Organometallics

DOI: 10.1002/ange.201403788

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

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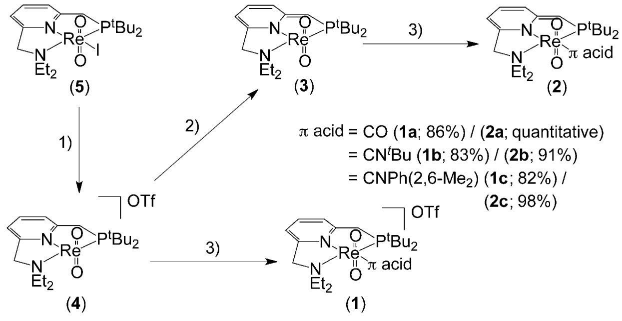
Abstract: *Aromatized cationic [(PNN)Re(π acid)(O)$_2$]$^+$ (**1**) and dearomatized neutral [(PNN*)Re(π acid)(O)$_2$] (**2**) complexes (where π acid = CO (**a**), tBuNC (**b**), or (2,6-Me$_2$)PhNC (**c**)), possessing both π-donor and π-acceptor ligands, have been synthesized and fully characterized. 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*-diethylaminomethyl)-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 alongside 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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[**] Funding for this research was provided by DOE-BES, Grant no. DE-FG-02-06ER15794. We thank Dr. John S. Harwood and Dr. Huaping Mo of Purdue University for their assistance with NMR experiments. This research was supported through computational resources provided by Information Technology at Purdue—Rosen Center for Advanced Computing, West Lafayette, Indiana. PNN = 6-(di-*tert*-butylphosphinomethylene)-2-(*N*,*N*-diethylaminomethyl)-1,6-dihydropyridine.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201403788.

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 δ = 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.

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

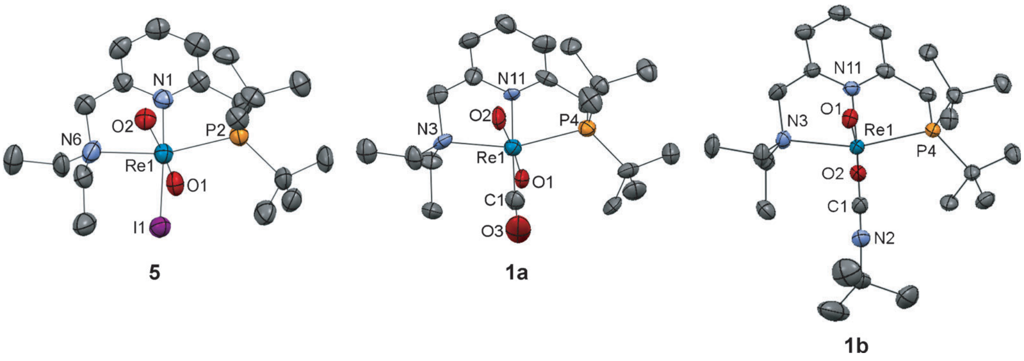
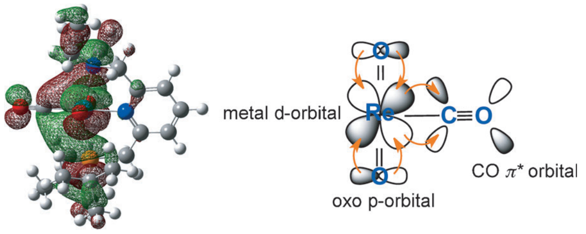


Figure 1. ORTEP drawing of compounds **5**, **1a**, and **1b** with partial atom labeling. Ellipsoids are set at 50% probability. Hydrogen atoms and anions (**1a** and **1b**) are omitted for clarity.[13]

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**).



1a

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.

Received: March 27, 2014

Keywords: carbon monoxide · isocyanide ligands · oxo ligands · pincer ligands · rhenium

[1] a) M. S. Malarek, D. J. Evans, P. D. Smith, A. R. Bleeker, J. M. White, C. G. Young, *Inorg. Chem.* **2006**, *45*, 2209–2216; b) S. Thomas, E. R. T. Tiekink, C. G. Young, *Inorg. Chem.* **2006**, *45*, 352–361; c) S. Thomas, E. R. T. Tiekink, C. G. Young, *Organometallics* **1996**, *15*, 2428–2430; d) K. A. Hall, J. M. Mayer, *J. Am. Chem. Soc.* **1992**, *114*, 10402–10411; e) S. G. Feng, L. Luan, P. White, M. S. Brookhart, J. L. Templeton, C. G. Young, *Inorg. Chem.* **1991**, *30*, 2582–2584; f) F. M. Su, J. C. Bryan, S. Jang, J. M. Mayer, *Polyhedron* **1989**, *8*, 1261–1277; g) D. C. Brower, J. L. Templeton, D. M. P. Mingos, *J. Am. Chem. Soc.* **1987**, *109*, 5203–5208; h) F. M. Su, C. Cooper, S. J. Geib, A. L. Rheingold, J. M. Mayer, *J. Am. Chem. Soc.* **1986**, *108*, 3545–3547; i) J. M. Mayer, D. L. Thorn, T. H. Tulip, *J. Am. Chem. Soc.* **1985**, *107*, 7454–7462.

[2] U. Jayarathne, P. Chandrasekaran, H. Jacobsen, J. T. Mague, J. P. Donahue, *Dalton Trans.* **2010**, *39*, 9662–9671.

[3] a) B. Liang, L. Andrews, *J. Phys. Chem. A* **2002**, *106*, 4042–4053; b) B. Liang, L. Andrews, *J. Phys. Chem. A* **2002**, *106*, 595–602; c) P. F. Souter, L. Andrews, *Chem. Commun.* **1997**, 777–778.

[4] a) M. J. Almond, *Chem. Soc. Rev.* **1994**, *23*, 309–317; b) M. J. Almond, J. A. Crayston, A. J. Downs, M. Poliakoff, J. J. Turner, *Inorg. Chem.* **1986**, *25*, 19–25.

[5] C. E. C. A. Hop, T. B. McMahon, *J. Am. Chem. Soc.* **1992**, *114*, 1237–1243.

[6] a) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon, D. Milstein, *Nat. Chem.* **2011**, *3*, 609–614; b) C. Gunanathan, D. Milstein in *Topics in Organometallic Chemistry*, *Vol. 37* (Eds.: T. Ikariya, M. Shibasaki), Springer, Berlin, **2011** p. 55; c) S. W. Kohl, L. Weiner, L. Schwartsburd, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David, M. A. Iron, D. Milstein, *Science* **2009**, *324*, 74–77; d) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790–792; e) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841.

[7] J. L. Smeltz, C. E. Webster, E. A. Ison, *Organometallics* **2012**, *31*, 4055–4062.

[8] a) S. K. Tahmassebi, W. S. McNeil, J. M. Mayer, *Organometallics* **1997**, *16*, 5342–5353; b) S. K. Tahmassebi, J. M. Mayer, *Organometallics* **1995**, *14*, 1039–1043; c) T. R. Cundari, R. R. Conry, E. Spaltenstein, S. C. Critchlow, K. A. Hall, S. K. Tahmassebi, J. M. Mayer, *Organometallics* **1994**, *13*, 322–331; d) R. R. Conry, J. M. Mayer, *Organometallics* **1993**, *12*, 3179–3186; e) R. R. Conry, J. M. Mayer, *Organometallics* **1991**, *10*, 3160–3166.

[9] K. R. Pichaandi, M. G. Mazzotta, J. S. Harwood, P. E. Fanwick, M. M. Abu-Omar, *Organometallics* **2014**, *33*, 1672–1677.

[10] J. C. Bryan, R. E. Stenkamp, T. H. Tulip, J. M. Mayer, *Inorg. Chem.* **1987**, *26*, 2283–2288.

[11] Gaussian, Inc., Wallingford CT **2009**, see Supporting Information for the full reference.

[12] GaussView, Version 5, R. Dennington,T. Keith, J. Millam, Semichem Inc., Shawnee Mission KS, **2009**.

[13] CCDC 993463, 993464 and 993465 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.