Group 9 open-shell organometallics: reactivity at the ligand
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Carbonyl Complexes of Rhodium with N-donor Ligands: Factors Determining the Formation of Terminal versus Bridging Carbonyls

R = H, Alkyl

R = 2-picoly

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3.1 Introduction

Carbonyl complexes of rhodium with the tridentate nitrogen-donor ‘scorpionato’ trispyrazolyl (Tp) type of ligands have received quite some attention over the past two decades. It was shown that complexes of the type Rh(Tp*)(CO)₂ (Tp* = tris(3,5-dimethylpyrazolyl)borate) photochemically activate C-H bonds of alkanes, show a high degree of fluxionality in solution and reveal interesting one-electron redox properties in the presence of a supporting phosphorous ligand.

The arrangement of the pyrazolyl moieties of the Tp-type ligands imposes a fac-coordination mode. Furthermore, Rh¹ complexes with Tp-type ligands reveal a hemilabile coordination mode through the κ²-κ³ equilibrium, producing diverse structures spanning from mononuclear square planar and trigonal bypiramidal or square pyramidal bis-carbonyls, to octahedral dinuclear triscarbonyl bridged species (Scheme 1). Similar structures (although κ²-κ³ isomerism was not reported) were found for cyclic fac- coordinating tri- and hexa-amines, with the latter ones forming tris-carbonyl bridged tetranuclear assemblies.

While these strictly fac-coordinating N₃-donor ligands have been thoroughly studied, surprisingly little attention has been given to rhodium carbonyl complexes with more flexible podal N₃-donor ligands that can adopt both fac- and mer- coordination modes.

Mathieu and Ros reported that bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine can bind in both fashions to a cationic rhodium carbonyl centre resulting in formation of either mono-carbonyl square planar or bis-carbonyl square pyramidal complexes (Scheme 2). The factors that determine the coordination mode of the N₃-donor ligand and as a result the number of carbonyl ligands per metal atom, were not investigated.

The above structural diversity of N₃-donor ligand Rh-carbonyl complexes is intriguing and could well result in different reactivities. For this reason we became interested in the factors that determine the coordination mode of both the carbonyl ligands and the N-donor ligands in cationic [(Rh(CO)x(N-donor ligand))₃]⁺ complexes with flexible podal N-donor ligands.

Given the rich chemistry of rhodium olefin complexes with bispicolylamine (bpa) type ligands and dual fac- and mer- coordination behavior of bpa, we were interested in the coordination modes of the flexible ligands shown in Scheme 3, and in
understanding the factors that drive the formation of mononuclear complexes with terminal carbonyl ligands versus binuclear carbonyl bridged complexes.

Scheme 3. Ligands used in this study.

Bridging carbonyl complexes are frequently ‘dormant state’ or ‘dead end’ species in several catalytic carbynylation reactions (e.g. hydroformylation) and therefore a better understanding of the factors that determine their formation might well be of synthetic relevance.

3.2 Results and discussion

For the tridentate bpa type of ligands we compared the Me-bpa and Bu-bpa ligands having a methyl or butyl substituent on the central amine donor, respectively, with the non-functionalized bpa ligand to investigate the influence of the electronic effects (stronger bpa donor vs. weaker Me-bpa or Bu-bpa) on the formation of mononuclear terminal vs. bridging carbonyl complexes (Scheme 3). We also investigated ditopic alkyl-bpa bridged complexes with an alkyl tether between two bpa units and their potential more favourable entropic factors associated with the formation of bridged carbonyl complexes. For the tetradentate tpa type ligands we compared the stronger non-functionalized tpa donor with the Me3tpa donor bearing methyl substituents on the pyridine-6 positions (Scheme 3). These substituents have some steric influence on the metal coordination which results in the pyridine units being weaker donors to the metal compared with non-substituted pyridines.

3.2.1 Rhodium carbonyl complexes with bis(picolyl)amine, N-methyl(bis(picolyl)amine) and N-butyl(bis(picolyl)amine)

Reaction of $\text{[Rh}(\kappa^3\text{-bpa})(\eta^4\text{-cod})]\text{PF}_6$ ([1]PF$_6$) (cod = cis,cis-1,5-cyclooctadiene) with CO at a pressure of 1 bar in dichloromethane results in formation of the tris-carbonyl bridged binuclear complex $\text{[Rh}_2(\kappa^3\text{-bpa})_3(\mu\text{-CO})_3][\text{PF}_6]_2$ ([2][PF$_6$]$_2$) (Scheme 4). The complex has $C_2$ symmetry and is not fluxional in solution on the NMR timescale, which results in separate NMR signals of the inequivalent pyridine and methylene groups of
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The inequivalence is a result of the coordination mode in which two CO ligands are trans to picolyl and amine moieties, whereas the third CO is trans to the two picolyl groups of the different bpa ligands. This coordination mode is similar to that previously reported for [Rh₂(μ-CO)₃Cl₂(Py)$_₂$] and was confirmed by single crystal X-ray diffraction. The crystal was grown by layering an acetone solution of [2](PF$_6$)$_₂$ with hexanes at −20 °C. Although the quality of the crystal data is hampered by severe PF$_6$ disorder, the molecular structure of the dication 2$^{2+}$ is unambiguously revealed by the X-ray data (Figure 1).

Scheme 4. Synthesis of [Rh₂(κ$^3$-bpa)$_2$(μ-CO)$_3$]$^{2+}$ (2$^{2+}$) and [Rh(κ$^3$-bpa)(CO)]$^+$ (3$^+$)

Figure 1. X-ray structure of [Rh₂(κ$^3$-bpa)$_2$(μ-CO)$_3$]$^{2+}$ (2$^{2+}$). Thermal ellipsoids are drawn with 50% probability. Hydrogen atoms bound to the carbon atoms, the PF$_6$$^-$ counter ions and acetone molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh(1)–C(1) 2.004(14); Rh(1)–C(1i) 2.019(12); Rh(1)–C(2) 2.019(18); Rh(1)–N(1) 2.165(11); Rh(1)–N(2) 2.176(12); Rh(1)–N(3) 2.184(12); Rh(1)–Rh(1i) 2.5710(18); C(1)–O(1) 1.140(16); C(2)–O(2) 1.14(2); C(1)–Rh(1)–C(1i) 82.1(6); C(1)–Rh(1)–C(2) 84.6(5); C(1)–Rh(1)–C(2) 84.2(5); C(1)–Rh(1)–N(1) 177.4(5); C(1)–Rh(1)–N(2) 98.6(5); C(1)–Rh(1)–N(3) 177.5(5); C(1)–Rh(1)–N(3) 98.3(5); N(1)–Rh(1)–N(2) 84.1(4); N(1)–Rh(1)–N(3) 84.2(5); C(1)–Rh(1)–C(1i) 177.5(5); C(1)–Rh(1)–C(2) 98.3(5); N(1)–Rh(1)–N(2) 84.1(4); N(1)–Rh(1)–N(3) 84.1(4); Rh(1)–C(1)–Rh(1i) 79.5(4); Rh(1i)–C(2)–Rh(1) 79.1(8).

The IR spectrum of the carbonyl region reveals two overlapping bands at 1835 and 1828 cm$^{-1}$ and $^{13}$C NMR spectroscopy reveals two triplets of intensity 2:1 at 215.8 and 210.4 ppm, with Rh–C coupling constants of 28.4 and 27.9 Hz, respectively. This complex is stable in the solid state for at least 2 months. In solution it slowly converts to the mono-carbonyl complex [Rh(κ$^3$-bpa)(η¹-CO)]PF$_6$ (3$^+$) (approx. 30% conversion in acetone after 10 days, heating under reflux in acetone for 2 h leads to quantitative
conversion) (Scheme 4). Complex 3+ reveals a single CO stretch band at 1989 cm⁻¹ and a ¹³C NMR resonance at 190.3 ppm with a Rh–C coupling constant of 77.5 Hz in MeCN.

In marked contrast to its bpa analog, reaction of the [(κ³-Me-bpa)Rh(η⁴-cod)]PF₆ complex ([4]PF₆) with 1 bar CO does not lead to a binuclear, tris-carbonyl bridged species analogous to 2²⁺. Instead, treatment of [4]PF₆ with 1 bar CO in CH₂Cl₂ results directly in a clean and facile substitution of cod by CO with formation of only the square planar carbonyl complex [(κ³-Me-bpa)Rh(CO)]PF₆ ([5]PF₆) (Scheme 5). In the conversion of the η⁴-cod to the monocarbonyl complexes the coordination mode of the Me-bpa ligand changes from fac to mer as evidenced by X-ray diffraction measurements (Figure 2).

![Scheme 5. Synthesis of [Rh(κ³-Me-bpa)(CO)]⁺ ([5]+).](image)

Crystals of [5]PF₆ suitable for X-ray diffraction were grown by layering MeCN solution of [5]PF₆ with diethyl ether. The structure of 5⁺ is shown in Figure 2.

![Figure 2. Coordination geometry of the rhodium atom in the complex [(κ³-Me-bpa)Rh(CO)]PF₆ ([5]PF₆). Hydrogen atoms and the PF₆⁻ counter ion are omitted for clarity. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths [Å] and angles [°]: Rh1–C1 1.834(3), Rh1–N2 2.034(2), Rh1–N1 2.039(2), Rh1–N3 2.079(3), C1–O1 1.144(4), C1–Rh1–N2 98.29(11), C1–Rh1–N1 98.82(11), N2–Rh1–N1 162.85(10), N2–Rh1–N3 177.53(13), N2–Rh1–N1 162.85(10), N1–Rh1–N3 81.16(10).](image)

The substantial different stabilities of the Rh(μ-CO)₂Rh bridged complexes with bpa versus Me-bpa is remarkable, considering the structural resemblance of these ligands. Formation of a square planar monocarbonyl rhodium complex was also observed for the Bu-bpa ligand. Interestingly, the formation of a Rh(μ-CO)₃Rh complex with Bu-bpa could be enforced at higher CO pressures.
Treatment of \([\text{Rh}(\kappa^2-\text{Bu-bpa})(\text{CO})_2]^+\)\([6]\)PF\(_6\) with 50 bar CO for approx. 7 days results in partial conversion (approx. 15\%) to a mixture of the dinuclear, dicationic complex \([\text{Rh}_2(\kappa^2-\text{Bu-bpa})(\mu-\text{CO})_3]^2+\)\([7]\)(PF\(_6\))\(_2\) and mononuclear, monocationic complex \([\text{Rh}(\kappa^2-\text{Bu-bpa})(\text{CO})_2]^+\)\([8]\)(PF\(_6\)) containing two terminal CO ligands as observed by mass spectrometry and IR spectroscopy (Scheme 6).\(^{16,17}\)

Scheme 6. Reaction of \([\text{Rh}(\kappa^2-\text{Bu-bpa})(\text{CO})]^+\)\([6]\) with 50 bar CO to form \([\text{Rh}_2(\kappa^2-\text{Bu-bpa})(\mu-\text{CO})_3]^2+\)\([7]\)\(_2^+\) and \([\text{Rh}(\kappa^2-\text{Bu-bpa})(\text{CO})_2]^+\)\([8]\)\(_+\).\(^{16}\)

FAB-MS (m/z = 945, 917) and IR spectra (\(\nu_{\text{CO}}\) = 1832 cm\(^{-1}\) (KBr)) of \([7]^2+\) are in accordance with the tris-\(\mu\)-carbonyl bridged structure while m/z 772 and \(\nu_{\text{CO}}\) = 1992 and 2042 cm\(^{-1}\) confirm the presence of the bis-carbonyl complex \([8]^+\). Attempts to prepare \([7]\)(PF\(_6\))\(_2\) in high yield were unsuccessful, which might indicate an equilibrium between \([7]^2+\) and \([6]^+\) in the presence of CO. In accordance with this, \([7]\)(PF\(_6\))\(_2\) is not stable in the solid state at room temperature in the absence of CO, and converts to \([6]\)PF\(_6\) within days. Heating of the isolated mixture of \([6]\)PF\(_6\) and \([7]\)(PF\(_6\))\(_2\) in acetonitrile to 50 \(^{\circ}\)C for 2 hours results in full conversion of the contained \([7]\)(PF\(_6\))\(_2\) to \([6]\)PF\(_6\).\(^{16}\)

Table 1. IR and \(^{13}\)C NMR spectroscopy data of the carbonyl ligands.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\nu_{\text{CO}}) solution</th>
<th>(\nu_{\text{CO}}) solid state</th>
<th>(J(\text{Rh,C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[cm(^{-1})]</td>
<td>[cm(^{-1})]</td>
<td>[Hz]</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{bpa})(\mu-\text{CO})_3]^2+)([2]^{2+})</td>
<td>1835 (sh. 1828)</td>
<td>1836, 1815</td>
<td>28.4, 27.9</td>
</tr>
<tr>
<td>([\text{Rh}(\text{bpa})(\text{CO})]^3^+)([3]^3^+)</td>
<td>1989</td>
<td></td>
<td>77.5</td>
</tr>
<tr>
<td>([\text{Rh}(\text{Me-bpa})(\text{CO})]^5^+)([5]^5^+)</td>
<td>1996 (DCM)</td>
<td></td>
<td>78.0</td>
</tr>
<tr>
<td>([\text{Rh}(\text{Bu-bpa})(\text{CO})]^6^+)([6]^6^+)</td>
<td>1994</td>
<td></td>
<td>79.1</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{Bu-bpa})(\mu-\text{CO})_3]^2+)([7]^{2+})</td>
<td>1832</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\text{Bu-bpa})(\text{CO})_2]^8^+)([8]^8^+)</td>
<td>1992, 2042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{tpen})(\text{CO})_2]^2+)([12]^{2+})</td>
<td>1999</td>
<td></td>
<td>67.5</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{tpn})(\text{CO})_2]^2+)([13]^{2+})</td>
<td>1994</td>
<td></td>
<td>79.0</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{tppn})(\mu-\text{CO})_3]^4+)([14]^4^+)</td>
<td>1838 (sh. 1828)</td>
<td></td>
<td>29.1, 29.1</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{tpbn})(\text{CO})_2]^2+)([15]^2+)</td>
<td>1992</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{tpbn})(\mu-\text{CO})_2]^2+)([16]^2+)</td>
<td>1843</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is difficult to imagine that substitution of a proton for an alkyl group will have any significant steric influence on the formation of the \([\text{Rh}(\mu-\text{CO})_3\text{Rh}]\) bridge (tethered alkyl substituted \text{bpa} complexes do form carbonyl bridged species, \textit{vide infra}). Therefore, the markedly different stability of the dirhodium triscarbonyl species \([2]^{2+}\) and \([7]^{2+}\) is most likely caused by the decrease in donor capacity of the ligand on going from \text{bpa} to Me-
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and Bu-bpa. The more electron rich rhodium atom of bpa complex $2^{2+}$ is expected to bind CO more strongly than the Bu-bpa ligated metal in the complex $7^{2+}$ which should result in relative stabilization of the $(\mu$-CO)$_3$ bridge in $2^{2+}$ compared to $7^{2+}$.

The CO stretch frequencies of the square planar complexes $3^{+}$ and $6^{+}$ (1989 cm$^{-1}$ vs. 1994 cm$^{-1}$ and 1996 cm$^{-1}$ for bpa, Bu-bpa, and Me-bpa respectively) confirm that Bu-bpa is indeed a weaker donor than bpa (Table 1). Although the difference in stretch frequencies (5 cm$^{-1}$) does not seem to be large, it is significant and might explain the different relative stability of the bridged carbonyl complexes $2^{2+}$ and $7^{2+}$.

3.2.2 Structure of cyclooctadiene and carbonyl rhodium complexes with tethered bpa ligands

Concluding that the Bu-bpa complex $7^{2+}$ is thermodynamically unstable, we decided to investigate the stabilization of tris-carbonyl bridged species by chelate cooperativity$^{18}$ of binuclear rhodium bpa species tethered with an alkyl chain. The reduction of the entropy of binding by tethering of the rhodium carbonyl complexes could lead to structures similar to the reported hexamine macrocyclic triscarbonyl bridged rhodium complexes.$^{8}$ For that reason we took a closer look at the corresponding cod and carbonyl complexes with ligands that have bpa moieties tethered by a chain of 2, 3 and 4 carbon atoms, and their reactivity with CO.$^{16}$

Analysis of the X-ray structures of $[\text{Rh}_2((\mu-(\text{bis-κ}^3)\text{tpen})_2(\eta^4\text{-cod})_2)]^{2+}$ ($9^{2+}$), $[\text{Rh}_2((\mu-(\text{bis-κ}^3)\text{tpbn})_2(\eta^4\text{-cod})_2)]^{2+}$ ($11^{2+}$) and the DFT optimized structure of $[\text{Rh}_2((\mu-(\text{bis-κ}^3)\text{tppn})_2(\eta^4\text{-cod})_2)]^{2+}$ ($10^{2+}$) (tpen = $N^1N^1N^2N^2$-tetrakis(pyridin-2-ylmethyl)ethane-1,2-diamine, tpnn = $N^1N^1N^2N^2$-tetrakis(pyridin-2-ylmethyl)propane-1,2-diamine, tpbn = $N^1N^1N^2N^2$-tetrakis(pyridin-2-ylmethyl)butane-1,2-diamine) indicates that the length of the methylene tether connecting bis(picolyl)amine moieties in tpbn, tpnn and tpbn influences the solid state structure of the binuclear complex. In complexes with 2 or 4 carbon atoms in the tether, the two metal centers are found to be on the opposite sides of the molecule, in a ‘one hand up, one hand down’ configuration. In complex $10^{2+}$ having a C3 linker the metal centers are on the same side, in a ‘hands up’ configuration (see Figure 3).

![Figure 3](image_url)

Figure 3. Molecular structures of $[\text{Rh}_2((\mu-(\text{bis-κ}^3)\text{tpen})_2(\eta^4\text{-cod})_2)]^{2+}$ ($9^{2+}$), $[\text{Rh}_2((\mu-(\text{bis-κ}^3)\text{tppn})_2(\eta^4\text{-cod})_2)]^{2+}$ ($10^{2+}$) and the previously reported $[\text{Rh}_2((\mu-(\text{bis-κ}^3)\text{tpbn})_2(\eta^4\text{-cod})_2)]^{2+}$ ($11^{2+}$).

We expect that the same structures should be also favored in solution since the zigzag conformation of the alkyl chain results in minimal steric interactions of the moieties coordinated to the rhodium centre. Above structural features of the tethered bpa-alkyl ligands proved to have an impact on the structure of corresponding rhodium carbonyl complexes (see below).

In contrast to the reaction of $[6]PF_6$, the reaction of $[\text{Rh}_2((\mu-(\text{bis-κ}^3)\text{tppn})(\text{CO})_2](PF_6)_2$, ([13](PF_6)_2) in CH3CN with 50 bar CO is nearly quantitative within 4 days. The
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tetranuclear complex $[\text{Rh}_4((\mu-\text{CO})_3)_2((\mu-(\text{bis-\kappa}^3)tppn)_2)]^{4+}$ [14]$^{4+}$ is formed, with two tris-$\mu$-carbonyl bridges (Scheme 7). The $\nu$(CO) bands at 1838 and 1828 cm$^{-1}$ (CH$_3$CN) and $^{13}$C-NMR triplets at $\delta = 215$ ($^1J_{C-Rh} = 29.1$ Hz) and $\delta = 213$ ($^1J_{C-Rh} = 29.1$ Hz) ppm in approx. intensity ratio of 2:1, are indicative for the tris-$\mu$-carbonyl bridges (Table 1). $^1$H NMR and $^{13}$C-NMR signals for the tppn ligand show that [14]$^{4+}$ has effective $D_{2h}$ symmetry in solution (8 equivalent pyridyl-fragments). The tppn ligand in [14]$^{4+}$ is fac-coordinated, as indicated by $^1$H NOESY NMR spectroscopy. The DFT optimized structure of [14]$^{4+}$ is presented in (Figure 4).

Scheme 7. Formation of a tetranuclear rhodium carbonyl complex $[\text{Rh}_4((\mu-\text{CO})_3)_2(tppn)_2]^{4+}$ (14$^{4+}$).$^{16}$

Figure 4. DFT optimized structure of 14$^{4+}$.

In contrast to 7$^{2+}$, 14$^{4+}$ is stable at room temperature both in the solid state and in solution. Heating 14$^{4+}$ in CH$_3$CN to 80 °C results in only approx. 20% conversion to 13$^{2+}$ in 2 hours.$^{16}$

The stability of the tetranuclear complex 14$^{4+}$ is most likely a result of the cooperative binding of the four rhodium atoms through carbonyl bridges. Formation of the first Rh(CO)$_3$Rh bridge (that is not thermodynamically stable for the binuclear analog of 14$^{4+}$ – the Bu-bpa complex 7$^{2+}$) enhances the effective local concentration of rhodium and entropically favors the formation of the second Rh(CO)$_3$Rh bridge. This effect is similar to the well-known chelate effect that results in stronger binding of multidentate versus monodentate ligands. Consequently, multivalent binding$^{18}$ (involving the interaction of four Rh atoms) stabilizes 14$^{4+}$ from fragmentation into terminal Rh-CO complexes and results in higher stability of 14$^{4+}$ compared to 7$^{2+}$. 
Under similar carbylization conditions the tpen carbyl complex $[\text{Rh}_2((\mu-(\text{bis-})\kappa^3)\text{tpen})(\text{CO})_2]^{2+}$ (12$^{2+}$) (nor the tpen cod complex 9$^+$) did not form any bridged carbyl species and only 12$^{2+}$ could be observed in the solution. Although formation of an intramolecular CO bridge should be disfavored because of the preferred ‘one hand up, one hand down’ conformation of the molecule, one could expect that intermolecular CO bridges could be formed, leading to polymeric structures. Formation of the CO bridged species from the Bu-bpa complex 6$^+$ (for which the partial conversion to the bridged species 7$^{2+}$ was observed) and tpen complex 13$^{2+}$ would have approximately the same unfavorable entropy contribution, but the enthalpy of formation of the bridged species is likely even lower for tpen because of electronic effects. The tpen ligand imposes a lower electron density on the metal ($\nu_{(\text{CO})} = 1999$ cm$^{-1}$, $J_{\text{C-Rh}} = 67.5$ Hz) compared to the Bu-bpa or tppn ligands ($\nu_{(\text{CO})} = 1994$ cm$^{-1}$, $J_{\text{C-Rh}} = 79$ Hz) (Table 1), which most probably does not allow for coordination of any extra CO molecule. The lower donor capacity of tpen ligand compared to Bu-bpa can be rationalized by the fact that the amine nitrogens of tpen are rivaling for the electrons from a very short C2 alkyl bridge, which effectively acts as an electron poor “CH$_2$• radical” substituent of the bpa moiety.

Treatment of the $[\text{Rh}_2((\mu-(\text{bis-})\kappa^3)\text{tpbn})(\eta^4\text{-cod})_2]^{2+}$ complex with 10 bar of CO at 50 ºC for 10 hours in acetonitrile results in formation of a yellow precipitate. IR measurements (KBr) showed the presence of bridging carbyls ($\nu_{(\text{CO})} = 1843$ cm$^{-1}$) and a minor amount of terminal carbyls ($\nu_{(\text{CO})} = 1993$ cm$^{-1}$) in the precipitate, while the filtrate after evaporation of the solvent gave signals at 1838 and 1992 cm$^{-1}$. This could indicate formation of polymeric Rh(μ-CO)$_3$Rh bridged species, which should be driven by precipitation.

### 3.2.3. Rhodium carbyl complexes with tris(picolyl)amine

The above results suggest that the formation of the Rh(μ-CO)$_3$Rh bridged species is driven by use of stronger σ-donating N$_3$-ligands and can be further stabilized by entropic factors in case of homoditopic ligands. To further investigate the effect of stronger σ-donors we studied the tetradentate tpa (tpa = tris(picolyl)amine) ligand that can be regarded as a bpa ligand functionalized with an additional picolyl group. This ligand can be compared with our previously reported Me$_3$tpa complexes in its coordinating behavior towards Rh-carbyl species.$^{20}$

Reaction of the $\text{in situ}$ generated $[\text{Rh}(\mu-(\text{Cl})(\text{CO})_2]^2$ with tpa (tpa = tris(picolyl)amine) in methanol yields $[\text{Rh}(\kappa^3\text{-tpa})(\text{CO})]PF_6$ ([15]$^+$ as a yellow powder after precipitation with KPF$_6$. Solution IR in low concentration shows only one CO absorption band at 1991 cm$^{-1}$, indicating that the complex has a 16VE square-planar geometry with the tpa ligand being in a $\kappa^3$-coordination mode. In polar solvents like acetone or acetonitrile, the mononuclear species 15$^+$ is in equilibrium with the dinuclear bis-μ-CO bridged species $[\text{Rh}(\kappa^3\text{-tpa})(\mu-(\text{CO})_2]^{2+}$ (16$^{2+}$) (Scheme 8) and at higher concentrations a weak IR absorption band at 1749 cm$^{-1}$ reveals the formation of bridging ketonic carbyls. After evaporation of the solvent a dark purple solid is obtained, showing an IR (solid state) absorption band of the bridging carbyls of the dinuclear complex 16$^{2+}$ at $\nu_{(\text{CO})} = 1740$ cm$^{-1}$ and a terminal carbyl band at 1985 cm$^{-1}$ (Table 1). Formation of 16$^{2+}$ is reversible and dissolution of the solid purple mixture of 15$^+$ and 16$^{2+}$ leads to disappearance of the bridging carbyl band. Such a monomer-dimer equilibrium is remarkable and has not been observed for the related $[\text{Rh}(\kappa^3\text{-Me}_3\text{tpa})(\text{CO})]^+$ complex.$^{20}$
This different behavior should be ascribed to the stronger donor capacity of tpa versus Me\textsubscript{3}tpa.

![Scheme 8. Dynamic equilibrium between the mononuclear [Rh(κ\textsuperscript{3}-tpa)(CO)]\textsuperscript{+} 15\textsuperscript{+} and dinuclear [Rh(κ\textsuperscript{4}-tpa)(μ-CO)]\textsubscript{2}\textsuperscript{2+} 16\textsuperscript{2+}.](image)

The equilibrium between the mononuclear and binuclear complexes could be studied by NMR spectroscopy in polar solvents like acetonitrile or acetone. Both the monomer and the dimer are fluxional on the NMR time scale, involving exchange of the axial and equatorial picolyl moieties. VT-NMR measurements further allowed us to calculate the thermodynamics for dimerization of 15\textsuperscript{+} in acetone through a van ’t Hoff plot in the range from 283 K to 225 K (Figure 5).

![Figure 5. Van ’t Hoff plot of the dimerization of 15\textsuperscript{+} to 16\textsuperscript{2+}: ΔH = –28.4 ± 1.7 kJ·mol\textsuperscript{-1}; ΔS = –134 ± 7 J·mol\textsuperscript{-1}\textcdot K\textsuperscript{-1}; (r\textsuperscript{2} = 0.9985). The equilibrium constant is defined as: \( K = \frac{[16\textsuperscript{2+}]}{[15\textsuperscript{+}]^2} \).](image)

Formation of binuclear complex 16\textsuperscript{2+} from 15\textsuperscript{+} is enthalpically favorable by −28 kJ·mol\textsuperscript{-1}, but entropically disfavored. The large negative entropy factor −134 J·mol·K\textsuperscript{-1} agrees well with a dimerization process and dominates at room temperature. The overall process at 298 K is slightly endergonic (ΔG\textsuperscript{298} = +11.5 kJ·mol\textsuperscript{-1}, K\textsuperscript{298} ≈ 9.5 · 10\textsuperscript{-3}).

The \textsuperscript{1}H NMR spectra recorded in the temperature range from 330 to 218 K are presented in Figure 6. At 330 K only the mononuclear form 15\textsuperscript{+} is visible (K\textsuperscript{330} ≈ 3.2 · 10\textsuperscript{-3}). All the picolyl arms of the ligand are equivalent, which indicates that at this temperature the molecule is fluxional on the NMR time scale. This process is frozen at 263 K where the protons of the coordinated and dangling picolyl groups show different signals. We expect that the mechanism of fluxionality of 15\textsuperscript{+} is the same as for the recently reported [Rh(Me\textsubscript{3}tpa)CO]\textsuperscript{+}, i.e. the dangling picolyl arm coordinates to the...
metal forming a transient 18 VE κ4 complex followed by dissociation of another picolyl moiety to reform the 16 VE square planar κ3 complex. 20

Figure 6. Variable temperature 1H NMR spectrum showing dimerization of 15+ and the fluxional behavior of 15+ and 162+ in acetone-d6. Legend: ♦ = 15+; ♠ = 162+.

The signals of the dinuclear species 162+ start to appear upon cooling the solution close to room temperature. Both the signals of mononuclear species 15+ and dinuclear species 162+ are substantially broadened at 308 K. Sharpening of the signals of both compounds appears in the same temperature range. This behavior indicates that the broadening is due to coalescence associated with the reversible dimerization of 15+ to 162+. The signals of all three picolyl arms of the dinuclear compound 162+ are equivalent down to 218 K. Clearly the dinuclear complex remains fluxional in the entire measured temperature range. At temperatures below 253 K the signals of the dimer are becoming broader and the signal of Py-H6 completely disappears at 218 K while approaching coalescence. 21 Since the fluxional behavior of 162+ down to 218 K is not caused by the dimer-monomer equilibrium, it has to originate from exchange of the picolyl moieties on the octahedral 18VE rhodium centre that is fast on the NMR timescale. Noticeably, the octahedral 18VE complex 22+ does not show a similar fluxional behavior in solution.
An important difference between $\text{2}^2^+$ and $\text{16}^2^+$ is the presence of a Rh–Rh bond in the former, absent in the latter (see below). We therefore propose that the exchange process of $\text{16}^2^+$ follows the sequence shown in Figure 7. Decoordination of one of the picolyl arms (Py$^\text{C}$ trans to Py$^\text{A}$) leads to a transient 16VE square pyramidal species that can rearrange the coordinated picolyl groups via a Berry-preudorotation mechanism (via a trigonal bipyramidal structure). Recoordination of the free picolyl group leads to reformation of the octahedral species with a different order of the picolyl groups. DFT calculations suggest that the detachment of the picolyl moiety of $\text{16}^2^+$ is facilitated by formation of a weak $\sigma$-type metal-metal interaction in the ‘unsaturated’ tbpy intermediate. $\text{2}^2^+$ already has a $\sigma$-type Rh–Rh bond and cannot easily increase its bond order and hence the pentacoordinate intermediate required for exchange should be less easily accessible.

**Figure 7.** Proposed mechanism of exchange of the pyridyl groups of $\text{16}^2^+$ leading to observed fluxionality of the complex.

Formation of the dinuclear species $\text{16}^2^+$ was confirmed by single-crystal X-ray diffraction. The molecular structure of $\text{16}^2^+$ is shown in Figure 8. The Rh–Rh distance of 3.0585(7) indicates little or no bonding interaction between the metal atoms, in agreement with the saturated 18 VE configuration of the two metals in the absence of a Rh–Rh bond. The Rh–C–Rh angle (100.9(2)$^\circ$) is considerably larger than the usual 80–90$^\circ$ bond of the ‘classical’ bridging rhodium carbonyls. Although the angle is somewhat more acute than most of the reported M–C–M angles for ketonic carbonyls (having more sp$^2$ character of the carbon atom) which are in the range of 107–120$^\circ$, the CO stretching frequency of 1749 cm$^{-1}$ (MeCN) is in full agreement with a ketonic character of the carbonyl group. To our best knowledge, complex $\text{16}^2^+$ is the first example of a binuclear bis-CO bridged rhodium species not supported by any other ancillary bridging ligands, nor a Rh–Rh bond. This seems to be also the first example of a dynamic equilibrium between a mononuclear terminal carbonyl Rh$^1$ species and binuclear Rh(μ-CO)$_x$Rh bridged species measured in solution.
Figure 8. X-ray structure of \([\text{Rh}(\kappa^4\text{-tpa})(\mu\text{-CO})]^{2+}\) \(16^{2+}\). Selected bond lengths [Å] and angles [°]: Rh1–C1 1.972(4), Rh1–C1a 1.993(4), Rh1–N2 2.088(3), Rh1–N1 2.111(3), Rh1–N4 2.201(3), Rh1–N3 2.242(3), C1–O1 1.205(5), N1–Rh1–N4 80.14(12), N1–Rh1–N3 81.07(12), N2–Rh1–N4 80.14(12), N1–Rh1–N3 81.07(12), N2–Rh1–N4 79.13(12), N2–Rh1–N3 93.62(12), C1–Rh1–C1a 79.05(18).

3.3 Conclusions

Synthesis of rhodium carbonyl complexes ligated with a series of different bis(2-picolyl)amine derivatives allowed us to study the factors that determine the relative stabilities of terminal mono-carbonyl and bridging tris-carbonyl bridged. Whereas for the relatively strong electron donating bpa ligand the formation of the \(\text{Rh}(\mu\text{-CO})_3\text{Rh}\) bridge is thermodynamically favorable at 1 bar of CO, weaker donors such as Me-bpa, Bu-bpa or tpen do not allow formation of such species under such conditions. The unfavorable entropy of formation of the carbonyl bridges can be reduced by tethering the bpa moieties with a propylene linker. This allows for cooperative binding of four rhodium centers to assemble a stable tetranuclear compound with two tris-carbonyl bridges.

Similarly, the stronger tris(2-picolyl)amine (tpa) \(N_4\)-donor allows formation of ketonic bis-carbonyl bridged species \(16^{2+}\) that exist in dynamic equilibrium with the mononuclear mono-carbonyl species \(15^+\) in solution, whereas Rh-carbonyl species with the weaker \(N_4\)-donor Me\(_3\)tpa (tris(2,6-lutidyl)amine) exist only in the mononuclear terminal carbonyl form. We thus showed that subtle changes in the ligand structure have a major impact on the stability of the carbonyl bridged compounds compared to their terminal mono-carbonyl analogs. The presented results clearly show that the stability of the bis- and tris-carbonyl bridged structures depends on a delicate balance between favorable enthalpic factors (enhanced with stronger \(\sigma\)-donor ligands) and unfavorable entropic factors (that can be reduced by multinuclear binding using ditopic ligands).

3.4. Experimental Section

General methods

All procedures were performed under N\(_2\) using standard Schlenk techniques. Solvents (p.a.) were deoxygenated by bubbling through a stream of N\(_2\) or by the freeze-pump-thaw method. The temperature indication r.t. corresponds to ca. 20 °C. \([\text{Rh}(\kappa^3\text{-bpa})(\eta^4\text{-cod})][\text{PF}_6] ([1][\text{PF}_6]), [\text{Rh}(\kappa^3\text{-Bu-bpa})(\eta^4\text{-cod})][\text{PF}_6] ([4][\text{PF}_6])\) and \([\text{Rh}_2(\mu-\kappa^2\text{-tpbn})(\eta^4\text{-cod})_2][\text{PF}_6]_2 ([11][\text{PF}_6]_2)^{11}\) were
prepared according to literature procedures. Synthetic procedures for [Rh(κ₃-Bu-bpa)(CO)]PF₆ (16)[PF₆], [Rh₂(μ-(bis-κ₃)tpen)(cod)₂](PF₆)₂ (19)[PF₆], [Rh₂((μ-(bis-κ₃)tppn)(cod)₂)](PF₆)₂ (10)(PF₆)₂, [Rh₂(μ-(bis-κ₃)tpen)(CO)]PF₆ (12)(PF₆)₂, [Rh₂((μ-(bis-κ₃)tppn)(CO)](PF₆)₂ (13)[PF₆]₂), [Rh₂((μ-(bis-κ₃)tppn)]((μ-CO)₃)₂)(PF₆)₄ (14)[PF₆]₄ are reported in reference 16. All other chemicals are commercially available and were used without further purification.

NMR experiments were carried out on a Bruker DRX300 (300 MHz and 75 MHz for ¹H and ¹³C respectively) and Varian Inova500 (500 MHz and 125 MHz for ¹H and ¹³C respectively). Solvent shift reference for ¹H NMR: acetone-d₆ δH = 2.05, CD₃CN δH = 1.98. For ¹³C-NMR: acetone-d₆ δC = 29.50, CD₃CN δC = 1.28. Abbreviations used are s = singlet, d = doublet, dd = doublet of doublets, t = triplet, p = pentet, m = multiplet and br = broad. The couplings between the protons in the pyridine ring are not fully resolved and hence we use a simplified assignment of the multiplicities of the signals as doublets, triplets and double triplets.

Elemental analyses (CHN) were carried out by H. Kolbe Mikroanalytisches Laboratorium (Germany). Solution on a Bruker Vertex 70 FTIR spectrometer. Solid state IR measurements were performed on a Shimadzu FTIR 8400S spectrometer equipped with a Specac MKII Golden Gate Single Reflection ATR system.

X-ray diffraction

The structures are shown in Figures 1 and 2 which include selected bond distances and angles. The crystal data are shown in Table 2. Crystals were mounted on glass needles. The intensity data of (2)(PF₆)₂ was collected at on a Nonius Kappa CCD single-crystal diffractometer, using Mo Kα radiation and applying φ and ω scan modes. The intensity data were corrected for Lorentz and polarization effects. A semi-empirical multiscan absorption correction was applied (SADABS) on [2]. The structures were solved by the PATTY option of the DIRDIF program system. All nonhydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed at calculated positions, and refined isotropically in riding mode.

[2](PF₆)₂: The crystal structure analysis was hampered by PF₆ disorder and the poor quality of the data. Because of the limited reliability of the higher order data all data above 25° θ were not used in the refinement. The least squares refinement showed a moderate racemic twinning (BASF = 0.113). The difference Fourier map showed a substantial residual density which could not be parameterized, and therefore the SQUEEZE procedure was used to account for this electron density. Nevertheless the final difference Fourier map showed rather large residual density, especially close to the rhodium atom. To a large extend this is probably due to absorption effects. The parameter set suggests a ratio of 1 dinuclear Rh-complex : 1.5 PF₆ moieties : 2 acetone moieties. Obviously, the correct charge balance of the dinuclear Rh-complex (as confirmed by the analytical and spectroscopic data of [2](PF₆)₂, see synthesis section below) requires the presence of 2 PF₆ moieties per complex, therefore we have to assume that the residual electron density stands for 0.5 PF₆ (4 PF₆ moieties in the whole unit cell). The SQUEEZE procedure shows 4 voids of 229 Å³ each, containing 52 electrons in the whole unit cell. These voids are centred around positions with y = 0.25 and y = 0.75, so around special positions with a multiplicity of 4, which is in accord with the number of missing PF₆ moieties. The number of electrons in these voids reported by the SQUEEZE procedure is rather low as a PF₆ moiety has 69 electrons. However, the voids are rather large and therefore merge to form channels through the structure running parallel to the c-axis. Measurements on crystals grown from acetone:diethyl ether did not result in improved data, indeed they were worse. However, these data showed indications of the missing PF₆ moieties on a general position in these channels, in which case an occupancy factor of 0.5 has to be assumed, together with the presence of some more, unidentified solvent moiety (acetone or diethylether). Despite the problems encountered with this structure we do believe that the structure and geometry of the dicationic dinuclear Rh-complex are correct and reliable. The physical properties given here are based on the presence of 2 PF₆ and 2 acetone moieties in the structure.
Table 2. Crystallographic data for [2](PF₆)₂ and [5](PF₆)₂.

<table>
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<tr>
<th>Crystallographic Data</th>
<th><a href="PF%E2%82%86">Rh₂(κ³-bpa)₂(μ-CO)₃</a>₂·2C₃H₆O</th>
<th>[Rh(κ³-bpa-Me)(CO)]PF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₁₂H₁₄F₁₄N₆O₆ P₁₀Rh₂</td>
<td>C₁₂H₁₄F₆N₃OPRh</td>
</tr>
<tr>
<td>Formula weight</td>
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<td>489.17</td>
</tr>
<tr>
<td>Temperature [K]</td>
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<td>110</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoKα (graphite mon.)</td>
<td></td>
</tr>
<tr>
<td>Wavelength [Å]</td>
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<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>I-4 2 d</td>
<td>P 2 1/c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>30.368(8)</td>
<td>11.0276(4)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>30.368(8)</td>
<td>12.3702(4)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>9.2873(4)</td>
<td>15.6878(4)</td>
</tr>
<tr>
<td>β [°]</td>
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<td>126.6770(10)</td>
</tr>
<tr>
<td>Volume [Å³]</td>
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<td>1716.34(10)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Density [Mg m⁻³]</td>
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<td>1.8931(1)</td>
</tr>
</tbody>
</table>

DFT calculations
Geometry optimizations were carried out with the Turbomole program package³² coupled to the PQS Baker optimizer³³ at the ri-DFT³⁴ level using the BP86³⁵ functional and SV(P) basis set.³⁶

Measurements of the equilibrium between 15⁺ and 16²⁺
Measurements were performed on a 0.036 M solution of 15⁺ in acetone-d₆ on a Bruker DRX300 NMR spectrometer. The sample temperature was calibrated by measuring the chemical-shift separation between the OH and CH₃ resonances of methanol. Relative concentrations of 15⁺ and 16²⁺ were estimated by integration of the -CH₂- proton signals of the tpa ligand.

Syntheses:
[Rh₂(κ³-bpa)₂(μ-CO)₃](PF₆)₂ ([2](PF₆)₂): 290 mg of [Rh(bpa)(cod)]PF₆ (0.522 mmol) were placed in a 100 ml schlenk flask and dissolved in 15 ml CH₂Cl₂. CO was bubbled through the solution for 25 minutes during which yellow precipitate has formed. The solution was stirred for additional 30 minutes under CO atmosphere and the yellow solid was filtered and dried in vacuo. Yield: 167 mg (0.170 mmol, 65.4%).

1H NMR (500 MHz, CD₃CN): δ = 8.62 (d, J(H,H) = 4.5 Hz, 1H; Py-H6); 8.52 (d, J(H,H) = 4.5 Hz, 1H; Py-H6'); 7.88 (dt, J(H,H) = 1.5 Hz, J(H,H) = 8.0 Hz, 2H; Py); 7.46 (m, 3H; Py); 7.38 (t, J(H,H) = 6.0 Hz, 1H; Py); 5.72 (t, J(H,H) = 4.0 Hz, 1H; NH); 4.87 (dd[AB], J(H,H) = 17.0 Hz, J(H,H) = 17.0 Hz, 2H; N-CH₂-Py); 4.78 (dd[AB], J(H,H) = 17.0 Hz, J(H,H) = 7.0 Hz, 2H; N-CH₂-Py); 4.33 (m, 4H; N-CH₂-Py).

13C NMR (125 MHz, CD₃CN): δ = 215.8 (t, J(C,Rh) = 28.4 Hz, 2xμ₂-CO), 210.4 (t, J(C,Rh) = 27.9 Hz, μ₂-CO); 161.1 (Py-C1); 160.9 (Py-C1'); 149.5 (Py-C5); 149.3 (Py-C5'); 140.8 (Py-C3); 140.7 (Py-C3'); 125.8 (Py); 124.8 (Py); 60.0 (N-CH₂-Py); 59.9 (N-CH₂-Py').

IR (MeCN): ν(C≡O) = 1835 with a shoulder at 1828 cm⁻¹, solid state: ν(C≡O) = 1836, 1815 cm⁻¹
Elemental Analysis: Calcd. (C₂₇H₂₆F₁₂N₇O₃P₂Rh₂·0.5CH₂Cl₂): C: 32.36; H: 2.67; N: 8.23;
Found: C: 32.34; H: 2.97; N: 8.43.

[Rh(κ³-bpa)(CO)]PF₆ ([3](PF₆)₂): 153 mg of [2](PF₆)₂ (0.156 mmol) were dissolved in 10 ml MeOH and kept under reflux for 3 hrs allowing the evolved CO to escape from the vessel. The unreacted [2](PF₆)₂ was filtered off and the filtrate was condensed to approx 5 ml causing precipitation of the product that was filtered off, and dried in vacuo. Yield: 59 mg (0.124 mmol, 39.6%).

1H NMR (300 MHz, CD₃CN): δ = 8.39 (d, J(H,H) = 5.4 Hz, 2H; Py); 7.92 (dt, J(H,H) = 1.5 Hz, J(H,H) = 7.8 Hz, 2H; Py); 7.34 (d, J(H,H) = 8.1 Hz, 2H; Py); 7.30 (t, J(H,H) = 6.9 Hz, 2H; Py); 5.57 (s, br, 1H, N-H); 4.60 (dd[AB], J(H,H) = 15.9 Hz, J(H,H) = 9.6 Hz, 2H; N-CH₂-Py); 4.46 (dd[AB], J(H,H) = 15.9 Hz, J(H,H) = 6.0 Hz, 2H; N-CH₂-Py).
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$^{13}$C NMR (75 MHz, CD$_3$CN): $\delta$=190.3 (d, $^1J$(Rh,C) = 77.5 Hz; (CO)); 165.2 (Py); 154.6 (Py); 139.8 (Py); 125.7 (Py); 123.4 (Py); 57.8 (N-CH$_2$-Py).

IR (MeCN): $\nu_{C=O}$=1989 cm$^{-1}$

Elemental Analysis: Calcd (C$_{13}$H$_{13}$F$_6$N$_3$OPRh): C, 32.86; H, 2.76; N, 8.84; Found: C: 32.93; H: 3.00; N: 8.72.

$\text{[Rh}(\kappa^3\text{-bpa-Me})(\eta^4\text{-cod})]\text{PF}_6 ([4]PF_6)$:
206 mg of $\text{[Rh(cod)(\mu-Cl)]}_2$ (0.836 mmol Rh) was suspended in 10 ml MeOH and 179 mg (0.839 mmol) of bpa-Me was added and the solution was stirred until the solution became clear. Next, 210 mg (1.14 mmol) of KPF$_6$ and 2 ml of water were added and the solvent partially evaporated, causing precipitation of a bright yellow solid, which was filtered and washed with 2 ml MeOH. Yield: 222 mg (0.38 mmol, 46.6 %), a second crop of 63 mg was obtained by leaving the filtrate at –20 ºC for 3 days giving combined yield of 285 mg (0.501 mmol, 60%).

$^1$H (300 MHz, acetone-d$_6$): $\delta$ = 9.26 (d, $^3J$(H,H) = 4.8 Hz, 2H; Py); 7.73 (dd, $^4J$(H,H) = 1.5 Hz, $^2J$(H,H) = 7.8 Hz, 2H; Py); 7.33 (d, $^3J$(H,H) = 7.5 Hz, 2H; Py); 7.28 (d, $^3J$(H,H) = 8.1 Hz, 2H; Py); 4.65 (d[AB] br, $^2J$(H,H) = 16.2 Hz, 2H; N-CH$_2$-Py); 4.16 (d[AB], $^2J$(H,H) = 16.2 Hz, 2H; N-CH$_2$-Py); 3.85 (s, br, 4H; CH=CH); 3.66 (s, 3H; N-CH$_3$); 2.67 (m, br, 4H; CH$_2$); 1.87 (m, br, 4H; CH$_2$).

$^{13}$C (75 MHz, acetone-d$_6$): $\delta$ = 161.1 (Py-C$_2$); 153.2 (Py); 140.3 (Py); 126.2 (Py); 124.8 (Py); 76.9 (d, $^1J$(Rh,C) = 13.6 Hz; (CH=CH)); 67.9 (N-CH$_2$-Py); 53.0 (N-CH$_3$); 32.8 (CH$_2$).


$\text{[Rh}(\kappa^3\text{-bpa-Me})(\text{CO})]\text{PF}_6 ([5]PF_6)$:
173 mg of $\text{[Rh(bpaMe)(cod)]PF}_6$ (0.304 mmol) were placed in a 100 ml schlenk and dissolved in 15 ml CH$_2$Cl$_2$. CO was bubbled through the solution for 20 minutes and the solution was stirred for additional 30 minutes under CO atmosphere. 30 ml of hexanes were added causing precipitation of yellow solid that was filtered, washed with hexanes and dried in vacuo. Yield: 137 mg (0.260 mmol, 85.5%).

$^1$H (500 MHz, acetone-d$_6$): $\delta$ = 8.42 (d, $^3J$(H,H) = 5.5 Hz, 2H; Py); 7.96 (dt, $^4J$(H,H) = 1.5 Hz, $^2J$(H,H) = 8.0 Hz, 2H; Py); 7.51 (d, $^3J$(H,H) = 7.5 Hz, 2H; Py); 7.35 (t, $^3J$(H,H) = 7.5 Hz, 2H; Py); 4.87 (d[AB], $^2J$(H,H) = 15.5 Hz, 2H; N-CH$_2$-Py); 4.19 (d[AB], $^2J$(H,H) = 15.5 Hz, 2H; N-CH$_2$-Py); 2.69 (s, 3H; N-CH$_3$).

$^{13}$C (125 MHz, acetone-d$_6$): $\delta$ = 190.3 (d, $^1J$(Rh,C) = 78 Hz; (CO)); 163.5 (Py); 153.2 (Py); 125.7 (Py); 123.4 (Py); 57.8 (N-CH$_2$-Py).

IR (CH$_2$Cl$_2$) ($\nu$($C\equiv O$)=1996 cm$^{-1}$).

Elemental Analysis: Calcd. C: 34.38; H: 3.09; N: 8.59; Found: C: 34.24; H: 3.26; N: 8.30.


$\text{[Rh}(\kappa^3\text{-tpa})(\text{CO})]\text{PF}_6 ([15]PF_6)$:
197 mg of $\text{[Rh(\mu-Cl)(coe)$_2$]}_2$ (0.275 mmol) was suspended in 10 ml of MeOH and 167 mg of tpa (0.575 mmol) was added. CO was bubbled until all the solid dissolved and the solution turned yellow-brown. The solution has been stirred for additional 20 minutes under CO atmosphere after which 143 mg of KPF$_6$ (0.781 mmol) was added causing precipitation of yellow solid that was filtered off and washed twice with 2 ml of MeOH. Yield: 213 mg (0.376 mmol). Compound was recrystallized from 10 ml of hot MeOH to yield 140 mg (0.247 mmol, 45.0 %) of analytically pure product.


$^1$H NMR (500 MHz, acetone-d$_6$, –5 ºC): $\delta$ = 8.44 (d, $^3J$(H,H) = 5.0 Hz, 2H; Py$^C$-H6); 8.35 (d, $^3J$(H,H) = 3.5 Hz, 1H; Py$^D$-H6); 8.02 (t, $^3J$(H,H) = 7.5 Hz, 2H; Py$^C$-H4); 7.98 (d, $^3J$(H,H) = 7.5 Hz, 1H; Py$^D$-H3); 7.65 (t, $^3J$(H,H) = 7.5 Hz, 1H; Py$^D$-H4) 7.61 (d, $^3J$(H,H) = 8.0 Hz, 2H; Py$^C$-H3); 7.40 (t, $^3J$(H,H) = 7.0 Hz, 2H; Py$^D$-H5); 7.14 (t, $^3J$(H,H) = 6.0 Hz, 1H; Py$^D$-H5); 5.23
Carbonyl Complexes of Rhodium with N-Donor Ligands

(d[AB], 2$\nu$(H,H) = 15.5 Hz, 2H; N-CH$_2$-Py$^C$); 4.84 (d[AB], 2$\nu$(H,H) = 15.5 Hz, 2H; N-CH$_2$-Py$^C$); 4.38 (s, 2H; N-CH$_2$-Py$^D$).

$^{13}$C NMR (125 MHz, acetone, –27 °C): $\delta$ = 190.8 (d, $^1$$J$(Rh,C) = 79.5 Hz; (CO)); 165.1 (Py$^C$); 155.3 (Py$^C$); 155.2 (Py$^D$); 154.2 (Py$^D$); 140.7 (Py$^D$); 129.5 (Py); 129.3 (py); 66.4 (N-CH$_2$-Py); 65.9 (N-CH$_2$-Py).

IR (MeCN): $\nu$(C≡O)=1991 cm$^{-1}$.

Elemental Analysis: Calcd. (C$_{19}$H$_{18}$F$_6$N$_4$OPRh) C: 40.30; H: 3.20; N: 9.89; Found: C: 40.63; H: 3.57; N: 9.83.

$[\text{Rh}(\kappa^4-$tpa)(CO)$_2$(PF$_6$)$_2$ ([16](PF$_6$)$_2$):

After dissolution of 15$^+$ in acetone, the compound 16$^{2+}$ exists in equilibrium with 15$^+$. Signals of 15$^+$ were omitted for clarity.

$^{1}$H (500 MHz, acetone-d$_6$, –5 °C): $\delta$ = 8.52 (d, 3$\nu$(H,H) = 5.0 Hz, 3H; Py-H$_6$); 7.82 (d, 3$\nu$(H,H) = 7.5 Hz 4$\nu$(H,H) = 1.0 Hz, 3H; Py-H$_4$); 7.46 (d, 3$\nu$(H,H) = 7.5 Hz, 3H; Py-H$_3$); 7.25 (t, 3$\nu$(H,H) = 6.5 Hz, 3H; Py-H$_5$); 5.08 (s, 6H; N-CH$_2$-Py).

$^{13}$C (125 MHz, acetone, –60 °C, all peaks broad): $\delta$ = 208.3 (t, 1$\nu$(Rh,C) = 19.6 Hz; (CO)); 162.5 (Py); 153.2 (Py); 140.4 (Py); 140.1 (Py); 126.4 (Py); 126.1 (Py); 125.2 (Py); 65.7 (N-CH$_2$-Py).

IR (MeCN): $\nu$(C≡O)=1749 cm$^{-1}$.

3.5 Acknowledgements

We thank Jan Meine Ernsting for his assistance with the low temperature NMR experiments. Jan Smits and Maxime Siegler are acknowledged for the X-ray structure determination of complexes 2 and 5 respectively. Ferry van Nisselroij and Caroline Schouten are acknowledged for the synthesis and characterization of compounds 6-14. Charlotte Creusen is acknowledged for the initial studies on complex 15.

3.6 Notes and References


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14  Due to the low yield of $5^+$ and $7^+$ it was not possible to distinguish between their NMR signals that were generally overlapping with the signals of $5^-$. For that reason the structure of $6^+$ with two CO ligands being trans to two picolyl donors and one trans to two amine donors is tentative and it cannot be ruled out that the actual structure is similar to the structure of $2^+$ with one CO trans to two picolyl groups and two CO trans to one amine and one picolyl moiety.

15  We use the term chelate cooperativity (as defined by Hunter and Anderson) exchangeably with the multivalency definition by Mulder, Huskens and Reinhoudt. Essentially, both the chelate cooperativity and multivalency describe the same effect of increased local concentration and entropic contributions associated with binding of the tethered receptor to the binding site (a) Mulder, A.; Huskens, J.; Reinhoudt, D. N. Org. Biomol. Chem. 2004, 2, 3409-3424. (b) Hunter, C. A.; Anderson, H. L. Angew. Chem. Int. Ed. 2009, 48, 7488-7499.

16  The X-ray structure of the $\left[Rh_2(\eta^2-bpn)(\eta^4-cod)\right](PF_6)_2$ has shown such connectivity, however very large disorder made the structure unsuitable for publication.

17  (a) see Chapter 2 of this thesis. (b) Dzik, W. I.; Smits, J. M. M.; Reek, J. N. H.; de Bruin, B. Organometallics 2009, 28, 1631-1643.

18  Unfortunately, we were not able to record spectra below 218K because of the NMR spectrometer restrictions.


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28 Sheldrick, G. M. SADABS; University of Göttingen: Germany, 1996.
33 PQS version 2.4, 2001, Parallel Quantum Solutions, Fayetteville, Arkansas (USA); the Baker optimizer is available separately from PQS upon request; Baker, J. J. Comput. Chem. 1986, 7, 385-395.