Towards Rhodium and Iridium Oxo Complexes

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"To dream anything that you want to dream. That is the beauty of the human mind. 
To do anything that you want to do. That is the strength of the human will. 
To trust yourself to test your limits. That is the courage to succeed."

(Bernard Edmonds)

1. Gutachter: Prof. Dr. P. Burger
2. Gutachter: Prof. Dr. J. Heck
Dedicated to my parents

(Посвећено мојим драгим родитељима)
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List of abbreviations:

Al(pftb)$_4$ Perfluorotertbutoxyaluminate
B3LYP Becke-3 parameter functional with Lee-Yang-Parr correlation
BP-86 Becke-Perdew
Bn-tpen N-benzyl-N,N’,N’-tris(2-pyridyl-methyl)-1,2-diaminoethane
CCDC Cambridge Crystallographic Data Center
C$_6$H$_6$ Benzene
CH$_2$Cl$_2$ Dichloromethane
CH$_3$CN Acetonitrile
DMAN 1,8-bis-(dimethylamino)naphthalene
DFT Density functional theory
DME 1,2-Dimethoxyethane
Et$_2$O Diethyl ether
EPR Electron Paramagnetic Resonance
HMBC Heteronuclear Multiple Bond Correlation
HOMO Highest Occupied Molecular Orbital
HPLC High Performance Liquid Chromatography
HSQC Heteronuclear Single Quantum Coherence
$^3$Pr Isopropyl
IRC Intrinsic Reaction Coordinante
LACVP Los Alamos Core Valence Potential
LUMO Lowest Unoccupied Molecular Orbital
Me Methyl
MeOH Methanol
MLCT Metal to Ligand Charge Transfer
NMR Nuclear Magnetic Resonance
NOE Nuclear Overhauser Effect
N$_4$Py N,N-bis(2-pyridylmethyl)-bis(2-pyridyl)methylamine
ORTEP Oak Ridge Thermal Ellipsoid Plot Program
Ph Phenyl
PPNC1 Bis-(triphenylphosphoranylidene)-ammonium chloride
TASF Tris-(dimethylamino)sulfonium-difluorotrimethylsilicate
TBAF Tetrabutyl-ammoniumfluoride
TDAE  Tetrakisdimethylaminoethylene
TD-DFT Time Dependent Density Functional Theory
TEMPO 2,2,6,6-Tetramethyl-1-piperidinyloxo radical
THF Tetrahydrofuran
TMC 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane
TZVP Triple Zeta Split Valence

Abbreviations for the multiplicity of the NMR signals:
s (singlet), d (doublet), t (triplet), q (quartet) br (broad).
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1 Introduction

1.1 Functionalization of alkanes to alcohols

The selective oxidation and functionalization of alkenes under ambient conditions is an exciting scientific challenge and a highly valuable economic goal. Alkanes from natural gas and petroleum are the world’s most abundant feedstocks (Fig. 1.1). The primary component of natural gas is methane (CH₄). It may also contain heavier gaseous hydrocarbons such as ethane, propane and butane, as well as other gases, in varying amounts. During the geological formation of oil (and coal), large natural gas deposits are also formed. In former times, methane was released to the atmosphere when the oil (or coal) was extracted or it was simply burned at the oil field due to difficulties related to transportation. Most of the countries have abandoned this way of wasting methane, specifically because of environmental pressures. Nowadays, natural gas is transported through pipelines or by using tankers where the gas is liquefied. Although pipelines are economically feasible for inland gas transportation, they are not used across oceans. Alternatively, using tankers the cost of transport rises and safety problems emerge. In contrast, some platforms, where oil is extracted, pump the gas back into the ground in the hope that one day a new profitable method will be found to exploit this resource.

![Fig. 1.1 Abundance of natural gas and petroleum (left) and offshore platforms in California.](image)

Fig. 1.1 Abundance of natural gas and petroleum (left) and offshore platforms in California.
Currently, alkanes derived from both petroleum and natural gas are converted to energy, fuel and chemicals at high temperatures and multiple steps leading to inefficient environmentally and economically processes.

The development of a catalyst, which would selectively functionalize alkanes to alcohols under mild conditions, could lead to a new concept in production of energy in the 21st century.\textsuperscript{1,2,3} The \textit{selective} catalytic aerobic oxidation (O\textsubscript{2}) of one of the most inert substrates, methane, to methanol is still one of the "holy grails" of chemistry.\textsuperscript{4,5} In the past decades, there is an intense interest in C-H activation reactions, which are usually part of the catalytic cycle in functionalization of hydrocarbons to more useful products. However, there are very few examples of catalyst systems, that are capable of achieving this process and there are large gaps in our fundamental knowledge in how to design such a catalyst.\textsuperscript{3,5}

\subsection{1.1.1 Examples in nature}

The best examples of a selective alkane oxidation to a corresponding alcohol are found in nature. There are enzymes that can utilize dioxygen to oxidize saturated hydrocarbons to alcohols at ambient pressure and temperature (eq. 1.1).

\begin{equation}
\text{RH} + \text{NADH} + \text{H}^+ + \text{O}_2 \xrightleftharpoons{\text{enzyme}} \text{ROH} + \text{NAD}^+ + \text{H}_2\text{O} \quad (1.1)
\end{equation}

The best known of these enzymes are cytochrome P450 and methane monooxygenase (MMO), which in the resting state contain an Fe(III) protoporphyrin IX and a µ-oxo diiron or di-copper complex, respectively. The active species in the case of P450, is a terminal oxo-Fe(IV) porphyrin \textpi-radical cation (Fig. 1.2-left), which can oxidize organic substrates by oxygen atom transfer. In methanotrophic organisms, there are two types of MMO: a soluble form (sMMO) containing oxygen bridged non-heme diiron (Fe(IV)) active sites, and particulate form (pMMO), which contains Cu(III) oxygen bridged metal centers (Fig. 1.2-right).\textsuperscript{6,7,8}
A variety of Fe porphyrin complexes are able to mimic cytochrome P450 reactions \textit{in vitro} using iodosylbenzene (PhIO) as the primary oxidant.\textsuperscript{9,10}

Recently, it was reported that Cu loaded zeolite (ZSM-5) after activating with oxygen, converts methane to methanol at 398 K.\textsuperscript{11} In this case, the active core, containing a µ-oxo bridged di-copper is responsible for methane oxidation, which was also proposed for pMMO.\textsuperscript{12}

Only few examples are known in mimetics of non-heme iron enzymes. Wieghardt et al. postulated the formation of Fe(IV)-oxo compound $[\text{Fe(O)}(\text{cyclam-acetate})]^{+}$ in the reaction of corresponding Fe(II) complex and ozone.\textsuperscript{13} This compound was characterized only by Mössbauer spectroscopy. The first crystal structure of the terminal $[\text{Fe}^{IV}(\text{O})(\text{TMC})(\text{MeCN})](\text{OTf})_2$ complex was reported by Que Jr. et al.\textsuperscript{14} It was obtained in high yield in the reaction of the related Fe(II) complex with iodosylbenzene. The corresponding Fe(IV)=O complex with pentadentate N5 ligands (N4Py or Bn-tpen) hydroxylates triphenylmethane or ethylbenzene to related alcohols.\textsuperscript{15}

It is also worth mentioning that many of the postulated mechanisms involve radical pathways, which can be related to Fenton or Haber-Weiss chemistry. In 1898, Fenton reported the catalytic hydroxylation of alkanes with hydrogen peroxide and Fe(II) salts albeit with very low yield and conversion.\textsuperscript{16} The mechanism of Fenton´s reaction was discovered later by Willstätter, Haber and Weiss. They proposed that the actual oxidant in this reaction is the hydroxyl radical $·\text{OH}$ (eqs. 1.2 and 1.3).\textsuperscript{17,18}

\begin{align*}
\text{Fe(II)} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe(III)} + \text{HO}^+ + \text{HO}^- \quad (1.2) \\
\text{Fe(III)} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe(II)} + \text{H-O-O}^+ + \text{H}^+ \quad (1.3)
\end{align*}
They also worked on the mechanism of catalase (the enzyme which disproportionates hydrogen peroxide to water and oxygen) and proposed that a radical chain reaction takes place, which can be compared with their already proposed mechanism.\textsuperscript{19, 20, 21} This reaction activated further research in the field of biomimetics.

### 1.1.2 Catalytic systems

The classical Shilov system is one of the first examples where methane is selectively oxygenated to methanol (eq. 1.4).\textsuperscript{22, 23, 24} The C-H bond in methane showed an 100 times higher reactivity than C-H in methanol.

\[
\text{CH}_4 + [\text{PtCl}_6]^{2-} + \text{H}_2\text{O} \xrightarrow{[\text{PtCl}_4]^{2-}} \text{CH}_3\text{OH} + \text{CH}_3\text{Cl} + [\text{PtCl}_4]^{2-} + 2\text{HCl} \quad (1.4)
\]

Unfortunately, this catalyst showed to be unpractical. Pt(II) disproportionates to Pt(0) and Pt(IV) leading to a metal precipitation with concomitant deactivation. Further investigations of this system showed its high selectivity towards a terminal alkyl chain in the presence of the hydroxyl group.\textsuperscript{25}

Another example of methane oxidation to methanol is known as “\textit{Catalytica}” process. This process involves either a Hg(II) or Pt(II) catalyst and sulfuric acid as the oxidant.\textsuperscript{26} Periana et al. improved the original Shilov system using a Pt(II) chloro complex with a bidentate 2,2’-dipyrimidine ligand (eq. 1.5).\textsuperscript{27} The conversion to methylsulfate yields up to 70 \%, selectivity of 90 \% and turnover number ~ 300.

Apart from low turn over number, the disadvantage of this system is the high cost for the recovery of methanol from sulfuric acid.

\[
\text{CH}_4 + \text{H}_2\text{SO}_4 \xrightarrow{\text{Cl}^-\text{Cl}^-} \text{CH}_3\text{OSO}_3\text{H} + \text{H}_2\text{O} + \text{SO}_2 \quad (1.5)
\]

So far, the Shilov and Periana catalysts are the closest to producing a practical system for selective methane oxidation.
1.2 Our approach and goal

The main goal in this work is to develop a novel selective catalyst for the aerobic functionalization of methane to methanol. Combining an organometallic and coordination approach in alkane functionalization, monomeric Rh, Ir(III) oxo complexes with a terminal oxo unit $L_n M=O$ were the key compounds of the catalytic cycle presented in Figure 1.3. 

![Proposed catalytic cycle for alkane hydroxylation with Ir, Rh(III) oxo complex.](image)

Starting from the oxo complex II, 1,2-C-H bond addition would lead to alkyl hydroxo complex 27. The next step involves C-O reductive elimination of an alcohol and the formation of a cationic complex 29. The latter gives a peroxo species III after $O_2$ activation. The metal oxo complex II is then restored from III and one equivalent of 29.
According to DFT calculations, the step from the peroxo III to oxo complex II is thermodynamically favored. If the energy barrier is greater than expected, suitable amines such as dimethylphenyl amine can be used as a cocatalyst to convert III to II. The amine would also play a role in oxygen transfer. When amine-N-oxide is formed, it reacts further with 29 giving the desired oxo complex II.

1.3 Late transition metal-oxo complexes

Terminal metal-oxo complexes for high valent early and middle transition metals are well known. Moving from left to right in the periodic table, the number of stable terminal oxo complexes decreases. For the systems with a dⁿ electron configuration with n > 4, the oxo ligand is destabilized by repulsion (*vide infra*).

The aforementioned Fe(IV)=O complexes reported by Que Jr. et al. together with the four coordinate trimesityl Ir(V) oxo complex have d⁴ configuration (Fig. 1.4).

![Fig. 1.4 Ir(V) trimesityl oxo complex.](image)

The latter was obtained under aerobic conditions from the corresponding Ir(III) trimesityl complex and O₂ and is the only example of a terminal Ir-oxo complex reported in the literature. In the case of d⁶ configuration, there are only two complexes isolated for which a crystal structure was determined. One is NaRe(O)(PhCCPh)₂ reported by Mayer et al. (Fig. 1.5-left) and the second is Pt(IV)=O complex (K₂Na₉[Pt(O)(H₂O)L₂], L = [PW₉O₃₄]⁻) (Fig. 1.5-right) recently isolated by Hill et al.. The platinum metal center is situated between two polyoxotungstate ligands, which are found to be highly effective π acceptors.

![Fig. 1.5 Re(I) and Pt(IV) terminal oxo complexes.](image)
However, square planar transition metal-oxo complexes with d\textsuperscript{8} configuration are unknown. They are destabilized and a metal-oxygen multiple bond (L\textsubscript{3}M=O) is less feasible. This was rationalized by qualitative molecular orbital theory for Ni, Pd and Pt complexes by Mayer et al.\textsuperscript{34} The lack of an available $\pi$ acceptor orbital on the metal center (d\textpi), leads to 4 electron 2 orbital repulsion and destabilization of the system (Fig. 1.6).

\begin{center}
\textbf{Fig. 1.6} Destabilization of d\textsuperscript{8} square planar L\textsubscript{3}M=O complexes.
\end{center}

Recently the group of Cinellu postulated the formation of a reactive terminal Au(III) oxo intermediate in the reaction of the related gold bis-$\mu$-oxo bispyridine [Au\textsubscript{2}(bipy\textsuperscript{Me})(\mu-O)\textsubscript{2}]\textsuperscript{2+} and norbornene.\textsuperscript{35} The square-planar intermediate would have d\textsuperscript{8} configuration.

In complexes of the type L\textsubscript{3}M=O with d\textsuperscript{6} electron configuration destabilization by 4 electron 2 orbital repulsion may be still present (Fig. 1.7-left). However, there is a possibility to overcome this problem. The electrons from d\textsubscript{xz} orbital (b\textsubscript{2}, HOMO) of the L\textsubscript{3}M fragment have to be promoted to a d\textsubscript{z}\textsuperscript{2} orbital (a\textsubscript{1}, LUMO). This way $\pi$ bonding of the O\textsuperscript{2-} ligand with b\textsubscript{2} symmetry is possible with the now empty d\textsubscript{xz} orbital of the same symmetry and the system is stabilized (Fig. 1.7-right).
The energy for promoting these electrons depends on the gap between the HOMO and LUMO. For the weaker donors, such as amines or imines, with smaller splitting of these levels, the estimated promotion energy is small.

Conversely, the terdentate pyridine, dimine ligands, show excellent \( \pi \)-acceptor abilities and have been chosen in this work.\(^{36, 37}\) It is believed that the \( \text{M}=\text{O} \) interaction will be stabilized through a push-pull-interaction.\(^{28, 38}\)

It is noteworthy that HOMO-LUMO gaps in \( \text{d}^6 \) configured \( \text{L}_3\text{M}=\text{O} \) complexes are anticipated to be small and that an open shell \( S=1 \) states might be encountered.\(^{38}\)

According to previous investigations in our group,\(^{28}\) it was calculated that the formation of an oxo complex with a pyridine diimine ligand is thermodynamically favored for Rh and Ir (eq. 1.6).
However, the dimerization process of the terminal oxo complexes to mono or bis-μ-oxo bridged compounds is also strongly thermodynamically favored (eq. 1.7).  

$$\Delta E = -29 \text{ kcal/mol} \quad (1.7)$$

To prevent dimerization, sterically demanding pyridine diimine ligands with alkyl (Me, iPr, t-Bu) substituted phenyl groups were suggested. Intermolecular steric repulsion between the substituents on the ligands will prevent two possible dimerization pathways, denoted as “head to head” and “top on top” (Fig. 1.8).

Fig. 1.8 Prevention of dimerization using steric repulsion of the ligand substituents.

Although, sterically demanding ligands will be used, facile access of substrates is still possible from above or below the metal ligand plane.
The bond dissociation enthalpy of the metal-oxo moiety for the model complexes (depicted in eq. 1.6) was calculated to be in the range from 70-105 kcal/mol\textsuperscript{28} These values are significantly lower than for early to middle transition metals. For the tungsten oxo complex (C\textsubscript{5}MeH\textsubscript{4})\textsubscript{2}W=O\textsuperscript{39} the BDE equals 132 kcal/mol (experimentally determined). It may be concluded that low BDE’s of M=O in late transition metal oxo complexes will imply a great reactivity of the latter, which is important for alkane oxidation.

Part of this research was related to provide evidence for every step of the proposed cycle for the selective alkane activation (\textit{vide supra}). The thesis is divided into three chapters. In Chapter 2, different approaches to the synthetic access to the desired oxo and peroxo species will be described. In Chapter 3 a focus on the C-H activation and C-O reductive elimination reactions of the catalytic cycle will be made. The last part explains different synthetic routes to cationic complexes.
2 Towards Ir and Rh oxo complexes

As mentioned in the introduction, the selective, aerobic oxidation of methane to methanol is believed to involve a monomeric late transition metal oxo complex (L₅M=O) with a terminal oxo unit of the proposed catalytic cycle (see Fig. 1.3). The focus of this chapter will be on the synthetic progress in the preparation and characterization of rhodium and iridium oxo complexes as shown in Figure 2.1.

Fig. 2.1 An example of a Rh or Ir(III) oxo complex.

This chapter is divided into four sections. The first section describes the synthesis of the starting materials. The other sections are related to different approaches to obtain oxo complexes: 1) by oxidizing an Ir(I) hydroxo complex, 2) reaction with amine N-oxides and a cationic triflate complex, and from peroxo complexes. Although not directly related to the chemistry of the oxo complexes, the last part describes the reactions of “Rh(0)” complexes. These are suspected as potential precursors for the formation of a Rh(II) oxo or peroxo complexes.

2.1 Starting materials

As indicated, in order to prevent dimerization of the terminal L₅M=O systems, terdentate pyridine diimine ligand systems, with sterically demanding alkyl substituted groups, have been selected for this study. The terdentate pyridine diimine ligands (N₃Me₄) are prepared by the condensation of two equivalents of the desired aniline with 2,6-diacetylpyridine in 80 % yield (eq. 2.1)\(^{40,41,42,43,44}\).
The chloro complexes 1 and 2 were prepared from the bis(μ-chloro) dimers [M(C₉H₄)₂Cl]₂ (M = Rh, Ir) in good yields. The other starting materials, 3 – 6 were prepared by methoxide or hydroxide metathesis of the chloro ligand in a straightforward procedure as previously described. Compounds 7 and 8 were obtained by oxidative addition of methyl triflate to 3 and 4 dissolved in toluene (or 1 and 2 in dichloromethane). Complex 9 was prepared in excellent yield by a 1e⁻ reduction of the Rh(III) methyl bistriflate 7 with either TDAE or cobaltocene (Cp₂Co) in THF (eq. 2.2).

As previously established by Nückel, according to the ¹H, ¹³C-NMR spectroscopic data and X-ray crystal structure analyses, complexes 1 – 6 have a square planar geometry with a C₂ᵥ symmetrical ligand environment. All complexes are soluble in THF and dichloromethane.
However, after two days at room temperature in dichloromethane, compounds 3, 4 reconverted to the starting material 1, 2 and methanol. The presence of methanol was observed by $^1$H-NMR spectroscopy in the reaction mixture as well in the transferred volatiles (singlet peak at $\delta = 3.43$ ppm in CD$_2$Cl$_2$). According to the $^1$H and $^{13}$C-NMR of the residual product in CD$_2$Cl$_2$, the formation of 1 and 2 was unambiguously confirmed. Incorporation of alkyl substituents on the pyridine and phenyl rings increases the overall complex solubility in less polar solvents such as benzene or toluene.

### 2.1.1 Synthesis of Ir(I) triflate complex

The novel complex 10 was synthesized in quantitative yield by a different route than Rh analogue,$^{44}$ starting from the methoxide complex 4 (eq. 2.3). The reaction between complex 4 and two equivalents of methyl triflate resulted in the formation of the light green Ir(III) methyl bis triflate complex 8, which was fully characterized by $^1$H, $^{19}$F and $^{13}$C-NMR spectroscopy. The desired triflate compound 10 was obtained in the second step, when an equimolar THF solution of 4 and 8 were stirred together, until the color changed from green to brown. Both steps lead to C-O bond formation yielding dimethyl ether. The latter was identified in the $^1$H-NMR of the transferred volatiles revealing a singlet peak at $\delta = 3.21$ ppm in THF-d$_8$ (the observed resonance was compared to a reference sample). A possible reaction mechanism of this transformation will be discussed in Chapter 3.

![Chemical structure of complex 10](image)

Complex 10 is soluble in THF and DME and completely insoluble in benzene, toluene, diethyl ether and pentane. $^{19}$F-NMR spectroscopy of 10 revealed a singlet peak at $\delta = -78.9$ ppm in THF-d$_8$. Proton resonances from the coordinated THF (in THF-d$_8$) are observed as multiplets at $\delta = 1.61$ and 1.81 ppm in the $^1$H-NMR spectrum. Based on the $^1$H, $^{13}$C and $^{19}$F-NMR spectroscopic data, it was concluded that compound 10 is ionic with a THF ligand coordinated to
the metal center. This was later unambiguously confirmed by X-ray crystal structure analysis (Fig. 2.2).

Brown crystals suitable for an X-ray crystal structure analysis were obtained from a THF/pentane solution. Selected structural parameters of complex 10 are summarized in Table 2.1.

**Fig. 2.2** ORTEP plot of complex 10 with 50% thermal ellipsoids (triflate group and hydrogen atoms were omitted for clarity).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Length/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>1.905(7)</td>
</tr>
<tr>
<td>Ir1-N2</td>
<td>1.999(7)</td>
</tr>
<tr>
<td>Ir1-N3</td>
<td>2.017(7)</td>
</tr>
<tr>
<td>Ir1-O1</td>
<td>2.102(8)</td>
</tr>
<tr>
<td>N1-Ir1-N2</td>
<td>80.0(3)</td>
</tr>
<tr>
<td>N1-Ir1-O1</td>
<td>179.6(3)</td>
</tr>
<tr>
<td>N2-Ir1-O1</td>
<td>100.4(3)</td>
</tr>
<tr>
<td>N3-Ir1-N1</td>
<td>78.8(3)</td>
</tr>
<tr>
<td>N3-Ir1-N2</td>
<td>158.8(3)</td>
</tr>
<tr>
<td>N3-Ir1-O1</td>
<td>100.8(3)</td>
</tr>
</tbody>
</table>

The geometry around the Ir(I) center is essentially square planar with the sum of the bond angles equaling 359°. The fourth coordination site is occupied by a THF molecule displaying an Ir1-O1 distance of 2.102(8) Å, which indicates a strong interaction between the oxygen atom and the
positively charged metal center. Literature values for Ir-O distances are in the range of 2.025 – 2.339 Å.\textsuperscript{44, 49, 50} The only crystal structure found in CCDC database, where a THF molecule is bound to iridium metal center, is [IrH\textsubscript{2}(THF)(H\textsubscript{2}O)(PPh\textsubscript{3})\textsubscript{2}]SbF\textsubscript{6}·THF with the Ir-O distance 2.308(8) Å. In the latter the Ir-O bond is greatly elongated due to the trans influence of the hydride ligand.\textsuperscript{51} The reactions of complex \textbf{10} will be discussed later in this chapter.

\textbf{2.2 Oxidation of the Ir(I) hydroxo complex – unexpected results}

The hydroxo complex \textbf{6} has been used as a starting material in a number of attempts to synthesize an oxo complex. It is obtained in 60 % yield from the methoxo complex \textbf{4} by the addition of excess degassed water (eq. 2.4).\textsuperscript{47}

\begin{equation}
\begin{array}{c}
\text{Ir-OMe} \\
\text{Ir-OH}
\end{array}
\end{equation}

(2.4)

Complex \textbf{6} was fully characterized by \textsuperscript{1}H, \textsuperscript{13}C - NMR, IR spectroscopy and elemental analysis.

Synthetic access to oxo complexes was sought via oxidation of the readily available basic Ir(I) hydroxide complex \textbf{6} to the presumed corresponding acidic Ir(III) compound \textbf{I}, followed by deprotonation of \textbf{I} to give the desired oxo complex \textbf{II}\textsuperscript{*} (eq. 2.5).

\begin{equation}
\begin{array}{c}
\text{Ir-OH} \\
\text{Ir=O}
\end{array}
\end{equation}

(2.5)

\textsuperscript{*} Isolated and postulated complexes are labelled using arabic and roman numbers, respectively.
In order to have a better insight into the oxidation of complex 6, cyclic voltammetry experiments were performed (Fig. 2.3).

Fig. 2.3 Cyclic voltammograms of complex 6 recorded in THF (working electrode, gold; reference electrode, Ag/Ag⁺; [Bu₄NPF₆] = 0.4 M; scan rates = 400 mV (left) and 250 mV (right)).

The redox response for complex 6 is *quasireversible* with ΔEₚ = 152 mV. The approximate redox potential of complex 6 is ca. –1.7 V vs Cp₂Fe⁺/Cp₂Fe.

The oxidation process is *irreversible*. Two oxidation waves are observed with potentials of 0.44 and 0.91 V vs Cp₂Fe⁺/Cp₂Fe. It is presumed that the first oxidation wave at 0.44 V corresponds to the [Ir⁺(N₃Me₄)OH] / [Ir⁺⁺(N₃Me₄)OH]⁺ pair and the second wave at 0.91 V to the [Ir⁺⁺(N₃Me₄)OH]⁺ / [Ir⁺⁺⁺(N₃Me₄)OH]²⁺ couple. However, it is not clear whether a simple E process (one electron transfer) or more complex mechanisms such as EC and ECE are involved in the oxidation of 6.

In order to oxidize complex 6, different oxidizing reagents such as [thianthrene]⁺⁺, [NO]⁺, [N-(C₆H₄Br-4)]⁺⁺, [TEMPO]⁺ with high formal potentials (E°⁺) in the range from 0.7 – 1.0 V have been used. Each are classified as very strong oxidants.52

2.2.1 Oxidation with [thianthrene]⁺⁺

When the green solution of complex 6 in DME was added to a violet solution of the radical cation thianthrene⁺⁺ in DME, the color changed to red. However, instead of the desired o xo
complex, a diamagnetic Ir(III) hydride complex 11, with a molecule of DME coordinated to the metal center was obtained in 46 % of yield (eq. 2.6).

\[
\begin{align*}
\text{6} & \quad \text{Ir(III) hydride complex} \\
\text{11} & \quad \text{46 % yield, eq. 2.6}
\end{align*}
\]

The product 11 was fully characterized by \(^1\text{H}, \ ^{13}\text{C}\) and \(^{19}\text{F}\)-NMR spectroscopy. The presence of the Ir-H moiety was confirmed by \(^1\text{H}\)-NMR spectroscopy (in CD\(_2\)Cl\(_2\)) through a singlet peak at \(\delta = -32.5\) ppm. The DME ligand reveals four different sets of peaks (two singlets and two multiplets) in the aliphatic region. This is in agreement with the adopted essential Cs symmetrical environment found around the Ir metal center observed in X-ray crystal structure of 11. Red crystals of 11 were obtained by layering a DME solution with pentane (Fig. 2.4). Selected bond lengths and angles of complex 11 were presented in Table 2.2.

![ORTEP plot of complex 11](image)

Fig. 2.4 ORTEP plot of complex 11 with 50% probability thermal ellipsoids (the PF\(_6^-\) groups and H atoms except for the hydride ligand were omitted for clarity).
Table 2.2 Selected bond lengths [Å] and angles [°] for complex 11.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>2.058(4)</td>
<td>Ir1-N2</td>
<td>1.921(5)</td>
<td>Ir1-N3</td>
</tr>
<tr>
<td>Ir1-O1</td>
<td>2.120(5)</td>
<td>Ir1-O2</td>
<td>2.263(5)</td>
<td>Ir1-H1</td>
</tr>
<tr>
<td>N2-Ir1-N3</td>
<td>159.4(2)</td>
<td>N2-Ir1-N1</td>
<td>79.8(2)</td>
<td>N3-Ir1-N1</td>
</tr>
<tr>
<td>O1-Ir1-O2</td>
<td>75.6(2)</td>
<td>N1-Ir1-O1</td>
<td>177.7(2)</td>
<td>N1-Ir1-O2</td>
</tr>
<tr>
<td>N2-Ir1-O1</td>
<td>98.2(2)</td>
<td>N2-Ir1-O2</td>
<td>103.3(2)</td>
<td>N3-Ir-O1</td>
</tr>
<tr>
<td>N3-Ir1-O2</td>
<td>93.8(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The sum of angles of the equatorial ligands is 359.8° and of N1-Ir1-O2 = 93.6(2)° and N2-Ir1-O2 = 103.3(2)°. This shows that the geometry around the Ir(III) center is slightly distorted octahedral. The position of the hydride was located in the difference Fourier map and was isotropically refined. The Ir1-H1 distance of 1.68 Å is in the expected range for Ir(III) hydrides (1.47 – 1.81 Å).\(^{53, 54, 55}\) As displayed in Figure 2.4, DME is coordinated to the metal center. The \textit{trans} influence of the hydride is reflected in the elongation of the \textit{trans} Ir1-O2 bond distance of 2.263(5) Å, compared to the shorter equatorial Ir1-O1 bond distance of 2.120(5) Å.

The origin of the hydride is still unclear, as well as the fate of the hydroxide ligand. Less likely, the hydride originates from the OH group, since the independent experiment presented in eq. 2.7 leads to the product 12, which differs from 11 only in the counter ion.

![Reaction Scheme](image)

Comparing with the \textsuperscript{1}H-NMR spectrum of 11, all proton signals except for the hydride peak display the same chemical shift. The hydride peak is slightly shifted (δ = −32.6 ppm,
$\Delta \delta = 0.1$ ppm) presumably caused by the change of the counter ion. Until now, it is assumed that the hydride originates either from the glassware or the solvent.

2.2.2 Oxidation with “magic blue”

In another attempt to produce an iridium oxo complex, two equivalents of a different oxidizing agent, N-(p-bromophenyl)$_3$SbCl$_6$, which is also known as “magic blue” was added to complex 6. After stirring for 2 h in THF, the color changed from green to brown. The reaction resulted in the formation of the unexpected dichloro iridium(III) complex 13 in 23% yield (eq. 2.8).

\[ \text{according to the } ^1\text{H-NMR spectrum, the diamagnetic complex 13 was formed, which was confirmed by an X-ray crystal structure analysis. Complex 13 displays } C_{2v} \text{ symmetry in the solution, as confirmed by the observation of two singlet peaks assigned to the methyl groups of the phenyl rings and the ketimine methyl group with the integration ratio 2:1. The peaks from coordinated THF in THF-d}_8 \text{ are found at } \delta = 1.58 \text{ and 3.36 ppm, indicating slow exchange on the NMR time scale at } 200 \text{ MHz as expected for a } d^6 \text{ configured octahedral complexes.} \]

The ORTEP plot of complex 13 is displayed in Fig. 2.5 and the corresponding data with selected distances are listed in Table 2.3.
Fig. 2.5 ORTEP plot of complex 13 with 50% probability thermal ellipsoids (the SbCl$_6^-$ group and hydrogen atoms and were omitted for clarity).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Bond Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>1.934(9)</td>
<td></td>
</tr>
<tr>
<td>Ir1-N2</td>
<td>2.098(9)</td>
<td></td>
</tr>
<tr>
<td>Ir1-N3</td>
<td>2.092(9)</td>
<td></td>
</tr>
<tr>
<td>Ir1-Cl1</td>
<td>2.347(3)</td>
<td></td>
</tr>
<tr>
<td>Ir1-Cl2</td>
<td>2.339(3)</td>
<td></td>
</tr>
<tr>
<td>N1-Ir1-N2</td>
<td>80.1(4)</td>
<td></td>
</tr>
<tr>
<td>N1-Ir1-N3</td>
<td>79.8(4)</td>
<td></td>
</tr>
<tr>
<td>Cl1-Ir1-Cl2</td>
<td>177.7(1)</td>
<td></td>
</tr>
<tr>
<td>O1-Ir1-O1</td>
<td>90.9(4)</td>
<td></td>
</tr>
<tr>
<td>N2-Ir1-O1</td>
<td>100.7(4)</td>
<td></td>
</tr>
<tr>
<td>N1-Ir1-Cl1</td>
<td>88.5(4)</td>
<td></td>
</tr>
<tr>
<td>N2-Ir1-Cl1</td>
<td>88.9(3)</td>
<td></td>
</tr>
<tr>
<td>N1-Ir1-Cl2</td>
<td>89.4(4)</td>
<td></td>
</tr>
<tr>
<td>N2-Ir1-Cl2</td>
<td>91.7(3)</td>
<td></td>
</tr>
</tbody>
</table>

The geometry at the Ir(III) center is slightly distorted octahedral. This is confirmed by the sum of angles for the equatorially coordinated ligands which is 360° and the angles: N1-Ir1-Cl1 = 88.5(4)°, and N2-Ir1-Cl1 = 88.9(3)°. The two chloro ligands are positioned trans to each other with an angle, Cl1-Ir1-Cl2, of 177.7(1)°. The iridium chloro distances Ir1-Cl1 = 2.347(3) Å and Ir1-Cl2 = 2.339(3) Å are in good agreement with typical Ir-Cl distances (2.35 Å) reported in the literature for octahedral Ir(III) complexes.\textsuperscript{56, 57} The fourth
equatorial site is occupied by THF molecule displaying Ir-O1 distance 2.121(9) Å, slightly longer than Ir-O distance in complex 10 (2.102(8) Å). The THF ring is coordinated to the Ir center in a chair conformation as opposed to [Rh(NCN)(THF)Cl2] where the THF ring has a tilted coordination.\(^{58}\)

**The source of the chloro ligand**

It appears that [SbCl\(_6\)]\(^-\) is not always innocent. It can as well be an oxidant and undergo dissociation (reduction) to [SbCl\(_4\)]\(^-\) and 2 Cl\(^-\) (eq. 2.9).\(^{52}\)

\[
[SbCl_6]^- + 2e^- \rightarrow [SbCl_4]^- + 2Cl^- \quad (2.9)
\]

Two chloro ligands in complex 13 presumably originate from the reaction according to equation 2.9. Similar chloride transfer was previously reported in the literature. Using N-(p-bromophenyl)\(_3\)SbCl\(_6\) in the oxidation of [Fe\(_2\)(µ-CO)\(_2\)(CO)\(_2\)Cp\(_2\)] the undesired chloro complex [FeCl(CO)\(_2\)Cp] was formed\(^{59}\) and the oxidation of [Mn(CO)(dppe)Cp\(^+\)] gave [MnCl(CO)(dppe)Cp\(^+\)]\(^+\).\(^{60}\)

The oxidation reaction of complex 6 with [TEMPO]PF\(_6\) and [NO]+PF\(_6\)\(^-\) was also attempted. However, it did not succeed owing to their low solubility in the non-polar solvents (eq. 2.10). Due to problems with polymerization of the solvent, THF could not been used.

According to Conelly and Geiger,\(^{52}\) nitrosonium salts are soluble in CH\(_3\)CN, but react with solvents such as diethyl ether, acetone, and alcohols. Hence, based on our experience acetonitrile would interfere with the reaction and possibly coordinate to the metal center.
2.2.3 Hydride abstraction with a trityl cation

The hydride abstraction with trityl (Ph$_3$CPF$_6$)$^{61}$ from complex 6 was another anticipated method to access the desired Ir(III) oxo complex. Upon addition of a solution of complex 6 in DME to solid trityl-hexafluorophosphate, a color change from green to red was observed (eq. 2.11).

\[
\begin{align*}
\text{Ir(OH)} & \xrightarrow{\text{1 equiv. Ph$_3$CPF$_6$, DME, RT}} \text{Ir}^+\text{PF}_6^- \\
6 & \rightarrow \text{14} \\
\end{align*}
\]

The $^1$H-NMR spectrum of the pentane extraction of the reaction mixture revealed a singlet resonance at $\delta = 5.40$ ppm in C$_6$D$_6$, which corresponds to triphenylmethane. The $^1$H-NMR of the residual product in THF-d$_8$ appears to be diamagnetic with sharp peaks in the aliphatic (singlets at $\delta = 0.92$, 1.83 and 1.89 ppm with 1:1:1 integration ratio) and aromatic region (multiplet at $\delta = 6.84$, doublet at $\delta = 7.37$ and triplet at $\delta = 7.7$ ppm).

The IR spectrum of 14 shows a sharp, medium intensity peak at 1967 cm$^{-1}$.

An electrospray mass spectrum of complex 14 (ESI-MS +ve ion mode) was recorded and revealed a single peak at 603.2 m/z. This mass matches the complex with a coordinated acetonitrile ligand. The latter could originate from the atmosphere of the glovebox.

In order to provide more evidence for acetonitrile coordination, an independent experiment was performed. Upon addition of CH$_3$CN to complex 10, the reddish brown acetonitrile complex 10-MeCN was formed in a quantitative yield (eq. 2.12).
The $^1$H-NMR spectrum of 10-MeCN in THF-d$_8$ revealed a new resonance at $\delta = 1.77$ ppm, which was assigned to the coordinated acetonitrile. The integration ratio of the observed peaks for the methyl groups (on the phenyl ring, diimine and acetonitrile) is 4:2:1. The stretching $\nu_{CN}$ frequency of the coordinated acetonitrile ligand in complex 10-MeCN was found at $\nu_{CN} = 2294$ cm$^{-1}$ (non-coordinated CH$_3$CN; $\nu_{CN} = 2250$ cm$^{-1}$).

Upon dissolving the obtained crystals of complex 14 in THF-d$_8$ and transferring the volatiles, a singlet peak at $\delta = 2.47$ ppm in $^1$H-NMR spectrum was observed*. It was later discovered that the water resonance in THF-d$_8$ appears at essentially the same chemical shift ($\delta = 2.48$ ppm). The same peak was observed when PPNCl was added to complex 14 and volatiles were transferred. The $^1$H-NMR of the residual compound confirmed the formation of 2.

Compound 14 can be reproduced and several X-ray crystal analyses have been undertaken. Red crystals were obtained from DME/pentane solution at $-35$ °C. The X-ray crystal structure analysis suggested a linear, possibly three-atom ligand, Q1-Q2-Q3. The residual electron density (Q1-Q2-Q3) as shown in Figure 2.6 is so far unresolved. The full pyridine-diimine ligand could be anisotropically refined and the R-values (I > 2sigma (I)) for the complete molecule are R1 = 0.0383, wR2 = 0.0843. The distances between Ir-N1 are 1.967(7) Å and Ir-N2 are 2.036(4) Å.

---

*The acetonitrile resonance in THF-d$_8$ displays a singlet peak at $\delta = 1.95$ ppm in $^1$H-NMR spectrum.
Fig. 2.6 ORTEP plot of complex 14 (Q1, Q2 and Q3 represent unresolved residual electron densities found in the difference Fourier map).

According to the literature, acetonitrile is mostly coordinated in the linear rather than bent fashion, due to increased overlap between the N donor and the metal center. However, there are also examples for the group 6 transition metals, where acetonitrile is coordinated to the metal center in $\eta^2$-fashion.62

In order to address this point, DFT calculations (B3LYP hybrid, LACVP** basis set) for the model complex 14a and 14b have been performed (Fig. 2.7).

Fig. 2.7 Energy diagram for the optimized structures 14a, b.
As displayed in Fig. 2.7, complex 14a is 20 kcal/mol lower in energy than the \( \eta^2 \) analogue 14b. During the optimization of structure 14b, the angle N-Ir-C was constrained. When constraints are released, 14b relaxes to 14a.

Comparing and summarizing all the results related to reaction according to eq. 2.11 allows us to exclude the coordination of acetonitrile.

Unfortunately, until now it has not been possible to establish the nature of the ligand that resides in the fourth coordination site in complex 14.

Due to the disorder observed in the PF\(_6^-\) anion (not shown in Fig. 2.6) in the crystal structure of complex 14 and aforementioned refinement, it was decided to exchange the PF\(_6^-\) counter ion of the trityl cation with a more bulky perfluorinated alkoxyaluminate anion.\(^\text{63, 64}\)

Unfortunately, the experiment could not be performed applying the same conditions as in eq. 2.11 using DME as solvent. The trityl-Al(pftb)\(_4\) reacts with DME very fast giving a violet-blue solution of unknown products. Therefore, benzene was used as solvent.

When complexes 5 or 6 were dissolved in benzene and added to Ph\(_3\)CAl(pftb)\(_4\) the color changed from green to reddish brown. Pentane extraction of the reaction mixture contained a 1:1 mixture of Ph\(_3\)CH (\(\delta = 5.40\) ppm) and Ph\(_3\)COH (\(\delta = 2.67\) ppm) according to the \(^1\)H-NMR in C\(_6\)D\(_6\) (eq. 2.13).

The \(^1\)H-NMR spectrum of II in THF-d\(_8\) revealed that a mixture of at least three different products was formed (three sets of triplet and doublet peaks at different chemical shifts were
observed in the aromatic region). The mixture could not be separated by either extraction or by precipitation due to comparative solubilities.

2.3 Ir(I) triflate as a precursor for an oxo complex

2.3.1 Reactions with amine N-oxides

Based on the previous investigations by our group, a straightforward route to Ir-oxo complex \( \text{II} \) from Ir(I) triflate \( \text{10} \) and amine N-oxides has been suggested (eq. 2.14). The proposed mechanism, supported by kinetics will be discussed later in more details.

\[
\begin{align*}
\text{10} & \quad + \text{OTf}^- \\
& \quad \xrightarrow{\text{O-NPh}_{3-x}\text{Me}_x \quad x = 1 - 3} \\
& \quad \text{10a} \\
& \quad \xrightarrow{\Delta \text{ or } h\nu} \text{II} \\
& \quad + \text{OTf}^-
\end{align*}
\]

Upon the addition of a solution of Ph\(_2\)MeNO or PhMe\(_2\)NO in THF to complex \( \text{10} \), the corresponding amine Ph\(_2\)MeN or PhMe\(_2\)N were formed, as confirmed by \(^1\)H-NMR spectroscopy in THF-\(d_8\) (Ph\(_2\)MeN: \(\delta = 3.28\) (s, 3 H, Me), 6.88 (tt, 2 H, CH\(_{\text{arom}}\)), 6.98 (dd, 4 H, CH\(_{\text{arom}}\)), 7.20 (tt, 4 H, CH\(_{\text{arom}}\)); PhMe\(_2\)N: \(\delta = 2.86\) (s, 6 H, Me), 6.56 (tt, 1 H, CH\(_{\text{arom}}\)), 6.66 (dd, 2 H, CH\(_{\text{arom}}\)), 7.10 (tt, 2 H, CH\(_{\text{arom}}\))). Unfortunately, the expected “Ir-oxo” complex \( \text{II} \) precipitated from solution as a dark brown solid.

The IR spectrum of the precipitate in Nujol revealed a sharp, medium intensity band at 723 cm\(^{-1}\), which can be tentatively assigned to Ir=O stretching frequency (note: this band was observed after subtracting the spectrum of precipitate in Nujol and Nujol\(^*\)). The only Ir-oxo complex in the literature by Wilkinson et al. reported that Ir=O band was found at 802 cm\(^{-1}\) (in Nujol) for the related Ir(V)(mes)\(_3\)(O) complex.\(^{31}\)

\(^*\)Nujol absorption bands were found at \(\nu = 2924\) (vs), 1462 (s), 1384 (s), 726 (vw) cm\(^{-1}\).
The reaction according to eq. 2.14 was also monitored by UV-Vis spectroscopy at room temperature during a period of 3 hours. The spectrum displayed in Figure 2.8 was observed.

**Fig. 2.8** Isobestic points for the reaction of complex 10 and excess of Me$_2$PhNO (left); decay of the absorbance at 800 nm (right).

The decay of the absorption bands at 404 and 455 nm corresponds to the decrease in the concentration of complex 10. As displayed in Fig. 2.8, there are three isobestic points at 357, 376 and 490 nm. The absorption, which has been tentatively assigned to a d-d transition at 800 nm decreases also with time.

The reaction is suggested to proceed via substitution of the THF ligand by the amine N-oxide group and formation of Ir-ONPh$_{3-x}$Me$_x$ intermediate 10a. The latter dissociates to an Ir=O complex and a free amine (see eq. 2.14). This proposed mechanism is supported by the previous isolation of [Rh(N$_3$Me$_4$)ONMe$_3$]OTf which was fully characterized and the crystal structure was determined.\(^{47}\)

In order to obtain an Ir analogue, the similar reaction between complex 10 and Me$_3$NO has been performed (eq. 2.15). However, due to the low solubility of the obtained complex 10a, the same reaction with Me$_3$NO after anion exchange of OTf with BAr$_4^F$ was attempted. Upon addition of Me$_3$NO to a THF solution of complex 10-BAr$_4^F$, the color changed from brown to green and complex 10b was formed.
The coordination of Me₃NO to the Ir center is confirmed by $^1$H-NMR spectroscopy, revealing a singlet peak at $\delta = 2.45$ ppm (in THF-d₈). This peak is considerably shifted in comparison to free Me₃NO, which reveals a singlet peak at $\delta = 3.06$ ppm. The integration ratio of the methyl groups on the N-oxide, phenyl rings and diimine ligand is 3:4:2. Unfortunately, the crystals obtained were not of suitable quality for an X-ray structure analysis.

Photolytic studies (using a mercury medium-pressure lamp 125HPKW, shielded by a Quartz jacket water cooling mantle and K₂CrO₄ or H₂O UV-Vis cutoff filters) were performed on complex 10b in order to cleave the N-O bond and therefore obtain an oxo complex. The photolysis reaction was done in a Young’s NMR tube in THF-d₈. Unfortunately, an insoluble black precipitate was formed. However, the $^1$H-NMR spectrum of the supernatant revealed a singlet peak at $\delta = 2.1$ ppm assigned to free trimethylamine. The fate of the oxygen from Me₃NO is unclear.

There are a few structurally characterized transition-metal complexes with Me₃NO as a ligand in the literature. Examples involve the octahedral rhenium dinuclear complex $\{[(\mu-H)Re₂(CO)₇(\mu-NC₅H₄)(Me₃NO)]\}^{65}$, tetrahedral $[\text{Co(ONMe₃)}]I₂^{66}$ and pseudo tetrahedral
Further, Herrmann et al.\textsuperscript{68} reported the formation of an air stable trinuclear Rh $\mu^3$-oxo complex $[(\text{Cp}*\text{Rh})_3(\mu-CO)(\mu-O)]$ in the reaction of Me$_2$NO and Cp$^*$Rh(CO)$_2$. If we address the reaction according to eq. 2.14 as a deoxygenation of an amine N-oxides to amines, there are examples where Cp$_2$TiCl$_2$/In or FeCl$_3$·6H$_2$O/In convert the N-oxide into the corresponding amines under ultrasonication.\textsuperscript{69, 70} This process is also well known in the catalytic cycle of enzymes such as trimethylamine-N-oxide reductase where the active site is Mo(IV) metal center.\textsuperscript{71}

As already established by DFT calculations,\textsuperscript{28} for the model compound, the formation of the Ir-oxo complex II is expected to be thermodynamically more favorable for amine N-oxide of the type O-NPh$_{3-x}$Me$_x$ with a larger number of phenyl groups (Fig. 2.9).

As shown in Figure 2.9, there is a nearly linear trend observed for the N-O bond strength in O-NPh$_{3-x}$Me$_x$ vs. number of methyl groups. When all methyl groups are substituted with phenyl groups, N-O bond is weakened by 22 kcal/mol.

To establish whether the N-O bond length changes by increasing the number of phenyl groups (as might be expected according to the calculations), Me$_2$PhNO and MePh$_2$NO were synthesized. The N-oxides (Me$_2$PhNO or MePh$_2$NO) were prepared according to the literature by using a tertiary N-amine and m-chloroperbenzoic acid\textsuperscript{72} in 70% yield and high purity (eq. 2.16).
Colorless crystals of Me₂PhNO and MePh₂NO suitable for X-ray structure analyses were obtained from concentrated acetone/pentane solutions. The crystal structures and the selected bond distances are presented in Figure 2.10a, b and Table 2.4.

Both N-oxides crystallize in the orthorhombic crystal system. PhMe₂NO crystallizes in the Pbca (Z = 8) space group, whilst Ph₂MeNO crystallizes in the Pna2₁ space group (Z = 8) with two
independent molecules in the asymmetric unit. They display a pseudo tetrahedral geometry around the N atom with average O-N-C bond angle of 109.6° for PhMe$_2$NO and 109.0° for Ph$_2$MeNO. The N-O distances, 1.388 Å for Me$_3$NO, $^{73}$ 1.388(1) Å for PhMe$_2$NO and 1.401(4) Å for Ph$_2$MeNO do not differ significantly, when one methyl group is replaced with phenyl group.

The dihedral angle O1-N1-C1-C2, which is 17.4° for PhMe$_2$NO and 13.7° for Ph$_2$MeNO is of particular interest since it suggested C-H-O hydrogen bonding. In order to address this point, DFT calculations were performed. In this case, the recently published X3LYP hybrid functional and 6G-311G** basis set was used to describe hydrogen bonding and Van-der-Waals interactions.$^{74}$ According to the calculations, the minimum energy corresponds to the structure with the dihedral angle O-N-C-C = 0° (Fig. 2.11). Increasing the dihedral angle from 0–90°, the energy rises and the maximum is reached when the angle is 90°.

![Fig. 2.11](image)

**Fig. 2.11** Energy diagram of PhMe$_2$NO (■) and Ph$_2$MeNO (▲) based on the change of the dihedral angle O-N-C1-C2 from 0–90°.

The calculated energy difference between the optimized and the crystal structure is approximately 0.5 kcal/mol for both N-oxides. A likely explanation for this observed difference is the additional intramolecular and intermolecular (calculated above) hydrogen bonding observed in the crystal packing (Fig. 2.12).
Fig. 2.12 Intramolecular and intermolecular CHO hydrogen bonding in Me₂PhNO.

The positions of all hydrogen atoms were located in the difference Fourier map and refined isotropically. Note: All C-H distances were averaged to 0.96 Å.

Non-linear intramolecular hydrogen bonding is apparent between O1····H1-C1 with the bond distance O1-H1 = 2.345 Å for PhMe₂NO (O1-H1a = 2.314 Å for Ph₂MeNO). The C1-H1····O1 angle is 102°, which is the lower limit for what can be accepted as bent hydrogen bonding according to the classification of Desiraju. An example of hydrogen bonding with a small angle (116°) is reported for the case of methoxy substituted cyclopenta[a]phenantrenes. Intermolecular CH····O hydrogen bonding, depicted in Figure 2.12, with the distances from 2.2 – 2.6 Å and an average angle from 170°, is classified as a strong CH····O hydrogen bond.

With respect to equation 2.14, the deoxygenation reaction of PhMe₂NO and Ph₂MeNO to the corresponding free amines under mild conditions with complex 10 is observed. However, the fate of the oxygen atom is still unclear due to the low solubility of the obtained compound.

2.3.2 Reaction with TBA-Oxone

“Oxone”, i.e. monopersulfate tetrabutylammonium salt has been used as an oxidant (for example it oxidizes sulfides to sulfoxides) and as an efficient single oxygen transfer reagent. It contains an unsymmetrical O-O bond that can be heterolytically cleaved with various transition metal
complexes.\textsuperscript{78, 79} It is also used in the asymmetric epoxidation of alkenes with Mn(III)-salen complexes as a cocatalyst.\textsuperscript{80}

The direct conversion of complex 10 to the oxo complex II with tetrabutylammonium monopersulfate (Bu\textsubscript{4}NHSO\textsubscript{5}) or for increased solubility with dodecylammonium monopersulfate (C\textsubscript{12}H\textsubscript{25})\textsubscript{4}NHSO\textsubscript{5}), was attempted (eq. 2.17).

![Diagram of the conversion of complex 10 to oxo complex II](image)

\textsuperscript{10} \textsuperscript{II}

Unfortunately, complete characterization of the obtained compound was not possible due to its low solubility. The solubility can be improved by changing the anion with more sterically demanding group. Alternatively, the methyl groups located on the phenyl rings could be exchanged by \textit{tert}-butyl groups. Both suggestions are left for future work.
2.4 Rh, Ir(III) peroxo complexes

The activation of dioxygen at transition metal centers is a fundamentally important process in the aerobic oxidation of organic molecules\textsuperscript{81, 82} and many other biological systems.\textsuperscript{83, 84, 85, 86} According to the literature, most of the available evidence shows that bound dioxygen is not very reactive, compared to a metal-oxo species.\textsuperscript{87, 49}

Based on the previous investigations,\textsuperscript{28} a different approach to an oxo moiety was planned through the synthesis of a peroxo complex III (eq. 2.18).

\[
\begin{align*}
\text{N} & \quad \text{M} - \text{THF} \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\text{N} & \quad \text{M} + \text{O}_2 \\
\end{align*}
\]

The overall proposed pathway involves cleavage of an M-O bond and formation of the superoxo transient \(a\). Addition of one equivalent of the cation complex would lead to the \(\mu\)-peroxo bridged species \(b\), which transforms into oxo complex II. In general, the formation of an oxo complex is expected to be smooth because it does not involve energetically too high lying species.

Exposure of a diethyl ether solution of complex 10-Al(pftb)\textsubscript{4} (synthesis – see Chapter 4) to an excess of dioxygen resulted in the formation of reddish-brown precipitate. After the solvent was evaporated, a microcrystalline product III was obtained (eq. 2.19).
The IR spectrum of complex III (in methylene chloride or diethyl ether) exhibited a new band (when compared to starting materials) at 976 cm\(^{-1}\), which was tentatively assigned to an O-O stretching frequency \(\nu_{\text{O-O}}\). This band is blue shifted by approximately 100 cm\(^{-1}\) when compared Rh, Ir(III)- peroxo chloride complexes.\(^8\) The O-O stretching frequency is used in the classification of peroxo complexes (930-740 cm\(^{-1}\)) and superoxo complexes (1200-1700 cm\(^{-1}\)).\(^88\) This criterion failed in our case and it was also reported by Theopold et al. for TpCo(O\(_2\)) (Tp = hydrotrispyrazolyl-borate).\(^87\) The O-O stretching frequency in the latter was found at 961 cm\(^{-1}\).

The \(^1\)H-NMR spectrum of III (M = Ir) in THF-d\(_8\) revealed three broad resonances (at \(\delta = 2.1, 7.2\) and 8.3 ppm), which suggested that the complex III is paramagnetic. In the \(^19\)F-NMR, a singlet peak assigned to the counter ion is slightly shifted to \(\delta = -73.7\) ppm when compared to the starting material 10-Al(pftb)\(_4\) (\(\delta = -75.6\) ppm). These observations are supported by DFT calculations, which revealed a preference of \(\sim 4\) kcal/mol for \(S = 1\) over \(S = 0\) state when the peroxo ligand is perpendicular to the IrNNN plane (Fig. 2.13 left).
Fig. 2.13 Energy diagram for the model complexes IIIa (left) and IIIb (right) calculated for the different ground states.

In the case for IIIb, the singlet ground state is thermodynamically more favorable than triplet, with the energy difference of ~ 30 kcal/mol.

The calculations also showed that the coordination of dioxygen perpendicular to the IrNNN rather than in the plane is preferred. The energy differences between the singlet (or triplet) states of IIIa and IIIb are 60 kcal/mol (or 80 kcal/mol) favored for IIIa.

Unfortunately, until now, suitable crystals for X-ray analysis were not obtained. In order to provide the evidence for the coordination of dioxygen to the metal center, PPh$_3$ was added to a THF solution of III (eq. 2.20).

\[
\begin{align*}
&\text{III} + \text{Al(pftb)$_4$}^- \\
\text{PPh$_3$, THF} &\rightarrow \\
&\text{Rh, IVa; Ir, IVb}
\end{align*}
\]

The $^1$H-NMR spectrum of IVa in THF-d$_8$ displays sharp singlet resonances in the aliphatic region at $\delta = 1.81$ and 1.93 ppm with an integration ration 1:2, which are assigned to the methyl
groups on the ketimine and phenyl rings. In the aromatic region a multiplet at $\delta = 7.10 - 7.70$ ppm, a doublet at $\delta = 8.15$ ppm and a triplet at $\delta = 8.38$ ppm (from the pyridine protons) were observed.

In the $^{31}$P-NMR spectrum, a singlet peak at $\delta = 24$ ppm was assigned to $\text{Ph}_3\text{PO}$ (and compared to the reference value). According to the $^{31}$P-NMR spectrum of complex IVa, a doublet peak at $\delta = 30$ ppm was obtained and assigned to the phosphorous atom bound to the Rh metal center. The Rh-P coupling constant is $J_{\text{RhP}} = 175$ Hz, which is in the expected range for Rh(I) square planar complexes.$^{89}$ For IVb, a singlet at $\delta = 10$ ppm was detected in the $^{31}$P-NMR spectrum and assigned to the coordinated $\text{PPh}_3$ ligand.

The $^1$H-NMR spectrum of IVb (in THF-d$_8$) in the aliphatic region revealed a two singlet peaks ($\delta = 1.54$ and 1.91 ppm) with the integration ratio 1:2 assigned to the methyl groups on the ketimine and phenyl rings. In the aromatic region, typical set of signals (multiplet at $\delta = 7 - 7.3$ ppm, doublet at $\delta = 8.36$ ppm and triplet at $\delta = 8.65$ ppm) was observed. All resonances are strongly downfield shifted in the $^1$H-NMR spectrum when compared to complex 10.

Complex IVb was obtained in an independent experiment by adding $\text{PPh}_3$ to a THF solution of 10 (eq. 2.21).
2.5 The reactivity of formal Rh”(0)” complexes towards small molecules

Homogeneous catalytic reactions mostly involve closed shell complexes. In contrast, metallo-enzymes, especially oxygenases (such as P450) employ paramagnetic, radical species in their further transformations. Most of the known organometallic radicals are 17 or 19 electron species. They can be obtained via different routes such as photolytic homolysis of metal-hydride or metal-metal bonds, electron transfer processes or atom abstraction. The unpaired electron spin density can be located at the metal center or it can be transferred to a π-acceptor ligand. Such ligand radical character is reported for iridium olefin complexes with a formal oxidation (0) and (II), and also very well known in case of P450 in which the active species is high valent (porphyrin*)FeIV=O complex. Organometallic radicals are usually very reactive and can easily dimerize if there is no steric hindrance. They can readily abstract halogens or hydrides and react with other organic radical traps. Furthermore, a reactivity toward a variety of substrates such as CO, H₂, CH₄, etc has been reported.

In this part the focus will be on the synthesis and the chemistry of the novel Rh”(0)” complexes. The latter are thought to be a good precursors to obtain Rh(II) peroxo or related imido compounds.

The reduction of Rh(I) diimine, pyridine chloro complexes carried out under an argon atmosphere leads to the formation of the stable violet complex V (or Va*), which is believed to be a radical species (eq. 2.22).

\[
\begin{align*}
\text{Rh}^{I} & \xrightarrow{\text{Na/Hg, THF, Argon, } - \text{NaX}} \text{Rh}^{*} \\
\text{I} & \xrightarrow{\text{R = Me, iPr}} \text{V} \\
\text{R'} & \xrightarrow{\text{R' = H, t-Bu, X = Cl}} \text{V} \\
\end{align*}
\]

*Until now the crystal structure of V has not been determined. For simplicity, the above depicted formula (V) will be used.
The difficulties in preparation and handling of complex V, deserves a special mention. The lifetime of V depends strongly on the quality (purity) of the solvent (HPLC solvents required) as well as on the quality of argon. However, even when the synthesis of V was performed under very rigorous Schlenk conditions, the lifetime of the methyl substituted complex V was in order of 1 hour at −35 °C. Therefore, it was anticipated that by changing the methyl groups (on the phenyl rings) with isopropyl groups would lead to a more stable radical complex. This was indeed accomplished, and the isopropyl substituted compound can be stored for days at low temperatures. Unfortunately, after many attempts, the crystals of V suitable for an X-ray analysis were not obtained. The lifetime of V can be related to a color change from violet to green or brown.

The UV-Vis spectrum of complex V in THF shows a relatively intense band at 459 nm and a weaker at 508 nm. Since the molecular weight of V was unknown, in order to support the band assignment, TD-DFT calculations were performed. Calculated extinction coefficients for the model compounds Vb and Vc (vide infra) were in the order of 10^4 l/mol cm, which is in agreement with literature values for MLCT bands. The shape of the spectrum is identical to the one obtained experimentally. The other bands in the visible region found at 581 nm and 650 nm with weaker intensities are assigned to a d-d transition (calculated $\varepsilon = 10^3$ l/mol cm). The corresponding UV-Vis spectrum of the complex V is displayed in Figure 2.14 together with the related chloro complex and the ligand for comparison.

![Fig. 2.14 UV-Vis spectra of the chloro complex 1 (---), the radical complex V (----) and the ligand (----).](image)
The dimerization of the 15 electron complex $V$ and the formation of metal-metal bond is prevented by sterically demanding ligand. However, coordination of the THF at the rhodium "(0)" metal center was not excluded. According to DFT calculations (B3LYP, LACVP** basis set), the preference for THF coordination in $V_c$ is approximately 18 kcal/mol (eq. 2.23).

\[ \Delta E = -18 \text{ kcal/mol} \] (2.23)

The electronic structure was also of particular interest. Based on DFT calculations (B3LYP, LACVP** basis set) on the model compounds $V_b$ and $V_c$, the spin density of the electron is essentially located within the pyridine diimine ligand (Fig. 2.15).

**Fig. 2.15** Calculated spin density for the model compounds $V_b$ and $V_c$.

The non-innocent behavior of the pyridine diimine ligands has already been established. They are readily engaged in to a metal-to-ligand charge transfer and sometimes undergo alkyl migrations. DFT calculations of $V$ showed that the pyridine diimine ligand demonstrates a great capacity to accept an additional electron. This was also observed for the Rh"(0)" dinitrogen complex (see part 2.5.3).
Since compound $\text{V}$ has a “delicate” structure, different anticipated trapping reactions were attempted.

In dichloromethane, complex $\text{V}$ immediately changed color from violet to green yielding the chloro complex $\text{I}$ (eq. 2.24).

\begin{align*}
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{Rh} \quad \bullet \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array}
\quad \begin{array}{c}
\text{CH}_2\text{Cl}_2 \\
\text{V} \\
\quad \text{Cl} \\
\text{I} \\
\end{array}
\end{align*}

According to the $^1\text{H}-\text{NMR}$ spectrum (in CD$_2$Cl$_2$), the observed resonances ($\delta = 1.03$ (d, 12 H, CH(CH$_3$)$_2$); $1.12$ (d, 12 H, CH(CH$_3$)$_2$); $1.64$ (s, 6 H, CH$_3$); $3.02$ (sept, 4 H, CH(CH$_3$)$_2$); $7.19$-$7.27$ (m, 6 H, CH$_{\text{arom}}$); $7.69$ (d, 2 H, CH$_{\text{pyr}}$); $8.52$ (t, 1 H, CH$_{\text{pyr}}$)) and their integration ratio unambiguously confirmed the formation of $\text{I}$.

Complex $\text{V}$ was completely un-reactive towards hexamethydisilane (Me$_6$Si$_2$) at room temperature. In the reaction of $\text{V}$ with triethylsilane (Et$_3$SiH), only a mixture of different unknown compounds was observed with no hydride resonance in the expected region in the $^1\text{H}-\text{NMR}$ spectrum (eq. 2.25).

\begin{align*}
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{Pr}^i \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Pr}^i \\
\end{array}
\quad \begin{array}{c}
\text{Pr}^i \\
\text{Pr}^i \\
\text{Pr}^i \\
\text{Pr}^i \\
\end{array}
\quad 1/2 \text{Me}_6\text{Si}_2, \text{THF} \\
\quad \text{Pr}^i \\
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{Pr}^i \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Pr}^i \\
\end{array}
\quad \begin{array}{c}
\text{Pr}^i \\
\text{Pr}^i \\
\text{Pr}^i \\
\text{Pr}^i \\
\end{array}
\quad \text{Et}_3\text{SiH} \\
\quad \text{Pr}^i \\
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{Pr}^i \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{Pr}^i \\
\end{array}
\quad \begin{array}{c}
\text{Pr}^i \\
\text{Pr}^i \\
\text{Pr}^i \\
\text{Pr}^i \\
\end{array}
\quad \text{Et}_3\text{SiH} \\
\quad \text{- (Et}_3\text{Si}_2 \text{)} \\
\end{align*}
2.5.1 The formation of the Rh(I) azido complex

Rh-imido complexes are of general interest, since they are isoelectronic to the related oxo ligand. The focus of this section will be to describe attempts to isolate a Rh(II) imido complex. As a preparative route to the desired Rh(II) imido complex, trimethylsilyl azide and adamantyl-1-azide have been used. According to the literature, the facile Si-N cleavage and elimination of N\textsubscript{2} has been used as a successful method in synthesis of organic imides and imines.\textsuperscript{104}

However, in this case, addition of one equivalent of Me\textsubscript{3}SiN\textsubscript{3} to a THF solution of complex V resulted in the formation of the green Rh(I) azido complex 15 in quantitative yield based on starting material 1 (eq. 2.26).

\[
\begin{align*}
\text{V} & \quad \xrightarrow{\text{Me}_3\text{SiN}_3, \text{THF}} \quad \textbf{15} \\
\text{Me}_3\text{SiN}_3, \text{THF} & \quad -1/2\text{Me}_6\text{Si}_2
\end{align*}
\]

The loss of hexamethyldisilane was confirmed by \textsuperscript{1}H-NMR spectroscopy of the transferred volatiles from the reaction mixture in THF-d\textsubscript{8}. A singlet peak at \(\delta = 0.04\) was observed and compared to a standard reference.

The IR spectrum of complex 15 in toluene showed a strong characteristic absorption band at \(\nu = 2031\) cm\textsuperscript{-1} (Fig. 2.16 left). This band is assigned to the \(\nu_{\text{as}}\) stretching frequency of the coordinated azido ligand. The expected \(\nu_s\) band for the azido ligand was not detected. This was also reported by Werner et al. for [Rh\textsuperscript{3}(Pr\textsubscript{3}P\textsubscript{2})(C\textsubscript{2}CPh\textsubscript{2})N\textsubscript{3}] (\(\nu_{\text{as}} = 2050\) cm\textsuperscript{-1}).\textsuperscript{105}

The UV-Vis spectrum of 15 in THF revealed three bands, at 474 nm (strong intensity) and at 615 and 676 nm (weak intensity) (Fig. 2.16 right).
Fig. 2.16 IR and UV/Vis spectra of complex 15 recorded at RT.

Crystals of 15 suitable for X-ray crystal structure analysis were obtained from a THF/pentane solution.

Fig. 2.17 ORTEP plot of complex 15 with 50% probability ellipsoids (hydrogen atoms were omitted for clarity).
Complex 15 adopts a square planar coordination with the sum of angles around Rh center equaling 360°. The azido ligand N4-N5-N6 displays an angle of 175.0(1)°. The angle Rh1-N4-N5 of 132.2(7)° suggests sp² hybridisation of nitrogen atom N4, while the bond distances N4-N5 (1.204(1) Å) and N5-N6 (1.159(1) Å) describe nitrogen atom N5 as sp² hybridised.

As displayed in Figure 2.17, the molecule has an approximate Cs symmetry in the solid state. However, the integration ratio between the methyl groups on the ketimine and phenyl rings, in the (time averaged) ¹H-NMR spectrum (in THF-d₈) at RT, is 1:2. This indicates C₂ᵥ symmetry of 15 in the solution.

To address this point, DFT calculations on a model complex 15a were performed. The geometry of the ground state (S=0) has Cs symmetry and a bent conformation of the azido ligand. The azido ligand can rotate fast around the Rh-N bond or it can move as a “windshield wiper” going through a linear structure, which could explain the observed C₂ᵥ symmetry (Fig. 2.18). Both suggested processes are much faster than the NMR time scale.
The linear structure was found to be a transition state, with the energy barrier of approximately 5 kcal/mol. The Walsh diagram (displayed in Fig. 2.19) shows an increase in energy by ~1 kcal/mol when angle $\alpha$ was increased by 10°. Since the energy barrier is so small, the calculation related to the rotation around the Rh-N bond were not performed.

Further, calculated bond distances for the model complex (B3LYP, LACVP** basis set) are in good agreement with those found in the X-ray structure analysis. This is the best illustrated with N4-N5 = 1.217 Å (1.204(1) Å) and N5-N6 = 1.156 Å (1.159(1) Å) bond distances.
2.5.2 The reaction of V with adamantyl-1-azide

Addition of one equivalent of adamantyl-1-azide (AdN₃) to a THF solution of the radical complex V at room temperature resulted in the evolution of gas bubbles (presumably N₂) accompanied by a color change from violet to burgundy to yield complex VI as a plausible product (eq. 2.27).

\[ \text{R=Me, iPr} \]
\[ \text{R'=H, t-Bu} \]

The UV-Vis spectrum of VI in THF showed two bands at 465 nm and 520 nm. In the \(^1\)H-NMR spectrum (THF-d₈), broad peaks at δ = 4.3 and 7.2 ppm were observed, indicating the presence of a paramagnetic compound, most likely a Rh(II) species. A group of resonances at δ = 1.1 ppm were assigned to the adamantyl protons. Fast relaxation of the unpaired electron does not affect significantly adamantyl moiety since it is further away (Fermie and through space coupling decreases with the increase in distance (~1/r² and 1/r³)). Therefore, the observed peaks were not broad. The EPR spectroscopy reveals a sharp signal with g = 1.997 (3500 G) at RT (Fig. 2.20). Measurements at low temperature showed only minor splitting.

![EPR spectra of complex VI](image)

**Fig. 2.20** EPR spectra of complex VI.
In the literature p-tolyl azide or adamantyl azide have been used to generate imido complexes. Meyer et al. described the formation of the d^6 low spin (S=0) Co(III) imido complex, supported by a tris-carbene ligand, using p-tolyl azide.\(^{106}\) An open shell Co(III) imido complex (S=1) was obtained with a Tp ligand system using adamantyl azide, as described by Theopold et al.\(^{107}\) High reactivity of the β-diketiminato Co(I) arene complex towards organic azides and the formation of diverse imido complexes have been described by Warren et al.\(^ {108}\)

### 2.5.3 The activation of dinitrogen with complex V

Dinitrogen is inert to reactions due to its low polarity and strong triple bond. In comparison to the isoelectronic CO ligand, chemistry of dinitrogen is less well developed owing to its weak σ donor and poor π acceptor characteristics. Depending on the metal, oxidation state and the neighboring ligands, dinitrogen can be bonded to the metal center in different ways. For example, it can bind to the metal in end-on or side-on mode, forming mono or dinuclear complexes.\(^ {109}\)

Dinitrogen complexes can be obtained by displacement of weakly coordinated ligands. They can also be prepared by reduction of metal complexes and formation of low-valent metal center that can activate and bind N\(_2\). It is also possible, that during the reaction a vacant site is formed on the metal center where N\(_2\) may coordinate.\(^ {109}\) As it will be described in this part, the activation of dinitrogen with complex V has been accomplished.

**Dinuclear dinitrogen complex 16**

When the tentative radical violet complex V, with the methyl groups on the aryl substituents was exposed to a nitrogen atmosphere, the color immediately changed from violet to dark brown and complex 16 is formed in quantitative yield (eq. 2.28). Complex 16 can be independently synthesized by the reduction of Rh(I) chloro or methoxo complex with Na/Hg under N\(_2\) atmosphere. The synthesis and characterization of complex 16 as well as magnetic properties have already been described by Nückel.\(^ {47}\)
Both metal centers in complex 16 have a formal Rh(0) oxidation state. According to the crystal structure analysis, the N-N bond in complex 16 is 1.129(7) Å, slightly elongated in comparison to free N₂ (1.0975 Å). The elongation of the N-N bond is often related with the reactivity of dinitrogen complexes (*vide infra*).

Complex 16 reacts with chlorinated solvents such as dichloromethane and 1,2-dichloroethane forming the complex 1 in quantitative yield (eq. 2.29). The formation of 1 was unambiguously confirmed by ¹H-NMR spectroscopy in CD₂Cl₂ and compared with reference.

The reaction between complex 16 and two equivalents of methyl-triflate leads to the formation of the Rh (I) triflate complex 9 (eq. 2.30).
The $^1$H-NMR analysis of the transferred volatiles (in THF-d$_8$) revealed a singlet peak at $\delta = 2.94$ ppm. Based on the $^1$H-NMR spectrum, the formation of Me$_2$N$_2$ as a side product is proposed.\textsuperscript{110, 111} The chemical shift for Me$_2$N$_2$ reported in the literature was found at $\delta = 3.76$ ppm in CDCl$_3$ and $\delta = 2.84$ ppm in D$_2$O.\textsuperscript{112} (No reference was found for THF-d$_8$). Further supporting evidence was obtained by GC-MS of the volatiles displaying a peak at 58 m/z as expected for N$_2$Me$_2^{+*}$.

**Mononuclear dinitrogen complex 17**

When the violet complex $V$ with ortho isopropyl aryl substituents was exposed to N$_2$ atmosphere the color changed to brown and the mononuclear dinitrogen complex 17 was formed in quantitative yield (eq. 2.31). Alternatively, complex 17 can be obtained by reduction of the chloro complex with Na/Hg under N$_2$ atmosphere. To the best of our knowledge, this is the first example of a mononuclear Rh(0) dinitrogen complex. The cationic cobalt(I) complex was reported by Gibson et al.\textsuperscript{113}

\[
\begin{array}{c}
\text{N}
\end{array} \begin{array}{c}
\text{N}
\end{array} \begin{array}{c}
\text{Rh}^*
\end{array} \text{N}_2
\]

Based on NMR and EPR spectroscopy, complex 17 is paramagnetic with the formal oxidation state of (0) for Rh center. In the $^1$H-NMR spectrum in C$_6$D$_6$, broad peaks typical for paramagnetic compounds were detected at $\delta = 2.28$, 3.55 and 5.60 ppm. The IR spectrum in toluene revealed a N-N stretching frequency at $\nu = 2139$ cm$^{-1}$ (Fig. 2.21). A small shoulder at $\nu = 2101$ cm$^{-1}$ presumably originates from the solvent.
According to the IR spectrum, it can be concluded that there is no enhanced back bonding to the N₂ ligand. The observed frequency at $\nu_{\text{NN}} = 2139 \text{ cm}^{-1}$ reveals that the N₂ molecule is polarized but still retains its triple bond character (free N₂ is IR inactive, whilst in the Raman spectrum displays a frequency at $\nu_{\text{NN}} = 2331 \text{ cm}^{-1}$).\textsuperscript{114}

Crystals suitable for an X-ray structure analysis were obtained from a concentrated toluene solution of 17 at –35 °C. The molecular representation of 17 and selected bond distances and angles are displayed in Figure 2.22 and Table 2.6.

**Fig. 2.21** IR spectrum of complex 17 in toluene (*– toluene).

**Fig. 2.22** ORTEP plot of complex 17 with 50% probability ellipsoids (hydrogen atoms were omitted for clarity).
Table 2.6 Selected bond lengths [Å] and angles [°] for complex 17.

<table>
<thead>
<tr>
<th>Bond Description</th>
<th>Bond Length [Å]</th>
<th>Bond Description</th>
<th>Bond Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-N1</td>
<td>1.914(1)</td>
<td>Rh1-N2</td>
<td>2.011(1)</td>
</tr>
<tr>
<td>Rh1-N4</td>
<td>1.950(2)</td>
<td>N4-N5</td>
<td>1.087(3)</td>
</tr>
<tr>
<td>N1-Rh1-N4</td>
<td>179.3(1)</td>
<td>Rh1-N4-N5</td>
<td>178.8(3)</td>
</tr>
<tr>
<td>N1-Rh1-N2</td>
<td>79.55(7)</td>
<td>N1-Rh1-N3</td>
<td>79.05(7)</td>
</tr>
<tr>
<td>N2-Rh1-N3</td>
<td>158.6(7)</td>
<td>N4-Rh1-N2</td>
<td>100.6(8)</td>
</tr>
<tr>
<td>N4-Rh1-N3</td>
<td>100.8(8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The geometry of complex 17 at the Rh center is square planar with the sum of bond angles equaling 360°. The N₂ ligand completes the fourth coordination site of the N1-N2-Rh1-N3 plane. The molecule adopts approximate C₂ᵥ symmetry. The N1-Rh1-N4 angle is 179.3(1)°. The distance between N4-N5 bond is 1.087(3) Å and it is comparable with the N-N distance in free N₂ (1.0975 Å). The dinitrogen distance in the cationic cobalt system is 1.112(6) Å.¹¹³

**EPR spectroscopy and DFT calculations**

The EPR spectrum revealed a sharp signal at room temperature measurement with g = 1.999 (3500 G). However, the unpaired electron did not show hyperfine splitting either with the¹⁰³Rh metal center (I=1/2) or ¹⁴N atoms (I = 1). At low temperature measurements (100 K), a small shoulder is observed. No hyperfine coupling for either complex 16 and 17 was detected (Fig. 2.23).

![EPR spectra of complex 17 at RT and 100 K.](image)

**Fig. 2.23** EPR spectra of complex 17 at RT and 100 K.
According to DFT calculations, the spin density of the electron is delocalized within the pyridine ligand (Fig. 2.24-left). This could be a possible explanation why hyperfine splitting was not observed in the EPR experiment.

Calculated distances for the model compound 17a (B3LYP, LACVP** basis set) are in good agreement with those found in the X-ray crystal analysis (Fig. 2.24-right).

Fig. 2.24 Calculated bond distances and spin density for the model complex 17a.

In this part, it was shown that the activation of N₂ is feasible with very reactive radical complex V. The reactivity of the isolated complexes 16 and 17 with different reagents (such as H₂, O₂, etc.) will be of great interest in the future.
3 C-H activation by Rh, Ir(I) square planar complexes – mechanistic aspects

3.1 Improved synthesis of Ir(I) methyl complex

It has been previously shown that the methyl complex 18 can be synthesized from complex 4 by the addition of AlMe₃. However, the trimethoxy aluminium Al(OMe)₃ side product formed is difficult to remove from the reaction mixture. If traces of Al(OMe)₃ remain in the solution together with complex 18, for a prolonged period of time, a mixture of unknown products is obtained. Therefore, an improved synthesis of 18, employing the alternative methylating agent, ZnMe₂, was performed. Complex 18 can be prepared by the addition of ZnMe₂ to a THF solution of complex 4 or complex 6 in approximately 70 % yield for both reactions (eq. 3.1).

\[
\begin{align*}
\text{Ir} - \text{OMe} & \quad \xrightarrow{(1/3 \text{AlMe}_3, 1/2 \text{ZnMe}_2, \text{THF})} \quad \text{Ir} - \text{Me} \\
4 & \quad \text{Ir} - \text{OH} & \quad \text{Ir} - \text{OMe} & \quad \xrightarrow{\text{ZnMe}_2, \text{toluene}, \text{ZnO, CH}_4} \quad \text{Ir} - \text{OH}
\end{align*}
\]

(3.1)

The insoluble byproducts (Zn(OMe)₂ and ZnO) can be easily removed by filtration. However, the stability of 18 in diethyl ether or THF solution even at the lower temperatures (−35 °C) is still a great problem. Interestingly, by using this route (especially from complex 6), decomposition of complex 18 is much slower than in the previously reported synthesis, suggesting that less side products remained in the solution.

3.2 C-H activation of benzene

The facile intermolecular C-H activation of complex 18 in benzene under ambient temperature leads quantitatively to the phenyl complex 19 and methane (eq. 3.2). This reaction, as well as the DFT analysis of the proposed mechanism were previously reported in some detail by our group.³⁶
The proposed mechanism for this reaction is anticipated to proceed via a two-step mechanism, via oxidative addition followed by C-H reductive elimination rather than σ-bond metathesis (Fig. 3.1). The oxidative addition pathway leads to an octahedral Ir(III) intermediate, with a “square-pyramidal” transition state.

The crucial step in the C-H activation mechanism is the bending of the Ir-Me bond out of the metal-NNN ligand plane. This bending process in 18 requires energy of approximately 12 kcal/mol for \( \alpha = 70^\circ \). However, if the ketimine methyl groups are replaced with CF\(_3\) groups, enhancing the \( \pi \)-acceptor properties of the ligand, the bent over the square-planar structure is preferred (Fig. 3.2).

**Fig. 3.1** The proposed two-step mechanism for C-H activation process.\(^{36}\)
Fig. 3.2 Calculated minimum for model complex 18_{CF3}.

To probe experimentally, the synthesis of methyl complex 18_{CF3} was attempted. The ligand was synthesized according to the procedure of Brookhart et al. The first step of ligand synthesis involves the sequential treatment of 2,6-dibromopyridine with n-BuLi and methyltrifluoroacetate at −90 °C and the formation of 2,6-bis(trifluoroacetyl)pyridine. The following step is a simple condensation reaction between the diketopyridine derivative and 2,4,6-trimethylaniline (eq. 3.3).

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\uparrow \quad \downarrow & \quad \uparrow \\
\text{N} & \quad \text{N} \\
\text{CF}_3 & \quad \text{CF}_3 \\
\text{N} & \quad \text{N} \\
\text{F}_3 & \quad \text{C} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{2 n-BuLi,} & \quad 2\text{CF}_3\text{CO}_{2}\text{Me} \\
\text{THF/Et}_2\text{O} & \quad -90^\circ\text{C} \\
\text{N} & \quad \text{CF}_3 \\
\text{F}_3 & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{CSA} & \quad \text{toluene} \\
\text{NH}_2 & \quad \text{NH}_2 \\
\text{2} & \quad \text{2} \\
\text{N} & \quad \text{N} \\
\text{CF}_3 & \quad \text{CF}_3 \\
\text{50}\% & \quad \text{(3.3)}
\end{align*}
\]

The syntheses of the chloro and methyl complexes (2a and 18_{CF3}) according to eq. 3.4 were attempted.

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{N} \\
\text{Me} & \quad \text{Me} \\
\text{F}_3 & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{Ir} & \quad \text{Ir} \\
\text{Cl} & \quad \text{Cl} \\
\text{F}_3 & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{Ir} & \quad \text{Ir} \\
\text{Me} & \quad \text{Me} \\
\text{F}_3 & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{Ir} & \quad \text{Ir} \\
\text{Cl} & \quad \text{Cl} \\
\text{F}_3 & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{Ir} & \quad \text{Ir} \\
\text{Me} & \quad \text{Me} \\
\text{F}_3 & \quad \text{C} \\
\end{align*}
\]

According to the $^1$H-NMR in C$_6$D$_6$, no reaction proceeds when the CF$_3$-ligand and [Ir$_2$(C$_2$H$_4$)$_4$(µ-Cl)$_2$] was mixed together and heated up to 150 °C over a period of 6 days.
In one step reaction, by using freshly prepared $[\mu$-Me)$_2$Ir$_2$(COE)$_4$ and CF$_3$-ligand (in THF) at −78 °C and warming up the reaction mixture gradually to room temperature (eq. 3.4), the isolation of methyl complex 18$_{\text{CF}_3}$ failed.

The unsuccessful complexation could be traced to strongly reduced $\sigma$-donor properties of the diimine ligand, which originate from a very strong electron withdrawing nature of the CF$_3$ groups.

**Low temperature NMR studies**

In order to learn more about the bending process of the Ir methyl moiety, low temperature NMR studies were performed (Fig. 3.3).

![Fig. 3.3 Temperature dependent NMR of complex 18.](image)

The $^1$H-NMR of the Ir methyl group in complex 18 shows an unusual down field shift at 6.91 ppm. As displayed in Figure 3.3, by decreasing the temperature, the Ir methyl signal is shifted towards higher field (6.91 − 6.76 ppm). The signals (doublet and triplet) from the pyridine ring are slightly shifted towards lower field. As previously described, complex 18 has
a very shallow potential for the “bending process” of the methyl group. This low energy barrier may provide a possible explanation for the observed strong dependence in the low temperature NMR study. The ability of phenyl rings to induce a ring-current effect and shift the protons towards higher field is similar to the previous observations made by Crabtree et al.\textsuperscript{117}

### 3.2.1 Evidences for Ir(III) intermediate

In the context of the aforementioned C-H activation process, support for the proposed mechanism with an Ir(III) intermediate was obtained by the reaction of the iridium phenyl complex \textbf{19} with excess hydrogen. The reaction leads to the formation of the trihydride complex \textbf{20a} (eq. 3.5).

The trihydride peak was observed as a broad “triplet” at −8.76 ppm in toluene-d\textsubscript{8}. The integration ratio between the proton in the \textit{para} position on the pyridine ring and the trihydride peak is approximately 1:3 as required. The broadness of the triplet is attributed to the fast exchange process between the hydride ligands. It is proposed that complex \textbf{20a} is in equilibrium with the dihydrogen hydride complex \textbf{20b}, which will be discussed below.

#### Low temperature NMR studies

In an attempt to gain a better insight into the dynamic processes of the hydride ligands, the low temperature NMR behavior of complex \textbf{20a} was studied. NMR investigations between 313 and 183 K in toluene demonstrated a classical (incoherent) exchange process (Fig. 3.4).
Fig. 3.4 $^1$H-NMR spectra of the hydride resonances at different temperatures.

As the temperature was decreased, a broadening of the signal at $-8.76$ ppm was observed. Also, the integral, starting from 233 K, became smaller (in comparison to the *para* proton from the pyridine ring). The value is reduced by half at 193 K. Starting from 223 K, (Fig. 3.3 right) peaks at $-11.3$ and $-13.1$ ppm were observed with increasing signal intensity at lower temperatures. Unfortunately the shapes of the peaks do not appear as a doublet and a triplet, which might be expected for the trihydride complex 20a. However, the integration ratio of these newly observed signals at 183 K is approximately 2:1.

The unsymmetrical shape of the triplet and its further broadening, when the temperature is decreased, did not allow for the coupling constants in complex 20a to be measured.

According to the overall data from the low temperature NMR study, it is proposed that at room temperature, equilibrium between 20a and 20b is present. Fast exchange between the hydride ligands resulted in the broadness of the “triplet” peak at $-8.76$ ppm. Upon decreasing the temperature, the exchange process (between the hydride ligands) slows down and at 183 K the predominantly structure observed is 20a.
According to the literature, if the barrier is too low (between dihydrogen and hydride complexes), fluxional behavior (incoherent process) will be observed rather than the coherent exchange process \( \textit{vide infra} \). A barrier between 8.7 and 16.7 kcal/mol must be present in order that two species can be observed by NMR.

**\( T_1 \) measurements**

The determination of relaxation time for the hydride resonances of complex 20a was carried out using the standard inversion recovery method. The obtained \( T_1 \) value was 276 ms at room temperature (400 MHz), confirming the presence of a classical trihydride complex. Unfortunately, due to technical problems of the NMR spectrometer, \( T_{1\text{min}} \) measurements were not performed, thus it was not possible to show the existence of a dihydrogen hydride species 20b.

![Graph](image)

**Fig. 3.5** \( T_1 \) for complex 20.

Short \( T_{1\text{min}} \) values (< 80 ms) are usually diagnostic to the presence of dihydrogen bound to the metal center, such as in the case of Ir(PCy\(_3\))\(_2\)H\(_6\). In contrast, larger \( T_{1\text{min}} \) values (> 150 ms) imply that the relaxation time is much slower, the distance between the hydrogen nuclei is larger and that classical hydrides are present.
**DFT calculations**

DFT calculations have been used extensively in order to provide a fundamental understanding of both structure and bonding, as well as the dynamic processes in dihydrogen complexes.\textsuperscript{122, 126} DFT calculations with the BP-86 functional were therefore performed on complex \textit{20} (Fig. 3.6).\textsuperscript{127} The distance between the hydrogen atoms was varied from 1 Å (\(\eta^2\)-dihydrogen hydride complex) up to 1.7 Å (trihydride complex).

![Energy diagram](image)

**Fig. 3.6** Energy diagram for the conversion of the complex \textit{20a} to \textit{20b} by varying the H-H distance (DFT model, BP-86; basis set: TZVP (for Ir) and SV(P) (for the rest of atoms)).

The minimum for complex \textit{20} was found to be the trihydride complex \textit{20a}, lying 2 kcal/mol below the \(\eta^2\)-dihydrogen hydride complex \textit{20b}. This energy difference between the two structures is very small, which is the reason why \textit{20a} and \textit{20b} could not be distinguished by NMR spectroscopy.

Also, molecular dynamics calculations were undertaken for complex \textit{20a}. The intramolecular H-H site exchange between hydrogen atoms is displayed in Figure 3.7.
Fig. 3.7 H-H site exchange in complex 20a.

The extrusion of dihydrogen from the trihydride (model) complex 20c was calculated (eq. 3.6).

$$\Delta E_{\text{calc}} = +21 \text{ kcal/mol} \quad (3.6)$$

It was found to be a thermodynamically unfavorable process (+ 21 kcal/mol). If an entropical contribution (∼ 10 kcal/mol at RT for the formation of dihydrogen and monohydride complex 20c) is also considered, then $\Delta G$ for the overall process is in the order of 10 kcal/mol. This encountered problem may be the reason why the crystals of complex 20a were not obtained.

### 3.2.2 Si-H activation process

Further evidence for a two-step C-H activation mechanism was provided by low temperature NMR studies of complex 4 for the Si-H activation process in trimethylsilane. It is assumed that upon the addition of Me₃SiH to complex 4, Ir(III) intermediate 21a is formed (eq. 3.7).
The reaction was carried out on the NMR scale in THF-d$_8$. Excess of Me$_3$SiH was condensed to a frozen solution of complex 4, the tube sealed and then allowed to warm up to −80 °C.

The $^1$H-NMR spectrum of the reaction mixture was monitored starting from −80 °C. Upon warming up to −59 °C, two hydride resonances at −28.30 and −11.50 ppm started to grow in. Both of the signals appeared as singlets and no $^{29}$Si satellites were detected. The $^{29}$Si satellites have been observed in cases of $\eta^2$-silane complexes.$^{128, 129}$ Therefore, it is anticipated that octahedral intermediate isomers (cis/trans) 21a and 21b are present (eq. 3.8).

![Diagram](image)

Upon warming to −50 °C, the peak at $\delta = −28.30$ ppm disappeared and the intensity of the hydride resonance at $\delta = −11.50$ ppm increased. At −35 °C, another singlet peak in the hydride region ($\delta = −6.20$ ppm) begins to appear while the other peak (at $\delta = −11.50$ ppm) starts to decrease in intensity. This newly observed hydride peak has been tentatively assigned to the Ir-H complex 20c. An additional resonance at $\delta = 3.36$ ppm, later assigned to free Me$_3$SiOMe*, appeared. The Ir-OMe peak at $\delta = 4.67$ ppm decreased in intensity upon warming up the reaction mixture with a small shift (~ 0.1 ppm) towards lower field. Finally, upon reaching room temperature only the hydride resonance assigned to the monohydride (at $\delta = −6.10$ ppm) remained. Unfortunately, after 1-2 hours at room temperature, the postulated monohydride complex decomposed to a mixture of unknown products (a broad peak at $\delta = 18$ ppm was detected, similar to the one observed for the dinitrogen complex 16; N$_2$ residue originates from THF).

The same reaction with trimethylsilane was investigated for the Rh analogue 3 (eq. 3.9).

---

* $^1$H-NMR of the Me$_3$SiOMe: in THF-d$_8$ $\delta = 0.06$ ppm (Me$_3$SiOMe), 3.36 ppm (Me$_3$SiOMe); in C$_6$D$_6$ $\delta = 0.06$ ppm (Me$_3$SiOMe), 3.24 ppm (Me$_3$SiOMe).
The mixture of 3 and Me₃SiH was gradually allowed to warm up (from the frozen solution to room temperature) and the ¹H-NMR spectra were recorded over a period of 30 minutes. The reaction proceeded rapidly and broad signals at δ = 5 ppm and 21 ppm were detected after only 5 min. No hydride peak was detected during the reaction. By comparing the observed, characteristic broad resonances (at δ = 5.01, 5.26, 17.2 and 20.2 ppm), the formation of the dinuclear Rh dinitrogen complex 16 was confirmed. The peak at δ = 0.58 and 3.24 ppm was assigned to free Me₃SiOMe.

Based on the ¹H-NMR experiments, the mechanism presented in Figure 3.8 for the Si-H activation is proposed. DFT calculations on the model complex (B3LYP, LACVP** basis set), excluding the aryl substituents and the ketimine methyl groups, were performed.

Fig. 3.8 The proposed mechanism for Si-H activation.
The oxidative addition of Me$_3$SiH to 4a leads initially to the octahedral intermediate 21a, which is 8 kcal/mol higher in energy. The second step of the reaction involves reductive elimination of Me$_3$SiOMe, which is thermodynamically favourable by 14 kcal/mol relative to the reactants (4a + Me$_3$SiH). The transition state (TS) for the reductive elimination of Me$_3$SiOMe is 12 kcal/mol uphill starting from 4a and silane.

IRC calculations were also carried out (B3LYP, LACVP** basis set) starting at the saddle point to check the connections between the transition state, intermediate and the final product. As expected, the forward step leads to the product (20c + Me$_3$SiOMe) and reverse to the intermediate (21a).

DFT calculations for the reductive elimination of methanol from the intermediate 21b, were also performed. The reaction is uphill by 13 kcal/mol in comparison to the reactants, presumably because of the formation of weaker Ir-Si bond (compared with 20c Ir-H).

### 3.3 Ir, Rh(I) fluorides – precursors for the hydride complexes

It has been shown that fluoride complexes provide a convenient synthetic route to hydride complexes.$^{130}$ With respect to the mechanistic studies related to C-H activation, suitable synthetic routes to the rhodium and iridium hydrides via the appropriate fluoride complexes were investigated. It is also believed that a rhodium hydride compounds would provide a good starting materials for the synthesis of a rhodium hydroperoxo complex, which is anticipated to be one of the intermediates in catalytic epoxidation of ethylene observed in previous studies.$^{47}$ The F$^-$ ligand is classified as a strong π-donor. It was expected that a pyridine diimine ligand could stabilize the Ir(Rh)-F bond due to its good π-acceptor abilities, as in the case for methoxo ligand in complex 4.$^{44}$

In the last decade, adequately characterized fluoro complexes started to appear in the literature.$^{131, 132, 133, 134}$ The difficulties involved in isolating pure metal-fluoro compounds arises from the great affinity of the fluoride anion towards protic reagents. Often, the target compounds are contaminated with hydroxide or bifluoride moiety. Another obstacle to isolate metal fluoride complexes is the possible reactions with glassware. Often plastic containers are used to overcome this problem. Elemental fluorine and hydrogen fluoride are not convenient reagents in
the metal fluoride synthesis owing to difficulty in handling and safety. However, there are quite a few fluorinating reagents available (mostly inorganic, i.e. \( \text{XeF}_2 \) and organic salts), which are more suitable.

In this part, the synthesis and characterization of Rh and Ir(I) fluorides, using the previously successfully employed\textsuperscript{135} tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) and tetrabutylammonium fluoride (TBAF) will be described.

When the Rh or Ir(I) triflate complex, dissolved in THF was added to solutions of TASF in THF, the color changed from brown to green and provided complex 22 or 23 in 60% yield (eq. 3.10). Trimethylsilylfluoride is precipitated from the solution with pentane and removed by filtration. Both complexes co-crystallize with one molecule of tris-(dimethylamino)sulfonium. The possible explanation for this phenomenon (co-crystallization) will be discussed later in this chapter.

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{M} & \quad \text{O} \\
\text{N} & \quad \text{M} \quad \text{F} \\
\text{N} & \quad \text{F} \\
\text{N} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{−} & \quad \text{Me}_3\text{SiF}^+ \\
\text{OTf}^- & \quad \text{(3.10)} \\
\end{align*}
\]

\( \text{M} = \text{Rh} \quad 9 \quad \text{Ir} \quad 10 \)

\( \text{Rh} \quad 22 \quad \text{Ir} \quad 23 \)

**Rh(I) fluoride complex - 22**

In the \( ^1\text{H}-\text{NMR} \) spectrum of the aliphatic region (in THF-\( \text{d}_8 \)), three singlet peaks were observed at \( \delta = 1.64, 2.14 \) and 2.76 ppm with an integration ratio 1:2:3. These resonances were assigned to the methyl groups on the ketimine ligand, phenyl rings and sulfonium cation. A multiplet at \( \delta = 7.05 \) ppm, doublet at \( \delta = 7.85 \) ppm and a triplet at \( \delta = 8.49 \) ppm assigned to the aromatic protons on the phenyl and pyridine ring were also observed.

According to the \( ^19\text{F}-\text{NMR} \) spectrum of complex 22 in THF-\( \text{d}_8 \), only singlet peaks at \( \delta = -158 \) ppm and \( -80 \) ppm were detected. The latter was assigned to the triflate anion. For the
rhodium fluoride complex a doublet in the $^{19}$F-NMR due to the direct $^1J_{RhF}$ coupling would be expected. In the literature there is also an example of RhF(COD)(PPh$_3$) where coupling between Rh-F was not observed in the $^{19}$F-NMR even at $-90^\circ$C presumably due to the fast Rh-F dissociation.\textsuperscript{136} This could also apply for complex 22.

Crystals suitable for an X-ray structure analysis were obtained from a THF/pentane solution (Fig. 3.9).

![Fig. 3.9 ORTEP plot of 22 shown at 50% thermal ellipsoid probability (hydrogen atoms and triflate anion were omitted for clarity).](image)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-F1</td>
<td>2.000(5)</td>
<td>Rh1-N1</td>
<td>1.854(6)</td>
</tr>
<tr>
<td>Rh1-N3</td>
<td>2.015(6)</td>
<td>S1-N4</td>
<td>1.626(6)</td>
</tr>
<tr>
<td>S1-N6</td>
<td>1.697(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1-Rh1-N2</td>
<td>99.9(2)</td>
<td>F1-Rh1-N3</td>
<td>100.3(2)</td>
</tr>
<tr>
<td>N1-Rh1-N3</td>
<td>80.4(2)</td>
<td>N2-Rh1-N1</td>
<td>79.3(2)</td>
</tr>
</tbody>
</table>

Table 3.1 Selected bond lengths [Å] and angles [°] for complex 22.
Complex 22 is isostructural with complex 23. It crystallizes in an orthorhombic Pbca space group. The bond distance Rh1-N1 is 1.854(6) Å, a significantly shorter than for chloro analogue (Rh-N1 = 1.889(2) Å). The N-S bond distances are in agreement to the literature values for a sulfonium moiety. A possible explanation why complexes 22 and 23 co-crystallize with a molecule of sulfonium triflate will be discussed later (vide infra).

**Ir(I) fluoride complex – 23**

The $^1$H-NMR spectrum of 23 displays singlet peaks assigned to the methyl groups on the ketimine ($\delta = 1.01$ ppm), phenyl rings ($\delta = 1.98$ ppm) and sulfonium cation ($\delta = 2.73$ ppm) with an integration ratio 1:2:3.

In the $^{19}$F-NMR spectrum of 23 (in THF-d$_8$), besides the triflate peak at $\delta = -80$ ppm an additional peak at $\delta = -128$ ppm was found and was assigned to Ir-F ligand.

Crystals suitable for an X-ray diffraction of complex 23 were obtained from a THF/pentane (2:1) solution (Fig. 3.10). Selected bond distances and angles are given in the Table 3.2.

Fig. 3.10 ORTEP plot of complex 23 (hydrogen atoms and triflate anion are omitted for clarity).
Table 3.2 Selected bond lengths [Å] and angles [°] for complex 23.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
<th>Bond</th>
<th>Length</th>
<th>Bond</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-F1</td>
<td>1.983(5)</td>
<td>Ir1-N1</td>
<td>1.825(6)</td>
<td>S1-N5</td>
<td>1.611(9)</td>
</tr>
<tr>
<td>Ir1-N2</td>
<td>1.992(8)</td>
<td>Ir1-N3</td>
<td>1.998(9)</td>
<td>S1-N4</td>
<td>1.627(2)</td>
</tr>
<tr>
<td>S1-N6</td>
<td>1.699(9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1-Ir1-F1</td>
<td>177.5(4)</td>
<td>N2-Ir1-F1</td>
<td>100.4(3)</td>
<td>N3-Ir1-F1</td>
<td>100.5(4)</td>
</tr>
<tr>
<td>N2-Ir1-N1</td>
<td>78.9(4)</td>
<td>N1-Ir1-N3</td>
<td>80.3(4)</td>
<td>N2-Ir1-N3</td>
<td>159.1(4)</td>
</tr>
</tbody>
</table>

Complex 23 has a square planar geometry with the sum of the angles equaling 360°. The Ir-F distance is 1.983(5) Å, while the distance between Ir1-N1 = 1.825(6) Å is significantly shorter than in other iridium(I) complexes of this type (Table 3.3).\(^{47,44}\)

![HOMO of complex 23](image-url)

Fig. 3.11 HOMO of complex 23 (DFT, B3LYP hybrid, LACVP** basis set).
The aforementioned co-crystallization of the sulfonium triflate was of particular interest. A possible explanation for this behavior might be attributed to hydrogen bonding between the C-H···F atoms. The position of the protons on the tris-(dimethylamino)sulfonium cation were located in the difference Fourier map and were isotropically refined. As depicted in Figure 3.12, H···F1 distances are 2.43 Å and 2.15 Å, respectively. Both protons are only 0.62 Å (0.52 Å) above the IrNNF plane, whilst the sulphur atom is out of the plane by 2.32 Å. The H···F distances are in agreement with the values reported by Mews et al. between one of the axial fluoride from Me$_3$SiF$_2$ anion and protons from (Me$_2$N)$_2$CF$_3$S cation.$^{138}$ Other groups, such as Desiraju$^{139}$ and Scheiner$^{140}$ investigated hydrogen C-H···F bonding in fluorobenzenes and fluoromethanes and reported similar to CH···F distances.

According to the literature, hydride complexes can be obtained from fluoride complexes through reaction of the latter with organosilanes. The driving force is the formation of a very strong Si-F bond (approximately 159 kcal/mol)$^{141}$

The reactivity of complex 22 and 23 towards triethyilsilane was tested. However, neither the formation of a metal hydride nor Si-F bond was detected in the $^1$H and $^{19}$F-NMR experiment. The reaction did not take place probably because the fluoride is shielded by the sulfonium cation (eq. 3.11).
In another attempt to obtain rhodium and iridium fluoride complexes, tetrabutylammonium fluoride (TBAF) was used. It has been recently reported that TBAF exceeds the reactivity of other nucleophilic fluorinated reagents. Anhydrous TBAF has been synthesized from tetrabutylammonium cyanide and hexafluorobenzene at low temperature through nucleophilic aromatic substitution reaction.$^{142}$

When a cold THF solution of triflate complex 9 or 10 was added to a cold solution of freshly prepared TBAF in THF (−35 °C) and stirred for 1 hour at room temperature, complexes 24 or 25 were formed in 70 % yield (eq. 3.12).

Complexes 24 and 25 have been characterized by $^1$H and $^{19}$F-NMR spectroscopy. The $^1$H-NMR spectrum (in THF-d$_8$) of 24, 25 and 26 revealed the traces of tetrabutylammonium chloride, which could not be removed. Proton resonances of 24 and 25 are slightly shifted in the aliphatic region (0.1 ppm) when compared to the $^1$H-NMR of 22 and 23. The resonances of the aromatic region are on the same shift. The presence of doublet in $^{19}$F-NMR spectrum at δ = −151.5 ppm
with the coupling constant $^{1}J_{\text{RhF}} = 121 \, \text{Hz}$, confirms the formation of Rh-F bond in complexes 24 and 26. The peak at $\delta = -262.3 \, \text{ppm}$ ($^{19}$F-NMR) was assigned to the fluoride for complex 25, which is significantly shifted in comparison to complex 23. This observation could be attributed to the less shielded fluoro ligand in 25 leading to a shift towards higher fields in the $^{19}$F-NMR spectrum.

It is worth mentioning that metathesis of the chloro ligand (by fluoro ligand) in 1a could be also accomplished. In the cases with different substituents on the phenyl ligand, chloride could not be substituted with the fluoride via this route.

In order to obtain a mono-hydride complex, complex 24 and 26 were treated with excess hydrogen (eq. 3.13). The released HF was trapped with a base 1,8-bis-(dimethylamino)naphthalin, known as proton sponge. Since the reaction was not stoichiometrically controlled and hydrogen was used in excess, a mixture of mono and tri-hydride species were formed in the solution according to the $^{1}$H-NMR where several singlet peaks in the range from $-9$ to $-35 \, \text{ppm}$ were observed.

In order to use the formation of the strong Si-F bond (vide supra) as a driving force for the formation of Rh-H, trimethylsilane (Me$_3$SiH) was added to complex 26 (eq. 3.13). Trimethylsilane was prepared from Me$_3$SiCl by the reduction with LiAlH$_4$.\textsuperscript{143, 144} As Me$_3$SiH has a boiling point of $-10 \, \text{°C}$, it was treated as a gas and transferred to the THF-d$_8$ solution of complex 26 using a known volume bulb manometer. The color of the reaction mixture changed from green to violet and then brown.

A doublet at $\delta = -29.9 \, \text{ppm}$ in the $^{1}$H-NMR spectrum was observed and assigned to the hydride complex 20$_{\text{cRh}}$. In the $^{19}$F-NMR spectrum, the doublet from Rh-F coupling (at $\delta = -151.5 \, \text{ppm}$)
disappears and the singlet peak at $\delta = -158.4$ ppm assigned to Si-F appears. The Si-F resonance for Me$_3$Si-F can be compared with the literature value found at $\delta = -159$ ppm (Fig. 3.13).$^{145}$

Fig. 3.13 $^{19}$F-NMR before and after reaction of 26 with Me$_3$SiH.

Although, the obtained crystals of complex 20c$_{\text{Rh}}$ were not of good enough quality for the X-ray structure analysis, the NMR spectroscopy indicated that the formation of the Rh(I) hydride from the fluoride analogue is feasible.

The formation of the Rh(I) hydride species from Rh(I) fluoride was calculated for the model compounds 20c$_{\text{Rh}}$ and 26a at B3LYP/LACVP** level (Fig. 3.14).

Fig. 3.14 DFT calculations for the formation of 20c$_{\text{Rh}}$.

As depicted above, the formation of the hydride complex 20c$_{\text{Rh}}$ is thermodynamically favorable by 20 kcal/mol.
3.4 C-O reductive elimination

The formation of a C-O bond by reductive elimination is an important part in an alkane functionalization process. The final products are usually alcohols, amines, ethers and esters. Despite the great importance of this reaction in homogeneous catalysis\textsuperscript{24, 27} a limited number of the directly observed metal centered C-O bond formation reactions are known.\textsuperscript{146, 147, 148, 149, 150}

The reductive elimination from d\textsuperscript{6} octahedral complexes mostly proceeds via ligand dissociation and formation of five-coordinate intermediate prior to the actual reductive elimination step.\textsuperscript{151, 152, 153} The energy barriers for the C-O or C-C reductive elimination in square-pyramidal penta-coordinated systems are much smaller than the energy barriers for same process which occurs without the ligand loss, from the six-coordinated complexes. This process has been studied by Goldberg et al. for the Pt(IV) complexes.\textsuperscript{154, 155}

The C-O bond formation is one important part in the proposed catalytic cycle for methane functionalization (Chapter 1). Based on the DFT calculations for the Ir model complex (eq. 3.14), C-H bond addition, which is strongly thermodynamically favorable, leads to the hydroxy alkyl intermediate 27a. The second step involves reductive elimination of methanol, which leads to the formation of the cationic species 10a.

\[
\begin{align*}
\text{Ir}=\text{O} & \quad + \quad \text{H-CH}_3 \quad \xrightarrow{1,2-\text{C-H add.}} \quad \text{CH}_3 \quad \text{Ir}=\text{OH} \\
\text{(I)} & \quad \text{27a} & \quad \text{C-O red. elim.} & \quad -\text{MeOH} & \quad \text{Ir} \quad \text{+} & \quad \text{(10a)} \\
\text{−37 kcal/mol} & \quad & \quad & & & \quad \text{(3.14)}
\end{align*}
\]

In order to provide support for C-O reductive elimination of methanol via intermediate 27a (eq. 3.14), a low temperature NMR experiment of the reaction 3.15 was performed (\textit{vide infra}).

Addition of MeOTf to a toluene solution of 6 at room temperature leads to the fast and clean formation of complex 10 and methanol. To provide the evidence for intermediate 27, low temperature NMR experiment was performed.
The reaction shown in eq. 3.15 was monitored from –80 °C to 25 °C for 2 hours in toluene-d₈. During, the first 45 minutes, the temperature was held at –80 °C. Even after 2 minutes at –80 °C, three new singlet peaks appeared at δ = 2.60, 2.98 and 5.30 ppm. The resonances at δ = 2.60 (Ir-CH₃) and 5.30 ppm (OH-broad) were tentatively assigned to the intermediate species 27. When the reaction mixture was further warmed up, the intensity of peaks at 2.60 and 5.30 ppm decreased, while the peak at 2.98 ppm gained intensity. At –30 °C, of these three peaks the singlet resonance at δ = 2.98 ppm remained. This resonance was assigned to free methanol (¹H-NMR of MeOH in toluene-d₈: δ = 3 ppm).

In the ¹⁹F-NMR spectra (at –80 °C) three peaks are observed at: δ = –76.0 ppm assigned to the free MeOTf (¹H-NMR of MeOTf in toluene-d₈: δ = 3.03 ppm; ¹⁹F-NMR: δ = –76.1 ppm), δ = –79.2 ppm assigned to the intermediate 27 and δ = –80.0 ppm assigned to the triflate complex 8. After the reaction was completed, the solvent was evaporated. The ¹H and ¹⁹F-NMR spectra of the final product (in THF-d₈) unambiguously confirmed the formation of complex 10.

**Mechanistic aspects**

The highly nucleophilic character of d⁸-configured metal centers in the square planar coordination geometry is based on the ¹H-NMR experiment.²⁸ A nucleophilic attack on the carbon as the first step followed by reductive elimination of methanol is proposed. It was also observed in the ¹H-NMR study that the nucleophilic substitution step in MeOTf is significantly faster than the C-O reductive elimination of methanol. The presence of an intermediate provided further support for the proposed mechanism.
DFT calculations presented in Fig. 3.15 are concerned with the C-O reductive elimination part starting from the proposed intermediate 27a. The calculations were carried out at the B3LYP/LACVP** level in toluene.

Fig. 3.15 Reaction profile for the C-O reductive elimination of methanol from 27a.

The reductive elimination (27a → 10a) is exothermic with an energy difference of ~12 kcal/mol and a calculated energy barrier for this process of 10 kcal/mol. In the transition state TS, the C-Ir-O angle becomes more acute (starting from 100° in 27a to 50° in TS) with concomitant elongation of the Ir-Me bond. By decreasing the angle between the methyl group and the hydroxide, the C-O bond distance shortens and methanol is formed.

C-O bond formation is independently observed in the synthesis of the triflate complex 10 (Chapter 2.1.1). When 4 and 8 were stirred together dimethyl ether was formed (eq. 3.16).

\[
\text{[Ir]-OMe} + \text{[Ir]-OTf} \rightarrow \text{Me} \text{Me}_2\text{O} \rightarrow 2 \text{[Ir]-OTf} \quad (3.16)
\]
The mechanism proposed for the reaction according to eq. 3.16 was adopted from the C-C coupling reaction of 7 and Rh(I) methyl complex.  

In both cases (C-C or C-O bond formation), the methyl group on the Rh, Ir(III) centers has attributed an *electrophilic* character. To address this point, $^{13}$C labeled bistriflate complexes (7 and 8) were prepared and $^1$H-NMR spectra in CD$_2$Cl$_2$ were measured. The coupling constant ($^1J_{CH}$) of the methyl group, in complex 7 is $^1J_{CH} = 140$ Hz and 135 Hz in 8. According to the literature, polar substituents in alkanes (for example CH$_4$) influence on the coupling constant and hybridization of the carbon. Depending on the nature of the substituent, the carbon centers are more *electrophilic* or *nucleophilic*, which is determined by field-gradient factor $F$. As a result, by comparison to the literature values, it was proposed that carbon bonded to metal centers have an *electrophilic* character in complexes 7 and 8.

In addition, it is worth mentioning that the methyl group exhibits a strong *trans* influence. Therefore, the bond distances between the metal and the oxygen from the triflate group, in the apical position is elongated (Rh-O$_{ap}$ = 2.305(4) Å) in comparison to the Rh-O$_{eq}$ equatorial bond (2.093(3) Å). After spectroscopic (IR, $^{19}$F-NMR) and conductivity measurements, the triflate *trans* to the methyl group was described with partially ionic character. The same observations were reported by Brookhart et al. for the Rh(III)-methyl-bistriflate complex with the isopropyl groups on the phenyl rings. In this complex Rh-O$_{ap}$ distance is 2.358 Å and the author describes the Rh metal center as pentacoordinate. For this reason, it could be expected that the triflate in the apical position would be substituted in further reactions.

Addition of acetonitrile to the light green complex 8, resulted in the color change to red and the formation of 28 in quantitative yield (eq. 3.14). 

$$\text{MeCN} \quad \text{8} \quad \text{MeCN}$$

\[
\begin{align*}
\text{Ir} & \quad \text{MeCN} \\
\text{OTf} & \quad \text{OTf} \\
\text{Me} & \quad \text{Me} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\end{align*}
\]
Complex 28 is fully characterized by $^1$H, $^{13}$C and $^{19}$F-NMR spectroscopy. The $^1$H-NMR spectrum in CD$_2$Cl$_2$ revealed a new singlet peak at $\delta = 2.21$ ppm assigned to the acetonitrile ligand. The integration ratio between different methyl groups is 1:1:2:4. Two singlets at $\delta = -79.50$ and $-79.62$ ppm were observed in the $^{19}$F-NMR spectrum.

Crystals suitable for an X-ray structure analysis were obtained from a THF/pentane solution. The molecular structure and the selected bond distances and angles were presented in Figure 3.16 and Table 3.4.

Fig. 3.16 ORTEP plot of complex 28 with 50% thermal ellipsoids (non–coordinated triflate and hydrogen atoms were excluded for clarity).
Table 3.4 Selected bond lengths [Å] and angles [°] for complex 28.

<table>
<thead>
<tr>
<th></th>
<th>Bond Length [Å]</th>
<th></th>
<th>Bond Length [Å]</th>
<th></th>
<th>Bond Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>1.88(4)</td>
<td>Ir1-N2</td>
<td>2.10(3)</td>
<td>Ir1-N3</td>
<td>2.05(4)</td>
</tr>
<tr>
<td>Ir1-N4</td>
<td>1.95(4)</td>
<td>Ir1-C1</td>
<td>2.05(4)</td>
<td>Ir1-O1</td>
<td>2.26(2)</td>
</tr>
<tr>
<td>N1-Ir1-N4</td>
<td>178.1(1)</td>
<td>N2-Ir1-N1</td>
<td>80.1(1)</td>
<td>N3-Ir1-N1</td>
<td>79.1(1)</td>
</tr>
<tr>
<td>C1-Ir1-O1</td>
<td>177.6(1)</td>
<td>N1-Ir1-O1</td>
<td>88.2(1)</td>
<td>N1-Ir1-C1</td>
<td>94.1(1)</td>
</tr>
<tr>
<td>N2-Ir1-O1</td>
<td>93.0(9)</td>
<td>N2-Ir1-C1</td>
<td>86.9(1)</td>
<td>N2-Ir1-N4</td>
<td>101.8(1)</td>
</tr>
<tr>
<td>N3-Ir1-O1</td>
<td>91.2(1)</td>
<td>N3-Ir1-C1</td>
<td>89.8(1)</td>
<td>N3-Ir1-N4</td>
<td>99.0(1)</td>
</tr>
<tr>
<td>N3-Ir1-N2</td>
<td>158.6(1)</td>
<td>N4-Ir1-C1</td>
<td>85.9(1)</td>
<td>N4-Ir1-O1</td>
<td>91.8(1)</td>
</tr>
</tbody>
</table>

The ligand environment around the Ir(III) center is octahedral with the sum of the equatorial angles equaling 360° and N2-Ir1-O1 = 93.0(9)° N2-Ir1-C1 = 86.9(1)°. The methyl group is trans to the triflate group with the C1-Ir1-O1 angle equaling 177.6°. The bond distance Ir1-O1 (2.26(2) Å) is in the range of the reported values.\textsuperscript{44, 49, 50, 48} Compared to Rh1-O1 bond distance in 7, Ir1-O1 is shortened by 0.1 Å. Nevertheless, the trans influence of the methyl group is still evident. The equatorial coordination site is occupied by the acetonitrile ligand with Ir1-N4 = 1.95(4) Å. The ligand shows an almost linear arrangement with the angle Ir1-N4-C2 = 170.0° and N4-C2-C3 = 176.4° similar to the one found in cationic [Rh(PPh\textsubscript{3})\textsubscript{3}(CH\textsubscript{3}CN)]BF\textsubscript{4} or neutral [Rh(PNP)(CH\textsubscript{3}CN)] complexes.\textsuperscript{157, 158}

The results reported in this section are focused on the first two steps proposed in the catalytic cycle (Chapter1); C-H activation and C-O reductive elimination. Further evidence that C-H activation occurs via a two-step process (oxidative addition and reductive elimination) was provided. This was supported by the formation of Ir(III) trihydride intermediate as well as the Si-H activation in trimethylsilane. The second part was related to C-O bond formation, which was investigated by NMR spectroscopy and compared to the findings from our previous research.\textsuperscript{47, 28}
4 Cationic complexes

This chapter focuses on different approaches for the synthesis and isolation of three-coordinated cationic complexes. The syntheses and characterization of cationic compounds 9 and 10 with a THF molecule coordinated to the metal center have been described in Chapter 2.1.1. However, the main goal of this work is the isolation of cationic complex or related compounds with more weakly coordinated ligands such as, for example, diethyl ether. As will be described later, the purity of the solvents plays an important role in the crystallization process of these types of compounds. Cationic complexes are part of the proposed alkane functionalization cycle (Chapter 1) and several reactions were anticipated as good routes to the desired species 29 (eq. 4.1).

\[
\begin{align*}
2 & \quad \text{IrCl} \\
19 & \quad \text{IrPh} \\
4 & \quad \text{IrOMe} \\
29 & \quad \text{IrOMe} (4.1)
\end{align*}
\]
Based on results of Brookhart et al., one promising route was to use sodium salts of weakly coordinated anions (such as NaBAR$_4$F$_4$) together with complex 2 in non-coordinated solvent to form complex 29 in salt–metathesis reaction. In order to avoid further reaction between complex 29 and chlorinated solvents such as CH$_2$Cl$_2$ or C$_2$H$_4$Cl$_2$ (vide infra), diethyl ether was used. However, the reaction did not take place even after 3 days of stirring at room temperature (no visible changes in the $^1$H-NMR spectrum were observed).

This contrasts results reported by Brookhart et al. for the formation of Rh analogue. For the synthesis of the latter, dichloromethane was used. The different reactivity observed for the Ir complex 29 and the Rh analogue could be attributed to the change in solvent.

4.1 Unexpected formation of the Ir(III) hydride

Upon addition of a dichloromethane solution of tris-(pentafluorophenyl)borane into complex 4, the color changed from green to reddish-brown and complex 30 was formed in 60 % yield (eq. 4.2).

\[
\begin{align*}
\text{Ir-OMe} & \quad + \quad \text{B} \left( \begin{array}{c} F \\ F \\ F \\ F \\
\end{array} \right)_3 & \quad \text{CH}_2\text{Cl}_2 & \quad \rightarrow & \quad \begin{array}{c} \text{Ir} \\ \text{Cl} \\ \text{H} \\
\end{array} \\
\text{4} & \quad & \quad & \quad & \quad \text{30} 
\end{align*}
\]

The presence of an Ir-H moiety was confirmed by $^1$H-NMR spectroscopy, revealing a singlet peak at $\delta = -18$ ppm in CD$_2$Cl$_2$. The methyl groups on the phenyl rings are chemically non-equivalent (opposite as in the square planar complexes), leading to two sets of singlet peaks at $\delta = 2.02$ and 2.40 ppm with an integration ratio of 1:1. Finally, the formation of 30 was confirmed by an X-ray crystal structure analysis. The crystals were obtained from CH$_2$Cl$_2$/pentane solution at $-35$ °C. A molecular representation of 30 and selected bond distances and angles are presented in Figure 4.1 and Table 4.1.
Fig. 4.1 ORTEP plot of complex 30 with 50% probability level (hydrogen atoms except H1 were excluded for clarity).

Table 4.1 Selected bond lengths [Å] and angles [°] for complex 30.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Bond</th>
<th>Length [Å]</th>
<th>Bond</th>
<th>Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>1.945(2)</td>
<td>Ir1-N2</td>
<td>2.050(2)</td>
<td>Ir1-N3</td>
<td>2.049(2)</td>
</tr>
<tr>
<td>Ir1-Cl1</td>
<td>2.354(5)</td>
<td>Ir1-Cl2</td>
<td>2.502(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2-Ir1-N3</td>
<td>158.2(6)</td>
<td>N2-Ir1-N1</td>
<td>78.1(7)</td>
<td>N3-Ir1-N1</td>
<td>81.0(6)</td>
</tr>
<tr>
<td>Cl1-Ir1-Cl2</td>
<td>93.7(2)</td>
<td>N1-Ir1-Cl1</td>
<td>177.5(5)</td>
<td>N1-Ir1-Cl2</td>
<td>83.9(4)</td>
</tr>
<tr>
<td>N2-Ir1-Cl1</td>
<td>101.3(5)</td>
<td>N2-Ir1-Cl2</td>
<td>92.4(4)</td>
<td>N3-Ir1-Cl1</td>
<td>99.8(4)</td>
</tr>
<tr>
<td>N3-Ir1-Cl2</td>
<td>91.4(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The coordination geometry around the iridium center is pseudo octahedral with the equatorial angles equaling 359.3° and N2-Ir1-Cl2 = 92.4(4)°. Two chloro ligands are arranged cis to each other with a Cl1-Ir1-Cl2 angle 93.7(2)°. The position of the hydride was located in the difference Fourier map and was isotropically refined. The Ir1-Cl2 bond distance is elongated (2.502(5) Å) when compared to the Ir1-Cl1 bond distance (2.354(5) Å), due to the trans influence of the hydride ligand. It is in the range of Ir-Cl distances found for other complexes containing chloro ligands trans to the hydride ligand, as reported for [Ir(η^3-cyclooctenyl)(SbPr_3)_2Cl(H)]^{160},
[Ir(PN)(PPh₃)ClH₂] (PN = (4S)-2-(2-(diphenylphosphino)phenyl)-4-isopropyl-1,3-oxazoline)¹⁶¹ or [Ir(NH=O)(PPh₃)₂Cl₂H]¹⁶²

In complex 30, it may be assumed that the chloro ligands originate from the solvent. Complex 4 is not stable in chlorinated solvents (dichloromethane or 1,2-dichloroethane), forming 2 after 3 days (Chapter 2.1). The origin of the hydride is still unclear.

Similar reactions with B(C₆F₅)₃ in dichloromethane and the formation of chloro complexes were already reported in the literature. For example, the exchange reaction between a methyl and a chloro ligand in dichloromethane have been described for [CpTi(NP-tBu₃)(NC₅H₄NMe₂)Cl][B(C₆F₅)₄] and [CpTi(µ-Cl)(NPPh₂(NP-tBu₃))]₂[B(C₆F₅)₄]₂.¹⁶³,¹⁶⁴

In order to avoid the formation of chloro complex 30, the reaction (equation 4.2) was repeated using diethyl ether as a solvent. A color change from green to reddish-brown was observed and according to the spectroscopic data, complex 31 was obtained in 62 % yield.

Compound 31 is soluble in THF, diethyl ether and DME, partially soluble in non-polar solvents such as benzene or toluene and insoluble in pentane. According to the ¹H-NMR spectrum in THF-d₈, the obtained complex is diamagnetic displaying sharp resonances in the aliphatic and aromatic region comparable to resonances observed for complex 10 (see Experimental part). The resonance assigned to the methoxo ligand in 4 was shifted from 4.67 ppm to 2.97 ppm (broad) in the newly formed complex 31. The integration ratio of the different methyl groups is 4:2:1 as in 4. The ¹⁹F-NMR spectrum in THF-d₈ revealed three resonances at δ = −133.9, −165.4 and −168.4 ppm assigned to the ortho, para and meta fluorine in [MeOB(C₆F₅)₃]⁻ anion. Minor shifts are observed when compared with the resonances of free B(C₆F₅)₃ (δ = −135, −159.6 and −166.3 ppm).
4.2 The formation of methanol from complex 4

The addition of the strong cationic Brønsted acid \([\text{H(Et}_2\text{O)}_2][\text{Al(pftb)}_4]\) to a THF solution of complex 4 at room temperature, resulted in the formation of the Ir(I) cationic complex 10-Al(pftb)_4. The color immediately changed to reddish-brown and complex 10-Al(pftb)_4 was formed with concomitant elimination of methanol (eq. 4.4).

\[
\begin{align*}
\text{4} & \quad \text{[H(Et}_2\text{O)}_2][\text{Al(pftb)}_4] \quad \text{THF, } -\text{MeOH} \\
& \quad \text{THF} \quad (4.4) \\
\text{10-Al(pftb)}_4 & \quad \text{95 }\% \\
\end{align*}
\]

Compound 10-Al(pftb)_4 was fully characterized with \(^1\text{H}, \ ^{13}\text{C} \) and \(^{19}\text{F}-\text{NMR spectroscopy. The solubility of 10-Al(pftb)}_4 \) is comparable with 31. However, in benzene or toluene, 10-Al(pftb)_4 precipitates and turns to an oily material.

![Fig. 4.2](image)

**Fig. 4.2** The \(^1\text{H}-\text{NMR spectrum of the reaction mixture in eq. 4.4 and 10-Al(pftb)}_4 \text{ in THF-d}_8.**

According to the \(^1\text{H}-\text{NMR spectrum of the (1:1) reaction mixture (4 : [H(Et}_2\text{O)}_2]^+) \text{ in THF-d}_8, the methoxide resonance (δ = 4.67 ppm) disappeared. New peaks, doublet at δ = 3.26 ppm and quartet at δ = 3 ppm appeared, which were assigned to methanol (Fig. 4.2 - left).
Methanol resonances are also found in the transferred volatiles at the aforementioned chemical shift. The coupling between the methyl group and hydroxide proton through the oxygen atom was observed, revealing a doublet and a quartet peak with the coupling constant $^3J_{HH} = 5$ Hz. Diethyl ether from the acid was also observed in the transferred volatiles. In the $^{13}$C-NMR spectrum in THF-$d_8$, the methanol resonance appeared at $\delta = 50$ ppm.

The proton resonances of $10$-$\text{Al(pftb)}_4$ (Fig. 4.2 - right) are found at the same chemical shift as in the complexes $10$ and $31$ leading to the conclusion that no influence of the different anion is present.

### 4.2.1 Proposed mechanism for the methanol formation

The following mechanism for the formation of complex $10$-$\text{Al(pftb)}_4$ is proposed. Initially, protonation at the metal center occurs and compound $32$ is formed. Consecutively, reductive elimination of methanol and formation of $10$-$\text{Al(pftb)}_4$ takes place. This part of the proposed mechanism is equal to the mechanism anticipated for eq. 3.15 (Chapter 3.4). As it will be discussed later, another process involves further protonation of $32$ on the methoxide ligand and formation of Ir(III) hydrido methanol complex $32a$ is observed.
In order to provide a support for the proposed mechanism, the reaction according to eq. 4.5 was monitored from −90 °C to 50 °C over a period of 6 hours by $^1$H-NMR spectroscopy. Both components (4 and [H(Et$_2$O)$_2$]$^+$) were placed in the NMR tube and the solvent (THF-d$_8$) was condensed over (at liq. N$_2$ temperature). The mixture was then warmed up to −90 °C and placed into the pre-cooled probe–head of the NMR spectrometer. In the first spectrum obtained at −90 °C, two peaks in the high field region were observed at $\delta = −32.90$ and −33.30 ppm. The peak at −33.30 ppm was assigned to the hydride ligand in 32 (Fig. 4.3).

![Temperature dependent NMR of the reaction according to eq. 4.5 (hydride region).](image)

Fig. 4.3 Temperature dependent NMR of the reaction according to eq. 4.5 (hydride region).

The methoxy ligand (in 32) was found at $\delta = 2.33$ ppm, significantly shifted towards higher field when compared to chemical shift in 4 ($\delta = 4.67$ ppm). The assignment derived from the $^1$D-NOE NMR experiment. When the hydride peak at $\delta = −33.30$ ppm is irradiated, the peak at $\delta = 2.33$ ppm showed NOE enhancement. The resonance of protonated methanol in 32a appeared at $\delta = 2.90$ ppm. During a period of 1 hour, the temperature was increased gradually by 10 °C and the spectra recorded every 3 min. Nevertheless, apart from the slight shift of the hydride peak at $\delta = −32.90$ towards higher field no significant changes were observed. At −5 °C methanol was eliminated. The two hydride peaks crossed-over giving only one resonance at
\[ \delta = -33.40 \text{ ppm} \text{ (see spectrum at 268 K in Fig. 4.3). At +5 °C, the second hydride peak} \]
\[ \text{at } \delta = -33.45 \text{ ppm) reappeared again reducing the intensity with further temperature rise and it} \]
\[ \text{completely disappeared at 25 °C. Also, at 10 °C a new hydride resonance was observed at} \]
\[ \delta = -33.10 \text{ ppm which was assigned to complex 33. This resonance was the only one that} \]
\[ \text{remained when the temperature was elevated to 50 °C. In the aromatic region two sets of doublet} \]
\[ \text{and triplet peaks were detected. The triplet at } \delta = 8.5 \text{ ppm and the doublet at } \delta = 7.91 \text{ ppm were} \]
\[ \text{assigned to 10-Al(pftb)}_4 \text{ whilst the doublet at } \delta = 8.36 \text{ and triplet at } \delta = 8.21 \text{ ppm were assigned} \]
\[ \text{to complex 33. At the end, the mixture of 10-Al(pftb)}_4, 33 \text{ and methanol remained.} \]

Complex 33 was synthesized independently when two equivalent of the aforementioned acid were added to a THF solution of 4 and the color changed from green to red (eq. 4.6).

\[
\begin{align*}
\text{4} & \xrightarrow{2[H(\text{Et}_2\text{O})_2][\text{Al(pftb)}_4]} \text{THF, } -\text{MeOH} \\
\text{33} & 
\end{align*}
\]

This compound was characterized with \(^1\text{H}, ^{13}\text{C}, \text{and} ^{19}\text{F-NMR spectroscopy. Methanol was found}
\[ \text{in the transferred volatiles. According to the } ^1\text{H-NMR spectrum (in THF-d}_8\text{) the symmetry of the} \]
\[ \text{obtained compound is lowered, suggesting solvent coordination to the metal center. Methyl} \]
\[ \text{groups attached to the phenyl displayed a 1:1 integration ratio. The resonance of the methyl} \]
\[ \text{group on the diimine part of the ligand is shifted downfield revealing a peak at } \delta = 2.84 \text{ ppm.} \]
\[ \text{The assignments of the proton resonances were confirmed with 2D-HSQC and HMBC (} ^1\text{H}/^{13}\text{C) NMR spectra.} \]

**4.2.2 Alternative syntheses**

Complex 10-Al(pftb)_4 can be obtained via different routes. One way is by adding LiAl(pftb)_4 to a THF solution of 10. This procedure is straightforward employing only one equivalent of lithium salt in comparison to the reaction of 10 with NaBArF_4 where 7 equivalents of latter were used in order to complete the exchange of the triflate anion. The other method to synthesize
10-Al(pftb)$_4$ was by adding a THF solution of [H(Et$_2$O)$_2$][Al(pftb)$_4$] to a THF solution of 19 (eq. 4.7). The yield in both reactions is approximately 90 %.

According to the $^{19}$F-NMR spectrum in THF-d$_8$ for the reaction of LiAl(pftb)$_4$ and 10 the resonance for the triflate anion at $\delta = -$79.0 ppm disappeared and the new peak at $\delta = -$75.6 ppm was assigned to Al(pftb)$_4$ anion. This observation showed that the anion exchange was complete. The proton resonances are on the same chemical shift (see Experimental part).

In the $^1$H-NMR spectrum in THF-d$_8$ for the reaction of 19 and [H(Et$_2$O)$_2$][Al(pftb)$_4$], peaks from the phenyl group attached to the metal center (d, 5.57; t, 5.81; t, 6.58) disappeared and the resonances of the methyl groups at $\delta = 0.67$ and 1.97 ppm (in 19) shifted to $\delta = 1.78$ and 2.24 ppm in newly formed complex 10-Al(pftb)$_4$. The other aromatic peaks from the pyridine ligand were also shifted by 0.35 ppm towards higher field (comparing 19 and 10-Al(pftb)$_4$). The formation of benzene was confirmed in the transferred volatiles (in THF-d$_8$), revealing a singlet peak at $\delta = 7.25$ ppm in $^1$H-NMR and at $\delta = 130$ ppm in the $^{13}$C-NMR spectrum.

In order to crystallize complex 10-Al(pftb)$_4$, different ether solutions (THF, Et$_2$O or DME) were layered with non-polar solvents (pentane, toluene or benzene) or vapor diffusion was used. In this case, the crystals were obtained by slow vapor diffusion of pentane into a diluted Et$_2$O solution of 10-Al(pftb)$_4$ at $-35$ °C. After a long period of time, during crystallization, complex 34 was obtained (eq. 4.8). Dehydrogenation of diethyl ether and coordination of the ethoxyethene could be the possible explanation for the formation of complex 34.
The $^1$H-NMR spectrum of the crystals was measured in Et$_2$O-d$_{10}$ revealing two resonances at lower field (at $\delta = 4.08$ ppm and 5.44 ppm), with an integration ratio 2:1. These peaks were assigned to the $\eta^2$-coordinated vinyl ether ligand and compared with the literature values.\textsuperscript{166, 167, 168} The other resonances from the ethyl group were found at higher field (at $\delta = 1.01$ and 1.42 ppm). In the $^{19}$F-NMR spectrum, a singlet peak at $\delta = -79$ ppm was observed for the Al(pftb)$_4^-$ anion. Unfortunately, the concentration of 34 in Et$_2$O-d$_{10}$ was too low to perform $^{13}$C or 2D-NMR analyses.

Molecular representation of 34 and selected bond distances and angles are displayed in Figure 4.4 and Table 4.2.

![Molecular representation of 34 with selected bond distances and angles](image)

**Fig. 4.4** ORTEP plot of 34 with 50% probability level (hydrogen atoms and Al(pftb)$_4^-$ anion were omitted for clarity.)
Table 4.2 Selected bond lengths [Å] and angles [°] for complex 34.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>1.948(5)</td>
</tr>
<tr>
<td>Ir1-C26</td>
<td>2.139(7)</td>
</tr>
<tr>
<td>C27-O5</td>
<td>1.340(9)</td>
</tr>
<tr>
<td>C30-C31</td>
<td>1.379(1)</td>
</tr>
<tr>
<td>N2-Ir1-N3</td>
<td>157.4(2)</td>
</tr>
<tr>
<td>N1-Ir1-C26</td>
<td>168.7(3)</td>
</tr>
<tr>
<td>C26-Ir1-C27</td>
<td>36.8(3)</td>
</tr>
<tr>
<td>O5-C29-C30-C31</td>
<td>113.6(8)</td>
</tr>
</tbody>
</table>

The square planar coordination around the Ir center is slightly distorted with the sum of the angles equalling 359.2°. The ligand occupying the forth coordination site is perpendicular to the IrNNN plane. The bond distance Ir1-C26 = 2.139(7) Å is by 0.086 Å shorter than Ir1-C27. Both are in the range of reported Ir-C\textsubscript{sp2} distances.\textsuperscript{169, 170} The C26-C27 distance is 1.381(1) Å, comparable with the C=C bonds reported for the metallo vinyl ether complexes.\textsuperscript{168, 171} According to the literature, the C=C distance in the free vinyl ether is 1.340(5) Å.\textsuperscript{172} The atoms from C29-C32 are disordered.

4.3 Synthesis of the novel formaldehyde complex 35

The methoxide abstraction with trityl (Ph\textsubscript{3}CAI(pftb)\textsubscript{4}) from complex 4 was another anticipated method to access the desired Ir(I) cation complex in non polar, less coordinative solvents (see eq. 4.1). Upon addition of a green solution of complex 4 in benzene to a yellow solution of Ph\textsubscript{3}CAI(pftb)\textsubscript{4} and stirring for 2 hours a color change to reddish-brown was observed. However, instead of the desired cationic compound, the novel dihapto-Ir(III) formaldehyde complex 35 was obtained in 64 % yield (eq. 4.9).
The $^1H$-NMR spectrum of the colorless pentane extraction of the reaction mixture revealed a singlet resonance at $\delta = 5.4$ ppm in $C_6D_6$, which corresponds to triphenylmethane. Complex 35 was fully characterized with $^1H$, $^{13}C$ and $^{19}F$-NMR spectroscopy and elemental analysis. The $^1H$-NMR spectrum of 35 in THF-$d_8$ is consistent with $C_2v$ symmetry, indicating a fast rotation of the formyl group in solution. The formaldehyde ligand revealed a proton resonance at $\delta = 4.0$ ppm and $^{13}C$ resonance at $\delta = 69.1$ ppm, which are highfield in comparison with the free aldehyde. These chemical shifts are in the good agreement with the ones reported for complexes with a $\eta^2$-coordinated formaldehyde, for example $[(\text{tmeda})\text{Ni}(\eta^2$-$\text{CH}_2\text{O})(\text{C}_2\text{H}_4)]$ (in THF-$d_8$: $^1H$ $\delta = 3.64$, $^{13}C$ $\delta = 70.9$ ppm)$^{173}$ and $[\text{Cp'}\text{\text{2}\text{Nb}(\eta^2$-$\text{CH}_2\text{O})]}$ (in $C_6D_6$: $^1H$ $\delta = 3.37$ ppm, $^{13}C$ $\delta = 67.8$ ppm).$^{174}$ The integration ratio of the formaldehyde ligand and the methyl groups is 1:6:3. The $^{13}C$-NMR resonance at $\delta = 69.2$ ppm, which was assigned to CH$_2$ group is based on a DEPT-135 experiment. In the coupled $^{13}C\{^1H\}$-NMR experiment, the CH$_2$ group revealed a triplet with a coupling constant $^{1}J_{CH} = 166$ Hz, typical for sp$^2$-hybridized carbon. According to the literature, $^{1}J_{CH}$ coupling constants depend also on the nature of the neighboring atom. Electronnegative substituents lead to an increase of the $^{1}J_{CH}$ value.$^{175}$ In case for 35, it is anticipated that the carbon atom (in CH$_2$O group) is sp$^3$-hybridized, which is in agreement with results obtained by X-ray crystal structure analysis. For the $^1H$ and $^{13}C$ resonances of the formaldehyde ligand a cross peak in the HSQC experiment was observed (Fig. 4.5).
The ν(CO) stretching frequency at 1031 cm$^{-1}$ in toluene strongly suggested an η$^2$ coordination of the formaldehyde ligand for which typical stretching frequencies vary from 1000-1200 cm$^{-1}$.\cite{176} Opposite to η$^2$, η$^1$ formaldehyde ligands show much higher energy C-O stretching frequencies (~ 1600 cm$^{-1}$).\cite{177,178} It is noteworthy that the assigned frequency is indicative for back donation and lengthening of the C-O bond which is confirmed by X-ray crystal structure analysis.

Reddish-brown crystals were obtained from Et$_2$O/pentane solution by vapor diffusion (Fig. 4.6). Selected bond lengths and angles of 35 are presented in Table 4.3.
Fig. 4.6 ORTEP plot of complex 35 with 50% probability thermal ellipsoids (the Al(pftb)$_4$ anion and hydrogen atoms (except the formyl ones) were excluded for clarity).

Table 4.3 Selected bond lengths [Å] and angles [°] for complex 35.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir1-N1</td>
<td>1.962(1)</td>
<td>Ir1-N2</td>
<td>2.098(1)</td>
</tr>
<tr>
<td>Ir1-O5</td>
<td>2.146(1)</td>
<td>Ir1-C27</td>
<td>2.172(2)</td>
</tr>
<tr>
<td>N2-Ir1-N3</td>
<td>152.9(6)</td>
<td>N2-Ir1-N1</td>
<td>75.5(6)</td>
</tr>
<tr>
<td>N1-Ir1-C27</td>
<td>164.3(7)</td>
<td>N2-Ir1-C27</td>
<td>89.5(7)</td>
</tr>
<tr>
<td>N1-Ir1-O5</td>
<td>156.9(8)</td>
<td>N2-Ir1-O5</td>
<td>127.1(7)</td>
</tr>
<tr>
<td>C27-Ir1-O5</td>
<td>37.6(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The molecule adopts a square planar geometry around the metal center with the sum of the angles equaling 358.8°. The formyl ligand lies in the IrNNN plane. The angle between the plane defined by Ir1-C27-O1 is 37.6°. The C27-O5 bond distance (1.390(2) Å) is in the range of the other formaldehyde complexes reported.\textsuperscript{179, 174, 173} The observed lengthening of the C-O bond, compared to free formaldehyde (1.225 Å)\textsuperscript{180} strongly suggested $\pi$ back-bonding. In the literature, the osmium complex [Os(PPh$_3$)$_2$(CO)$_2$(η$_2$-CH$_2$O)] with the unusually long C-O bond (1.59(1) Å) was reported and the interaction between osmium and formaldehyde was described as the oxirane like structure.\textsuperscript{181} It is worth noticing that the C-O bond distance in the starting material 4...
(1.392(8) Å) is only 0.002 Å longer than in 35 (vide infra), which suggests that the ligand (C-O) retained the same hybridization after the reaction. The Ir1-O5 bond distance (2.146(1) Å) is shorter than the Ir-C27 distance (2.172(2) Å). This behaviour is mostly observed when the metal centers have an oxophilic character as it could be suggested in case for complex 35.

4.3.1 Mechanistic aspects

There are several different routes for the synthesis of aldehyde complexes. Mostly, they are prepared by using paraformaldehyde as the source of the desired ligand or reduction of the carbon monoxide by appropriate metal hydrides. The third possibility for the synthesis of aldehyde complexes is β-hydride elimination of alkoxide complexes to give hydridoformaldehyde intermediates. Formation of such an intermediate is anticipated for the reaction according to eq. 4.9.

The proposed mechanism (Fig. 4.7), involves the formation of the formyl hydrido complex. The hydride ligand is then abstracted by the trityl cation giving 35 and triphenylmethane. DFT calculations (B3LYP, LACVP** basis set) on the model complex 4a were performed for the formation of the formyl hydride.

![Diagram](image.png)

**Fig. 4.7** Energy barrier for the formation of formyl hydrido complex.

Previously, the preference for the in-plane coordination of the methoxide group in 4a was established by our group, with an energy difference of 12 kcal/mol. The energy barrier from 4a
to the formyl hydride is 26 kcal/mol. The transition state (TS) resembles the product and can be described as late transition state according to the Hammond postulate. The imaginary frequency for the transition state corresponds to shortening of Ir-H bond distance. The formyl hydridro complex is 14 kcal/mol higher in energy than 4a with the hydride and oxygen in the cis position.

In order to confirm the reaction pathway, IRC calculations were carried out (B3LYP, LACVP** basis set). Starting from the saddle point (TS), the forward direction led to the formyl hydride and the reverse reaction mode to the starting material 4a.

The second part of the proposed mechanism involves hydride abstraction. According to DFT calculations, the reaction is thermodynamically favored (in the gas phase) for the formation of the formaldehyde complex and triphenylmethane by 23 kcal/mol (eq. 4.10).

\[
\begin{align*}
\text{H} &= \text{N} \quad \text{Ir} \quad \text{H} \\
\text{H} &= \text{N} \quad \text{Ir} \quad \text{H} \\
\text{H} &= \text{N} \quad \text{Ir} \quad \text{H} \\
\text{O} &= \text{CH}_2 \\
\end{align*}
\]

\[
\text{N} \quad \text{N} \quad \text{H} \\
\text{H} \quad \text{Ir} \quad \text{H} \\
\text{H} \quad \text{Ir} \quad \text{H} \\
\text{O} \quad \text{CH}_2 \\
\]

\[
\begin{align*}
+ & \text{Ph}_3\text{C}^+ \quad \rightarrow \quad + & \text{Ph}_3\text{CH} \\
\end{align*}
\]

\[
\Delta E = -23 \text{ kcal/mol}
\]

The β-hydride elimination from methoxo complexes was already reported by Bryndza et al. in the case for Pt(II)(DPPE)(OMe)\textsubscript{2}. The thermolysis of the latter, which generates methanol and formaldehyde oligomers at 30 °C, was explained by a mechanism involving a pre-equilibrium with a β-hydride elimination. Milstein et al. established the same mechanism for an octahedral Ir(III)Cl(H)(OMe)(PR\textsubscript{3})\textsubscript{3} complex.

To the best of our knowledge this is the first fully characterized and isolated iridium η\textsuperscript{2}-formaldehyde complex. The reactivity of latter, especially towards H\textsubscript{2} and CO, is still unexplored and will be left for further studies.
4.3.2 Different reactivity of the Rh(I) methoxo complex 3

The reaction according to equation 4.9 was repeated for the Rh analogue. Upon addition of a green solution of 3 in benzene to a yellow solution of Ph₃CAI(pftb)₄, a color change to brown was observed. However, instead of formaldehyde compound, the cationic complex 36 was obtained (eq. 4.11).

![Reaction diagram]

The ¹H-NMR spectrum of the colorless pentane extraction of the reaction mixture revealed singlet resonances at δ = 5.40 ppm (for the CH group) and 2.96 ppm (for the methyl group) in C₆D₆ with a 1:1 integration ratio, which correspond to triphenylmethane and trityl-methyl ether (Note: the residual compound is not soluble in pentane). The ¹H-NMR spectrum of 36 in THF-d₈ revealed two singlet peaks of the methyl groups (at δ = 1.98 and 2.30 ppm) with an 1:2 integration ratio as expected for Cᵥ symmetry in complex 36. In the ¹⁹F-NMR spectrum, one resonance at δ = −76.30 ppm assigned to the Al(pftb)₄ anion was observed.

The alternative route to synthesize complex 36 was by mixing THF solutions of 3 and [H(Et₂O)₂][Al(pftb)₄]. As in the reaction according to eq. 4.4, methanol was eliminated (see section 4.2). Proton and carbon resonances of 36 can be compared with the resonances from triflate complex 9¹⁷, confirming that there is no anion effect involved.

The crystals were grown by a slow vapor diffusion of pentane to a diluted diethyl ether solution of 36. During crystallization, compound 37 was obtained, which was confirmed by X-ray crystal structure analysis (eq. 4.12).
Molecular presentation and selected bond distances and angles were displayed in Figure 4.8 and Table 4.4.

Fig. 4.8 ORTEP plot of complex 37 at 50% probability level (hydrogen atoms and the Al(pftb)$_4^-$ anion were omitted for clarity).
Table 4.4 Selected bond lengths [Å] and angles [°] for complex 37.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-N1</td>
<td>1.946(6)</td>
</tr>
<tr>
<td>Rh1-N2</td>
<td>2.053(6)</td>
</tr>
<tr>
<td>Rh1-N3</td>
<td>2.046(6)</td>
</tr>
<tr>
<td>Rh1-C26</td>
<td>2.160(8)</td>
</tr>
<tr>
<td>C27-O5</td>
<td>1.308(1)</td>
</tr>
<tr>
<td>N2-Rh1-N3</td>
<td>157.4(2)</td>
</tr>
<tr>
<td>N2-Rh1-N1</td>
<td>79.0(2)</td>
</tr>
<tr>
<td>Rh1-N1-C26</td>
<td>167.7(3)</td>
</tr>
<tr>
<td>Rh1-C26</td>
<td>98.2(3)</td>
</tr>
<tr>
<td>C27-O5</td>
<td>113.9(6)</td>
</tr>
<tr>
<td>O5-C29-C30</td>
<td>74.0(2)</td>
</tr>
<tr>
<td>C26-Rh1-C27</td>
<td>34.9(3)</td>
</tr>
<tr>
<td>N1-Rh1-C26</td>
<td>167.7(3)</td>
</tr>
<tr>
<td>N2-Rh1-C26</td>
<td>98.2(3)</td>
</tr>
<tr>
<td>N3-Rh1-C26</td>
<td>103.4(3)</td>
</tr>
<tr>
<td>C26-Rh1-C27</td>
<td>105.3(4)</td>
</tr>
<tr>
<td>N1-Rh1-C27</td>
<td>96.1(3)</td>
</tr>
<tr>
<td>C27-O5-C29</td>
<td>114.6(9)</td>
</tr>
<tr>
<td>N1-Rh1-C27</td>
<td>157.3(4)</td>
</tr>
<tr>
<td>N2-Rh1-C27</td>
<td>105.3(4)</td>
</tr>
<tr>
<td>N3-Rh1-C27</td>
<td>96.1(3)</td>
</tr>
<tr>
<td>C26-Rh1-C27</td>
<td>34.9(3)</td>
</tr>
<tr>
<td>Rh1-C27-O5</td>
<td>113.9(6)</td>
</tr>
<tr>
<td>C27-O5-C29</td>
<td>114.6(9)</td>
</tr>
</tbody>
</table>

Complex 37 is isostructural with complex 34, crystallizing in the space group P2_1/n. The geometry around the Rh center is distorted square planar with the sum of the angles equaling 359°. The alkene, as the forth ligand is oriented perpendicularly to the plane defined by Rh1, N1, N2 and N3 atoms. The rhodium center is bound to C26 and C27 with the distance Rh-C26 = 2.160(8) Å and Rh-C27 = 2.195(1) Å, respectively. The C26-C27 bond distance (1.310(1) Å) is slightly longer than in Ir analogue. The R values are less than 10 % for both complexes (R_1(34) = 0.0661, R_1(37) = 0.0772).

In this chapter, syntheses of novel cationic complexes were presented. In comparison to the synthesis of complex 10, a new, straightforward synthesis was described for preparation of the 10-Al(pftb)_4 followed by the elimination of methanol. This reaction was studied by low temperature NMR and the mechanism was proposed.

Synthesis and characterization of the novel [Ir(N_3Me_4)(η^2-CH_2O)]^+ complex as well as DFT calculations concerning the mechanism for the formation of the latter was also described.
5 Summary

The research described herein is an extension and continuation of previous research work developed within the group, in the area of C-H activation of alkanes to alcohols via square planar late transition metal monomeric Rh, Ir(III) oxo complexes with a terminal oxo unit L₄M=O. The central theme of the current work was to try and provide further evidence for each sequential step of the proposed catalytic cycle for this process. Syntheses and characterization of the desired complexes and direct observation or isolation of reactive intermediates and products was the focus of the experimental work.

A range of square planar starting materials (1-10) using sterically demanding terdentate pyridine diimine ligands was prepared. The first approach to an Ir oxo complex was the direct oxidation of the Ir(I)-hydroxo complex 6 with different strong oxidizing reagents. However, unexpected compounds were obtained. Using 2 equivalents of the thianthrene radical cation and 6 in a dimethoxyethane (DME) solution, the Ir(III)-hydride complex 11 with DME coordinated to the metal center was isolated. The source of the hydride was not conclusive. An independent experiment (formation of 12) showed that the hydride did not originate from the hydroxide group in 6. The use of a different oxidizing reagent, “magic blue” led to the formation of the Ir(III)-dichloro complex 13 with THF coordinated to the metal center.

Another route to the oxo complex II by hydride abstraction from the hydroxide group in 6 was pursued with trityl-PF₆. However, due to crystallographic problems, the ligand occupying the fourth site on the metal center in 14 was not resolved. It is noteworthy, that several X-ray crystal structure analyses were undertaken and apart from the fourth ligand, all the other atoms from the terdentate ligand were anisotropically refined with small R-values.

According to DFT calculations, amine N-oxides were proposed as possible co-catalysts in the catalytic cycle that can react with the cationic complex 29 to yield II. It was also calculated that by increasing the number of phenyl groups coordinated to the nitrogen of the amine N-oxide, starting from trimethylamine N-oxide, the formation of II would be thermodynamically more favorable. Therefore, Me₂PhNO and MePh₂NO were synthesized and their X-ray crystal structures determined. The distances between two amine N-oxides (including Me₃NO) were comparable. This finding was opposite from what was expected, since electron withdrawing
phenyl groups were introduced. Through a crystal packing analysis, it was found that strong 
intermolecular and intramolecular CH···O hydrogen bonding is present and presumably 
responsible for the aforementioned result. In the reaction of the triflate complex 10 and 
Me₂PhNO, the formation of free amine was confirmed. Unfortunately, the fate of the oxygen 
atom is still unclear.

The activation of molecular oxygen and the formation of a peroxo species was also at the center 
of this work. In order to improve the solubility of the desired complexes, the exchange of the 
triflate anion in 10 was accomplished either with NaBAR₄ or LiAl(pftb)₄ giving complexes 
10-BAR₄ and 10-Al(pftb)₄, respectively. When the latter was reacted with oxygen, the tentative, 
paramagnetic peroxo complex III was obtained. DFT calculations indeed confirmed that a triplet 
state (S=1) is preferable. In the reaction with Ph₃P and III, the cationic phosphine complex IV 
and free Ph₃PO were formed.

The reaction chemistry of the formal Rh”(0)” complexes was a significant part of this project. 
Compound V was synthesized by the reduction of the Rh(I) chloro or methoxo complexes 
(1a or 3a) with Na/Hg in THF solution under argon atmosphere. Paramagnetic character of V 
was confirmed with EPR experiment. DFT calculations revealed that the spin density of the 
electron is essentially located within the pyridine diimine ligand. Unfortunately, attempts to 
occur crystals for an X-ray crystal structure analysis were unsuccessful.

The reactivity of V was tested with different reagents. In dichloromethane, it reconverts to the 
chloro complex 1a. Upon addition of Me₃SiN₃ in V, the Rh(I) azido complex 15 was obtained. In 
the reaction with adamantyl-1-azide, the paramagnetic, species VI was formed. Although further 
characterization was unsuccessful, the structure of VI was tentatively assigned to a Rh(II) imido 
species.

Alternatively, when the reduction of 1a was performed under an N₂ atmosphere, depending on 
the alkyl substituents on the phenyl rings, dinuclear or mononuclear dinitrogen complexes 16 
and 17 were isolated. To the best of our knowledge, 17 is the first example of a mononuclear 
Rh(0) dinitrogen complex. As in the case of V, DFT calculations showed that the spin density is 
delocalized within the pyridine diimine ligand.
Further focus of this research was the improvement of the synthesis of methyl complex 18 and establish evidence for the Ir(III) intermediate proposed for the mechanism in the case of intermolecular C-H activation of 18 in benzene. In the reaction of the phenyl complex 19 and H₂, the Ir(III) trihydride 20a was obtained. This compound showed fluxionality of the hydrido ligands in the ¹H-NMR spectra. Low temperature NMR and T₁ measurements confirmed the presence of a trihydride species. DFT calculations revealed that the energy difference between the trihydride 20a and the dihydrogen hydride 20b complexes is very small.

Further evidence for a two-step C-H activation mechanism (oxidative addition and reductive elimination) was the extended low temperature NMR study of the Si-H activation process in trimethylsilane of the methoxy complex 4. The Ir(I) mono-hydride 20 was obtained, followed by the formation of trimethysilylmethoxide.

A suitable route to both iridium and rhodium mono-hydride complexes from the related fluoride complexes was investigated. Using TASF as a fluorinating reagent in the reaction with the triflate complexes 9 and 10, the Rh,Ir(I)-fluoro complexes 22 and 23 were obtained. Both complexes crystallize with (Me₂N)₃SOTf. Using a new fluoride source, TBAF, by metathesis of the chloride ligand from 1, 1a or 2, the fluoro complexes 24, 25 and 26 were obtained.

One of the most important reactions in the alkane functionalization is the C-O reductive elimination process. During this study, C-O elimination of methanol (from the hydroxo complex 6 and methyltriflate) was followed by low temperature ¹H-NMR spectroscopy. The formation of the hydroxo, methyl intermediate 27 was detected. DFT calculations on the mechanism of C-O reductive elimination were also investigated. Another example of C-O bond formation was observed in the reaction of the methoxy complexes 3 or 4 and two equivalents of methyltriflate. In both examples dimethyl ether was eliminated.

Finally, different approaches to obtain cationic complexes were pursued. In the reaction of 4 and tris-(pentafluorophenyl)borane, depending on the solvent, complexes 30 and 31 were obtained. If the reaction was performed in dichloromethane, the Ir(III)-dichloro hydride 30 was isolated. In the case when diethyl ether was used, the cationic complex 31 was formed.

When one equivalent of the Brønsted acid [H(Et₂O)₂][Al(pftb)₄] was added to the methoxy complex 4, complex 10-Al(pftb)₄ was formed and methanol was eliminated. Low temperature
$^1$H-NMR measurements were undertaken in order to provide evidence for the proposed mechanism. The formation of the Ir(III)-hydrido methoxide complex 32, followed by reductive elimination of methanol strongly support the mechanistic scenario. However, a competing reaction also takes place and depending on the concentration of the acid, the Ir(III)-hydrido complex 33 can be obtained.

Complex 10-Al(pftb)$_4$ can be synthesized via different routes, either by the simple metathesis of the triflate anion from 10 with LiAl(pftb)$_4$ already described above or upon addition of the aforementioned acid to the phenyl complex 19.

In the reaction of 4 and trityl-Al(pftb)$_4$, the novel η$^2$-Ir(III) formaldehyde complex 35 was prepared. A possible mechanism for this reaction was investigated with DFT calculations. The proposed mechanism involves the formation of the formaldehyde hydride species obtained by β-hydride elimination from the methoxide ligand, followed by a hydride abstraction with trityl. The outcome for the reaction of the analogous Rh(I) methoxo complex 3 and trityl-Al(pftb)$_4$, was different. Instead of the formaldehyde complex, a cationic species 36 was obtained. The same compound was independently synthesized when 3 was reacted with the acid, [H(Et$_2$O)$_2$][Al(pftb)$_4$].
6 Experimental Section

6.1 General Procedures

Unless otherwise noted, all manipulations were performed at room temperature under an atmosphere of purified nitrogen or argon either in a glove box (M. Braun) or using standard Schlenk/vacuum line techniques. Solvents used for syntheses were dried thoroughly using appropriate drying agent and distilled under nitrogen atmosphere. Deuterated NMR solvents were purified dried and degassed with “freeze-pump-thaw” method. Pentane used for the preparation of the cation complexes was purified by following procedure from the literature.\textsuperscript{191}

Instruments used for characterization:

$^1$H-NMR spectra were recorded on Varian Gemini 2000 and Bruker Avance 400 spectrometers operating at 200 and 400 MHz respectively.

$^{13}$C($^1$H)-NMR spectra were recorded on a Varian Gemini 2000 and Bruker Avance 400 spectrometer operating at 50 and 100 MHz respectively.

$^{19}$F($^1$H)-NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 188.1 MHz.

$^{31}$P($^1$H)-NMR spectra were recorded on Bruker Avance 400 spectrometer operating at 162 MHz.

Chemical shifts are given in ppm and were referenced to the residual $^1$H solvent shift or $^{13}$C-NMR solvent shift. If not specially noted, all spectra were recorded at RT.

The assignment of $^1$H NMR and $^{13}$C NMR resonances is based on C-H correlation in 2D-NMR spectra (DEPT, HSQC and HMBC experiments).

IR spectra were measured on a FT-IR Perkin Elmer Spectrometer 1720.
ESI mass spectra were measured on a Bruker *ESQUIRE-LC* quadrupole ion trap instrument equipped with a combined Hewlett-Packard Atmospheric Pressure Ion (API) source at the University of Zürich.

Mass spectra were measured on Finnigan MAT 8430 spectrometer at the University of Zürich.

ESR spectra were recorded in the X-Band (9.45-9.75 GHz) on a Bruker ESP-300E instrument.

UV/VIS spectra were measured on a Cary 50 Scan UV-VIS spectrophotometer.

X-ray crystal structure analyses were performed on a STOE-IPDS image plate system with monochromated Mo-$K\alpha$ (0.70713 Å) beam at the University of Zürich and on a Bruker SMART CCD diffractometer with Mo-$K\alpha$ (0.70713 Å) beam at the University of Hamburg. For the structure determination and refinement SHELXS-86 and SHELX-97 programs were used.\textsuperscript{192,193}

Elemental analyses were measured on a Heraeus CHN Rapid analyzer.

Cyclic voltammetry was carried out in THF/0.4 M Bu$_4$NPF$_6$ using a three-electrode configuration in the glove box at room temperature. The potential was controlled with a BAS-100W potentiostat (Bionalytical Systems Inc.).

DFT calculations were performed with Jaguar (version 6.0) using B3LYP (X3LYP) hybrid and LACVP** (6G-311G**++) basis set.
6.2 Synthesis and characterization of the novel Rh and Ir complexes

The below mentioned compounds were synthesized following the procedure from the literature:

- Di-µ-chloro-tetrakis(ethene)dirhodium(I) \([\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2\) \(^{194}\)
- Di-µ-chloro-tetrakis(cyclooctene)diiridium(I) \([\text{Ir}(\text{COE})_2\text{Cl}]_2\) \(^{194}\)
- Di-µ-chloro-tetrakis(ethene)diiridium(I) \([\text{Ir}(\text{C}_2\text{H}_4)_2\text{Cl}]_2\) \(^{46}\)
- Tetrabutylammonium-fluoride TBAF\(^{142}\)
- Dimethylphenyl amine N-oxide Me\(_2\)PhNO \(^{72}\)
- Diphenylmethyl amine N-oxide MePh\(_2\)NO \(^{195, 72}\)
- Trimethylsilane Me\(_3\)SiH \(^{144}\)
- LiAl(\text{pftb})\(_4\), AgAl(\text{pftb})\(_4\) \(^{196}\)
- Ph\(_3\)CAI(\text{pftb})\(_4\) \(^{63}\)
- [H(\text{Et}_3\text{O})_2][\text{Al(\text{pftb})}_4] \(^{165}\)
- 2,6-Bis-[1-(2,6-Dimethylphenylimino)ethyl]pyridine N\(_3\)Me\(_4\) and 2,6-Bis-[1-(2,6-Diisopropylphenylimino)ethyl]pyridine \(^{1\text{Pr}_3}\)N\(_3\) \(^{41, 197}\)
- 4-tert-butyl-2,6-diacetylpyridine and related ligand \(^{44}\)
- Complexes 1-7, 9 and 17, 19, 20 \(^{44, 47}\)

The general numbering scheme used for the assignment of proton and carbon resonances in the \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\)-NMR spectra for all complexes 1 - 36 is shown in Fig. 6.1.

![Fig. 6.1 Numbering scheme for NMR resonances used in complexes 1 - 36.](image)
6.2.1 Syntheses from Chapter 2

[Ir(N\textsubscript{3}Me\textsubscript{4})Me(OTf)\textsubscript{2}] - 8

[Ir(N\textsubscript{3}Me\textsubscript{4})OMe] 4 (840 mg, 1.51 mmol) was dissolved in 10 ml of toluene. MeOTf (0.33 ml, 3 mmol) was added via syringe at room temperature. The mixture was stirred over night. The solvent was removed in vacuum and a light green product was obtained. The crude product was washed with pentane (2 × 10 ml).

Yield: 96 % (1.26 g, 1.44 mmol).

\textsuperscript{1}H-NMR (CD\textsubscript{2}Cl\textsubscript{2}): \(\delta = 1.08\) (s, 3 H, Ir-CH\textsubscript{3}); 2.12 (s, 6 H, CH\textsubscript{3}); 2.40 (s, 6 H, CH\textsubscript{3}); 2.79 (s, 6 H, CN-CH\textsubscript{3}); 7.18 (m, 6 H, CH\textsubscript{arom}); 7.95 (s, 3 H, CH(2,3,4)).

\textsuperscript{13}C\{\textsuperscript{1}H\}-NMR (CD\textsubscript{2}Cl\textsubscript{2}): \(\delta = 18.3\) (CN-CH\textsubscript{3}); 19.5 (CH\textsubscript{3}); 19.8 (CH\textsubscript{3}); 21.4 (Ir-CH\textsubscript{3}); 127.6 (CH(2,4)); 128.7, 129.3, 129.5 (C\textsubscript{arom}-H); 134.1 (C\textsubscript{arom}-CH\textsubscript{3}); 138.5 (CH(3)); 144.6 (C\textsubscript{arom}N); 184.0 (C=N).

\textsuperscript{19}F\{\textsuperscript{1}H\}-NMR (CD\textsubscript{2}Cl\textsubscript{2}): \(\delta = -80.1\) (s, 3 F, OTf); -80.7 (s, 3 F, OTf).

[Ir(N\textsubscript{3}Me\textsubscript{4})(THF)]OTf - 10

[Ir(N\textsubscript{3}Me\textsubscript{4})Me(OTf)\textsubscript{2}] 8 (506 mg, 579 µmol) was dissolved in 10 ml of THF. A solution of [Ir(N\textsubscript{3}Me\textsubscript{4})OMe] 4 (344 mg, 579 µmol) in THF (10 ml) was added at room temperature to the reaction vial. The mixture was stirred for 2 hours. The color changed from green to dark brown. The solvent was evaporated. The crude product was recrystallized from THF/pentane (−35 °C).

Yield: 94 % (778 mg, 994 µmol).

\textsuperscript{1}H-NMR (THF-d\textsubscript{8}): \(\delta = 1.80\) (s, 6 H, CN-CH\textsubscript{3}); 1.61 (m, 4 H, THF); 1.81 (m, 4 H, THF) 2.24 (s, 12 H, CH\textsubscript{3}); 7.23 (m, 6 H, CH\textsubscript{arom}); 8.10 (d, 2 H, J = 8 Hz, CH(2,4)); 8.55 (t, 1 H, J = 8 Hz, CH(3)).

\textsuperscript{13}C\{\textsuperscript{1}H\}-NMR (THF-d\textsubscript{8}): \(\delta = 17.6\) (CN-CH\textsubscript{3}); 18.5 (CH\textsubscript{3}); 123.9 (C\textsubscript{arom}-CH\textsubscript{3}); 125.1 (CH(2,4)); 128.2 128.5, 129.7 (C\textsubscript{arom}H); 131.9 (CH(3)); 150.0 (C\textsubscript{arom}N); 166.4 (C(1,5)); 179.8 (C=N).
$^{19}$F-$^1$H-NMR (THF-d$_8$): $\delta = -78.92$ (s, 3 F, OTf).

Elemental analysis:
Calculated for C$_{30}$H$_{35}$N$_3$O$_4$F$_3$Ir: C 46.00, H 4.47, N 5.37;
    Found: C 45.73, H 4.13, N 5.65.

[Ir(N$_3$Me$_4$)(THF)]$^{10}$-Bar$_4^F$ - 10-Bar$_4^F$

[Ir(N$_3$Me$_4$)THF]OTf 10 (100 mg, 0.13 mmol) was dissolved in 10 ml of THF and added to NaBar$_4^F$ (0.8 g, 0.91 mmol). The mixture was stirred for 1 h, filtered and the solvent was evaporated. The crude product was extracted with diethyl ether and left at $-35$ °C to crystallize off the excess of NaBar$_4^F$. The latter was filtered and the solvent was evaporated. Yield: 33 % (61 mg, 43 µmol).

$^1$H-NMR (THF-d$_8$): $\delta = 1.77$ (s, 6 H, CN-CH$_3$); 2.22 (s, 12 H, CH$_3$); 7.24 (m, 6 H, CH$_{arom}$); 7.57 (s, 4 H, BAr$_4^F$); 7.79 (s, 8 H, BAr$_4^F$); 7.92 (d, 2 H, $J = 8$ Hz, CH(2,4)); 8.45 (t, 1 H, $J = 8$ Hz, CH(3)).

$^{19}$F-$^1$H-NMR (THF-d$_8$): $\delta = -64.0$ (s, 24 F, BAr$_4^F$).

[Ir(N$_3$Me$_4$)ONMe$_3$]Bar$_4^F$ - 10b

Me$_3$NO (3.3 mg, 44 µmol) was added to a solution of [Ir(N$_3$Me$_4$)THF]OTf 10 (50 mg, 33 µmol) in THF (10 ml). The mixture was stirred for 15 min. The solvent was evaporated and the crude product was washed with pentane (2 x 5 ml). The crude product was dissolved in THF and left to crystallize at $-35$ °C.

$^1$H-NMR (THF-d$_8$): $\delta = 1.11$ (s, 6 H, CN-CH$_3$); 2.10 (s, 12 H, CH$_3$); 2.45 (s, 9 H, Me$_3$NO); 7.15 (m, 6 H, CH$_{arom}$); 7.57 (s, 4 H, BAr$_4^F$); 7.80 (s, 8 H, BAr$_4^F$); 8.05 (d, 2 H, $J = 8$ Hz, CH(2,4)); 8.75 (t, 1 H, $J = 8$ Hz, CH(3)).
[Ir(N₃Me₄)(H)DME](PF₆)₂ - 11

[Ir(N₃Me₄)OH] 6 (50 mg, 92 µmol) was dissolved in 5 ml of DME and added to a violet solution of thianthrene⁺PF₆ (66 mg, 184 µmol) in DME. The color changed from violet to dark red. The solvent was evaporated in vacuo and the crude product was crystallized from DME/pentane (−35 °C).

Yield: 46 % (48 mg, 43 µmol).

¹H-NMR (CD₂Cl₂): δ = −32.50 (s, Ir-H); 2.25 (s, 6 H, CH₃); 2.28 (s, 6 H, CH₃); 2.82 (s, 6 H, CN-CH₃); 3.10 (m, 2 H, DME); 3.32 (s, 3 H, DME); 3.48 (m, 2 H, DME); 3.67 (s, 3 H, DME); 7.02-7.32 (m, 6 H, CHₐrom); 8.26 (s, 1 H, CH(3)).

¹⁹F{¹H}-NMR (CD₂Cl₂): −71.2 (6 F, PF₆); −75.69 (6 F, PF₆).

¹H-NMR (THF-d₈): δ = −31 (Ir-H); 1.94 (s, 6 H, CH₃); 2.18 (s, 6 H, CH₃); 2.49 (s, 6 H, CN-CH₃); 2.79 (m, 2 H, DME); 3.27 (s, 3 H, DME); 3.43 (m, 2 H, DME); 6.62 (d, 2 H, CH(2,4)); 7.04-7.30 (m, 6 H, CHₐrom); 8.38 (t, 1H, CH(3)).

¹⁹F{¹H}-NMR (THF-d₈): δ = −72.5 (6 F, PF₆); −76.3 (6 F, PF₆).

³¹P{¹H}-NMR (THF-d₈): δ = −143.4 (sept, PF₆).

[Ir(N₃Me₄)(DME)(H)]PF₆OTf - 12

[Ir(N₃Me₄)THF]OTf 10 (50 mg, 64 µmol) was dissolved in 5 ml of DME and added to a solution of thianthrene⁺PF₆ (64 µmol) in DME. The color changed from dark brown to red. The mixture was stirred for 15 min and solvent was evaporated. The crude product was extracted with DME and filtered. The solvent was evaporated. The complex was crystallized from DME/pentane (−35°C).

¹H-NMR (THF-d₈): δ = −32.7 (Ir-H); 1.94 (s, 6 H, CH₃); 2.18 (s, 6 H, CH₃); 2.49 (s, 6 H, CN-CH₃); 2.79 (m, 2 H, DME); 3.27 (s, 3 H, DME); 3.43 (m, 2 H, DME); 6.62 (d, 2 H, CH(2,4)); 7.04-7.30 (m, 6 H, CHₐrom); 8.38 (t, 1H, CH(3)).
\[^{13}\text{C}\{^1\text{H}\}\text{-NMR (THF-}d_8\text{)}: \delta = 15.3 \text{ (CH}_3\text{, DME); 15.5 \text{ (CH}_2\text{, DME); 16.6 \text{ (CH}_3\text{-CN); 23.3 \text{ (CH}_3\text{ overlaps with THF signal}); 127.1, 128, 128.4 \text{ (C}_{\text{arom-H}); 129.3 \text{ (C}_{\text{arom-CH}_3}; 130.1 \text{ (C}_{\text{arom-CH}_3}; 134.5 \text{ (CH}(3); 140.2 \text{ (CH}(2,4); 143.8 \text{ (C}_{\text{arom-N); 160.7 \text{ (C}(1,5); 184.6 \text{ (C=N).}}\n
\[^{19}\text{F}\{^1\text{H}\}\text{-NMR (THF-}d_8\text{): } \delta = -72.5 \text{ (3 F, PF}_6; -76.2 \text{ (3 F, PF}_6; -80.4 \text{ (3 F, OTf).}\n
\[\text{[Ir(N}_3\text{Me}_4)(\text{THF})\text{Cl}_2\text{]SbCl}_6 - 13\]

\[\text{[Ir(N}_3\text{Me}_4)\text{OH]} \text{ 6 (53 mg, 97.6 } \mu\text{mol) was dissolved in 5 ml THF and added to a solution of N-}(\text{p-bromophenyl})_5\text{SbCl}_6 \text{ (159 mg, 195 } \mu\text{mol) in THF. The reaction mixture was stirred for 2 hours. The color changed from green to brown. The solvent was evaporated. The crude product was dissolved in THF and filtered through a glass filter. The solvent was reduced to half of its volume and pentane was added (} -35^\circ\text{C).\]

Yield: 23% (23 mg, 22 } \mu\text{mol).\]

\[^1\text{H-NMR (THF-}d_8\text{): } \delta = 1.58 \text{ (m, 4 H, CH}_2\text{thf); 2.44 \text{ (s, 12 H, CH}_3; 3.10 \text{ (s, 6 H, CN-CH}_3; 3.36 \text{ (m, 4 H, CH}_2\text{-Othf); 7.20 \text{ (m, 6 H, CH}_{\text{arom}); 8.43 \text{ (t, 1 H, CH}(3); 8.55 \text{ (d, 2 H, CH}(2,4).}\n
\[^{13}\text{C}\{^1\text{H}\}\text{-NMR (THF-}d_8\text{): } \delta = 19.1 \text{ (CN-CH}_3; 21.7 \text{ (CH}_3; 26.4 \text{ (CH}_2\text{thf); 74.9 \text{ (CH}_2\text{-Othf); 129.4, 131.4, 133.0 \text{ (C}_{\text{arom-H); 130.8 \text{ (C}_{\text{arom-CH}_3}; 142.2 \text{ (CH}(2,4) \text{ or CH}(3); 145.7 \text{ (C}_{\text{arom-N); 160.3 (C}(1,5)); 186.7 \text{ (C=N).}}\n
Elemental analysis:
Calculated for C_{36}H_{49}Cl_{10}IrN_{3}O_{13}Sb: C 36.98, H 4.22, N 3.59;
Found: C 36.46, H 4.44, N 3.64.

\[\text{[Rh(N}_3\text{Pr}_4)\text{OMe]} - 3a\]

\[\text{[Rh(N}_3\text{Pr}_4)\text{Cl]} \text{ 1a (300 mg, 485 } \mu\text{mol) and NaOMe (42 mg, 775 } \mu\text{mol) were placed in a Schlenk tube and 20 ml of methanol was added. The mixture was stirred for 1h and the solvent was evaporated. The crude product was washed with pentane (2×5 ml) and dried in vacuum. The} \]
product was extracted into toluene and filtered through a glass filter. The solvent was removed in vacuo. Green crystals were obtained from a toluene/pentane by vapor diffusion (−35 °C).

Yield: 71 % (212 mg, 344 µmol).

\(^1\)H-NMR (C\(_6\)D\(_6\)): \(\delta = 1.09 \) (d, 12 H, \(^3J = 7\) Hz, CH(CH\(_3\))\(_2\)); 1.24 (d, 12 H, \(^3J = 7\) Hz, CH(CH\(_3\))\(_2\)); 2.10 (s, 6 H, CN-CH\(_3\)); 3.16 (sept, 4 H \(^3J = 7\) Hz, CH(CH\(_3\))\(_2\)); 4.28 (s, 3 H, OCH\(_3\)); 6.98-7.19 (m, 6 H, CH\(_{\text{arom}}\)); 6.80 (d, 2H, CH (2,4)); 7.82 (t, 1H, \(^3J = 8\) Hz, CH (3)).

\(^{13}\)C\{\(^1\)H\}\(-NMR (C\(_6\)D\(_6\)): \(\delta = 17.5\) (CN-CH\(_3\)); 24.0 (CH(CH\(_3\))\(_2\)); 24.2 (CH(CH\(_3\))\(_2\)); 28.8 (CH(CH\(_3\))\(_2\)); 121.8 (CH(3)); 123.6 (C\(_{\text{arom}}\)H); 124.5 (CH(2,4)); 127.1 (C\(_{\text{arom}}\)H); 140.5 (C\(_{\text{arom}}\)\(^i\)Pr); 146.2 (C\(_{\text{arom}}\)N); 156.3 (C(1,5)); 166.9 (C=N).

Elemental analysis:
Calculated for C\(_{34}\)H\(_{46}\)N\(_3\)ORh: C 66.33, H 7.53, N 6.83;
Found: C 64.16, H 7.22, N 6.82.

\([\text{Rh}(\text{N}^3\text{iPr}_4)\text{N}_3]\) - 15

The rhodium radical \(\text{V}\) (20 mg) was dissolved in 5 ml of THF and Me\(_3\)SiN\(_3\) (4.6 µl, 34.2 µmol) was added. The mixture was stirred for 2 hours. The color changed from violet to green. The solvent was evaporated and the crude product was washed with pentane (2 x 2 ml). Crystals were obtained from a solution of THF/pentane at −35 °C.

Yield: 71 % (15.6 mg, 24 µmol – based on complex \(1\)a).

\(^1\)H-NMR (THF-d\(_8\)): \(\delta = 1.05\) (d, 12 H, \(^3J = 7\) Hz, CH(CH\(_3\))\(_2\)); 1.14 (d, 12 H, \(^3J = 7\) Hz, CH(CH\(_3\))\(_2\)); 1.65 (s, 6 H, CN-CH\(_3\)); 3.06 (sept, 4 H \(^3J = 7\) Hz, CH(CH\(_3\))\(_2\)); 7.08-7.20 (m, 6 H, CH\(_{\text{arom}}\)); 7.87 (d, 2 H, \(^3J = 8\) Hz, CH (2,4)); 8.47 (t, 1 H, \(^3J = 8\) Hz, CH (3)).

\(^{13}\)C\{\(^1\)H\}\(-NMR (THF-d\(_8\)): \(\delta = 16.4\) (CN-CH\(_3\)); 22.7 (CH(CH\(_3\))\(_2\)); 27.9 (CH(CH\(_3\))\(_2\)); 122.2 (CH(3)); 122.5 (C\(_{\text{arom}}\)H); 124.5 (CH(2,4)); 126.1 (C\(_{\text{arom}}\)H); 139.5 (C\(_{\text{arom}}\)\(^i\)Pr); 145.3 (C\(_{\text{arom}}\)N); 155.2 (C(1,5)); 166.6 (C=N).

IR (toluene): \(\nu_{\text{NN}} = 2031\text{cm}^{-1}\).
Elemental analysis results were not adequate after repeating the measurements several times.

[Rh(N$_3$Pr$_4$)N$_2$] - 17

[Rh(N$_3$Pr$_4$)Cl] 1a (100 mg, 161 µmol) was dissolved in 5 ml of THF and added to Na/Hg (550 mg, 183 µmol) in THF. The mixture was stirred for 1.5 h. The color of the mixture changed from green to brown. The solvent was evaporated and the crude product was washed with pentane (2×5 ml). After removing pentane in vacuum, the brown product was extracted into toluene and filtered. The solvent was evaporated. The crystals were obtained from toluene/pentane solution at –35 °C.

Yield: 76 % (75 mg, 122 µmol).

$^1$H-NMR (C$_6$D$_6$): $\delta = 2.28$ (br); 3.55(br); 5.60 (br).

IR (toluene): $\nu_{NN} = 2139$ cm$^{-1}$

ESR (in toluene): $g = 1.99$ (3500 G) at RT.

Elemental analysis:
Calculated for C$_{33}$H$_{43}$N$_5$Rh: C 64.70, H 7.07, N 11.43;

6.2.2 Syntheses from Chapter 3

[Ir(N$_3$Me$_4$)Me] - 18

Alternative syntheses

a) [Ir(N$_3$Me$_4$)OMe] 4 (21 mg, 36 µmol) was dissolved in 5 ml of toluene and cooled down to –35°C. A 2M solution of ZnMe$_2$ in toluene (9 µl, 18 µmol) was added. The reaction mixture was allowed to warm up to room temperature and was stirred for 2 days. The solvent was evaporated
and the crude product was extracted into diethyl ether. After filtration, the solvent was evaporated and $^1$H-NMR recorded.

Yield: 70 % (14 mg, 24 µmol).

b) [Ir(N$_3$Me$_4$)OH] 6 (20 mg, 34 µmol) was dissolved in 5 ml of THF and cooled down to −35°C. A 2M solution of ZnMe$_2$ in toluene (17 µl, 34 µmol) was added. The mixture was stirred until room temperature was reached. The mixture was filtered and the solvent was evaporated.

Yield: 72 % (15 mg, 26 µmol).

$^1$H-NMR (THF-d$_8$): 0.21 (s, 6 H, CN-CH$_3$); 1.97 (s, 12 H, CH$_3$); 6.91 (s, 3 H, Ir-CH$_3$); 7.0 – 7.19 (m, 6 H, CH$_{arom}$); 8.40 (d, $J$ = 8 Hz, 2 H, CH(2,4)); 8.91 (t, $J$ = 8 Hz, 1 H, CH(3)).

[Rh(N$_3$Me$_4$)F](Me$_2$N)$_3$SOTf - 22

[Rh(N$_3$Me$_4$)THF]OTf 9 (100 mg, 144 µmol) was dissolved in 10 ml of THF and added to a solution of TASF (40 mg, 144 µmol) in THF. The color changed from brown to dark green. The mixture was stirred for 15 min and then filtered through a glass filter. The solvent was evaporated. The crude product was dissolved in 5 ml of THF and 1 ml of pentane was added to precipitate colorless crystals (of Me$_3$SiF). The product was re-filtered to yield green crystals.

Yield: 61 % (71 mg, 88 µmol).

$^1$H-NMR (THF-d$_8$): $\delta$ = 1.64 (s, 6 H, CN-CH$_3$); 2.14 (s, 12 H, CH$_3$); 2.76 (18 H, (Me$_2$N)$_3$S); 7.03-7.08 (m, 6 H, CH$_{arom}$); 7.85 (d, 2 H, $J$ = 8 Hz); 8.49 (t, 1 H, $J$ = 8 Hz).

$^{13}$C{$^1$H}-NMR (THF-d$_8$): $\delta$ = 16.5 (CN-CH$_3$); 18.5 (4 CH$_3$); 38.2 ((Me$_2$N)$_3$S); 122.9 (CH(3)); 126.1 (CH(2,4)); 128.7, 131.2 (C$_{arom}$H); 149.1 (C$_{arom}$-N); 158.1 (C(1,5)); 168.1 (C=N).

$^{19}$F{$^1$H}-NMR (THF-d$_8$): $\delta$ = −80.0 (3 F, OTf), -158.1 (1 F, Rh-F).
Elemental analysis:
Calculated for C_{32}H_{45}F_{4}N_{6}O_{3}RhS_{2}: C 47.76, H 5.64, N 10.44, S 7.97;
Found: C 47.46, H 5.65, N 10.49, S 7.69.

[Ir(N_{3}Me_{4})F](Me_{2}N)_{3}SOTf - 23

[Ir(N_{3}Me_{4})THF]OTf 10 (73.3 mg, 94 µmol) was dissolved in 10 ml of THF and added to a solution of TASF (26 mg, 94 µmol) in THF. The color changed from brown to dark green. The mixture was stirred for 15 min and filtered through a glass filter. The solvent was evaporated. The crude product was dissolved in 5 ml of THF and 1 ml of pentane was added to precipitate colorless crystals (of Me_{3}SiF). After a second filtration product was placed at –35 °C and green crystals were obtained.

Yield: 60 % (50 mg, 56 µmol).

^{1}H-NMR (THF-d_{8}): δ = 1.01 (s, 6 H, CN-CH_{3}); 1.98 (s, 12 H, CH_{3}); 2.73 (18 H, (Me_{2}N)_{3}S); 7.03-7.05 (m, 6 H, CH_{arom}); 8.01 (d, 2 H, J = 8 Hz); 8.45 (t, 1 H, J = 8 Hz).

^{13}C{^{1}H}-NMR (THF-d_{8}): δ = 18.6 (CN-CH_{3}); 18.4 (4 CH_{3}); 38.3 ((Me_{2}N)_{3}S); 120.4 (CH(3)); 123.9 (CH(2,4)); 126.7, 128.6, 131.6 (C_{arom}H); 153.8 (C_{arom}-N); 165.5 (C(1,5)); 172.7 (C=N).

^{19}F{^{1}H}-NMR (THF-d_{8}): δ = −79.6 (3 F, OTf); −128.0 (1 F, Ir-F).

Elemental analysis:
Calculated for C_{32}H_{45}F_{4}N_{6}O_{3}IrS_{2} (.3THF): C 47.59, H 5.07, N 7.57;
Found: C 47.47, H 4.97, N 6.97.

[Ir(N_{3}Me_{4})(Me)(OTf)(CH_{3}CN)]OTf - 28

[Ir(N_{3}Me_{4})(Me)(OTf)]_{2} 8 (20 mg, 23 µmol) was dissolved in acetonitrile. The color from green changed to red. The solvent was evaporated and the product was dissolved in THF/pentane and left to crystallize. The reaction was quantitative.

^{1}H-NMR (CD_{2}Cl_{2}): δ = 0.84 (s, 3 H, Me); 2.18 (s, 6 H, 2 CH_{3}); 2.21 (s, 3 H, CH_{3}CN); 2.40 (s, 6 H, 2 CH_{3}); 2.80 (s, 6 H, 2 CH_{3}-CN); 7.23 (m, 6 H, CH_{arom}); 8.24-8.35 (m, 3 H, CH(2, 3, 4)).
13C{1H}-NMR (CD2Cl2): δ = 2.0 (s, CH3CN); 16.9 (CN-CH3); 17.4 (CH3); 17.6 (CH3); 23.3 (Ir-CH3); 120.5 (CH(2,4); 126.5-128.5 (C aromH); 139.3 (CH(3)); 141.6 (C arom-CH3); 155.5 (C aromN); 181.0 (C=N).

19F{1H}-NMR (CD2Cl2): δ = -79.50 (s, 3F, OTf); -79.62 (s, 3F, OTf).

6.2.3 Syntheses from Chapter 4

[Ir(N3Me4)(H)Cl2] - 30

Tris-(pentafluorophenyl)borane (44 mg, 86 µmol) was dissolved in 5 ml of dichloromethane and added to solid [Ir(N3Me4)OMe] 4 (50 mg, 84 µmol). The reaction mixture was stirred for 15 min. The color changed from green to brown. The solvent was evaporated and the crude product was washed with pentane (2 × 2 ml) and dried in vacuo. The complex was recrystallized from CH2Cl2/pentane (−35 °C).

Yield: 60 % (32 mg, 51 µmol).

1H-NMR (CD2Cl2) δ = -18 (s, 1 H, Ir-H); 2.02 (s, 6 H, CH3); 2.40 (s, 6 H, CH3); 2.60 (s, 6 H, CN-CH3); 7.12 – 7.22 (m, 6 H, CH arom); 7.87 (t, 1 H, J = 8 Hz, CH(3)); 8.27 (d, 2H, J = 8 Hz, CH(2,4)).

13C{1H}-NMR (CD2Cl2) δ = 18.6 (CN-CH3); 22.1 (CH3); 22.3 (CH3); 129 (CH(3)); 129.8 (CH(2,4); 132.4, 133.0, 133.8 (C aromH); 134.0 (C arom-CH3); 142.7 (C aromN); 154.0 (C=N).

[Ir(N3Me4)][MeOB(C6F5)3] - 31

Tris-(pentafluorophenyl)borane (17 mg, 33 µmol) was dissolved in 5 ml of diethyl ether and added to [Ir(N3Me4)OMe] 4 (20 mg, 33 µmol). The mixture was stirred for 30 min and the color changed from green to reddish-brown. The solvent was evaporated and the crude product was washed with pentane (3 x 5 ml). After drying in vacuum no further purification was necessary.

Yield: 64 % (25 mg, 21 µmol).
\[ ^1H\text{-NMR (THF-d}_8\text{): } \delta = 1.78 \text{ (s, 6 H, CN-CH}_3\text{); 2.23 (s, 12 H, CH}_3\text{); 2.99 (s, br, 3 H, BOME(C}_6\text{F}_3\text{)_3}; 7.25 (m, 6 H, CH}_\text{arom}\text{); 7.93 (d, 2 H, } J = 8 \text{ Hz, CH(2,4)); 8.48 (t, 1 H, } J = 8 \text{ Hz, CH(3))}. \]

\[ ^{13}C\{^1H\}\text{-NMR (THF-d}_8\text{): } \delta = 17.4 \text{ (CN-CH}_3\text{); 18 \text{ (CH}_3\text{); 25.3 (OMeB(C}_6\text{F}_3\text{)); 124.2 (CH(2,4)); 123.9 (C}_\text{arom}\text{-CH}_3\text{); 128.2, 129.7 (C}_\text{arom}\text{H); 132 (CH(3)); 151.3 (C}_\text{arom}\text{-N); 160.0 (C(1,5)); 178.0 \text{ (C=}\text{N)}. \]

\[ ^{19}F\{^1H\}\text{-NMR (THF-d}_8\text{): } \delta = -133.9 \text{ (m, 6 F, o-F); } -165.4 \text{ (t, 3 F, p-F); } -168.4 \text{ (m, 6 F, m-F). } \]

\[ [\text{Ir(N}_3\text{Me}_4\text{(THF)}][\text{Al(pftb)}_4] - 10-\text{Al(pftb)}_4 \]

**Alternative syntheses**

1) from complex 4

\[ [\text{H(Et}_2\text{O)}_2][\text{Al(pftb)}_4] \text{ (37 mg, 33 } \mu\text{mol) was dissolved in 5 ml of THF and added into a THF solution of } [\text{Ir(N}_3\text{Me}_4\text{O)}\text{Me}] \text{ 4 (20 mg, 33 } \mu\text{mol). The color changed immediately from green to brownish-red. The mixture was stirred for 15 min and the solvent was evaporated. No further purification was necessary.} \]

Yield: 94 % (50 mg, 31 } \mu\text{mol).}

\[ ^1H\text{-NMR (THF-d}_8\text{): } \delta = 1.78 \text{ (s, 6 H, CN-CH}_3\text{); 2.24 (s, 12 H, CH}_3\text{); 7.26 (m, 6 H, CH}_\text{arom}\text{); 7.93 (d, 2 H, } J = 8 \text{ Hz, CH(2,4)); 8.51 (t, 1 H, } J = 8 \text{ Hz, CH(3))}. \]

\[ ^{13}C\{^1H\}\text{-NMR (THF-d}_8\text{): } \delta = 17.6 \text{ (CN-CH}_3\text{); 18.2 (CH}_3\text{); 120.9, 123.9 (C}_\text{arom}\text{-CH}_3\text{); 124.4 (CH(2,4)); 128.5, 129.9 (C}_\text{arom}\text{H); 132.0 (CH(3)); 150.1(C}_\text{arom}\text{-N); 163.5 (C(1,5)); 178.0 \text{ (C=}\text{N)}. \]

\[ ^{19}F\{^1H\}\text{-NMR (THF-d}_8\text{): } \delta = -75.6 \text{ (s, 36 F, Al(pftb)}_4\text{).} \]

**Elemental analysis:**

Calculated for C_{45}H_{35}AlF_{36}IrN_{3}O_{5}: C 33.76, H 2.20, N 2.62;  
Found: C 33.33, H 2.29, N 2.38.
2) from complex 10

[\text{Ir(N}_3\text{Me}_4\text{)THF}O\text{Tf} 10] (30 mg, 38 µmol) was added to a solution of LiAl(pftb)_4 (37 mg, 38 µmol) in diethyl ether (10 ml). The mixture was stirred for 45 min. The color slightly changed from brown to reddish–brown. The mixture was filtered and the solvent was evaporated. The crude product was recrystallized from THF/pentane at -35 °C.

Yield: 95 % (55 mg, 36 µmol).

\( ^1\text{H-NMR (THF-d}_8\): } \delta = 1.78 (s, 6 \text{ H, CN-CH}_3); 2.23 (s, 12 \text{ H, CH}_3); 7.26 (m, 6 \text{ H, CH}_\text{arom}); 7.93 \text{ (d, 2 H, } J = 8 \text{ Hz, CH(2,4)); 8.51 (t, 1 \text{ H, } J = 8 \text{ Hz, CH(3))}.

\( ^{13}\text{C\{}^1\text{H}\}_\text{-NMR (THF-d}_8\): } \delta = 17.6 \text{ (CN-CH}_3); 18.2 \text{ (CH}_3); 120.9, 123.9 \text{ (C}_\text{arom-CH}_3); 124.4 \text{ (CH(2,4)); 128.5, 129.9 (C}_\text{arom-H); 132.0 \text{ (CH(3)); 150.1(C}_\text{arom-N) 163.5 (C(1,5)); 178.0 (C=\text{N)).}

\( ^{19}\text{F\{}^1\text{H}\}_\text{-NMR (THF-d}_8\): } \delta = -75.6 \text{ (s, 36 F, Al(pftb)_4).}

3) from complex 19

[\text{H(Et}_2\text{O})_2\text{][Al(pftb)_4}] (38 mg, 34 µmol) was dissolved in 5 ml of THF and added to a THF solution of [\text{Ir(N}_3\text{Me}_4\text{)Ph}] 19 (22 mg, 33 µmol). The color changed immediately from green to brownish-red. The mixture was stirred for 15 min and the solvent was evaporated.

Yield: 92 % (48 mg, 29 µmol).

\[\text{Ir(N}_3\text{Me}_4\text{)H][Al(pftb)_4]}_2 - 33\]

[\text{H(Et}_2\text{O})_2\text{][Al(pftb)_4}] (37 mg, 33 µmol) was dissolved in 5 ml of THF and added into a THF solution of [\text{Ir(N}_3\text{Me}_4\text{)OMe}] 4 (10 mg, 17 µmol). The color changed immediately from green to red. The mixture was stirred for 20 min and the solvent was evaporated. No further purification was necessary.
\[ \text{H-NMR (THF-d}_8\text{): } \delta = -33.1 \text{ (s, 1 H, Ir-H); 2.17 (s, 6 H, CH}_3\text{); 2.40 (s, 6 H, CH}_3\text{); 2.83 (s, 6 H, CN-CH}_3\text{); 7.15-7.33 (m, 6 H, CH}_\text{arom}\text{); 8.36 (t, 1 H, } J = 8 \text{ Hz, CH}(3)\text{); 8.22 (d, 2 H, } J = 8 \text{ Hz, CH}(2,4)\text{).} \]

\[ \text{^{13}C\{^1\text{H}\}-NMR (THF-d}_8\text{): } \delta = 16.8 \text{ (CH}_3\text{); 17.0 (CN-CH}_3\text{); 18.1 (CH}_3\text{); 119.1, 125.0 (C}_\text{arom-CH}_3\text{); 128.8 (CH}(2,4)\text{); 123.5, 130.3 (C}_\text{arom-H); 142.0 (CH}(3)\text{); 145.3 (C}_\text{arom-N) 162.9 (C}(1,5)\text{); 186.0 (C=\text{N).} \]

\[ \text{^{19}F\{^1\text{H}\}-NMR (THF-d}_8\text{): } \delta = -76.3 \text{ (s, 72 F, Al(pftb)}_4\text{).} \]

\[ \text{[Ir(N}_3\text{Me}_4\text{)C}_5\text{H}_10\text{O}[\text{Al(pftb)}_4]\text{ - 34} \]

As already mentioned in Chapter 4, complex \textbf{10-Al(pftb)}_4 is soluble in diethyl ether, THF and DME and insoluble in non-polar solvents such as pentane, benzene and toluene. In order to obtain crystals from \textbf{10-Al(pftb)}_4 different solvent mixtures were tried either by layering non-polar solvent on top of the ether solution of \textbf{10-Al(pftb)}_4, or by vapor diffusion. Crystals were obtained from a diluted solution of Et\textsubscript{2}O/pentane at −35 °C by vapor diffusion. During crystallization of \textbf{10-Al(pftb)}_4, compound \textbf{34} was obtained.

\[ \text{^1H-NMR (Et\textsubscript{2}O-d}_{10}\text{): } \delta = 1.01 \text{ (m, -OCH}_2\text{CH}_3\text{); 1.42 (m, -OCH}_2\text{CH}_3\text{); 2.03 (s, 6 H, CN-CH}_3\text{); 2.21 (s, 12 H, CH}_3\text{); 4.21 (s, 2 H, CH=CH}_2\text{); 5.57 (s, 1 H, } CH=CH}_2\text{); 7.43 (m, 6 H, CH}_\text{arom}\text{); 8.28 (d, 2 H, } J = 8 \text{ Hz); 9.07 (t, 1 H, } J = 8 \text{ Hz).} \]

\[ \text{^{19}F\{^1\text{H}\}-NMR (Et\textsubscript{2}O-d}_{10}\text{): } \delta = -79.0 \text{ (s, 36 F, Al(pftb)}_4\text{).} \]

\[ \text{[Ir(N}_3\text{Me}_4\text{)(\eta}^2\text{-CH}_2\text{O)}[\text{Al(pftb)}_4]\text{ - 35} \]

\[ \text{[Ir(N}_3\text{Me}_4\text{)OMe] 4 (38 mg, 64 µmol) was dissolved in 5 ml of C}_6\text{H}_6\text{ and then added to a yellow solution of Ph}_3\text{CAI(pftb)}_4 \text{ (77 mg, 64 µmol) in C}_6\text{H}_6\text{. The mixture was stirred for 2 hours. The color changed from green to redish-brown. The solvent was evaporated and the crude product was washed with pentane to remove Ph}_3\text{CH (until colourless solution). The crude product was dissolved in diethyl ether. Crystals were obtained from a diluted solution of Et\textsubscript{2}O/pentane at −35 °C by vapor diffusion.} \]
Yield: 64 % (64 mg, 41 µmol).

$^1$H-NMR (THF-d$_8$): $\delta = 1.94$ (s, 6 H, CN-CH$_3$); 2.10 (s, 12 H, CH$_3$); 4.00 (s, 2 H, CH$_2$O); 7.29 (m, 6 H, CH$_{arom}$); 8.27 (d, 2 H, $J = 8$ Hz); 8.84 (t, 1 H, $J = 8$ Hz).

$^{13}$C{$^1$H}-NMR (THF-d$_8$): $\delta = 16.4$ (CH$_3$); 17.3 (CN-CH$_3$); 69.1 (CH$_2$O); 125.6 (CH(2,4)); 128.4, 128.5, 129.1 (C$_{arom}$H); 136.0 (CH(3)); (C(1,5)); 150.0 (C$_{arom}$-N); 178.0 (C=N).

$^{19}$F{$^1$H}-NMR (THF-d$_8$): $\delta = -74.3$ (s, 36 F, Al(pftb)$_4$).

IR (toluene): $\nu_{CO} = 1031$ cm$^{-1}$ (tentative).

Elemental analysis:
Calculated for C$_{42}$H$_{37}$IrN$_3$O$_5$AlF$_{36}$: C 32.33, H 2.37, N 2.69;
Found: C 33.35, H 2.25, N 2.55.

$[\text{Rh}(N_3\text{Me}_4)(\text{THF})][\text{Al}(\text{pftb})_4] – 36$

$[\text{H}(\text{Et}_2\text{O})_2][\text{Al}(\text{pftb})_4]$ (38 mg, 34 µmol) was dissolved in 5 ml of THF and added to a THF (5 ml) solution of $[\text{Rh}(N_3\text{Me}_4)\text{OMe}]$ 3 (17 mg, 34 µmol). The mixture was stirred over the night and the color changed from green to reddish-brown. The solvent was evaporated. The crude product was left to crystallize from THF/pentane solution at –35 °C.

Yield: 88 % (45 mg, 30 µmol).

$^1$H-NMR (THF-d$_8$): $\delta = 1.98$ (s, 6 H, CN-CH$_3$); 2.30 (s, 12 H, CH$_3$); 7.19 (m, 6 H, CH$_{arom}$); 7.92 (d, 2 H, $J = 8$ Hz, CH(2,4)); 8.39 (t, 1 H, $J = 8$ Hz, CH(3)).

$^{13}$C{$^1$H}-NMR (THF-d$_8$): $\delta = 16.5$ (CN-CH$_3$); 18.4 (CH$_3$); 119.5, 125.3 (C$_{arom}$-CH$_3$); 126.9 (CH(2,4)); 127.7, 129.7 (C$_{arom}$H); 131 (CH(3)); 148.1(C$_{arom}$-N) 158.8 (C(1,5)); 172.1 (C=N).

$^{19}$F{$^1$H}-NMR (THF-d$_8$): $\delta = -76.3$ (s, 36 F, Al(pftb)$_4$).
Elemental analysis:
Calculated for C\(_{45}\)H\(_{35}\)AlF\(_{36}\)N\(_3\)O\(_5\)Rh: C 35.76, H 2.33, N 2.78;
Found: C 39.63, H 3.18, N 3.76.

**Alternative synthesis**

[Rh(N\(_3\)Me\(_4\))OMe] (35 mg, 69.4 \(\mu\)mol) dissolved in C\(_6\)H\(_6\) was added in to a yellow solution of Ph\(_3\)CAl(pftb)\(_4\) (84 mg, 69.4 \(\mu\)mol) in C\(_6\)H\(_6\). The mixture was stirred for 30 min. The color changed from green to reddish-brown. The solvent was evaporated and the crude product was washed with pentane to remove Ph\(_3\)CH and Ph\(_3\)COMe (until a colorless solution). The crude product was dried in high vacuum and was left to crystallize from THF/pentane solution at \(-35^\circ\)C.  

Yield: 38 \% (40 mg, 26 \(\mu\)mol).

[Rh(N\(_3\)Me\(_4\))C\(_6\)H\(_{10}\)O][Al(pftb)\(_4\)] - 37

Complex 36 is soluble in diethyl ether, THF and DME and insoluble in non-polar solvents such as pentane, benzene and toluene. In order to obtain crystals from 36, different solvent mixtures were attempted. Crystals were obtained by slow diffusion of pentane into a diethyl ether solution of 36 at \(-35^\circ\)C. During crystallization compound 37 was obtained.

\(^1\)H-NMR (Et\(_2\)O-d\(_{10}\)): \(\delta = 0.87\) (m, -OCH\(_2\)CH\(_3\)); \(2.07\) (s, 6 H, CN-CH\(_3\)); \(2.30\) (m, -OCH\(_2\)CH\(_3\)); \(2.43\) (s, 12 H, CH\(_3\)); \(3.12\) (br, CH=CH\(_2\)); \(5.45\) (s, CH=CH\(_2\)); \(7.43\) (m, 6 H, CH\(_{arom}\)); \(7.95\) (d, 2 H, \(J = 8\) Hz); \(8.56\) (t, 1 H, \(J = 8\) Hz).

\(^19\)F{\(^1\)H}-NMR (Et\(_2\)O-d\(_{10}\)): \(\delta = -78.1\) (s, 36 F, Al(pftb)\(_4\)).
7 References

38. Susnjar, N., unpublished results, **2004**.


8 Appendix

8.1 Starting materials (1 – 7, 9)$^{44,49}$

8.2 Isolated complexes (8-36)
8.3 Summary of postulated complexes
$\text{Rh, IVa; Ir, IVb}$

$\text{V}$

$\text{Va}$

$\text{VI}$

$\text{R} = \text{Me, iPr}$

$\text{R'} = \text{H, t-Bu}$
### 8.2 X-ray crystallographic data and parameters

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<td>([\text{Ir} (\text{N}_3\text{Me}_4)\text{F})((\text{Me}_2\text{N})_3\text{SOTf})] 23</td>
<td>([\text{Ir} (\text{N}_3\text{Me}_4)(\text{H})\text{Cl}_2]\cdot \text{CH}_2\text{Cl}_2) 30</td>
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<td>---------</td>
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<td>Empirical formula</td>
<td>(\text{C}<em>{32}\text{H}</em>{45}\text{F}_4\text{IrN}_6\text{O}_3\text{S}_2)</td>
<td>(\text{C}<em>{26}\text{H}</em>{30}\text{Cl}_4\text{Ir}_3)</td>
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<td>(\text{C}2/c, \text{No.15})</td>
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<td>(\alpha [^\circ])</td>
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<td>[Ir(N₃Me₄)(Me)(MeCN)OTf]^+ ²⁸</td>
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<td>$\text{C}<em>{47}\text{H}</em>{41}\text{AlF}_{36}\text{RhN}_3\text{O}_5$</td>
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<td>$D_{\text{calc.}}$ [g/cm$^3$]</td>
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<td>$\lambda$ [Å], Mo-K$\alpha$</td>
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<td>0.71073</td>
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<td>$2 \Theta$ [°]</td>
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<td>0.743, -0.722</td>
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</table>
8.3 Lebenslauf

Persönliche Daten

Name: Nevena Šušnjar

Geboren am: 23.09.1976

Geburtsort: Belgrad

Nationalität: Serbisch

Ausbildung

1983 - 1991 Grundschule “Karadjordje”
1995 - 2001 Universität Belgrad, Fakultät der Chemie

06/2001 - 11/2001 Diplomarbeit im Institut für Anorganische Chemie, Universität Belgrad
bei Prof. Dr. S. Sovilj
Thema: Co(II), (III), Ni(II) and Cu(II) dithiocarbamato Complexes

19/11/2001 Dipl. Chemiker

2002 - 2006 Doktorandin bei Prof. Dr. P. Burger zum
Thema: Towards Rhodium and Iridium oxo complexes

2002 - 2003 Anorganisch-chemischen Institut der Universität Zürich
2003 - 2006 Institut für Anorganische und Angewandte Chemie der Universität Hamburg

Anstellungsverhältnis

10/2003 - 02/2006 Wissenschaftliche Mitarbeiterin an der Universität Hamburg

Konferenzen und Fortbildungen

08/2003 XV Fechem - Zürich, Switzerland - Posterbetrag
09/2003 Summer school on computational chemistry - Heidelberg, Germany
09/2004 Molecular modeling and DFT calculations - Heidelberg, Germany
09/2005 XVI Fechem - Budapest, Hungary – Posterbetrag
The research presented within, was carried out by the author at the University of Zürich and University of Hamburg. It is the author’s original work and contains nothing that is a result of the work carried out in collaboration and has not been submitted in whole or in part for a degree at any other university.

Hamburg, February 2006