Group 9 open-shell organometallics: reactivity at the ligand
Dzik, W.I.

Citation for published version (APA):
Dzik, W. I. (2011). Group 9 open-shell organometallics: reactivity at the ligand
Chapter 4

Base Assisted Selective Reduction of Organometallic Rh$^{II}$ and Ir$^{II}$ Radicals
4.1 Introduction

Hydrogen atom transfer (HAT) plays an important role in inorganic chemistry and is of fundamental importance in many biochemical transformations and some industrially relevant synthetic reactions. Transfer of a hydrogen atom from the substrate to a metal coordinated oxygen atom is one of the key steps in biotransformations catalyzed by galactose oxidase\(^1\), lipoxygenase,\(^2\) cytochrome \(\text{P}_{450}\),\(^3\) methane monooxygenases\(^4\) and class I ribonucleotide reductase.\(^5\) HAT reactions are essential for chain transfer during metal-mediated radical polymerization of olefins,\(^6\) but can also lead to catalyst deactivation in cyclopropanation reactions.\(^7\)

Open-shell second and third row transition metal complexes are excellent models to study HAT reactions, because the products are generally well defined NMR-characterizable diamagnetic compounds. This has been exploited by a number of groups over the past years, providing information on the fundamental reactivity of transition metal radical complexes towards \(Y\)-H bonds (\(Y = C, H, Si, S\)). The pioneering work of the group of Wayland on rhodium and iridium complexes has demonstrated that \(C\)-\(H\)\(^8\) and \(H\)-\(H\)\(^8c\) bonds can be broken homolytically between two metalloradicals. Ligand radicals generated on these metals are also capable of abstracting hydrogen atoms from the reaction medium.\(^9\) Recently, the group of Grützmacher elegantly presented a galactose oxidase mimic based on an iridium aminyl radical complex.\(^10\) The study of hydrogen atom transfer at open-shell second and third row transition metal complexes clearly deserves much more attention as we are only beginning to understand such reactivity.

Recently, our group investigated the reactivity of paramagnetic rhodium and iridium compounds with the general formula \([\text{M}^{II}(\text{N}_3\text{-ligand})(\text{cod})]^2+\) (\(\text{cod} = \text{cis,cis-1,5-cyclooctadiene}\)).

![](image)

Scheme 1. Hydrogen atom transfer of allylic hydrogen in \([\text{M}^{III}(\text{N}_3\text{-ligand})(\text{cod})]^2+\) complexes (\(\text{R}_1, \text{R}_2 = \text{H or Me, R}_3 = \text{H or Bn}\)).

These complexes undergo interesting bimolecular HAT reactions, and the rate of the HAT pathway proved to be markedly dependent on the nature of the used bis-picolylamine (bpa) type \(\text{N}_3\)-ligand. Irrespective of the \(\text{R}\) groups introduced in the bpa moiety (\(\text{R}_1, \text{R}_2 = \text{H or Me, R}_3 = \text{H or Bn}\)) the paramagnetic complexes spontaneously transform into a 1:1 mixture of \([\text{M}^{III}(\text{allyl})(\text{N}_3\text{-ligand})]^2+\) and protonated \(\text{M}(\text{cod})\).
complexes (in the form of $[\text{M}^\text{I}(\text{olefin})(\text{N}_3\text{-ligand}+\text{H})]^\text{2+}$ for $\text{M} = \text{Rh}$ or $[\text{M}^{\text{III}}(\text{H})(\text{olefin})(\text{N}_3\text{-ligand})]^\text{2+}$ for $\text{M} = \text{Ir}$, Scheme 1).\textsuperscript{11} The rate of decomposition depends strongly on the nature of the substituents and only the complexes with $R_1, R_2 = \text{Me}$, $R_3 = \text{Bn}$ were stable enough to be isolated and fully characterized. The low stability of complexes with secondary amine bpa-type ligands ($R_3 = \text{H}$) raises the question if the decomposition to the allyl and hydride complexes could proceed via the involvement of aminyl radicals (Scheme 2).

![Scheme 2](image)

**Scheme 2.** Possible hydrogen atom transfer of the allylic hydrogen of the cod ligand via a putative aminyl radical species.

The possible involvement of aminyl radicals in the $[\text{M}^{\text{II}}(\text{cod})(\text{N}_3\text{-ligand})]^\text{2+}$ system seems plausible. Aminyl radicals can be stabilized by coordination to a metal centre and several examples of such stable species have been reported.\textsuperscript{12,13} Reversible H-atom transfer (HAT) from a nitrogen atom of transition metal complexes with ligands possessing an amine functionality can occur and this has been extensively studied in the last decade by the group of Mayer.\textsuperscript{14} Recently, Grützmacher et al. showed that aminediolefin Rh I and Ir I complexes can form stable, $d^8$ transition metal aminyl radical complexes upon deprotonation of the amine and subsequent one-electron oxidation.\textsuperscript{10,15} These aminyl radical complexes abstract hydrogen atoms from activated Y-H bonds. Moreover, bispicolylamine (bpa) is also prone to single and double deprotonation when coordinated to rhodium or iridium diolefin species,\textsuperscript{16} and can subsequently form transient ligand-centered radical species upon one electron oxidation.

To study the possible aminyl radical reactivity of the bpa-type ligand we need a diene ligand that is more robust than cyclooctadiene (innocent towards allylic C-H bond activation or C-C coupling). Therefore we decided to synthesize rhodium and iridium complexes with dibenzo[a,e]cyclooctatetraene (dbcot) as the supporting diolefin.\textsuperscript{17} Since the steric shielding of the metal centre proved to have a positive effect on the stability of $[\text{M}^{\text{II}}(\text{cod})(\text{N}_3\text{-ligand})]^\text{2+}$ complexes, we chose bis-lutidylamine (bla) as the N3-donor ligand.
4.2 Results and discussion

4.2.1 Synthesis and characterization of [M(\(\mu\beta\))\(\eta^4\)-dbcot\)(\(\kappa^3\)-bla)]\(PF_6\) \([1]PF_6\) and [Ir(\(\eta^4\)-dbcot)(\(\kappa^3\)-bla)]\(PF_6\) \([2]PF_6\) complexes were synthesized from the bla ligand and the corresponding dinuclear [M(\(\mu\Cl\))(\(\eta^4\)-dbcot)]\(_2\) compounds in methanol followed by precipitation as a \(PF_6^-\) salt by adding KPF\(_6\) (Scheme 3).

\[
\begin{align*}
\text{dbcot} & = \text{dibenzo}[a,e]\text{cyclooctatetraene}, \text{bla} = \text{bis-N,N-(6-methyl-2-pyridylmethyl)amine}
\end{align*}
\]

Scheme 3. Synthesis of [Rh(\(\eta^4\)-dbcot)(\(\kappa^3\)-bla)]\(^+\) \([1]^+\) and [Ir(\(\eta^4\)-dbcot)(\(\kappa^3\)-bla)]\(^+\) \([2]^+\).

[Rh(\(\mu\Cl\))(\(\eta^4\)-dbcot)]\(_2\) used for the synthesis of \(1^+\) could be generated \textit{in situ} from [Rh(\(\mu\Cl\))(\(\eta^2\)-coe)]\(_2\) (coe = \textit{cis}-cyclooctene) and dbcot. A similar approach to synthesize the iridium complex \(2^+\) failed and resulted in unexpected formation of a new complex [Ir(\(\kappa^3\)-bla)(H)(\(\sigma\)-C\(_8\)H\(_{13}\))(\(\eta^2\)-C\(_8\)H\(_{14}\))]\(PF_6\) \([3]PF_6\) by oxidative addition of a vinylic C-H bond of coe to the iridium metal centre (Scheme 4). Therefore the successful synthesis of \([2]PF_6\) required the use of the isolated [M(\(\mu\Cl\))(\(\eta^4\)-dbcot)]\(_2\).

\[
\begin{align*}
\text{dbcot} & = \text{dibenzo}[a,e]\text{cyclooctatetraene}, \text{bla} = \text{bis-N,N-(6-methyl-2-pyridylmethyl)amine}
\end{align*}
\]

Scheme 4. Synthesis of [Ir(\(\kappa^3\)-bla)(H)(\(\sigma\)-C\(_8\)H\(_{13}\))(\(\eta^2\)-C\(_8\)H\(_{14}\))]\(^+\) \([3]^+\).

Oxidative addition of the vinylic C–H bond of cyclooctene was previously reported for iridium complexes with \(\text{HB(Pz)}_3\)\(^18\) and \(\text{Cn}(\text{N}_3)\)-supporting ligands (\(\text{HB(Pz)}_3 = \text{tris(pyrazolyl)borate}, \text{Cn} = 1,4,7-	ext{triazacyclononane}\)). Such reactivity is in line with comparable electronic properties of tris(pyrazolyl)borate and bis-lutidylamine type ligands, which resulted in similar reactivity of the iridium biscarbonyl complexes towards nucleophiles.\(^20\) Other electron rich (PNP) tridentate ligands also allow for such reactivity on the iridium centre.\(^21\) X-ray quality crystals of \([3]PF_6\) were grown by layering an acetone solution of \([3]PF_6\) with hexanes (Figure 1). The structure of \(3^+\) is noteworthy and is an interesting example of a metal-olefin-hydride complex that does not undergo spontaneous olefin insertion into the M–H bond in coordinating solvents (\textit{e.g.} acetone). \([\text{Ir}(\kappa^3\)-bla)(H)(\(\sigma\)-C\(_8\)H\(_{13}\))(\(\eta^2\)-C\(_8\)H\(_{14}\))]PF_6\) has a distorted octahedral geometry with the bla ligand being coordinated in a \textit{fac}-mode. The most sterically hindered position \textit{trans} to the \textit{N3} amine nitrogen is occupied by the least sterically demanding hydride anion. The cyclooctenyl group coordinates \textit{trans} to the \textit{N1} lutidyl...
nitrogen and its C9–C10 bond has a clear double bond character (1.326(4) Å). This vinylic double bond has no significant interaction with the metal. The cyclooctenyl group has a large \textit{trans} influence on the lutidyl N1 atom, which results in a rather large (> 2.23 Å) Ir–N1 distance. The cyclooctene ligand coordinates \textit{trans} to the N2 lutidyl nitrogen. As expected for an olefin coordinated to an electron deficient metal, the double bond of the cyclooctene ligand does not reveal substantial elongation.

**Figure 1.** X-ray structure of [Ir(H)(σ-C8H13)(η2-C8H14)(κ3-blk)]\(^+\) (3\(^+\)). Thermal ellipsoids are drawn with 50% probability (hydrogen atoms and the PF\(_6\)– counterion were omitted for clarity). Selected bond distances (Å) and angles (°): Ir1–N1 2.239(3); Ir1–N2 2.136(2); Ir1–N3 2.174(3); Ir1–C1 2.200(3); Ir1–C2 2.168(3); Ir1–C9 2.041(3); Ir1–H1 1.490(3); C1–C2 1.387(5); C9–C10 1.326(4); N1–Ir1–N3 79.31(10); N1–Ir1–N2 82.12(10); N2–Ir1–N3 78.12(9); C1–Ir1–C2 37.02(12); Ir1–C9–C10 123.04(2); N1–Ir1–C9 167.63(11); N2–Ir1–C9 88.13(11); N3–Ir1–C9 91.29(11); N3–Ir1–H1 170.0(11); N2–Ir1–H1 92.2(11); N1–Ir1–H1 97.0(11); H1–Ir1–C9 91.0(11)

Single crystals of [1]PF\(_6\) and [2]PF\(_6\) suitable for X-ray structure determination were grown from acetone solutions layered with hexanes or diethyl ether respectively. The two compounds are isostructural in the solid state (Figure 2) and are best described as distorted trigonal bipyramids (\textit{tbpy}). The axial positions of the trigonal bipyramid are occupied by the lutidyl (N1) nitrogen atom and a double bond of the dbcot ligand (C5–C6). The M–N1 distance is the same for both complexes within the experimental error while the axially coordinated double bond binds more strongly to iridium (resulting in shorter M–C5 and M–C6 distances and longer C5–C6 distance in 2\(^+\) compared to 1\(^+\)). The equatorial sites are coordinated with lutidyl N2, amine N3 and the C1–C2 double bond of dbcot. For both complexes there is no significant difference between their M–N2 and M–N3 distances, however these nitrogen atoms are bond more strongly to iridium with on average 0.03 Å shorter M–N bonds for 2\(^+\) compared to the rhodium analogue 1\(^+\). The axially coordinated lutidyl moiety (N1) is bound more strongly to the metal than the equatorially bound N2 and N3 donors, as expected for a d\(^8\) \textit{tbpy} complex.\(^{22}\) Due to stronger \(\pi\)-back bonding in the equatorial plane of \textit{tbpy} complexes,\(^{22}\)
the C1–C2 double bond is bound stronger compared to the axially coordinated C5–C6 bond. The metal C1–C2 interaction has a significant metalla(III)cyclopropane character, resulting in a remarkable elongation of the C1–C2 distance (1.32, 1.44 and 1.47 Å for free dbcot, 1+ and 2+ respectively). This substantial elongation of the double bonds of coordinated dbcot is indicative of strong π-acidity of this ligand.

![Figure 2](image)

**Figure 2.** X-ray structure of [Rh($\eta^4$-dbcot)(κ3-bla)]+ (1+) (left) and [Ir($\eta^4$-dbcot)(κ3-bla)]+ (2+) (right). Thermal ellipsoids are drawn with 50% probability (hydrogen atoms, the PF6− counter ions and solvent molecules are omitted for clarity). The crystal of 1+ reveals the presence of two independent but isostructural cations in the asymmetric unit. See Table 1 for selected bond distances and angles.

<table>
<thead>
<tr>
<th></th>
<th>1a+</th>
<th>1b+</th>
<th>2+</th>
<th>2a2+</th>
<th>2b2+</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–N1</td>
<td>2.116(2)</td>
<td>2.113(2)</td>
<td>2.114(4)</td>
<td>2.111(3)</td>
<td>2.093(3)</td>
</tr>
<tr>
<td>M–N2</td>
<td>2.257(3)</td>
<td>2.259(3)</td>
<td>2.229(3)</td>
<td>2.095(3)</td>
<td>2.112(3)</td>
</tr>
<tr>
<td>M–N3</td>
<td>2.261(3)</td>
<td>2.249(3)</td>
<td>2.224(4)</td>
<td>2.184(3)</td>
<td>2.185(3)</td>
</tr>
<tr>
<td>M–C1</td>
<td>2.103(3)</td>
<td>2.101(3)</td>
<td>2.066(4)</td>
<td>2.189(3)</td>
<td>2.189(4)</td>
</tr>
<tr>
<td>M–C2</td>
<td>2.064(3)</td>
<td>2.062(3)</td>
<td>2.130(5)</td>
<td>2.159(3)</td>
<td>2.182(4)</td>
</tr>
<tr>
<td>M–C5</td>
<td>2.139(3)</td>
<td>2.147(3)</td>
<td>2.128(4)</td>
<td>2.191(3)</td>
<td>2.165(3)</td>
</tr>
<tr>
<td>M–C6</td>
<td>2.155(4)</td>
<td>2.155(4)</td>
<td>2.097(4)</td>
<td>2.184(4)</td>
<td>2.183(4)</td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.440(5)</td>
<td>1.436(5)</td>
<td>1.472(6)</td>
<td>1.414(5)</td>
<td>1.410(5)</td>
</tr>
<tr>
<td>C5–C6</td>
<td>1.397(5)</td>
<td>1.400(5)</td>
<td>1.411(6)</td>
<td>1.390(5)</td>
<td>1.408(5)</td>
</tr>
<tr>
<td>C1–M–C6</td>
<td>40.42(13)</td>
<td>40.34(13)</td>
<td>41.41(17)</td>
<td>37.94(12)</td>
<td>37.65(13)</td>
</tr>
<tr>
<td>C2–M–C5</td>
<td>37.96(14)</td>
<td>37.99(14)</td>
<td>38.72(17)</td>
<td>37.05(13)</td>
<td>37.77(13)</td>
</tr>
<tr>
<td>N1–M–N2</td>
<td>88.97(9)</td>
<td>89.12(10)</td>
<td>91.48(12)</td>
<td>92.17(11)</td>
<td>89.91(11)</td>
</tr>
<tr>
<td>N1–M–N3</td>
<td>75.63(10)</td>
<td>75.00(9)</td>
<td>75.09(13)</td>
<td>76.57(11)</td>
<td>79.80(11)</td>
</tr>
<tr>
<td>N2–M–N3</td>
<td>76.18(10)</td>
<td>76.46(10)</td>
<td>76.55(12)</td>
<td>79.97(11)</td>
<td>76.93(12)</td>
</tr>
</tbody>
</table>
In solution $1^+$ is fluxional on the NMR time scale, leading to averaged $^1$H and $^{13}$C NMR signals for both lutidyl groups of the bla ligand and averaged signals of the two olefinic HC=CH moieties and the aromatic rings of the dbcot ligand. Analogous behavior was observed for $2^+$. Strong $\pi$-back bonding from the metal to the dbcot ligand results in substantial upfield shifts of both the proton and carbon resonance frequencies (6.78, 4.50, and 4.37 ppm in $^1$H and 133.2, 74.6 and 58.3 ppm in $^{13}$C for free dbcot, $1^+$ and $2^+$ respectively). Thus, both the X-ray and NMR analyses confirm a very strong $\pi$-bonding of dbcot to the metal.

The redox properties of $1^+$, $2^+$ were investigated using cyclic voltammetry. All complexes reveal reversible one-electron oxidation waves in the scan range between 10 and 200 mV/s. The redox potential of the bla rhodium complex is higher by 47 mV compared to the iridium analogue, which is in line with previous results showing that a variety of [Ir(cod)(N$_3$-ligand)]$^+$ complexes are oxidized at lower potentials than their rhodium analogs ($E_{1/2}$ lowered by 70-100 mV in those cases).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_a$ (V)</th>
<th>$\Delta E$ (mV)</th>
<th>$E_{1/2}$ (V)</th>
<th>$I_a/I_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh($\eta^4$-dbcot)(κ$^3$-bla)]PF$_6$ ([1]PF$_6$)</td>
<td>0.410</td>
<td>101</td>
<td>0.359</td>
<td>1.0</td>
</tr>
<tr>
<td>[Ir($\eta^3$-dbcot)(κ$^2$-bla)]PF$_6$ ([2]PF$_6$)</td>
<td>0.364</td>
<td>104</td>
<td>0.312</td>
<td>1.0</td>
</tr>
<tr>
<td>[Rh($\eta^4$-dbcot)(κ$^3$-Bn-bla)]PF$_6$ ([4]PF$_6$)</td>
<td>0.477</td>
<td>70</td>
<td>0.443</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$\Delta E =$ peak separation, $E_a =$ anodic peak potential, $E_{1/2} =$ half-wave potential, $I_a/I_b =$ anodic peak current/cathodic peak current.

### 4.2.2 Synthesis and characterization of paramagnetic [M$^\text{II}$(dbcot)(bla)]$^{2+}$ complexes

In contrast to the abundant chemistry of $d^8$-metal olefin complexes, fully characterized, stable $d^7$ rhodium(II) and iridium(II) olefin compounds are rather scarce. This is caused by the general low stability of organometallic radicals, coupled with relative facile allylic C–H bond activation and C$_{\text{alkene}}$–C$_{\text{alkene}}$ coupling reactions triggered by the open-shell metal centre. We expected that the use of the robust dbcot diolefin should block such undesired decomposition pathways involving the metal centre and allow for exclusive reactivity on the nitrogen atom of the coordinated bis-lutidylamine.

Scheme 5. Synthesis of open shell species [Rh($\eta^4$-dbcot)(κ$^3$-bla)]$^{2+}$ ([1]$^{2+}$) and [Ir($\eta^4$-dbcot)(κ$^3$-bla)]$^+$ ([2]$^+$).

The electrochemical data suggest that stable $d^7$ M$^\text{II}$ complexes should be obtainable from $1^+$ and $2^+$ by one-electron oxidation. Hence we investigated their chemical oxidation in solution. Treatment of $1^+$ and $2^+$ with appropriate oxidants led to formation of $1^{2+}$ and $2^{2+}$, respectively (Scheme 5). Compound $2^{2+}$ proved to be
sufficiently stable to obtain X-ray quality crystals by layering an acetone solution of $2^{2+}$ onto dichloromethane at $-20 \, ^\circ\text{C}$.

Figure 3. X-ray structure of $[\text{Ir(} \eta^4\text{-dbco})(\kappa^3\text{-bla})]^{2+} (2^{2+})$. Thermal ellipsoids are drawn with 50% probability (hydrogen atoms, the PF$_6^-$ counter ions and a disordered CH$_2$Cl$_2$ molecule are omitted for clarity). The crystal contains two independent cations in the asymmetric unit, only one of them is shown. See Table 1 for selected bond distances and angles.

One-electron oxidation of $2^+$ to $2^{2+}$ results in a change of the coordination geometry from trigonal bipyramidal to a distorted square pyramid ($sqpy$) with the two lutidyl donors and the two olefinic double bonds coordinated in the basal plane and the amine at the apical position, as evidenced by the single crystal X-ray diffraction. The Ir–N$_1$ and Ir–N$_2$ distances of $2^{2+}$ are not significantly different ($\Delta r < 3\sigma$). The same is observed for the distance between iridium and the olefinic bonds. Lower electron density on the metal after oxidation results in increased Ir–N and decreased Ir–olefin interactions as compared to $2^+$. The N$_1$, N$_2$ atoms and the centroids of the double bonds
are not in one plane, due to a slight ‘twist’ of the dbcot moiety (Figure 3). The measured crystal contained two independent molecules: the first isomer has the dbcot moiety twisted clockwise, whereas the other counterclockwise. Optimization of the X-ray structure using DFT resulted in convergence to a structure where N1, N2 and the centroids of the double bonds are aligned in a plane. The slightly ‘twisted’ geometry thus seems to be a result of crystal packing forces.

The observed change of the coordination geometry from \( \textit{tbpy} \) to \( \textit{sqpy} \) is more frequently observed when the electron configuration of a transition metal changes from \( \textit{d}^8 \) to \( \textit{d}^7 \), and is most likely a result of the Jahn-Teller effect.\(^{28}\) For that reason we expect that compound \( \text{1}^{2+} \) has a structure similar to \( \text{2}^{2+} \).

We used EPR spectroscopy to further investigate the (electronic) structure of \( \text{1}^{2+} \) and \( \text{2}^{2+} \). Measured X-band EPR spectra of \( \text{1}^{2+} \) and \( \text{2}^{2+} \) could be simulated as rhombic spectra (\( \text{i.e. } g_1 \neq g_2 \neq g_3 \)) with well resolved (super)hyperfine interactions with the metal centre and a single nitrogen atom along the \( g_3(z) \) axis (Figure 4 and Table 3). The measured \( g \) values are indicative of metal-centered radicals. As expected for heavier transition metals with larger spin-orbit couplings, the \( g \)-anisotropy (rhombicity) of the iridium complex \( \text{2}^{2+} \) is larger than that of the rhodium analogue \( \text{1}^{2+} \).

The spectrum of the iridium(II) compound \( \text{2}^{2+} \) is influenced by the presence of large Ir-quadrupole interactions causing the appearance of two weak ‘forbidden’ transitions as indicated by the arrows in Figure 4.\(^{11,29}\) Since the spectrum does not reveal any resolved hyperfines in this region of the spectrum that could be influenced by these quadrupole interactions we did not take these interactions into account in the spectral simulations.

To get a better insight in the electronic structure of both complexes we calculated the EPR properties with DFT (Table 3). In line with the experiments, DFT predicts that \( \text{1}^{2+} \) and \( \text{2}^{2+} \) are metal centered radicals with Mulliken spin densities of 72% and 73% on rhodium and iridium respectively, and 16.5% on the amine nitrogen atom.
Table 3. Simulated (exp) and calculated (DFT) g-values and (super)hyperfine interactions (MHz) for compounds 1\(^{2+}\), 2\(^{2+}\) and 4\(^{2+}\) (n.r. = not resolved). Directions of the principal axes of the g tensor in the molecular axis system of complexes are shown.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Property</th>
<th>g(_{11}) (x)</th>
<th>g(_{22}) (y)</th>
<th>g(_{33}) (z)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp</td>
<td>DFT</td>
<td>exp</td>
<td>DFT</td>
</tr>
<tr>
<td>1(^{2+})</td>
<td>g-value</td>
<td>2.181</td>
<td>2.133</td>
<td>2.158</td>
</tr>
<tr>
<td></td>
<td>HFI(_{\text{Rh}})</td>
<td>n.r.</td>
<td>-7.67</td>
<td>n.r.</td>
</tr>
<tr>
<td></td>
<td>HFI(_{\text{N}})</td>
<td>n.r.</td>
<td>36.8</td>
<td>n.r.</td>
</tr>
<tr>
<td>2(^{2+})</td>
<td>g-value</td>
<td>2.368</td>
<td>2.320</td>
<td>2.294</td>
</tr>
<tr>
<td></td>
<td>HFI(_{\text{Ir}})</td>
<td>n.r.</td>
<td>97.0</td>
<td>n.r.</td>
</tr>
<tr>
<td></td>
<td>HFI(_{\text{N}})</td>
<td>n.r.</td>
<td>38.4</td>
<td>n.r.</td>
</tr>
<tr>
<td>4(^{2+})</td>
<td>g-value</td>
<td>2.211</td>
<td>2.128</td>
<td>2.184</td>
</tr>
<tr>
<td></td>
<td>HFI(_{\text{Rh}})</td>
<td>n.r.</td>
<td>-8.67</td>
<td>n.r.</td>
</tr>
<tr>
<td></td>
<td>HFI(_{\text{N}})</td>
<td>n.r.</td>
<td>34.1</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

The radical species 1\(^{2+}\) and 2\(^{2+}\) are sterically shielded around the metal, which is reflected by their relative inertness towards dioxygen in solution. Bubbling air through the solutions of 1\(^{2+}\) or 2\(^{2+}\) did not give rise to the formation of superoxo species nor to a noticeable decrease of the EPR signal. Apparently, shielding of the metal centre by the methyl groups of the bla ligand prevents any rapid radical type reactivity at the metal centre. However, somewhat surprisingly, in solution the complexes slowly convert to the one-electron reduced diamagnetic compounds 1\(^{+}\) and 2\(^{+}\), as evidenced by NMR spectroscopy.\(^{30}\) This process is not a disproportionation reaction (as commonly observed for Rh\(^{II}\) and Ir\(^{II}\) complexes), because the one-electron reduced species 1\(^{+}\) and 2\(^{+}\) are the only observed products.

Our initial hypothesis was that the increased charge of the metal (changing from 1\(^{+}\) to 2\(^{+}\) upon one electron oxidation) results in an increased acidity of the NH group of the bla ligand. Spontaneous deprotonation of the amine group would then lead to formation of an aminyl radical via an intramolecular redox reaction between the metal and the nitrogen atom. Subsequently, this aminyl radical could then abstract a hydrogen atom from the reaction medium, thus reforming the reduced complex 1\(^{+}\) or 2\(^{+}\) (Scheme 6). To check whether the re-formation of compounds 1\(^{+}\) and 2\(^{+}\) indeed proceeds via the pathway shown in Scheme 6, we studied the reactivity of 1\(^{2+}\) and 2\(^{2+}\) towards Brønsted bases. We also performed radical trapping experiments.

![Scheme 6](image)

Scheme 6. Hypothetical deprotonation-HAT pathway leading to net reduction of the paramagnetic species 1\(^{2+}\) and 2\(^{2+}\).

Reaction of complexes 1\(^{2+}\) and 2\(^{2+}\) with solid K\(_2\)CO\(_3\) in acetone or acetonitrile resulted in disappearance of the characteristic EPR signals and no signal of the putative aminyl radical could be detected.\(^{31}\) Instead, quantitative formation of the one-electron reduced diamagnetic complexes 1\(^{+}\) and 2\(^{+}\) was observed with \(^{1}\)H NMR. Remarkably, the NMR
spectroscopy data further reveal that the reactions retain the N-H hydrogen atoms for a large part whereas formation of the N-D deuterated analogs of $1^+$ and $2^+$ would be expected if the reactions would proceed via the pathway depicted in Scheme 6. This makes the aminyl radical pathway rather doubtful, unless the reaction would be associated with a very large kinetic isotope effect. Radical trapping experiments did not allow for unambiguous detection of the proposed aminyl radicals, nor of solvent radicals.

4.2.3 Synthesis of paramagnetic N-protected [Rh$^{II}$](Bn-bla)(dbcot)$^{2+}$ complex and its reactivity with K$_2$CO$_3$

Since the above results are inconclusive about the role of the amine/amminyl radical in the observed reduction of $1^{2+}/2^{2+}$ to $1^+/2^+$, we decided to perform a control experiment using a similar compound in which the amine is protected with a benzyl moiety. Hence we investigated the reactivity of the complex [Rh(dbcot)(Bn-bla)](PF$_6$)$_2$ ($[4](PF_6)_2$).

The precursor complex [Rh($\eta^4$-dbcot)(κ$_3$-Bn-bla)]PF$_6$ ($[4]$PF$_6$) was prepared using the method described for $[1]$PF$_6$ (Scheme 7). The $^1$H NMR signals of the dbcot moiety in compound $4^+$ are broadened compared to the signals of Bn-bla at room temperature and contrary to $1^+$ and $2^+$ the olefinic signals of dbcot are magnetically inequivalent giving two broad signals at $\delta = 4.75$ and 4.24 ppm. This suggests that the rotation of dbcot is much slower in case of $4^+$ than in $1^+$ and $2^+$.

![Scheme 7. Synthesis of [Rh($\eta^4$-dbcot)(κ$_3$-Bn-bla)]$^+$ ($4^+$).](image)

CV measurements reveal that the redox potential of the [Rh(Bn-bla)(dbcot)]$^+$ ($4^+$) is higher by 67 and 170 mV compared with [Rh(bla)(dbcot)]$^+$ ($1^+$) and the previously reported [Rh(Bn-bla)(cod)]$^{11+}$ respectively, showing that exchange of either the bla ligand for Bn-bla ligand or cod for dbcot results in a considerable destabilization of the +II oxidation state of rhodium (see Table 2). For that reason we used AgPF$_6$ in DCM as the oxidizing reagent to form $4^{2+}$.

The EPR spectrum of $4^{2+}$ is very similar to the spectrum of $1^{2+}$ showing a rhombic, almost axial g-tensor, and hyperfine couplings with rhodium and nitrogen (see Table 3). As for $1^{2+}$ and $2^{2+}$ the DFT calculated EPR parameters are in good qualitative agreement with the experiment. The DFT calculated Mulliken spin densities at rhodium (67%) and nitrogen (18%) are comparable to those of $1^{2+}$ and $2^{2+}$.

Stirring an acetone-d$_6$ solution of $4^{2+}$ with solid K$_2$CO$_3$ again results in a color change from dark green to bright yellow, with quantitative formation of the reduced species $4^+$, (as evidenced by NMR spectroscopy). This is similar to the reactions observed for $1^{2+}$ and $2^{2+}$ and shows that the presence of the N-H group is not essential for the reduction of the M$^{II}$ oxidation state radical species to their M$^+$ precursors. Hence, the reaction does not necessarily involve the intermediacy of aminyl radicals and the role of the Brønsted base has to be different than originally anticipated.
Base assisted oxidation of solvent\textsuperscript{35} seems to be a viable pathway for the reduction of species $1^{2+}/2^{2+}$ (Scheme 8). Judging from the redox potentials, the dicationic radical metal complexes $1^{2+}/2^{2+}$ and acetone must exist in a redox equilibrium with the closed shell metal complexes $1^+/2^+$ and the acetone radical cation.\textsuperscript{36} Without a base, this equilibrium lays far to the left, but the acetone radical cation formed in small quantities can be easily deprotonated by the base, shifting the redox equilibrium between acetone and $1^{2+}/2^{2+}$ completely to the right. Alternatively, in the presence of small quantities of water the hydroxide anion can be generated, which is known as a potential one-electron reducing agent in organic solvents.\textsuperscript{37} Thus, depending on the water content in the solvent (or base) this seems to be a plausible mechanism as well.

\begin{center}
\begin{tikzpicture}


\end{tikzpicture}
\end{center}

\textbf{Scheme 8.} Regeneration of the diamagnetic complex by base promoted oxidation of solvent or hydroxide anion.

At this point we cannot exclude that the pathway involving deprotonation of the N-H group can take place, taking into account the reactivity of related amine complexes of rhodium and iridium. Instant hydrogen atom abstraction by an iridium coordinated aminyl radical has been recently reported by Grützmacher et al.\textsuperscript{15c} However, it is tempting to assume that base assisted solvent oxidation is the actual mechanism of reformation of $1^+/2^+$ from $1^{2+}/2^{2+}$ and that the aminyl radical pathway plays little (if any) role in this reaction.

\section*{4.3 Summary and conclusions}

Open shell rhodium(II) and iridium(II) complexes with dibenzocyclooctadiene and bislutidylamine (bla) type ligands were successfully synthesized. They represent rare examples of isolable open-shell olefin complexes. The chosen diolefin ligand is inert toward radical reactions, which allowed for investigations of possible radical reactivity pathways involving the aminyl nitrogen atom of the bla ligand.

An attempt to obtain the aminyl radical complexes by deprotonation the N-H group of the bla ligand using a base led to an unexpected, selective reduction of the paramagnetic species [M\textsuperscript{II}(dbcot)(bla)]\textsuperscript{2+} to their one-electron reduced closed-shell analogs [M\textsuperscript{I}(dbcot)(bla)]\textsuperscript{+} (M = Rh, Ir). Control experiments with the rhodium(II) complex [Rh\textsuperscript{II}(dbcot)(Bn-bla)]\textsuperscript{2+} containing the Bn-bla ligand (a bla derivative having the amine protected with a benzyl group) revealed similar reactivity.

These results show that the generation of aminyl radicals from the complexes of the general formula [M\textsuperscript{II}(diolefin)(N\textsubscript{3}-ligand)]\textsuperscript{2+} (M = Rh, Ir) is perhaps not occurring at all. At least it is rather unlikely that the observed reduction reactions occur via deprotonation of the amine followed by HAT. It is remarkable, however, that the
complexes studied are quantitatively reduced in the presence of bases to the M^I species. The reduction is most likely caused by a hydroxide anion or a solvent molecule that can be deprotonated in its oxidized form. Hence the [M
^n(dbcot)(N

_3-ligand)]

^{n+} (M = Rh, Ir; n = 1, 2) complexes seem to be stable redox transfer agents, perhaps allowing oxidation of organic compounds under basic conditions.

4.4 Experimental

X-ray diffraction

The structures are shown in Figures 1, 2 and 3.\textsuperscript{38} The crystal data are shown in Table 4. X-ray data were collected at low temperature under the control of the Nonius COLLECT software with a Nonius KappaCCD on rotating anode. The intensity data were corrected for absorption with the program SADABS. The structures were solved with the program DIRDIF and refined with SHELXL97. The Flack parameter for [1]PF

_6 was refined to 0.484(13) with a BASF/TWIN refinement. The structure of [2](PF

_6)_2 has solvent accessible voids filled with disordered solvent. Their contribution to the structure factors in the refinement was taken into account with the PLATON/SQUEEZE approach. The hydrogen atom on Ir for [3]PF

_6 was located in a difference density map.

| Crystal color | [Rh(κ

_3-bla)(dbcot)]PF

_6 · CH

_3COCH

_3 ([1]PF

_6): | [Ir(κ

_3-bla)(dbcot)]PF

_6 · (CH

_3CH

_2)O ([2]PF

_6): | [Ir(κ

_3-bla)(dbcot)](PF

_6)_2 · CH

_2Cl

_2 ([2](PF

_6)_2): | [Ir(κ

_3-bla)(H)(σ-C

_8H

_13)(η

_2-C

_8H

_14)]PF

_6 ([3]PF

_6)] |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>yellow</td>
<td>yellow</td>
<td>black</td>
<td>pale yellow</td>
</tr>
</tbody>
</table>
| Empirical formula | C

_30H

_29N

_3Rh, C

_3H

_6O, F

_6PC | C

_30H

_29IrN

_3, C

_4H

_10O, F

_6P | C

_30H

_45IrN

_3, 4(F

_6P), CH

_2Cl

_2 | C

_30H

_3IrN

_3, 3(F

_6P) |
| Formula weight | 737.52 | 842.87 | 1912.37* | 784.88 |
| Temperature [K] | 110 | 110 | 110 | 110 |
| Radiation | MoKα | MoKα | MoKα | MoKα |
| Wavelength [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | Cc | P 21/c | P 21/c | P 21/c |
| a [Å] | 28.5187(8) | 9.2911(4) | 21.5483(9) | 9.5523(7) |
| b [Å] | 11.2036(3) | 20.4418(9) | 16.7416(7) | 16.2517(5) |
| c [Å] | 19.4833(4) | 17.3595(7) | 20.9573(8) | 20.1842(7) |
| β [°] | 101.351(1) | 98.599(2) | 110.520(2) | 97.861(2) |
| Volume [Å

_3] | 6103.4(3) | 3260.0(2) | 7080.7(5) | 3104.0(3) |
| Z | 8 | 4 | 4 | 4 |
| Density [Mg m

_3] | 1.605 | 1.7173(1) | 1.7939(1)* | 1.6796(2) |
| Absorption coefficient [mm

_1] | 0.682 | 4.212 | 4.027* | 4.414 |
| Theta-max | 27.5 | 27.5 | 27.5 | 27.5 |
| F(000) | 3008 | 1672 | 3728* | 1568 |
| R1 | 0.0281 | 0.0333 | 0.0292 | 0.0234 |
| wR2 | 0.0600 | 0.0584 | 0.0759 | 0.0496 |
| S | 1.047 | 1.093 | 1.101 | 1.027 |

* Starred items are excluding the disordered solvent contribution.

DFT calculations: Geometry optimizations were carried out with the Turbomole program package\textsuperscript{39} coupled to the PQS Baker optimizer\textsuperscript{40} at the ri-DFT\textsuperscript{41} level using the BP86\textsuperscript{42} functional and SV(P) basis set.\textsuperscript{43} Calculated EPR spectra\textsuperscript{44} were obtained with ADF program\textsuperscript{45} at the DFT, BP86,\textsuperscript{46} TZP\textsuperscript{47} level, using the Turbomole optimized geometries.

General procedures: All manipulations were performed in an argon atmosphere by standard Schlenk techniques or in a glovebox. Methanol and dichloromethane were distilled under nitrogen from CaH\textsubscript{2}. Hexanes were distilled under nitrogen from Na wire. Acetone was deoxygenated using freeze-pump-thaw method. NMR experiments were carried out on a Bruker DRX300 (300 and 75 MHz for \textsuperscript{1}H and \textsuperscript{13}C respectively) on a Varian Inova 500 (500 and 125 MHz for \textsuperscript{1}H and \textsuperscript{13}C.
Chapter 4

respectively) spectrometers. Solvent shift reference: acetone-\(d_6\) \(\delta = 2.05\) and \(\delta = 29.84\) for \(^1\)H and \(^{13}\)C, CDCl\(_3\) \(\delta = 7.26\) and \(\delta = 77.23\) for \(^1\)H and \(^{13}\)C respectively. Abbreviations used are \(s = \text{singlet}, d = \text{doublet}, t = \text{triplet}, m = \text{multiplet}, \text{br} = \text{broad}\). Elementanalyses (CHN) were carried out by H. Kolbe Mikroanalytisches Laboratorium (Germany). X-band EPR spectroscopy measurements were performed with a Bruker EMX Plus spectrometer. Cyclic voltammograms of \(~2\text{mM}\) parent compounds in \(1\text{M Bu}_4\text{NPF}_6\) electrolyte solution were recorded in a gas-tight single-compartment three-electrode cell equipped with platinum working electrode (apparent surface of \(0.42\text{mm}^2\)), coiled platinum wire auxiliary, and silver wire pseudoreference electrodes. The cell was connected to a computer-controlled PAR Model 283 potentiostat. Redox potentials are reported against the ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple. Ferrocene was used as internal standard. Magnetic susceptibility was measured on a Magway MSB Mk1 magnetic balance. \([\text{Fe(}\mu\text{-C}_5\text{H}_4\text{COMe})\text{Cp}]\text{PF}_6\)\(^{27}\) \([\text{Ir(dbcot)(}\mu\text{-Cl})\text{]}_2\)\(^{48}\) \([\text{M(coe)}\text{2(}\mu\text{-Cl})\text{]}_2\)\(^{49}\) dibenzo[a,e]cyclooctatetraene\(^{50}\) \(N\)-Benzyl-\(N,\text{N-di[(6-methyl-2-pyridylmethyl)amine}^{51}\) bis((6-methyl-2-pyridyl)methyl)amine \(^{52}\) have been prepared according to previously reported procedures.

Dibenzo[a,e]cyclooctadiene:

Although various experimental procedures are available for the synthesis of dbcot, \(^{50}\) we did not find a full assignment of all \(^{13}\)C NMR signals of this compound.

\(^1\)H (500 MHz, CDCl\(_3\)): \(\delta = 7.17\) (m, 4H, Ar-H); 7.08 (m, 4H, Ar-H); 6.78 (s, 4H, olefinic).

\(^{13}\)C (125 MHz, CDCl\(_3\)): \(\delta = 137.27\) (CIV); 133.44 (olefinic); 129.31; 127.03.

Syntheses:

\([\text{Rh(}\kappa^3\text{-bla)(}\eta^4\text{-dbcot)}]\text{PF}_6\) (\([1]\text{PF}_6\)):

179 mg of \([\text{Rh(coe)}\text{2Cl}\text{]}_2\) (0.499 mmol Rh) and 107 mg of dbcot (0.524 mmol) were dissolved in 10 ml of CH\(_2\text{Cl}_2\) and the solution was stirred for 2 hours and the solution was evaporated to dryness. Next, 115 mg bla (0.506 mmol) and a mixture of 10 ml of MeOH and 10 ml of CH\(_2\text{Cl}_2\) were added and stirred for 1 hour. The unreacted solid was filtered off and the remaining solvent was removed \(in\ \text{vacuo}\). The thus formed solid was dissolved in 5 ml MeOH and 106 mg KPF\(_6\) were added causing precipitation of a bright yellow solid, which was filtered and washed with 2 ml MeOH. Yield: 168 mg (0.247 mmol, 49.5 %).

\(^1\)H (500 MHz, acetone-\(d_6\)): \(\delta = 7.80\) (t, \(^3\)J(H,H) = 7.5 Hz, 2H; Py); 7.44 (d, \(^3\)J(H,H) = 7.5 Hz, 2H; Py); 7.35 (d, \(^3\)J(H,H) = 7.5 Hz, 2H; Py); 6.62 (m, 8H; Bn); 5.29 (d[AB] br, \(^2\)J(H,H) = 15.5 Hz, 2H; N-CH\(_2\)-Py); 4.50 (d, \(^2\)J(Rh,H) = 1.5 Hz, 4H; Bn-CH-); 4.28 (d[AB], \(^2\)J(H,H) = 16.5 Hz, 2H; N-CH\(_2\)-Py); 3.39 (s br, 6H; Py-CH\(_3\)).

\(^{13}\)C (125 MHz, acetone-\(d_6\)): \(\delta = 161.3\) (Py); 161.2 (Py); 145.6 (Bn); 139.3 (Py-C4); 126.9 (Bn); 126.7 (Bn); 126.0 (Py-C5); 121.3 (Py-C3); 74.6 (d, \(^2\)J(Rh,H) = 12.6 Hz; CH=CH); 58.3 (N-CH\(_2\)-Py); 28.6 (Py-CH\(_3\)).

Elemental Analysis: Calcd. C, 53.03; H, 4.30; N, 6.18; Found: 52.77; H, 4.67; N, 5.98.

\([\text{Ir(}\kappa^3\text{-bla)(}\eta^4\text{-dbcot)}]\text{PF}_6\) (\([2]\text{PF}_6\)):

300 mg of \([\text{Ir(dbcot)Cl}\text{]}_2\) (0.695 mmol Ir) were suspended in 10 mL of methanol and 160 mg of bla (0.704 mmol) was added. The solution was stirred for 30 min and turned transparent yellow. 128 mg KPF\(_6\) (0.695 mmol) was added causing precipitation of a bright yellow solid, which was filtered and washed with 2 ml MeOH. Yield: 234 mg (0.304 mmol, 43.7 %).

\(^1\)H (500 MHz, acetone-\(d_6\)): \(\delta = 7.88\) (t, \(^3\)J(H,H) = 7.5 Hz, 2H; Py); 7.52 (d, \(^3\)J(H,H) = 7.5 Hz, 2H; Py); 7.48 (d, \(^3\)J(H,H) = 7.5 Hz, 2H; Py); 6.91 (m, 4H; Bn); 6.79 (m, 4H; Bn); 5.33 (d[AB], \(^2\)J(H,H) = 17.0 Hz, 2H; N-CH\(_2\)-Py); 4.52 (d[AB], \(^2\)J(H,H) = 17.0 Hz, 2H; N-CH\(_2\)-Py); 3.30 (s, 6H; Py-CH\(_3\)).

\(^{13}\)C (125 MHz, acetone-\(d_6\)): \(\delta = 162.9\) (Py); 161.5 (Py); 148.2 (Bn); 139.7 (Py-C4); 127.2 (Bn); 126.5 (Py-C5); 126.4 (Bn); 121.5 (Py-C3); 60.2 (N-CH\(_2\)-Py); 58.3(CH=CH); 29.5 (Py-CH\(_3\)).

Elemental Analysis: Calcd for \([2]\text{PF}_6\)·0.5H\(_2\)O: C, 46.33; H, 3.89; N, 5.40 Found: C: 46.58; H: 4.29; N: 5.12.
Base Assisted Selective Reduction of Organometallic Rh\textsuperscript{II} and Ir\textsuperscript{II} Radicals

\[\text{[Rh}(\kappa^3\text{-bla})(\eta^4\text{-dbcot})](\text{PF_6})_2 (1)(\text{PF_6})_2\]:
94.5 mg (0.139 mmol) of [1]PF_6 and 35.6 mg of AgPF_6 (0.141 mmol) were dissolved in 3 ml of acetone and left to react for 30 minutes. Solution was filtered using a syringe filter and the filtrate was condensed to black oil \textit{in vacuo}. 8 ml of CH_2Cl_2 were added causing precipitation of purple solid, which was centrifuged. Yield: 84 mg (0.102 mmol, 73.4 %).

Unfortunately, despite many attempts, due to intrinsic instability of [1](PF_6)_2 we were not able to obtain an analytically pure sample.

\[\text{[Ir}(\kappa^3\text{-bla})(\eta^4\text{-dbcot})](\text{PF_6})_2 \cdot \text{CH}_2\text{Cl}_2 (2)(\text{PF_6})_2\]:
136 mg (0.177 mmol) of [2]PF_6 and 50 mg of [Fe(\mu-C_5H_4COMe)Cp](PF_6) (0.15 mmol) were dissolved in 20 ml of dichloromethane and stirred for 45 minutes in which time a brown precipitate formed and the characteristic absorbance of acetylferrocenium was gone. Solution was filtered, washed with dichloromethane and dried \textit{in vacuo}. Yield: 80 mg (0.08 mmol, 53.3 %).

Magnetic susceptibility: \(\mu_{\text{eff}} = 2.06\) (corrected for diamagnetism of [2]PF_6, PF_6, Ir\textsuperscript{2+} and CH_2Cl_2; measured: 1.90).\textsuperscript{53}

Elemental Analysis: Calcd for [2](PF_6)_2·CH_2Cl_2: C, 37.28; H, 3.13; N, 4.21; Found: C: 37.24; H: 3.08; N: 4.36.

\[\text{[Ir}(\kappa^3\text{-bla})(\text{H})(\sigma\text{-C}_8\text{H}_{13})(\eta_2\text{-C}_8\text{H}_{14})](\text{PF_6})_2 (3)(\text{PF_6})_2\]:
An excess of dbcot (238, 1.17 mmol) and bla (265 mg, 1.17 mmol) were added to a suspension of \([\text{Ir(coe)Cl}_2]\) (523 mg, 1.16 mmol Ir) in dry methanol (40 mL) and was stirred for 18 h. The reaction mixture turned to a transparent green solution, to which NH_4PF_6 was added causing precipitation of a white solid. The product was filtered off and recrystallized. Yield: 270 mg, 30%.

Crystals suitable for X-ray diffraction were grown by layering an acetone solution of 3[PF_6] with hexanes.

\[\text{1H} (\text{acetone-d}_6, 300 \text{ MHz}): \delta = 7.79 \text{ (t, } 3J(\text{H,H}) = 7.8 \text{ Hz, 1H; Py}_A); 7.63 \text{ (t, } 3J(\text{H,H}) = 7.5 \text{ Hz, 1H; Py}_B); 7.46 \text{ (m, 2H; Py}_A); 7.25 \text{ (d, } 3J(\text{H,H}) = 7.5 \text{ Hz, 2H; Py}_B); 6.60 \text{ (s, br, 1H; N-H); 5.47 \text{ (dd[AB], } 2J(\text{H,H}) = 17.7 \text{ Hz, 3J(\text{H,H}) = 8.1 \text{ Hz, 1H; N-CH}_2\text{-Py}); 5.15 \text{ (dd[AB], } 2J(\text{H,H}) = 15.9 \text{ Hz, 3J(\text{H,H}) = 5.1 \text{ Hz, 1H; N-CH}_2\text{-Py); 5.05 \text{ (t, } 3J(\text{H,H}) = 7.5 \text{ Hz, 1H; (IrC-CH); 4.76 \text{ (dd[AB], } 2J(\text{H,H}) = 18.6 \text{ Hz, 1H; N-CH}_2\text{-Py); 4.68 \text{ (dd[AB], } 2J(\text{H,H}) = 15.6 \text{ Hz, 1H; N-CH}_2\text{-Py); 3.88 \text{ (m, 2H; CH=CH); 3.13 \text{ (s, 3H; Py}_A\text{-CH}_3); 3.02 \text{ (s, 3H; Py}_B\text{-CH}_3); 2.66 \text{ (m, 1H; coe); 2.25 \text{ (m, 1H; coe); 1.5 \text{ (m, 22H; coe); -15.84 \text{ (s, 1H, Ir-H).}}}}

\[\text{13C (75 MHz, acetone-d}_6): \delta = 164.5 \text{ (Py); 163.4 \text{ (Py); 162.3 \text{ (Py); 161.7 \text{ (Py); 140.5 \text{ (Py}_A); 139.6 \text{ (Py}_B); 127.9 \text{ (IrC=CH); 127.5 \text{ (PyA); 127.2 \text{ (Ir-C); 125.6 \text{ (PyB); 122.1 \text{ (Py}_A); 121.6 \text{ (Py}_B); 69.3 \text{ (CH=CH); 64.6 \text{ (N-CH); 63.9 \text{ (N-CH); 63.8 \text{ (CH=CH); 40.8 \text{ (CH=CH); 33.8 \text{ (CH=CH); 33.1 \text{ (CH=CH); 33.0 \text{ (CH=CH); 32.4 \text{ (coe); 32.2 \text{ (Py}_C\text{CH}_3); 31.8 \text{ (Py}_B\text{CH}_3); 29.9 \text{ (coe); 29.7 \text{ (coe); 28.8 \text{ (coe); 28.5 \text{ (coe); 25.5 \text{ (coe); 27.8 \text{ (coe); 27.6 \text{ (coe).}}}}}}

Elemental Analysis: Caled (C_{30}H_{45}F_6Ir_N_3P): C: 45.91, H: 5.78, N: 5.35, found C: 45.83, H: 5.86, N: 5.33.

\[\text{[Rh}(\kappa^2\text{-Bn-bla})(\eta^4\text{-dbcot})](\text{PF_6})_2 (4)(\text{PF_6})_2\):
180 mg of [Rh(coe)Cl_2] (0.499 mmol Rh) and 102 mg of dbcot (0.499 mmol) were dissolved in 10 ml of CH_2Cl_2 and the solution was stirred for 2 hours and the solution was evaporated to dryness. Next, 164 mg Bn-bla (0.517 mmol) and a mixture of 8 ml of MeOH and 8 ml of CH_2Cl_2 were added and stirred for 1 hour and the solvent was removed \textit{in vacuo}. The thus formed solid was dissolved in 6 ml MeOH and 126 mg KPF_6 were added causing precipitation of a bright yellow solid, 2 ml of H_2O was added and the solution was stirred for 15 minutes after which it was filtered and washed with 2 ml MeOH. Yield: 331 mg (0.430 mmol, 86.2 %).

\[\text{1H} (300 \text{ MHz, acetone-d}_6): \delta = 7.80 \text{ (t, } 3J(\text{H,H}) = 7.7 \text{ Hz, 2H; Py); 7.66 - 7.41 \text{ (m, 5H; Py, Ph); 7.36 (d, } 3J(\text{H,H}) = 7.6 \text{ Hz, 2H; Py); 7.03 \text{ (m, br, 4H; Bn-dbcot); 6.97 \text{ (m, br, 4H; Bn-dbcot); 5.04 \text{ (d[AB] br, } 2J(\text{H,H}) = 15.8 \text{ Hz, 2H; N-CH}_2\text{-Py); 4.91 \text{ (s, 2H; N-CH}_2\text{-Ph}; 4.75 \text{ (s, br, 4H; Bn-CH-), 4.24 (s, br, 4H; Bn-CH-); 3.86 (d[AB], } 2J(\text{H,H}) = 16.0 \text{ Hz, 2H; N-CH}_2\text{-Py); 3.60 \text{ (s, 6H; Py-CH}_3)\]
$^{13}$C (125 MHz, acetone-d$_6$): $\delta$ = 162.1 (Py); 160.6 (Py); 145.0 (Bn$_{\text{d}bcot}$-C1); 139.8 (Py-C4); 133.5 (Bn-C1); 132.7 (Ph-C2/6); 129.7 (Ph-C3/5); 129.7 (Ph-C4); 127.3 (Bn$_{\text{d}bcot}$-C2/3); 127.2 (Py-C5); 122.6 (Py-C3); 63.6 (N-CH$_2$-Ph); 61.6 (N-CH$_2$-Py); 30.0 (Py-CH$_3$). The $^{13}$C NMR signals of the double bond of dbcot could not be located due to the fluxional behavior of this moiety.

FAB$^+$-MS: Calcd for [4]$^+$ (C$_{37}$H$_{35}$N$_3$Rh) $m/z$: 624.1883; Found $m/z$: 624.1886 ($\Delta$ = -0.5 ppm).

$[$Rh($x^3$-Bn-bla)($\eta^4$-dbcot)](PF$_6$)$_2$ ([4](PF$_6$)$_2$):

89.4 mg of [4]PF$_6$ (0.116 mmol) and 29.4 mg AgPF$_6$ (0.116 mmol) were dissolved in 3 ml CH$_2$Cl$_2$ causing instant precipitation of metallic silver and [4](PF$_6$)$_2$. Due to a rather low stability of [4](PF$_6$)$_2$, the attempts to isolate an analytically pure sample were not successful. Hence for the reaction with base we used the approx 1:1 mol mixture of [4](PF$_6$)$_2$ and Ag black obtained after decanting the green supernatant and drying the black-green powder in vacuo.

**Reaction of radical species 1$^{2+}$, 2$^{2+}$ and 4$^{2+}$ with K$_2$CO$_3$:***

In a typical experiment 0.02 mmol of the metal complex 1$^{2+}$, 2$^{2+}$ or 4$^{2+}$ was dissolved in 1 ml of acetone-d$_6$ and stirred with 0.4 mmol of anhydrous solid K$_2$CO$_3$. After the solution turned yellow, NMR spectrum was recorded showing quantitative formation of 1$^+$, 2$^+$ or 4$^+$ respectively.

### 4.5 Acknowledgements

We thank Luis Fuente Arruga for his contributions to this chapter. We thank Dr. Maxime Siegler and Prof. Dr. Anthony Spek for the X-ray structure determinations. We thank Han Peeters for measuring the FAB$^+$-MS mass spectrum.

### 4.6 Notes and References

Base Assisted Selective Reduction of Organometallic Rh\textsuperscript{II} and Ir\textsuperscript{II} Radicals


19 Iimura, M.; Evans, D. R.; Flood, T. C. Organometallics 2003, 22, 5370-5373.


27 Both compounds could be oxidized by Ag\textsuperscript{+} in acetone. 2\textsuperscript{+} was prepared by oxidation with [Fe(η\textsuperscript{5}-C\textsubscript{3}H\textsubscript{4}COMe)Cp]\textsuperscript{+} in CH\textsubscript{2}Cl\textsubscript{2}, however this oxidant was too weak to oxidize I\textsuperscript{1-}. For a list of common redox agents in organometallic chemistry see: Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877-910.


In acetone,\textsubscript{d0}, a very slow rise of the signals of the diamagnetic precursor could be observed for both complexes, in case of the rhodium complex I\textsuperscript{1-} accompanied by the rise of signals of the free dbcot moiety. Kinetic measurements using UV/Vis spectrometry revealed that the decomposition of I\textsuperscript{1-} and 2\textsuperscript{+} proceeds according to a first order rate equation in the metal complex concentration with k\textsubscript{obs} = 1·10\textsuperscript{-8} and 4·10\textsuperscript{-9} \textsuperscript{s}\textsuperscript{-1} respectively. Addition of H\textsubscript{2}O increases the rate of decomposition considerably. However in case of I\textsuperscript{2+} in an aseletive manner.

The same results were obtained when exactly 1 equivalent of KOtBu was added. This base however proved to be less suitable, because if used in excess, some follow-up unselective reactivity was observed, possibly via doubly deprotonated bla complexes (ref 16).
32 If the aminyl radical would abstract a hydrogen atom from the solvent one would expect that mostly deuterium would be incorporated. Alternatively a very large kinetic isotope effect could explain the obtained hydrogen atom, see: Huynh, M. H. V.; Meyer, T. J. Proc. Natl. Acad. Sci. USA 2004, 101, 13138-13141.

33 Evans, C. A. Aldrichimica Acta 1979, 12, 23-29.

34 Radical trapping of species $^{1}_{2}$ in acetone solution using DMPO (DMPO $= 5,5$-dimethyl-1-pyrroline-N-oxide) revealed formation of at least two species A and B, however neither of these could not be assigned to a radical solvent and most probably a rhodium radical has been captured. These species existed in 1:0.1 ratio which changed in time. The simulated parameters: I (major): $g_{iso} = 2.007$, $A^{N} = 48.9$ MHz, $A^{N} = 56.6$ MHz, $A^{N} = 4.9$ MHz; II (minor) $g_{iso} = 2.0049$, $A^{N} = 46.3$ MHz, $A^{N} = 57.5$ MHz. Species $^{2}_{2}$ with DMPO and K$_{2}$CO$_{3}$ gave a complex, very low intensity signal which was impossible to simulate reliably.

35 The oxidation of CO$_{2}$/CO$_{3}$ to C$_{2}$O$_{6}^{2-}$ seems to be less probable. Although the redox potential of the C$_{2}$O$_{6}^{2-}$/C$_{2}$O$_{4}^{2-}$ couple in aqueous carbonate buffer is +0.67 V vs. Fe/Fc$^{+}$ (0.21 vs. SCE), the low concentration of carbonate anions in acetone makes this pathway energetically unfavorable. Zhang, J.; Oloman, C. W.; J. Appl. Electrochem. 2005, 35, 945-953.

36 This equilibrium lays on the side of $^{1}_{2}$/2$^{2}$ and acetone (the oxidation of acetone occurs over 1000 mV vs. the Fe/Fc couple$^{13}$ which gives the energy difference between the two sides of the equilibrium of roughly 600-700 mV or 14-16 kcal/mol).

37 The redox potential of the OH$^{-}$/OH couple in MeCN is only +0.29 vs Fe/Fc$^{+}$ (+0.96 vs NHE): (a) Sawyer, D. T.; Roberts, jr, J. K. Acc. Chem. Res. 1988, 21, 469-476. (b) calculated from the relationship NHE $- E_{1/2} Fe/Fc^{+} = 630$ mV. Pavlishchuk, V. V.; Addison, A. W. Inorg. Chim. Acta 2000, 298, 97-102.