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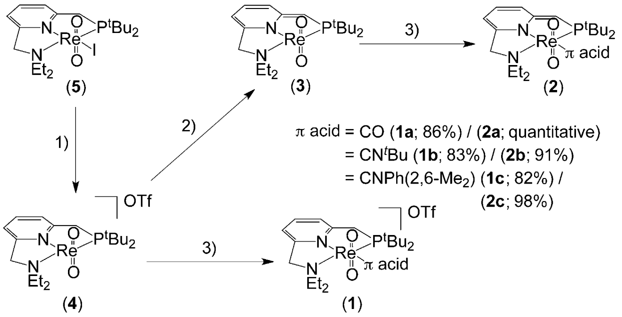
Concurrent Stabilization of π-Donor and π-Acceptor Ligands in Aromatized and Dearomatized Pincer [(PNN)Re(CO)(O)$_2$] Complexes**

*Michael G. Mazzotta, Kothanda Rama Pichaandi, Phillip E. Fanwick, and Mahdi M. Abu-Omar**

Abstract: *Aromatized cationic [(PNN)Re(π acid)(O)$_2$]$^+$ (**1**) and dearomatized neutral [(PNN*)Re(π acid)(O)$_2$] (**2**) complexes (where π acid = CO (**a**), tBuNC (**b**), or (2,6-Me$_2$)PhNC (**c**)), possessing both π-donor and π-acceptor ligands, have been synthesized and fully characterized. Reaction of [(PNN)Re(O)$_2$]$^+$ (**4**) with lithiumhexamethyldisilazide (LiHMDS) yield the dearomatized [(PNN*)Re(O)$_2$] (**3**). Complexes **1** and **2** are prepared from the reaction of **4** and **3**, respectively, with CO or isocyanides. Single-crystal X-ray structures of **1a** and **1b** show the expected trans-dioxo structure, in which the oxo ligands occupy the axial positions and the π-acidic ligand occupies the equatorial plane in an overall octahedral geometry about the rhenium(V) center. DFT studies revealed the stability of complexes **1** and **2** arises from a π-backbonding interaction between the d_{xy} orbital of rhenium, the π orbital of the oxo ligands, and the π* orbital of CO/isocyanide.*

Metal complexes with both π acids and π bases as ligands are fundamentally interesting because of the conflicting electronic requirements of the ligands. In this regard, CO, a π acid, and oxo, a strong π base, are heavily investigated.[1] These complexes are important for the green conversion of CO$_2$ into CO and the oxidation of CO by metal oxides. Mono-oxo carbonyl complexes of W^{IV} and Mo^{IV} reported by Mayer et al.[1d,f,h,i] and Young et al.[1a–c,e] as well as theoretical studies by Mingos and co-workers[1g] highlight the importance of these complexes. More recently, Donahue and co-workers demonstrated the utility of mono-oxo carbonyl tungsten complexes in a complete cycle of CO$_2$ reduction to CO and water.[2] However, complexes with multiple oxo and carbonyl ligands, such as [M(O)$_2$(CO)$_n$] ($n = 1$ or 2), have been isolated only in glass matrices from laser ablation of the reaction of CO$_2$ with metal oxides.[3] Almond et al.[4] and McMahon and Hop[5] studied these complexes in glass matrices by the photo-oxidation of metal carbonyl compounds in the presence of O$_2$. These complexes featuring opposing ligands may have interesting catalytic applications; however, the isolation of these multi-oxo carbonyl complexes has not been reported until now. Herein, we describe a series of rhenium(V) dioxo complexes possessing Milstein's PNN ligand system[6] (PNN = 6-(di-*tert*-butylphosphinomethylene)-2-(*N*,*N*-diethylamino-methyl)-1,6-dihydropyridine) in aromatized (**1**) and dearomatized form (**2**), and the π-acidic ligands CO and isocyanide (*t*BuNC and (2,6-Me$_2$)PhNC). These compounds are the first examples of isolable multi-oxo carbonyl metal complexes. Structural characterization of these complexes by NMR and IR spectroscopy, and X-ray techniques are described along-side DFT studies to illuminate their structure and bonding. In this context, Ison and co-workers have predicted a mono-oxo carbonyl d^2-rhenium intermediate in their investigation of the mechanism of CO oxidation by oxo rhenium(V) complexes.[7] Mayer et al. have also reported low valent oxo d^4-rhenium complexes with the π-acidic ligand MeC≡CMe.[1i,8]

The reaction of [ReI(O)$_2$(PPh$_3$)$_2$] with the PNN ligand in THF at room temperature gave bright orange crystals of [(PNN)Re(O)$_2$I] (**5**) in 85% yield. The syntheses of complexes **1**–**4** are depicted in Scheme 1. Salt metathesis of **5** with AgOTf or AgBF$_4$ afforded the cationic complex **4**. Subsequent addition of LiHMDS to **4** led to an immediate color



Scheme 1. Synthesis of complexes **1**–**5**. Reagents and conditions: 1) AgOTf or AgBF$_4$, THF, 25 °C. 2) LiHMDS, THF, −40 °C to 20 °C, 30 min. 3) CO gas. a) *t*BuNC, b) 2,6-Me$_2$PhNC, c) CH$_2$Cl$_2$, 25 °C.

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[*] M. G. Mazzotta, Dr. K. R. Pichaandi, Dr. P. E. Fanwick,
Prof. Dr. M. M. Abu-Omar
Department of Chemistry, Purdue University
West Lafayette, IN 47907 (USA)
E-mail: mabuomar@purdue.edu
Homepage: http://www.chem.purdue.edu/abu-omar/
Prof. Dr. M. M. Abu-Omar
School of Chemical Engineering, Purdue University
West Lafayette, IN 47907 (USA)

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change from orange to deep red with the formation of dearomatized [(PNN*)Re(O)$_2$] (**3**). Reaction of **3** or **4** with carbon monoxide gas or isocyanides resulted in an instantaneous color change (deep red to a lighter cherry red for **2**, from orange to bright yellow for **1**) to give complexes **2** and **1**, respectively, in high yields (Scheme 1).

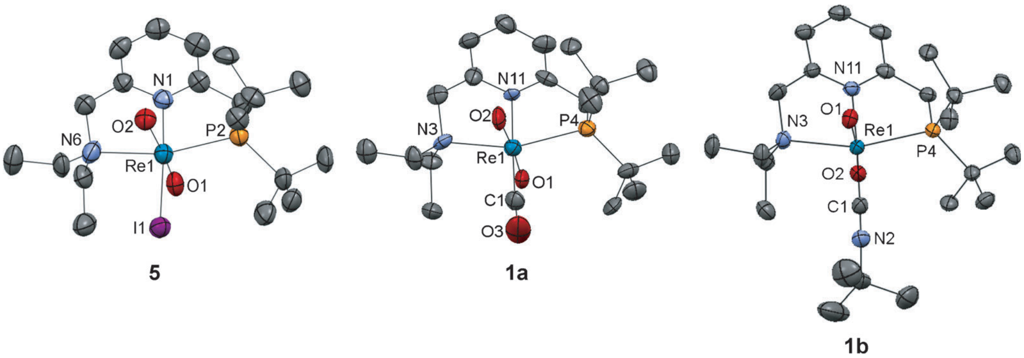
All complexes of **1** and **2**, except **2a**, were stable after removal of solvent and were isolated as solids, whereas **2a** was characterized only in solution. Upon removal of the solvent, complex **2a** decomposed to form unidentifiable products. All complexes **1**–**5** were fully characterized by ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, ^{13}C{^{1}H}-DEPT NMR experiments, IR spectroscopy, mass spectrometry, and elemental analysis.

The ^{1}H NMR resonance signals corresponding to the PNN ligand in the spectra of all the complexes showed no diastereotopic character, consistent with the *trans*-dioxo geometry having C_{2v} symmetry. The proton signals attributable to the pyridine ring for dearomatized complexes **2** and **3** showed a significant upfield shift when compared with their aromatized analogues **1**, **4**, and **5**. Similar shifts in the NMR spectrum have been documented by Milstein and co-workers for other dearomatized complexes.[6] The ^{13}C{^{1}H} NMR spectrum of molecule **1a** showed a doublet at $\delta = 194.6$ ppm with a coupling constant of 2 Hz, which we have assigned to the CO ligand.[9] Similar chemical shifts were observed for complexes **1b**, **1c**, and **2c** with coupling constants of 5, 5, and 7 Hz, respectively. Table 1 shows the ^{31}P{^{1}H} NMR chemical shifts and IR frequencies for complexes **1**–**5**. Upon introduction of the π-acidic ligands, the ^{31}P{^{1}H} NMR signals in the spectra of **1** and **2** shift downfield by approximately 9–14 ppm, reflecting the decrease in electron density at the rhenium center. The resonance signals in the ^{31}P{^{1}H} NMR spectra of the dearomatized complexes **2** and **3** are shifted approximately 3–6 ppm upfield compared to their aromatized counterparts **1** and **4**.

Table 1: The IR frequencies and ^{31}P{^{1}H} NMR chemical shifts for complexes **1**–**5**.

Complex	Re=O Stretch[a]	CO/CN Stretch[a]	^{31}P{^{1}H} NMR[c]
1a	896	2075 (2028)[b]	61.6
2a	938	2044 (1999)[b]	58.2
1b	896	2183	59.6
2b	932	2172	53.3
1c	896	2160	60.1
2c	934	2143	55.5
3	938	–	44.7
4	896	–	50.1
5	896	–	53.8

[a] IR spectra were recorded as CH_2Cl_2 solutions using KBr windows. [b] ^{13}C-labelled CO. [c] NMR spectra were recorded in CD_2Cl_2.



5 **1a** **1b**

Figure 1. ORTEP drawing of compounds **5**, **1a**, and **1b** with partial atom labeling. Ellipsoids are set at 50% probability. Hydrogen atoms and anions (**1a** and **1b**) are omitted for clarity.[13]

The IR spectra of **1a** and **2a** (Table 1) revealed CO absorption bands at 2075 and 2044 cm^{-1} (confirmed by ^{13}CO isotopic labeling), respectively. As anticipated, the absorption bands are higher than the CO stretching frequency observed for the matrix isolated complex [(O)$_2$Re(CO)] (2038 cm^{-1})[3b] and the isolated [(PNN)Re(CO)$_2$BrCl]$^{+}$ (2005, 1999 cm^{-1}),[9] in which rhenium has +4 and +3 oxidation states, respectively. The bands at 2183 cm^{-1} (**1b**) and 2172 cm^{-1} (**2b**) were assigned to CN stretching modes. They are approximately 40–70 cm^{-1} lower than in [ReOCl$_3$(CNCMe$_3$)$_2$] (2226 and 2239 cm^{-1}),[10] reflecting stronger backbonding in **1b** and **2b**. For Re=O bonds, the dearomatized complexes **2** and **3** exhibit ν_{ReO} at 932–938 cm^{-1}, whereas the ν_{ReO} for aromatized complexes **1**, **4**, and **5** occurs at 896 cm^{-1}. It is interesting to note that upon coordination of the π-acidic ligands, the ν_{ReO} is not affected.

X-ray crystallographic analysis of **1a**, **1b**, and **5** (Figure 1) revealed an octahedral arrangement of the ligands about the rhenium center with a *trans*-dioxo structure, where the oxo ligands occupy both axial positions. Selected bond lengths and bond angles are given in Table 2. The CO (**1a**), isocyanide (**1b**), and the iodide (**5**) ligands were almost perpendicular to the oxo groups. The Re–C(O) and C≡O bond lengths in **1a** are comparable to those in the rhenium(III) complex [(PNN)Re(CO)$_2$BrCl]$^{+}$.[9] The Re–C(N) and C≡N bond lengths in **1b** are 0.02 Å shorter and 0.01 Å longer, respectively, than those in [ReOCl$_3$(CNCMe$_3$)$_2$].[10] This is consistent with the IR observation of stronger backbonding in **1b**. No significant change in the Re=O bond lengths was observed for **1a** and **1b** when compared with **5**, which is consistent with the IR spectra of these complexes. This indicates that the Re=O bond is not affected appreciably by the incorporation of a π-acidic ligand into rhenium's coordination sphere. Attempts to obtain single crystals of the dearomatized complexes were unsuccessful as they formed a glass at −40°C. At room temperature, the dearomatized complexes either decomposed (**2a**) or re-aromatized (**2b** and **2c**) during the course of crystallization.

DFT studies were carried out to illuminate the nature of bonding interactions in **1** and **2**. In general bond lengths and

Table 2: The bond lengths and angles in **1a**, **1b**, and **5**.

Bond Lengths [Å] and Angles [°]	**1a**	**1b**	**5**
Re=O1	1.74	1.77	1.77
Re=O2	1.76	1.77	1.77
Re–Y[a]	2.02	2.06	2.79
C1–Z[b]	1.12	1.15	–
O-Re-O	174.9	173.1	170.2
O1-Re-Y[a]	89.4	92.0	94.5
O2-Re-Y[a]	89.0	91.3	92.5

[a] Y = C1 (**1a**, **1b**) and I1 (**5**). [b] Z = O3 (**1a**) and N2 (**1b**).

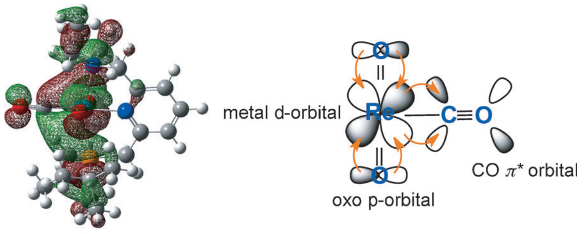


Figure 2. HOMO of **1a** predicted by DFT calculations (B3LYP density functional model with LANL2DZ basis sets within the Gaussian09[11] suite program, Gauss View 5.01[12] with an isovalue of 0.02 was used for generating the MOs). This interaction can be depicted as shown, where this π-backbonding interaction involves the oxo ligand p orbitals, Re d orbital and CO π* orbital.

bond angles calculated by DFT for **1a** and **1b** were in good agreement with experimental values obtained by X-ray structural determinations (Supporting Information). The dioxo–carbonyl and dioxo–isocyanide geometries in **1** and **2** are stabilized by π-backbonding between the metal center and the π* orbital of CO, facilitated by an interaction between the oxo p orbitals and the rhenium d_{xy} orbital (Figure 2 for **1a**; for **2a** and **2b**, see HOMO-1 in the Supporting Information). Mingos et al. made a similar observation from their DFT study of the oxo carbonyl complexes of tungsten and molybdenum.[1g] (For additional MOs that fall in the same category of π-backbonding interactions, see Supporting Information).

We have reported the first isolable dioxocarbonyl organometallic complex $[(PNN)Re(O)_2(CO)]^+$ (**1a**) and its molecular structure. Our synthetic methodology proved successful with the neutral, dearomatized complex and with isocyanide ligands, establishing the coexistence of both π-acidic and π-basic ligands in high-valent dioxorhenium(V) pincer complexes (**1** and **2**). Computational studies by DFT revealed π-backbonding as a key stabilizing interaction in these molecules. The ability to harness the opposing electronic effects of these ligands in conjunction with ligand cooperativity in catalytic applications will be a topic for further investigations.

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