Synthesis and characterization of bis- and tris-carbonyl Mn(I) and Re(I) PNP pincer complexes

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Abstract
A series of neutral bis- and cationic tris-carbonyl complexes of the types cis-[M(κ3 P,N,P-PNP)(CO)2Y] and [M(κ3 P,N,P-PNP)(CO)3]+ was prepared by reacting [M(CO)5Y] (M = Mn, Re; Y = Cl or Br) with PNP pincer ligands derived from the 2,6-diaminopyridine, 2,6-dihydroxy pyridine, and 2,6-lutidine scaffolds. With the most bulky ligand PNP NH-tBu, the cationic square-pyramidal 16e bis-carbonyl complex [Mn(PNP NH-tBu)(CO)2]+ was obtained. In contrast, in the case of rhenium, the 18e complex [Re(PNP NH-tBu)(CO)3]+ was formed. The dissociation of CO was studied by means of DFT calculation revealing in agreement with experimental findings that CO release from [M(κ3 P,N,P-PNP)(CO)3]+ is in general endergonic, while for [Mn(κ3 P,N,P-PNP NH-tBu)(CO)3]+, this process is thermodynamically favored. X-ray structures of representative complexes are provided.

Graphical abstract

Keyword Manganese · Rhenium · Pincer complexes · Carbonyl ligands · DFT calculations

Introduction
In recent years, manganese pincer complexes, where the metal centers adopt a formal oxidation state of +I, have received considerable importance in the field of homogeneous catalysis [1–6]. In comparison to manganese, rhenium pincer complexes remained comparatively unexplored until very recently but are becoming increasingly important as catalysts for hydrogenation/dehydrogenation reactions [7–10]. The most common ligand architecture is a PNP pincer system featuring an aromatic pyridine backbone with phosphine donors in the two ortho positions linked via CH2, O, NH, or NMe moieties. In particular, Mn(I) halo and hydride complexes of the type cis-[Mn(PNP)(CO)2Y] (Y = Cl, Br, H) as shown in Scheme 1 were found to be highly active catalysts in hydrogenation...
reactions of carbonyl compounds, including CO₂, as well as nitriles to yield alcohols, formate, and amines, respectively. Moreover, these types of complexes turned out to be also very active catalysts for the opposite process, i.e., dehydrogenation reactions of alcohols to obtain carbonyl compounds. These reactive intermediates are utilized for follow-up reactions such as condensation reactions in the presence of amines to yield functionalized amines, imines, or heterocycles such as pyridines, quinolines, or pyrroles [11, 12].

In the present work, we report on the synthesis and reactivity of a series of carbonyl Mn(I) and Re(I) PNP pincer complexes of the types cis-[M(κ₃P,N,P-PNP)(CO)₂Y] (Y = Cl or Br), [M(κ₃P,N,P-PNP)(CO)₃]⁺, and [M(κ₃P,N,P-PNP)(CO)₂]⁺ derived from the 2,6-diaminopyridine, 2,6-dihydroxypyridine, and 2,6-lutidine scaffolds.

**Results and discussion**

Treatment of the PNP ligands 1a–1d with the carbonyl precursors [Mn(CO)₅Br] in dioxane afforded complexes of the types cis-[Mn(κ₃P,N,P-PNP)(CO)₂Br] (2a–2d) and [Mn(κ₃P,N,P-PNP)(CO)₃]⁺ (3a–3d) (with Br⁻ as counterion 3aBr⁻–3dBr⁻) in high yields. The outcome of the reaction depends strongly on the reaction temperature (80 °C or 120 °C) and the reaction time (2–18 h) as well as on the nature of the ligand system itself (Scheme 2). At higher temperatures and longer reaction times, the formation of neutral bis-carbonyl complexes is favored, whereas at lower temperatures and shorter reaction times, the formation of cationic tricarbonyl species is preferred. Surprisingly, a triscarbonyl complex was not obtained with PNP ligand 1c. It has to be noted that the synthesis of cis-[Mn(PNPNH-iPr)(CO)₂Br] (2a) [13], cis-[Mn(PNPCH₂-iPr)(CO)₂Br] (2d) [14], and [Mn(PNPNH-iPr)(CO)₃]⁺ (3a) [13, 15] was already described in the literature. These authors, however, reported that with ligand 1a, they could only obtain an inseparable mixture of 2a and 3a [13]. All cationic complexes feature bromide as counterion which can be readily exchanged by other anions, if the bromide complexes are reacted with Ag⁺ salts. This was exemplarily shown for 3a and 3e, which upon treatment with AgOTf and AgBF₄, respectively, yielded complexes 3aOTf and 3eBF₄.
Likewise, ligands 1a–1e reacted with [Re(CO)₅Y] (Y = Cl or Br) to afford the rhenium(I) complexes cis-[Re(x³-P,N,P-PNP)(CO)₂Y] (4a, 4c) and [Re(x³-P,N,P-PNP)(CO)₅]⁺ (5a–5e) in high yields (Scheme 2). The synthesis of complex cis-[Re(PNPCH₂-i-Pr)(CO)₂Cl] (4a) was already described previously [16].

All neutral bis-carbonyl and cationic tricarbonyl complexes, respectively, are orange and off-white air-stable compounds. Selected NMR and IR spectroscopic data are provided in Table 1. In the IR spectrum, complexes 2 and 4 exhibit the two carbonyl stretching frequencies typical for a cis-CO arrangement. Complexes 3 and 5 give rise to two or three strong absorption bands typical of a mer CO arrangement. In ¹³C{¹H} NMR, the two or three CO ligands give rise to low field triplets in the range of 238–196 ppm. Due to the quadrupole moment of ⁵⁵Mn (I = ⁵/₂), the resonances of the manganese compounds are not always fully resolved giving rise to rather broad signals. Also, in ³¹P{¹H} NMR spectra, broad singlets are observed.

In the case of the most bulky PNP ligand 1e, with [Mn(CO)₃Br] the cationic 16e bis-carbonyl complex [Mn(PNP-i-Pr)(CO)₂]⁺ (3e) was obtained in 95% isolated yield as dark-violet solid (Scheme 2). This is in strong contrast to rhenium, where the 18e complex [Re(PNP-i-Pr)(CO)₃]⁺ (5e) was formed. It is interesting to note that also with the analogous 2,6-lutidine-based PNP ligand the cationic 18e complex [Mn(PNPCH₂-i-Pr)(CO)₃]⁺, rather than an unsaturated complex was formed instead [14]. The bromide counterion of 3eBr could be readily replaced by BF₄⁻ upon reaction of 3eBr with AgBF₄ affording 3eBF₄. Despite of being coordinatively unsaturated, these complexes are diamagnetic. Coordinatively unsaturated Mn(I) pincer complexes are not uncommon. In fact, several iso-electronic manganese PNP complexes were reported from the groups of Ozereov, Nocera, Boncella, Milstein, Liu, and Jones as shown in Scheme 3 [17–22].

In addition to the spectroscopic characterization of all complexes, the molecular structures of complexes [Mn(PNP²-Pr)(CO)₃]OTf (3aOTf), [Mn(PNPCH₂-i-Pr)(CO)₃]Br·CH₂Cl₂ (3dBr·CH₂Cl₂), [Mn(PNPNH-i-Pr)(CO)₂]BF₄ (3eBF₄), [Re(PNP²-Pr)(CO)₃]Br-acetone (5bBr-acetone) and [Re(PNPNH-i-Pr)(CO)₃]Br·acetone were determined by X-ray crystallography. Structural views are depicted in Figs. 1, 2, 3, 4, 5 with selected bond distances and angles given in the captions. Complexes 3aOTf, 3dBr, 5bBr, and 5eBr adopt a distorted octahedral geometry around the metal center. The PNP ligand is coordinated to the iron center in a typical tridentate meridional mode, with P-M-P angles between 154.1° and 164.8°. The C(CO)–M–C(CO) angles vary between 165.1 and 175.6°. The coordination geometry of Complex 3eBF₄ is a square pyramid with N(1), P(1), P(2), and C(23) defining the basal plane and C(22) defining the apex.

In the presence of a strong base such as NaH, [Mn(PNP²-Pr)(CO)₂]⁺ (3e) was readily deprotonated to afford the neutral 16e complex [Mn(PNP-i-Pr)(CO)₂] (6) in 95% isolated yield (Scheme 4). In the ³¹P{¹H} NMR spectrum, the now inequivalent phosphorus atoms of this complex exhibit a characteristic AB pattern with signals at 145.7 and 142.2 ppm (ţPP = 84.5 Hz). The carbonyl stretches (νCO = 1913, 1838 cm⁻¹) are indicative of an increased back-bonding effect relative to the cationic bis-carbonyl complex 3e (νCO = 1936, 1865 cm⁻¹). Recently, Sortais et al. [23] described the deprotonation of complex 2a to yield [Mn(PNPNH-i-Pr)(CO)₃].

The dissociation of one CO ligand from [M(PNP)- (CO)₃]⁺ (M = Mn, Re) was investigated by means of DFT/B3LYP calculations. The free energies ΔG° (in kJ/mol) for

### Table 1: Selected ¹³C{¹H} and ³¹P{¹H} NMR and IR data of complexes 2–6

| Complexes | δC/ppm | δP/ppm | νCO/cm⁻¹ |
|-----------|--------|--------|----------|
| [Mn(PNP²-Pr)(CO)₃]Br (2a) | 229.6 | 222.6 | 155.6 |
| [Mn(PNP²-Pr)(CO)₂]Br (2b) | 228.6 | 224.3 | 232.2 |
| [Mn(PNPCH₂-i-Pr)(CO)₂]Br (2d) | 85.8 | 80.9 | 1909 |
| [Mn(PNP²-Pr)(CO)₃]⁺ (3aBr) | 212.1 | 215.4 | 1943 |
| [Mn(PNP²-Pr)(CO)₂]Br (2c) | 220.3 | 215.4 | 2043 |
| [Mn(PNPCH₂-i-Pr)(CO)₂]⁺ (3bBr) | 216.9 | 207.4 | 2043 |
| [Mn(PNP²-Pr)(CO)₂]Br (2e) | 234.9 | 208.9 | 1910 |
| [Mn(PNPCH₂-i-Pr)(CO)₂]⁺ (3cBr) | 238.2 | 197.2 | 1913 |
| [Mn(PNP²-Pr)(CO)₃]⁺ (3dBr) | 208.9 | 197.2 | 1900 |
| [Mn(PNP²-Pr)(CO)₂]Br (2f) | 196.0 | 196.0 | 1928 |
| [Mn(PNPCH₂-i-Pr)(CO)₂]⁺ (3fBr) | 194.6 | 194.6 | 2045 |
| [Mn(PNP²-Pr)(CO)₂]Br (2g) | 203.6 | 193.9 | 1936 |
| [Mn(PNPCH₂-i-Pr)(CO)₂]⁺ (3gBr) | 233.1 | 224.0 | 1910 |

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**Synthesis and characterization of bis- and tris-carbonyl Mn(I) and Re(I) PNP pincer complexes**
the formation of the coordinatively unsaturated complexes 
[M(PNP)(CO)₂]⁺ are depicted in Scheme 5. In agreement
with experimental findings, the dissociation of CO is in
general endergonic ranging from 33.5 to 113.4 kJ/mol. In
the case of [Mn(κ₃P,N,P-PNP)(CO)₃]+ (3e), this process is
thermodynamically favored by −25.5 kJ/mol. This may be
attributed to the bulkiness of the PNP₃NH⁻Bu ligand, together
with the fact that the Mn–C CO bonds are weaker than the
Re–C CO bonds [24].

**Conclusion**

In sum, we have prepared a series of coordinatively satu-
rated neutral bis- and cationic tris-carbonyl complexes of the
types cis-[M(κ²P,N,P-PNP)(CO)₂]Y and [M(κ³P,N,P-PNP)-
(CO)₃]⁺ by reагing [M(CO)₅]Y (M = Mn, Re; Y = Cl or Br)
with PNP pincer ligands derived from the 2,6-diaminopyri-
dine, 2,6-dihydroxypyridine, and 2,6-lutidine scaffolds. In
the case of the most bulky ligand PNP₃NH⁻tBu, the cationic
square-pyramidal 16e bis-carbonyl complex [Mn(PNP$_{NH-tBu}$)(CO)$_2$]$^+$ was obtained, which in strong contrast to rhenium, where the 18e complex [Re(PNP$_{NH-tBu}$)(CO)$_3$]$^+$ was formed. The dissociation of CO from [M(κ$_3$P,N,P-PNP)(CO)$_3$]$^+$ is typically endergonic ranging from 33.5 to 113.4 kJ/mol. The only exception is [Mn(κ$_3$P,N,P-PNP$_{HH-tBu}$)(CO)$_3$]$^+$, where CO dissociation is thermodynamically favorable by −25.5 kJ/mol as established by DFT/B3LYP calculations. This may be attributed to the bulkiness of the PNP$_{NH-tBu}$ ligand, but also due to the fact that Mn–C CO bonds are generally weaker than Re–C CO bonds. Several complexes were also characterized by single crystal X-ray diffraction studies.

Experimental

All manipulations were performed under an inert atmosphere of argon by Schlenk techniques or in an MBraun inert-gas glovebox. Hydrogen (99.999% purity) was purchased
from Messer Austria and used as received. The solvents were purified according to standard procedures [25]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. The pincer ligands PNPNH-Pr (1a) [26], PNP′NMe-Pr (1b) [27], PNP0-Pr (1e) [28], PNPO-Pr (1d) [29], and PNPNH-PrBu (1e) [26] were prepared according to the literature. 1H, 13C{1H}, 19F{1H}, and 31P{1H} NMR spectra were recorded on Bruker AVANCE-250, 400, and AVANCE-600 spectrometers. 1H and 13C{1H} NMR spectra were referenced internally to residual protio-solvent and solvent resonances, respectively, and are reported relative to tetramethylsilane (δ = 0 ppm). 31P{1H} NMR spectra were referenced externally to H3PO4 (85%) (δ = 0).

cis-[Bromo[N2,N6-bis(diisoproplyphosphanyl)-N2,N6-dimethylpyridine-2,6-diamine](dicarbonyl)manganese(I)], cis-[Mn(PNP′NMe-Pr)(CO)2]Br (2b, C19H31BrMnN3O2P2) A solution of 185 mg PNP′NMe-Pr (1b, 0.50 mmol) and 137 mg [Mn(CO)3]Br (0.50 mmol) in 15 cm3 dioxane was stirred in a closed vessel at 120 °C for 18 h. The solvent was then removed under reduced pressure and the solid washed with 20 cm3 n-pentane. The yellow powder was dried under vacuum. Yield: 250 mg (89%); 1H NMR (600 MHz, acetone-d6, 20 °C): δ = 7.57 (t, JHH = 8.0 Hz, 1H, py4), 6.28 (d, JHH = 8.1 Hz, 2H, py5,6), 3.32 (s, 6H, NCH3), 3.09 (dt, J = 14.0, 7.2 Hz, 2H, CH), 2.98 (dt, J = 13.2, 6.8 Hz, 2H, CH), 1.65 (dd, J = 14.9, 7.1 Hz, 6H, CH3), 1.54 (dd, J = 14.7, 7.3 Hz, 6H, CH3), 1.49 (dd, J = 16.9, 7.1 Hz, 6H, CH3), 1.22 (dd, J = 13.3, 7.0 Hz, 6H, CH3) ppm; 13C{1H} NMR (151 MHz, acetone-d6, 20 °C): δ = 229.6 (CO), 222.9 (CO), 162.7 (vt, JCP = 10.4 Hz, py2,6), 139.3 (s, py6), 97.6 (vt, JCP = 3.1 Hz, py2,6), 35.3 (vt, JCP = 2.6 Hz, NCH3), 33.7 (vt, JCP = 8.9 Hz, CH), 30.2 (vt, JCP = 11.1 Hz, CH), 21.9 (CH3), 19.5 (CH3), 17.9 (CH3), 17.7 (vt, JCP = 5.4 Hz, CH3) ppm; 31P{1H} NMR (101 MHz, acetone-d6, 20 °C): δ = 155.6 ppm; IR (ATR): ν = 1929 (νCO), 1853 (νCO) cm⁻1.

cis-[Bromo[2,6-bis(diisoproplyphosphanyl)oxy]pyridine](dicarbonyl)manganese(I)], cis-[Mn(PNP0-Pr)(CO)2]Br (2c, C19H33BrMnNO4P2) A solution of 137 mg PNP0-Pr (1c, 0.40 mmol) and 110 mg [Mn(CO)3]Br (0.40 mmol) in 10 cm3 dioxane was stirred for 2 h at 80 °C. The solvent was removed under reduced pressure and the solid washed with n-pentane (3 × 15 cm3). The yellow powder was then dried under vacuum. Yield: 197 mg (92%); 1H NMR (250 MHz, acetone-d6, 20 °C): δ = 7.84 (t, JHH = 8.1 Hz, 1H, py4), 6.86 (d, JHH = 8.1 Hz, 2H, py5,6), 3.61 (m, 2H, CH), 3.03 (m, 4H, CH2), 1.56–1.20 (m, 24H, CH3) ppm; 13C{1H} NMR (151 MHz, acetone-d6, 20 °C): δ = 228.6 (CO), 224.3 (CO), 163.5 (vt, JCP = 5.6 Hz, py2,6), 142.9 (py5,6), 108.8 (vt, JCP = 2.6 Hz, CH2), 142.9 (py4, s, py6), 97.6 (s, CH3), 33.7 (vt, JCP = 8.9 Hz, CH), 30.2 (vt, JCP = 11.1 Hz, CH), 21.9 (CH3), 19.5 (CH3), 17.9 (CH3), 17.7 (vt, JCP = 5.4 Hz, CH3) ppm; 31P{1H} NMR (101 MHz, acetone-d6, 20 °C): δ = 155.6 ppm; IR (ATR): ν = 1943 (νCO), 1875 (νCO) cm⁻1.

 cis-[Bromo[N2,N6-bis(diisoproplyphosphanyl)pyridine-2,6-diamine](tricarbonylmanganese)] trifluoroacetone, [Mn(PNP′NMe-Pr)(CO)3]OTf (3aOTf, C19H33F3MnN3O9P3S) To a solution of 170 mg PNP′NMe-Pr (1a, 0.50 mmol) and 137 mg [Mn(CO)3]Br (0.50 mmol) in 15 cm3 dioxane 129 mg AgOTf (0.55 mmol) was added and the mixture was stirred at 80 °C for 4 h. Insoluble materials were removed by filtration and the solvent was then removed under reduced pressure. The solid was washed with 15 cm3 Et2O and 15 cm3 n-pentane and dried under reduced pressure. Crystals suitable for X-ray diffraction were grown by slow diffusion of n-pentane into an acetone solution of 3aOTf. Yield: 250 mg (89%); 1H
NMR (400 MHz, acetone-$d_6$, 20 °C): $\delta = 8.28$ (m, 2H, NH), 7.50 (t, $J_{HH} = 8.0$ Hz, 1H, py$^4$), 6.65 (d, $J_{HH} = 8.0$ Hz, 2H, py$^5$), 2.93 (m, 4H, CH), 1.53 (dd, $J_1 = 16.3$, 7.0 Hz, 12H, CH$_2$), 1.43 (dd, $J = 17.1$, 7.3 Hz, 12H, CH$_4$); $^{13}$C$^1$[H] NMR (151 MHz, acetone-$d_6$, 20 °C): $\delta = 221.0$ (CO), 215.4 (CO), 161.0 (vt, $J_{CP} = 7.4$ Hz, py$^2$, 2$^2$), 141.0 (py$^3$), 99.8 (vt, $J_{CP} = 3.3$ Hz, py$^3$), 30.9 (m, CH), 17.59 (CH$_3$), 17.58 (CH$_3$); $^{31}$P$^1$[H] NMR (101 MHz, acetone-$d_6$, 20 °C): $\delta = 134.4$ ppm; IR (ATR): $\nu = 2043$ (CO), 1941 (CO), 1927 (CO) cm$^{-1}$.

$[N^2,N^6$-Bis(diisopropylphosphanyl)-$N^2,N^6$-dimethylpyridine-2,6-diamine](tricarbonyl)manganese(I) bromide, [Mn(PNP$^\text{NMe}_2$-Pr)($CO$)$_2$Br (3eBr, $C_{19}$H$_{30}$ClNO$_4$P$^2$Re)] This complex was prepared analogously to 2c with 200 mg PNP$^\text{NMe}_2$-Pr (1e, 0.50 mmol) and 137 mg [Mn(CO)$_2$Br] (0.50 mmol) as starting materials. Yield: 228 mg (92%); $^1$H NMR (250 MHz, DMSO-$d_6$, 20 °C): $\delta = 9.14$ (m, 2H, NH), 7.74 (m, 1H, py$^4$), 6.63 (d, $J_{HH} = 8.9$ Hz, 2H, py$^5$), 1.36 (m, 36H, CH$_3$) ppm; $^{13}$C$^1$[H] NMR (151 MHz, DMSO-$d_6$, 20 °C): $\delta = 235.6$ (vt, $J_{CP} = 17.8$ Hz, CO), 165.6 (vt, $J_{CP} = 8.6$ Hz, py$^2$, 2$^2$), 144.6 (py$^3$), 99.6 (m, py$^3$), 28.4 (CH$_2$), 26.7 (CH$_3$) ppm; $^{31}$P$^1$[H] NMR (101 MHz, DMSO-$d_6$, 20 °C): $\delta = 147.6$ ppm; IR (ATR): $\nu = 1936$ (CO), 1865 (CO) cm$^{-1}$.

$[N^2,N^6$-Bis(di-tert-butylphosphanyl)pyridine-2,6-diamine](dicarbonylmanganese(I)) tetrafluoroborate, [Mn(PNP$^\text{NMe}$-Bu($CO$)$_2$BF$_4$ (3eBr, $C_{19}$H$_{30}$ClNO$_4$P$^2$Re)] Solution of 200 mg PNP$^\text{NMe}$-Bu (1e, 0.50 mmol) and 137 mg [Mn($CO$)$_2$Br] (0.50 mmol) in 15 cm$^3$ dioxane was stirred at 80 °C for 4 h. A dark-violet solid was formed which was filtered on a glass frit, washed with 15 cm$^3$ Et$_2$O and dried under vacuum. To a solution of this violet powder in 10 cm$^3$ acetone, 98 mg AgBF$_4$ (0.5 mmol) was added and the mixture was stirred for 1 h. The precipitate was removed by filtration over Celite and the solvent was then removed under reduced pressure. The solid was washed with 15 cm$^3$ Et$_2$O and 15 cm$^3$ n-pentane and finally dried under vacuum. Crystals suitable for X-ray diffraction were grown by slow diffusion of n-pentane into an acetone/EtOH (1:1) solution of 3eBF$_4$. Yield: 245 mg (82%); $^1$H NMR (250 MHz, acetone-$d_6$, 20 °C): $\delta = 8.49$ (m, 2H, NH), 7.75 (t, 1H, $J_{HH} = 8.0$ Hz, py$^4$), 6.80 (d, $J_{HH} = 8.0$ Hz, 2H, py$^5$), 1.36 (m, 36H, CH$_3$) ppm; $^{13}$C$^1$[H] NMR (151 MHz, acetone-$d_6$, 20 °C): $\delta = 234.9$ (vt, $J_{CP} = 17.2$ Hz, CO), 165.2 (vt, $J_{CP} = 8.3$ Hz, py$^2$, 2$^2$), 144.4 (py$^3$), 99.8 (vt, $J_{CP} = 3.2$ Hz, py$^3$), 39.7 (vt, $J_{CP} = 8.6$ Hz, C$_3$), 27.7 (vt, $J_{CP} = 2.0$ Hz, CH$_3$) ppm; $^{31}$P$^1$[H] NMR (101 MHz, acetone-$d_6$, 20 °C): $\delta = 148.6$ (s, 2P), 22 cm$^3$ n-pentane and finally dried under vacuum. The solution was washed with 10 cm$^3$ Et$_2$O and 20 cm$^3$ n-pentane and dried under vacuum. Yield: 228 mg (92%); $^1$H NMR (600 MHz, acetone-$d_6$, 20 °C): $\delta = 7.76$ (t, $J_{HH} = 8.1$ Hz, 1H, py$^4$), 6.80 (d, $J_{HH} = 8.1$ Hz, 2H, py$^5$), 3.59 (m, 2H, CH$_2$), 2.89 (m, 2H, CH$_2$), 1.29 (dd, $J = 12.9$, 7.0 Hz, 6H, CH$_3$), 1.23 (m, 12H, CH$_3$), 1.09 (dd, $J = 15.1$, 7.2 Hz, 6H, CH$_3$) ppm; $^{13}$C$^1$[H] NMR (151 MHz, acetone-$d_6$, 20 °C): $\delta = 203.6$ (CO), 193.9 (CO), 163.2 (vt, $J_{CP} = 3.7$ Hz, py$^2$, 2$^2$), 143.4 (py$^3$), 102.8 (vt, $J_{CP} = 1.9$ Hz, py$^3$), 27.9 (vt, $J_{CP} = 12.0$ Hz, CH), 17.6 (vt, $J_{CP} = 5.3$ Hz, CH), 17.1 (vt, $J_{CP} = 4.6$ Hz, CH$_2$), 16.7 (CH$_2$), 15.0 (CH$_3$) ppm; $^{31}$P$^1$[H]
[\text{[N}^2,\text{N}^6\text{-Bis(diisoproplyphosphanyl)pyridine-2,6-diamine-}
\text{(tricarbonyl)rhenum(I)] bromide, [Re(PNP\text{H}^+\text{-iPr})\text{(CO)}_3]\text{Br}
\text{(5aBr, C}_9\text{H}_3\text{BrN}_3\text{O}_3\text{P}_2\text{Re)]}]

A solution of 206 mg PNP-iPr (1a, 0.6 mmol) and 244 mg [Re(CO)_5Br] (0.6 mmol) in 10 cm³ dioxane was stirred for 2 h at 80 °C. The solvent was then removed under reduced pressure and the solid was washed with n-pentane (3×15 cm³). The colorless powder was then dried under vacuum. Yield: 394 mg (95%); 1H NMR (250 MHz, DMSO-d_6, 20 °C): δ = 9.21 (m, 2H, NH), 7.54 (t, J_HH = 8.0 Hz, 1H, py^3), 6.46 (d, J_HH = 8.1 Hz, 2H, py^3), 2.68 (m, 4H, CH), 1.35 (dd, J = 17.2, 6.9 Hz, 12H, CH_3), 1.21 (dd, J = 17.6 Hz, 7.3 Hz, 12H, CH_3) ppm; 13C{1H} NMR (63 MHz, DMSO-d_6, 20 °C): δ = 19.8 Hz, 6.9 Hz, 12H, CH_3) ppm; 31P{1H} NMR (101 MHz, DMSO-d_6, 20 °C): δ = 93.8 ppm; IR (ATR): ν = 2045 (υ_CO), 1926 (υ_CO) cm⁻¹.

[\text{[N}^2,\text{N}^6\text{-Bis(diisoproplyphosphanyl)pyridine-2,6-diamine-}
\text{(tricarbonyl)rhenum(I)] bromide, [Re(PNP\text{H}^+\text{-iPr})\text{(CO)}_3]\text{Br}
\text{(5bBr, C}_9\text{H}_3\text{BrN}_3\text{O}_3\text{P}_2\text{Re)]}]

This complex was prepared analogously to 5aBr with 199 mg PNP-H-iBu (1e, 0.50 mmol) and 203 mg [Re(CO)_5Br] (0.50 mmol) as starting materials. Crystals suitable for X-ray diffraction were grown by slow diffusion of n-pentane into an acetone solution of 5eBr. Yield: 360 mg (96%); 1H NMR (250 MHz, DMSO-d_6, 20 °C): δ = 9.04 (m, 2H, NH), 7.58 (t, J_HH = 7.9 Hz, 1H, py^3), 6.63 (d, J_HH = 7.9 Hz, 2H, py^3), 1.42 (m, 36H, CH_3) ppm; 13C{1H} NMR (151 MHz, DMSO-d_6, 20 °C): δ = 197.2 (CO), 196.6 (t, J_CP = 8.5 Hz, CO), 162.8 (py^3), 142.4 (py^4), 100.1 (py^3), 42.0 (t, J_CP = 10.9 Hz, C_6), 29.6 (t, J_CP = 2.4 Hz, CH_3) ppm; 31P{1H} NMR (101 MHz, DMSO-d_6, 20 °C): δ = 116.0 (s, 2P) ppm; IR (ATR): ν = 2034 (υ_CO), 1925 (υ_CO), 1910 (υ_CO) cm⁻¹.

[\text{[N}^2,\text{N}^6\text{-Bis(diisoproplyphosphanyl)-N}^2,\text{N}^6\text{-dimethylpyridine-}
\text{2,6-diamine(tricarbonyl)rhenum(I)] bromide, [Re(PNP(PNP\text{Me}_2)\text{-iPr})\text{(CO)}_3]\text{Br}
\text{(5cBr, C}_9\text{H}_3\text{BrN}_3\text{O}_3\text{P}_2\text{Re)]}]

This complex was prepared analogously to 5aBr with 222 mg PNPMe_iPr (1b, 0.60 mmol) and 244 mg [Re(CO)_5Br] (0.60 mmol) as starting materials. Crystals suitable for X-ray diffraction were grown by slow diffusion of n-pentane in an acetone solution of 5bBr. Yield: 405 mg (94%); 1H NMR (600 MHz, acetone-d_6, 20 °C): δ = 7.90 (t, J_HH = 8.3 Hz, 1H, py^3), 6.65 (d, J_HH = 8.3 Hz, 2H, py^3), 3.39 (m, 6H, NCH_3), 2.94 (m, 4H, CH), 1.46 (dd, J = 19.8 Hz, 6.9 Hz, 12H, CH_3), 1.22 (d, J = 19.8 Hz, 6.9 Hz, 12H, CH_3) ppm; 13C{1H} NMR (151 MHz, acetone-d_6, 20 °C): δ = 194.6 (CO), 190.8 (t, J_CP = 9.3 Hz, CO), 163.1 (t, J_CP = 7.2 Hz, py^3), 142.0 (s, py^3), 102.0 (t, J_CP = 2.6 Hz, py^3), 35.4 (NCH_3), 32.25 (vt, J_CP = 15.2 Hz, CH_2), 19.2 (vt, J_CP = 4.6 Hz, CH_3), 17.9 (CH_3) ppm; 31P{1H} NMR (101 MHz, acetone-d_6, 20 °C): δ = 120.9 ppm; IR (ATR): ν = 2045 (υ_CO), 1925 (υ_CO) cm⁻¹.

[\text{[N}(\text{di-tert-Butylphosphanyl})\text{-6-}[\text{(di-tert-butylphosphanyl})\text{-N}^2,\text{N}^6\text{-azanylidene}]
\text{(dicarbonyl)manganese(II)]},
\text{[Mn(PNP\text{H}^+\text{-Bu})\text{(CO)}_3]\text{Br} (5eBr, C}_9\text{H}_3\text{H}_6\text{Mn}_2\text{O}_3\text{P}_2\text{]}\]

To a suspension of 118 mg [Mn(PNP-H-iBu)(CO)_3]Br (5eBr, 0.20 mmol) in 15 cm³ THF, 11 mg NaH (0.46 mmol) was added. The suspension turned deep blue after 10 min and was stirred for an additional 2 h. Insoluble materials were removed by filtration over Celite. The solvent was then removed under reduced pressure. The crude product was redissolved in 20 cm³ n-pentane, filtered over Celite, and the solvent was removed under vacuum to afford 5eBr as blue solid. Yield: 96 mg (95%); 1H NMR (250 MHz, C_6D_6, 20 °C): δ = 6.91 (t, J_HH = 7.4 Hz, 1H, py^3), 6.79 (d, J_HH = 8.4 Hz, 1H, py^3), 5.13 (d, J_HH = 6.9 Hz, 1H, py^3), 4.27 (d, J_HH = 6.7 Hz, 1H, NH), 1.36 (d, J_HH = 13.0 Hz, 18H, CH_3), 0.94 (d, J_HH = 13.7 Hz, 18H, CH_3) ppm; 13C{1H} NMR (151 MHz, C_6D_6, 20 °C): δ = 238.2 (vt, J_CP = 16.2 Hz, CO), 174.6 (dd, J_CP = 8.4, 2.8 Hz, py^3), 162.0 (dd, J_CP = 12.7, 8.7 Hz, py^6), 139.6 (s, py^3), 108.6 (vd, J_CP = 20.9 Hz, py^3), 85.7 (vd, J_CP = 7.1 Hz, py^3), 118.1 (py^3), 39.4 (d, J_CP = 23.7 Hz, Cq), 38.2 (d, J_CP = 15.7 Hz, Cq), 28.5 (d, J_CP = 3.7 Hz, Cq), 27.9 (d, J_CP = 5.5 Hz, Cq) ppm; 31P{1H} NMR (101 MHz, C_6D_6, 20 °C): δ = 145.7 (A), 142.2 (B) (AB, J_CP = 84.5 Hz) ppm; IR (ATR): ν = 1913 (υ_CO), 1838 (υ_CO) cm⁻¹.

X-ray structure determination

X-ray diffraction data of [Mn(PNP\text{H}^+\text{-iPr})(CO)_3]Br·½acetone (5bBr·½acetone),
and [Re(PNP\textsubscript{NH-Bu})(CO)\textsubscript{3}]Br (5eBr) (CCDC numbers 1865227-1865231) were collected at \(T = 100\) K in a dry stream of nitrogen on a Bruker Kappa APEX II diffractometer system using graphite-monochromatized Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) and fine sliced \(q\)- and \(\omega\)-scans. Data were reduced to intensity values with SAIN'T and an absorption correction was applied with the multi-scan approach implemented in SADABS or TWINABS [30]. The structures were solved by the dual-space approach implemented in SHELXT [31] and refined against \(F^2\) with SHELXL [32]. Non-hydrogen atoms were refined anisotropically. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. The amine-Hs were located from difference Fourier maps and refined freely (3eBF\(_4\)) or restrained to a N–H distance of 0.87 Å (5eBr). The Mn atoms and CO ligands in 3eBF\(_4\) were refined as disordered about two positions. Contributions of disordered solvent molecules to the intensity data were removed for 5eBr using the SQUEEZE routine of the PLATON [33] software suite. Molecular graphics were generated with the program MERCURY [34].

Computational details

Calculations were performed using the GAUSSIAN 09 software package [35] with the B3LYP functional without symmetry constraints, the Stuttgart/Dresden ECP (SDD) basis set to describe the electrons of the manganese and rhodium atoms and a standard 6-31G** basis for all other atoms as already described previously [36].

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References

1. Gorgas N, Kirchner K (2018) Acc Chem Res 51:1558
2. Gorgas N, Kirchner K (2018) In: Morales-Morales D (ed) Pincer Compounds: Chemistry and Applications. Elsevier, Amsterdam
3. Garbe M, Junge K, Beller M (2017) Eur J Org Chem 129:4344
4. Maji B, Barman M (2017) Synthesis 49:3377
5. Kallmeier F, Kempe R (2018) Angew Chem Int Ed 57:46
6. Filonenko GA, van Putten R, Hensen EJM, Pidko EA (2018) Chem Soc Rev 47:1484
7. Wei D, Roisnel T, Darcel C, Clot E, Sortais JP (2017) Chem Cat Chem 9:80
8. Vogt M, Nerush A, Iron M, Leitus G, Diskin-Posner Y, Shimon LJW, Ben-David Y, Milstein D (2013) J Am Chem Soc 135:17004
9. Li H, Wei D, Bruenevo-Koine A, Ducamp M, Henrion M, Roisnel T, Dorcel V, Darcel C, Carpentier JF, Soule JF, Sortais JP (2018) Organometallics 37:1271
10. Pietl P, Peña-López M, Frey A, Neumann H, Beller M (2017) Chem Commun 53:3265
11. Mastalir M, Glatz M, Gorgas N, Stöger B, Pitenauer E, Allmaier G, Veiros LF, Kirchner K (2016) Chem Eur J 22:12316
12. Bertini F, Glatz M, Gorgas N, Stöger B, Peruzzi M, Veiros LF, Kirchner K, Gonsalvi L (2017) Chem Sci 8:5024
13. Tondreau AM, Boncella JM (2016) Polyhedron 116:96
14. Neumann J, Elangovan S, Spannenberg A, Junge K, Beller M (2017) Chem Eur J 23:5410
15. Bruenevo-Koine A, Wang D, Roisnel T, Darcel C, Sortais JP (2017) Catal Commun 92:1
16. Glatz M, Stöger B, Kirchner K (2017) Acta Cryst B 73:941
17. Radoseevich AT, Melnick JG, Stoian SA, Bacciu D, Chen CH, Foman BM, Ozorov OV, Nocera DG (2009) Inorg Chem 48:9214
18. Tondreau AM, Boncella JM (2016) Organometallics 35:2049
19. Mukherjee A, Nerush A, Leitus G, Shimon LJW, Ben-David Y, Jalapa NAE, Milstein D (2016) J Am Chem Soc 138:4298
20. Kulkarni NV, Breenessel WW, Jones WD (2018) ACS Catal 8:997
21. Fu S, Shao Z, Wang Y, Liu Q (2017) J Am Chem Soc 139:11941
22. Rao KR, Korobkov I, Gabidullin B, Richeson D (2018) Polyhedron 143:62
23. Bruenevo-Koine A, Wang D, Dorcel V, Roisnel T, Darcel C, Sortais JB (2017) J Catal 347:57
24. Simoes JAM, Beauchamp JL (1990) Chem Rev 90:629
25. Perrin DD, Armarego WLF (1988) Purification of laboratory chemicals, 3rd edn. Pergamon, New York
26. Benito-Garagorri D, Becker E, Wiedermann J, Lackner W, Polak M, Mereiter K, Kisala J, Kirchner K (2006) Organometallics 25:1900
27. Öztucu Ö, Holzhoacker C, Puchberger M, Weil M, Mereiter K, Veiros LF, Kirchner K (2013) Organometallics 32:3042
28. Salem H, Shimon LJW, Posner-Diskin Y, Leitus G, Ben-David Y, Milstein D (2009) Organometallics 28:4791
29. Leung WP, Ip QWY, Wong SY, Mak TCW (2003) Organometallics 22:4604
30. Bruker computer programs (2018) APEX2, SAINT, SADABS and TWINABS. Bruker AXS Inc., Madison
31. Sheldrick GM (2015) Acta Crystallogr A 71:3
32. Sheldrick GM (2015) Acta Crystallogr C 71:3
33. Acta Spek AL (2009) Crystallogr D 65:148
34. Acta Spek AL (2009) Crystallogr D 65:148
35. Macrae CF, Edginton PR, McCabe P, Pedcock E, Shields GP, Taylor R, Towler M, van de Streek J (2006) J Appl Cryst 39:453
36. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA Jr, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian 09, revision A.02. Gaussian Inc, Wallingford
37. Schröder-Holzhacker C, Gorgas N, Stöger B, Kirchner K (2016) Monatsh Chem 147:1023