Synthesis and characterization of unsaturated Manganese(I) and Rhenium(I) dicarbonyl complexes supported by an anionic PNP pincer

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Abstract
Syntheses of Re and Mn carbonyl complexes of the diarylamido/bis(phosphine) PNP pincer ligand are reported. The saturated (PNP)Re(CO)3 and (PNP)Mn(CO)3 react cleanly with HBr in acetic acid to undergo decarbonylation with concomitant addition of HBr across the N-M bond. The resultant (PNHP)MBr(CO)2 (M = Mn or Re) complexes can be dehydrobrominated with triethylamine to yield the unsaturated (PNP)M(CO)2. (PNP)Re(CO)2 has high affinity for CO and abstracts CO from (PNP)Mn(CO)3.

1. Introduction
Polycarbonyl complexes of group 7 metals Mn and Re have found utility in a number of reactions including C–H activation,[1] and electrocatalytic reduction of CO2 [2,3]. Carbonyl complexes of Mn and Re supported by anionic, nitrogen-centered, tridentate PNP pincer ligands have been studied in the context of catalysis of transfer (de)hydrogenation [4–9]. In the dehydrogenation chemistry, the active species is typically the unsaturated dicarbonyl complex (PNP)M(CO)2 with a central amido donor (M = Mn or Re), which is envisioned to accept a proton at the pincer and a hydride at the metal from a substrate such as alcohol (Scheme 1)[4–9] (see Scheme 2).

Synthetic access to such (PNP)M(CO)2 complexes has so far primarily relied on the reaction of the neutral (PNP)H proto-pincers [10] with XM(CO)5 (X = Cl or Br), isolation of the (PN(H)P)MX(CO)2 dicarbonyl intermediate, and subsequent dehydrohalogenation with a suitable base (Scheme 1) [4–8]. Isolation of (PN(H)P)MX(CO)2 is necessary, as dehydrohalogenation of it in situ would lead to the formation of the saturated tricarbonyl (PNP)M(CO)3. XM(CO)3 precursors are expensive relative to the other common precursors, such as M2(CO)10 or the carbonyl-free, inorganic Mn and Re derivatives.

Tricarbonyl (PNP)M(CO)3 compounds can be prepared via reactions of pincer-H with M2(CO)10 or by treatment with CO gas of various higher-oxidation state Re complexes ultimately accessible from perrenic acid [11]. However, removal [9] of CO from (PNP)M(CO)3 can be difficult because it binds to the electron-rich monovalent metal quite strongly, especially in the case of Re [12]. We hypothesized that CO may be lost if (PNP)M(CO)3 is treated with HX to give (PN(H)P)MX(CO)2, from which (PNP)M(CO)2 should be easily made via reaction with an appropriate base. Although a halide alone would not be expected to replace CO on an electron rich metal center, the presumed initial protonation of the pincer ligand would render the metal less electron-rich, and provide for an additional electrostatic effect favoring binding the halide. In the present work, we demonstrate the success of this approach with complexes of the diarylamido/bis(phosphine) ligand (MePNPiPr), wherein the previously reported [12] tricarbonyl complexes are converted into unsaturated dicarbonyl complexes. In addition, we show that (MePNPiPr)Re(CO)2 can be accessed without the initial use of polycarbonyl Re precursors.

2. Results and discussion
2.1. Synthesis of (MePNPiPr)M(CO)3 (M = Mn, Re)

(MePNPiPr)ReOBr2 was synthesized (Scheme 3-A) and isolated as a dark green, semi-crystalline powder in 88% yield via reaction of...
2.2. Hydrobrominative decarboxylation of (PNP)M(CO)3 (M = Mn, Re)

We previously reported that reaction of the strong acid HOTf with (MePNPiPr)M(CO)3 (M = Re, Mn) protonated the central nitrogen and furnished the ionic species, [(MePNPiPr)M(CO)3][OTf], in which the tricarbonyl motif was retained [12]. Protonation of the PNP nitrogen led to the increase of the average ν(CO) values by ca. 25-30 cm⁻¹ indicating significantly reduced back-donation to the carbonyl ligands. In light of this result, we surmised that addition of an acid with a more coordinating anion might result in a displacement of a carbonyl ligand. Treatment of toluene solutions of (MePNPiPr)M(CO)3 or (MePNPiPr)ReBr(CO)3 with a 30% HBr solution in acetic acid, and subjecting the resultant mixture to reflux conditions for 0.5–2 h resulted in a color change to yellow (Mn) or violet (Re) with concomitant formation of an unidentified orange precipitate which can be filtered off. After further workup, the decarboxylated products of HBr addition, (MePNPiPr)MnBr(CO)2 and (MePNPiPr)ReBr(CO)2, were obtained as yellow (Mn) and blue-green (Re) powders in high yield (Scheme 3-B). The 31P{1H} NMR spectra of (MePNPiPr)MnBr(CO)2 and (MePNPiPr)ReBr(CO)2 exhibited a single, broad resonance (Mn, δ 73.3; Re, δ 40.9 ppm). The 1H NMR spectra for (MePNPiPr)MnBr(CO)2 and (MePNPiPr)ReBr(CO)2 exhibited a resonance for the N-H proton (Mn, δ 7.20; Re, δ 7.21 ppm) and each featured isopropyl methyl resonances (24H total) diagnostic of C3-symmetry. Each showed two carbonyl C O stretches in their IR spectra (Mn, 1916 and 1836 cm⁻¹; Re, 1910 and 1830 cm⁻¹) with intensities in a ca. 1:1 ratio, supportive of a cis-dicarbonyl formulation.

2.3. Synthesis of unsaturated (MePNPiPr)M(CO)2 (M = Mn, Re)

(MePNPiPr)Mn(CO)2 was previously reported and spectroscopically characterized after loss of CO from (MePNPiPr)M(CO)3 under reflux. However, that procedure afforded only partial conversion to (MePNPiPr)Mn(CO)2 and it was not isolated as a pure material [12]. The thermal decarboxylative analogous chemistry with (MePNPiPr)Re(CO)3 was shown to remain entirely elusive.

Treatment of (MePNPiPr)MnBr(CO)2 or (MePNPiPr)ReBr(CO)2 with NET3 in toluene led to an immediate color change to blue (Mn) or red (Re) solutions with formation of a colorless precipitate (presumed to be [HNEt3][Br]). 31P{1H} NMR analysis indicated clean formation of (MePNPiPr)Mn(CO)2 (δ 83.7 ppm) and (MePNPiPr)Re(CO)2 (δ 63.9 ppm). (MePNPiPr)Mn(CO)2 and (MePNPiPr)Re(CO)2 were isolated as dark blue (Mn) and dark red (Re) powders in good to excellent yields (Scheme 3-B). (MePNPiPr)Mn(CO)2 and (MePNPiPr)Re(CO)2 exhibited C2v-symmetry in their 1H NMR spectra with two doublet of virtual triplet resonances for the isopropyl methyls (Mn, δ 1.27 and 1.07 ppm; Re, δ 1.23 and 0.98 ppm, 12H each), a single methine resonance (worth 4H), and three aromatic resonances (6H total). (MePNPiPr)Mn(CO)2 shows a triplet (JP = 19.6 Hz) carbonyl CO resonance in its 13C{1H} NMR spectrum at δ 239.5 ppm, and two rather low frequency CO stretches via IR spectroscopy at 1898 and 1824 cm⁻¹. The 13C{1H} NMR spectrum of (MePNPiPr)Re(CO)2 similarly reveals a triplet resonance (JP = 6.0 Hz) at δ 210.1 ppm, and two low frequency stretches in its IR spectrum at 1896 and 1820 cm⁻¹.

2.4. Structural study of (MePNPiPr)Re(CO)2

An X-ray diffraction study of a ruby-red, single crystal grown from CH2Cl2 and pentane confirmed the connectivity and revealed the C2v-symmetry of (MePNPiPr)Re(CO)2 in the solid state (Fig. 1). Similar to the previously reported structure of (MePNPiPr)Mn(CO)2 [12], (MePNPiPr)Re(CO)2 takes on a five-coordinate, Y-shaped...
geometry \( \tau = 0.33 \) in which the pincer PNP is bound meridionally \((P1-\text{Re1}-P2 = 158.65(7))\), and the two carbonyl ligands are of an expected cis-disposition to one another \((C1-\text{Re1}-C2 = 82.6(4))\). Notably, the Y-shaped geometry should allow for the optimization of amido \( \pi \)-donation into the Re \( \pi^* \)-orbital. This, in concert with the absence of CO or any other ligand directly trans to N, ostensibly contributes to the shortening of the Re1-N1 bond \( (2.078(6) \text{ Å}) \) versus that observed in the corresponding tri-carbonyl \((\text{MePNPiPr})\text{Re(CO)}_3 \) \( (2.191(4) \text{ Å}) \). The removal of one CO ligand also allows for a back-donation into the remaining CO \( \pi^* \) orbitals insofar as the Re-CO bonds \( (1.874(6) \text{ Å}) \) in \((\text{MePNPiPr})\text{Re(CO)}_2 \) are ca. 0.06 Å shorter than the shortest Re-CO bonds in the tricarbonyl \((\text{MePNPiPr})\text{Re(CO)}_3 \) \( (1.930(6) \text{ and } 1.972(5) \text{ Å}) \). 

2.5. Reactions of \((\text{MePNPiPr})\text{M(CO)}_2 \) (\( \text{M} = \text{Mn, Re} \))

Reaction of either \((\text{MePNPiPr})\text{Mn(CO)}_2 \) or \((\text{MePNPiPr})\text{Re(CO)}_2 \) with 1 atm of CO in \( C_6D_6 \) resulted in immediate formation of the tricarbonyl species, \((\text{MePNPiPr})\text{Mn(CO)}_3 \) and \((\text{MePNPiPr})\text{Re(CO)}_3 \), respectively. Showing that \((\text{MePNPiPr})\text{Re(CO)}_2 \) has a greater carbonyl affinity than \((\text{MePNPiPr})\text{Mn(CO)}_2 \), reaction of equimolar \((\text{MePNPiPr})\text{Mn(CO)}_3 \) with \((\text{MePNPiPr})\text{Re(CO)}_2 \) in \( C_6D_6 \) at room temperature for 1 h resulted in quantitative, clean conversion \((^{31}P\{^1H\text{NMR evidence}) \) to \((\text{MePNPiPr})\text{Mn(CO)}_2 \) and \((\text{MePNPiPr})\text{Re(CO)}_3 \) (Scheme 4). Thermolysis of this mixture at 80 \(^\circ\)C for 24 h did not result in any further observable changes. No further reactivity was observed between additional equivalents of \((\text{MePNPiPr})\text{Re(CO)}_2 \) and \((\text{MePNPiPr})\text{Mn(CO)}_2 \). On the other hand, \((\text{MePNPiPr})\text{Re(CO)}_2 \) did not react with benzaldehyde after 24 h at 100 \(^\circ\)C, showing that although \((\text{MePNPiPr})\text{Re(CO)}_2 \) possesses substantial thermodynamic affinity for binding CO, it is not capable of aldehyde decarbonylation [20–22].

3. Conclusions

The synthesis of \((\text{MePNPiPr})\text{Re(CO)}_3 \) via magnesium reduction of a Re(V)-oxo complex under a CO atmosphere has been disclosed. A new method of hydrobrominative decarbonylation has been reported allowing access to the six-coordinate Mn(I) and Re(I) complexes, \((\text{MePNPiPr})\text{MBr(CO)}_2 \). These complexes undergo facile dehydrohalogenation upon treatment with triethylamine to furnish the PNP-supported Mn and Re-dicarbonyls. A structural study of \((\text{MePNPiPr})\text{Re(CO)}_2 \) revealed a highly symmetric, five-coordinate, Y-shaped geometry with increased N-Re \( \pi \)-donation, as compared to \((\text{MePNPiPr})\text{Re(CO)}_3 \). Despite similar IR stretching frequencies, \((\text{MePNPiPr})\text{Re(CO)}_2 \) binds CO more strongly than \((\text{MePNPiPr})\text{Mn(CO)}_2 \), as might be expected for the 5d metal congener.

4. Experimental

4.1. General considerations

Unless otherwise stated, all experiments were carried out using
standard glovebox and Schlenk line techniques under a dry argon atmosphere. C6D6 was dried over NaK, benzophenone, and 18-crown-6, distilled, and stored over molecular sieves in an argon glovebox prior to usage. Diethyl ether, pentane, toluene, and tetrahydrofuran (THF) were dried and deoxygenated using a PureSolv MD-5 solvent purification system and were stored over molecular sieves in an argon-filled glovebox. All other deuterated solvents were degassed and stored over molecular sieves in an argon-filled glovebox. The [MePnP]Pr ligand [23] and ([PPh3]2ReOBr2(OEt)) [11] were synthesized using reported literature procedures. All other chemical reagents were purchased from commercial suppliers and were used as received. NMR spectra were recorded on a Varian iNova 500 (31P{1H} NMR, 125.670 MHz; 1H NMR, 499.678 MHz) spectrometer in given solvents. Chemical shifts are reported in ppm (δ). 31P{1H} NMR spectra were referenced externally to an 85% phosphoric acid standard at δ 0 ppm. 1H NMR spectra were internally referenced to residual solvent resonances.[24] In reporting spectral data, the following abbreviations were utilized: s = singlet; d = doublet; t = triplet; dd = doublet of doublets; v = virtual triplet; dvt = doublet of virtual triplets; m = multiplet; br = broad; br s = broad singlet; v = very broad. ATR-IR spectra were collected on an Agilent CARY 630 FT-IR spectrometer. Elemental analyses were performed by CALI, Inc. (Highland Park, NJ, USA).

4.2. Synthesis of ([MePnP]Pr)ReOBr2

This compound was synthesized using a modified literature procedure [8]. To a 50 mL Teflon tape culture tube equipped with magnetic stir bar was added ([PPh3]2ReOBr2(OEt)) (1.08 g, 1.16 mmol), [MePnP]Pr (525 mg, 1.22 mmol), and 15 mL toluene, forming a tan suspension which quickly turns dark violet. The violet suspension was then heated in an oil bath set to 100 °C for 2 h, over which time it became dark green and solids began to precipitate. The culture tube was cooled to room temperature, brought back into the glovebox, and 35 mL pentane was added, causing additional precipitation. The resultant mixture was then shaken briefly and placed in a freezer set to −38 °C for 1 h, allowing precipitation of the product. The solids were isolated on a fine frit, washed with pentane (2 × 5 mL) and dried in vacuo, to provide ([MePnP]Pr)ReOBr2 as a dark, microcrystalline powder. Yield: 805 mg (88%). 1H NMR (500 MHz, CDCl3): δ 7.74 (br, 2H, Ar CH), 7.15 (br m, 4H, Ar CH), 7.38 (br, 2H, 1′Pr methine), 3.39 (v br, 2H, 1′Pr methine), 2.51 (s, 6H, benzylic CH3), 1.54 (br, 18H, three overlapping 1′Pr CH3), 0.94 (br, 6H, 1′Pr CH3). 13C{1H} NMR (126 MHz, CDCl3): δ 165.5, 133.9, 131.2, 128.9, 128.2, 125.3, 28.2 (br, 2 overlapping benzylic CH4), 20.2 (br, overlapping CHMe2), 19.1 (br, 2 overlapping CHMe2), 18.4 (2 overlapping CHMe2). 31P{1H} NMR (202 MHz, CDCl3): δ 27.4 (d, Jp= 186 Hz), 21.9 (d, Jp= 186 Hz). IR: 940 (ν8=0) cm⁻¹ Elem Anal Found (calc): C: 39.19(39.50); H: 4.98(5.10).

4.3. Synthesis of ([MePnP]Pr)Re(CO)3

To a 200 mL Teflon stoppered Schlenk flask equipped with a magnetic stir bar was added ([MePnP]Pr)ReOBr2 (540 mg, 0.68 mmol), magnesium powder (332 mg, 13.7 mmol), and 10 mL THF, forming a dark green suspension. The resultant suspension was frozen, degassed, and allowed to thaw, prior to being refilled with 1 atm carbon monoxide. The vessel was then allowed to stir at room temperature for 24 h, over which time the solution became homogeneous and dark yellow. To this solution was added ca. 1 mL degassed H2O2, resulting in bubbling, and the precipitation of white solids. The resultant opaque, yellow solution was then filtered through silica and Celite on a fine frit, and solvent was removed in vacuo to provide the product as a bright yellow, free-flowing powder in >98% purity ([H NMR evidence). Yield: 459 mg (96%). Spectroscopic data matched that previously reported by Ozerov and Nocera et al. [12].

4.4. Synthesis of ([MePnP]Pr)ReBr(CO)2

In a 50 mL Schlenk flask equipped with a magnetic stir bar was added ([MePnP]Pr)ReOBBr2 (735 mg, 1.05 mmol) and 20 mL toluene, forming a yellow suspension. The flask was then placed under argon and a 30% HBr in AcOH (1.50 mL, 7.54 mmol HBr, not degassed) solution was added via syringe, resulting in a darkening of solution. The resultant mixture was then mixed with a reflux condenser and brought to reflux for 2 h under argon. Solvent was removed under reduced pressure, giving a light blue solid. The solid was extracted with 5 mL dichloromethane, filtered through a plug of Celite removing orange-brown solids, and then layered with 15 mL of pentane and stored at −37 °C for 12 h over which time additional orange-brown residue precipitated. The solvent was filtered cold through Celite, reduced under reduced pressure, washed with pentane and dried once more to provide the product as a blue-green solid. Yield: 585 mg (74%). 1H NMR (500 MHz, CDCl3): δ 7.39 (br, 2H, Ar CH), 7.21 (br 1H, N-H), 7.13 (br m, 4H, Ar CH), 2.97 (m, 2H, Pr methine), 2.89 (m, 2H, Pr methine), 2.42 (s, 6H, benzylic CH3), 1.47 (m, 18H, three 1′Pr CH3), 1.10 (dvt, J = 8.5, 7.1 Hz, 6H, 1′Pr CH3). 13C{1H} NMR (126 MHz, CDCl3): δ 206.1 (CO), 195.9 (CO), 148.5, 136.6, 135.9, 138.4, 130.6, 123.1, 27.4 (m), 26.3 (m), 21.8 (br), 21.0, 20.42, 20.38, 18.1. 31P{1H} NMR (202 MHz, CDCl3): δ 40.9 (br). ATR-IR: 3346(ν30-H), 1910(νCO), 1830(νCO) cm⁻¹. Elem Anal Found (calc): C: 44.41(44.74); H: 5.13(5.50).

4.5. Synthesis of ([MePnP]Pr)MnBr(CO)2

In a 25 mL Schlenk flask equipped with a magnetic stir bar was added ([MePnP]Pr)Mn(CO)3 (215 mg, 0.38 mmol) and 10 mL toluene, forming an orange suspension. The flask was fitted with a reflux condenser and brought to reflux. Upon achieving reflux a 30% HBr
in AcOH (300 µL, 1.50 mmol HBr) solution was added via syringe, resulting in an immediate color change to yellow as some dark solids were observed to form. Upon HBr addition, an observable increase in solution turbidity was noted, indicating evolution of gaseous CO. The solution was allowed to reflux an additional 30 min and then solvent was removed under reduced pressure to give a yellow residue. The residue was dissolved in CH2Cl2, filtered through Celite twice, and dried under reduced pressure to a yellow, oily solid. This was washed with pentane (2 x 3 mL) and dried again to provide the product as a bright yellow, free-flowing powder. Yield: 220 mg (94%). 1H NMR (500 MHz, CDCl3): δ 7.38 (br, 2H, Ar CH), 7.20 (s, 1H, N—H), 7.11 (m, 4H, Ar CH), 2.93 (m, 2H, ipr methine), 2.86 (m, 2H, ipr methylene), 2.40 (s, 6H, benzyl CH3), 1.49 (m, 18H, three ipr CH3), 1.20 (m, 6H, ipr CH3). 13C{1H} NMR (126 MHz, CDCl3): δ 135.9, 135.0, 132.3, 130.5, 122.7, 27.8 (m), 26.1 (m), 21.4, 21.2, 20.4, 19.7, 19.6. Resonances corresponding to the two CO ligands and remaining aromatic backbone signal could not be located, possibly due to overlap.

4.6. Synthesis of (MePNPiPr)Mn(CO)2

To a 20 mL scintillation vial equipped with a magnetic stir bar was added (MePNPiPr)MnBr(CO)2 (127 mg, 0.21 mmol) and CH2Cl2 (3 mL) and dried again with 1 atm of CO. Upon thawing of the solution and inverting the sample once, it immediately became a dull orange, and full, clean formation of (MePNPiPr)Mn(CO)2 was observed by 1H and 31P{1H} NMR spectroscopy [12].

4.11. Reaction of (MePNPiPr)Mn(CO)2 with CO

To a 20 mL scintillation vial equipped with a magnetic stir bar was added (MePNPiPr)MnBr(CO)2 (111 mg, 0.15 mmol) and 3 mL toluene, forming a yellow suspension. To this suspension was added triethylamine (34 µL, 0.22 mmol) causing an immediate color change to dark blue, with concomitant formation of solids (presumed to be HNEt3Br). The resultant suspension was allowed to stir for 10 min then filtered through a plug of Celite and silica, providing a homogeneous, dark blue solution. Volatiles were removed under reduced pressure and the dark blue residue was washed with pentane (3 x 2 mL) and dried again, giving the product as a dark blue, free-flowing powder. Yield: 85 mg (77%). 1H NMR (500 MHz, C6D6): δ 7.41 (d, J = 8.2 Hz, 2H, Ar CH), 6.89 (s, 2H, Ar CH), 6.72 (d, J = 8.2 Hz, 2H, Ar CH), 2.56 (m, 4H, ipr methine), 2.11 (s, 6H, benzyl CH3), 1.27 (d, J = 9.0, 7.0 Hz, 12H, ipr CH3). 13C{1H} NMR (126 MHz, C6D6): δ 239.5 (t, J = 19.6 Hz, two CO), 162.7 (t, J = 16.0 Hz), 132.1, 132.0, 122.2 (t, J = 14.5 Hz), 115.7 (m), 24.7 (br), 20.5, 18.3, 17.5. One of the expected aromatic resonances could not be identified, possibly due to overlap.

4.12. Reaction of (MePNPiPr)Mn(CO)2 with benzaldehyde

To a 20 mL scintillation vial equipped with a magnetic stir bar was added (MePNPiPr)Re(CO)2 (17.9 mg, 0.03 mmol) and C6D6, forming a red solution. The solution was then frozen, degassed, and refilled with 1 atm of CO. Upon thawing of the solution and inverting the sample once, it immediately became a scarlet red, and full, clean formation of (MePNPiPr)Re(CO)2 and (MePNPiPr)Mn(CO)2, indicating no reaction have occurred.

5. X-ray data collection, solution, and refinement for (MePNPiPr)Re(CO)2

A red, multi-faceted block of suitable size (0.26 x 0.24 x 0.09 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEX II CCD based diffractometer (Mo sealed X-ray tube, Kβ = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software [25]. An absorption correction was applied using SADABS [26]. The space group was determined on the basis of the observed absences and intensity

6. Reaction of (MePNPiPr)Re(CO)2 with (MePNPiPr)Mn(CO)3

To a J. Young tube was added (MePNPiPr)Re(CO)2 (10.5 mg, 0.016 mmol), (MePNPiPr)Mn(CO)3 (8.8 mg, 0.016 mmol), and C6D6. The resultant brown-orange suspension was placed on an NMR rotator for 1 h, over which time it became a dark green, homogeneous solution. Analysis by 1H and 31P{1H} NMR spectroscopy indicated full, clean conversion to (MePNPiPr)Re(CO)3 and (MePNPiPr)Mn(CO)2 in a 1:1 ratio.

7. Reaction of (MePNPiPr)Re(CO)2 with (MePNPiPr)Mn(CO)2

To a J. Young tube was added (MePNPiPr)Re(CO)2 (13.3 mg, 0.02 mmol), (MePNPiPr)Mn(CO)2 (10.7 mg, 0.02 mmol) and C6D6, forming a purple solution. This solution was heated at 80 °C and monitored spectroscopically. After 24 h, 31P{1H} and 1H NMR spectroscopy revealed a 1:1 ratio of (MePNPiPr)Re(CO)2 and (MePNPiPr)Mn(CO)2, indicating no reaction have occurred.

8. Reaction of (MePNPiPr)Re(CO)2 with (MePNPiPr)Mn(CO)3

To a J. Young tube was added (MePNPiPr)Re(CO)2 (17.9 mg, 0.03 mmol) and C6D6, forming a bright blue solution. The solution was then frozen, degassed, and refilled with 1 atm of CO. Upon thawing of the solution and inverting the sample once, it immediately became bright yellow, and full, clean formation of (MePNPiPr)Re(CO)3 was observed by 1H and 31P{1H} NMR spectroscopy [12].
statistics and the structure was solved by direct methods and refined by full-matrix least squares on $F^2$. The structure was solved in the orthorhombic Fdd2 space group using XS [27] (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on $F^2$) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program [28].

Acknowledgments

We are grateful for the support of this work by the Welch Foundation (grant A-1717 to O.V.O.) and the US National Science Foundation (NSF LSAMP Fellowship to A.J.K. via grant HRD-1406755).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.06.020.

References

[10] In Pyridine(bis(phosphine) Pincers, the Proton in the Neutral Ligand Is Not Located on the Central Nitrogen, but rather on an Atom (C or H) Connecting the Pyridine Ring to the Phosphine Donor.