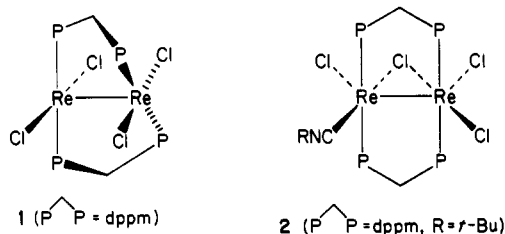


deprotonation up to about pH 9. The observed resistance to full ionization is due to a reluctance of the cyanide layer to form an energetically unfavorable lattice consisting of adjacent, mutually repelling anions.

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(18) Fulbright Scholar, University of Jordan, Amman, Jordan.

Department of Chemistry
University of California
Santa Barbara, California 93106

Bruce C. Schardt
John L. Stickney
Donald A. Stern
Douglas G. Frank
James Y. Katekaru
Stephen D. Rosasco
Ghaleb N. Salaita¹⁸
Manúel P. Soriaga*
Arthur T. Hubbard*

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Stabilization of Dinuclear Multiply Bonded Complexes Containing π -Acceptor Ligands: The Dirhenium(II)-Isocyanide System

Sir:

The cleavage of metal-metal bonds of dinuclear and trinuclear complexes by the π -acceptor ligands CO, NO, RNC (R = alkyl), and ArNC (Ar = aryl) is an important facet of multiple-metal-metal-bond chemistry.¹⁻³ In several instances these reactions have provided excellent synthetic routes to mononuclear complexes although little is yet known about their mechanisms. In this communication we report on the novel chemistry that is emerging from our studies of the reactions between the triply bonded dirhenium(II) complexes $\text{Re}_2\text{X}_4(\text{LL})_2$ (X = Cl, Br; LL = dppm, dppe, arphos)⁴ and isocyanide ligands. Dinuclear complexes that can be considered as intermediates in the bond cleavage process have been isolated, including the first example of a multiply bonded molecular A-frame-like complex, $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN}-t\text{-Bu})$.

While the $\text{Re}=\text{Re}$ bond of $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ (X = Cl, Br; PR_3 = monodentate tertiary phosphine) is readily cleaved by CO and RNC ligands to give mononuclear species,^{2a,e,5} the complexes $\text{Re}_2\text{Cl}_4(\text{LL})_2$, which contain the intramolecular bridging ligands dppm, dppe, or arphos, should be much more resistant to conversion to mononuclear fragments.⁶ We find that this is the case. The reaction of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (**1**)⁷ with 1 equiv of *tert*-butyl

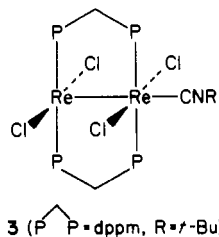
isocyanide (*t*-BuNC) in acetone for 30 min produces the red-brown 1:1 adduct **2** in very high yield (~90%). Analogous complexes have been obtained with use of the isocyanides MeNC and xylNC (xyl = xylyl). Recrystallization of **2** from dichloromethane-diethyl ether gave crystals of the CH_2Cl_2 hemisolvate $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN}-t\text{-Bu})\cdot 0.5\text{CH}_2\text{Cl}_2$.⁸ This diamagnetic complex is a nonelectrolyte in acetone and exhibits a well-defined 200-MHz ¹H NMR spectrum in CD_2Cl_2 that integrates in accord with this stoichiometry.⁹ The *t*-BuNC resonance is a sharp singlet at $\delta = +0.97$ (9 H), while the methylene protons of the dppm ligands appear as a basic AB pattern with superimposed P-H coupling ($\delta_A = +5.78$ (2 H); $\delta_B = +5.60$ (2 H); $J_{AB} = 12.7$ Hz; $J_{PH} = 4.8, 5.1$ Hz). This spectral pattern accords with **2** possessing an A-frame type structure.¹⁰⁻¹³ This has been confirmed by an X-ray crystal structure analysis.¹⁴ Unfortunately, refinement of the structure has been frustrated by a disorder problem that involves the Cl and *t*-BuNC ligands trans to the bridging Cl ligand. All that can be said at this time is that the Re-Re distance in **2** is somewhat longer than in the parent complex **1** (2.234 Å).¹⁵ The electrochemical properties of **2**, as measured by cyclic voltammetry (in 0.2 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ with a Pt-bead electrode),¹⁶ show the presence of two couples ($E_{1/2} = +0.21$ and $+1.30$ V vs. SCE), both of which correspond to one-electron oxidations. Both processes are characterized by $i_{p,c}/i_{p,a}$ ratios of unity and constant $i_p/\nu^{1/2}$ ratios for sweep rates (ν) between 50 and 400 mV/s in accord with diffusion control. Values for the potential separations between coupled anodic and cathodic peaks (ΔE_p) were 100 mV at $\nu = 200$ mV/s, and they increased with increase in sweep rate. These properties are consistent with the electron-transfer processes being electrochemically quasi-reversible. Chemical reversibility has been demonstrated by the oxidation of **2** (and its MeNC and xylNC analogues) to paramagnetic $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CNR})]\text{PF}_6$ using NOPF_6 or $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]\text{PF}_6$ in CH_2Cl_2 .¹⁷ The ready accessibility of two one-electron oxidations in **2** is a property that is characteristic of multiply bonded dirhenium species where the HOMO is an orbital of metal π or δ character.^{3,7} Accordingly,

- (1) Walton, R. A. "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, p 207 and references cited therein.
- (2) (a) Dunbar, K. R.; Walton, R. A. *Inorg. Chim. Acta* **1984**, *87*, 115. (b) Cameron, C. J.; Tetrack, S. M.; Walton, R. A. *Organometallics* **1984**, *3*, 240. (c) Cameron, C. J.; Wigley, D. E.; Wild, R. E.; Wood, T. E.; Walton, R. A. *J. Organomet. Chem.* **1983**, *255*, 345. (d) Bell, A.; Lippard, S. J.; Roberts, M.; Walton, R. A. *Organometallics* **1983**, *2*, 1562. (e) Allison, J. D.; Wood, T. E.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 3540. (f) Klendworth, D. D.; Welters, W. W., III; Walton, R. A. *Organometallics* **1982**, *1*, 336.
- (3) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982, and references cited therein.
- (4) Ligand abbreviations are as follows: dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; arphos = 1-(diphenylphosphino)-2-(diphenylarsino)ethane.
- (5) Hertzler, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2383.
- (6) There is considerable precedence for this reasoning. See, for example: Puddehatt, R. *J. Chem. Soc. Rev.* **1983**, *99*. Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *Organometallics* **1984**, *3*, 404.
- (7) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrack, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

- (8) Anal. Calcd for $\text{C}_{55.5}\text{H}_{54}\text{Cl}_5\text{N}_2\text{P}_4\text{Re}_2$: C, 47.32; H, 3.86; Cl, 12.58. Found: C, 46.57; H, 3.90; Cl, 12.82. IR (CH_2CH_2): $\nu(\text{C}=\text{N})$ 2133 s cm^{-1} .
- (9) The ^1H NMR spectrum of **2** in 3:1 CH_2Cl_2 -acetone- d_6 (vs. 85% aqueous H_3PO_4 with positive chemical shifts downfield) showed an AA'BB' pattern. Simulation of this spectrum gave the following parameters: $\delta_A = -6.39$; $\delta_B = -11.23$; $J_{AA'} = 232.3$ Hz; $J_{BB'} = 212.1$ Hz; $J_{AB} = 79.7$ Hz; $J_{AB'} = 1.2$ Hz.
- (10) Balch, A. L.; Hunt, C. T.; Lee, C. L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.
- (11) Lee, C. L.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2498.
- (12) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.
- (13) For a very recent account of the A-frame structure see: Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632 and references cited therein.
- (14) This structure determination was carried out by Dr. Douglas Powell of the Purdue University X-ray Crystallographic Facility.
- (15) Barder, T. J.; Cotton, F. A.; Dunbar, K. R.; Powell, G. L.; Schwotzer, W.; Walton, R. A., submitted for publication in *Inorg. Chem.*
- (16) For details of our experimental procedure, see: Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.
- (17) The properties of $[\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN}-t\text{-Bu})]\text{PF}_6$, which are characteristic of complexes of this type, are as follows: IR (CH_2Cl_2) $\nu(\text{C}=\text{N})$ 2151 s cm^{-1} ; IR (Nujol) $\nu(\text{C}=\text{N})$ 2149 s cm^{-1} ; CV (in 0.2 M TBAH- CH_2Cl_2) $E_{1/2}(\text{ox}) = +1.32$ V and $E_{1/2}(\text{red}) = +0.21$ V vs. SCE; X-band ESR (CH_2Cl_2 glass at -160 °C) broad complex signal between 500 and 4000 G centered at $g \approx 2.85$; μ_{eff} (CH_2Cl_2 solution) 1.4 μ_B ; elect absorption spectrum λ_{max} (in CH_2Cl_2) 770 ($\epsilon = 130$), 494 ($\epsilon = 1080$), 1175 nm ($\epsilon = 900$).

the electrochemical and redox characteristics of **2** strongly support the presence of multiple metal-metal bond character. Since **2** is diamagnetic, a formal Re-Re bond order of at least 2 is implied.

The isolation and structural identification of **2** provides insights into the intermediates that are formed when isocyanide ligands cleave M-M multiple bonds. In the solid state, structure **2** is apparently more stable than the alternative one **3**, which we can

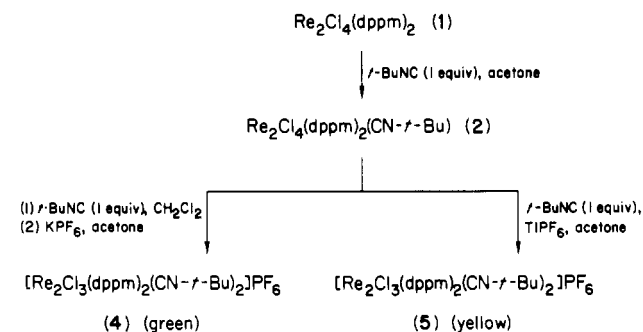


envisage as representing the species that is formed upon the initial interaction of isocyanide with **1**. The rearrangement **3** → **2** is clearly favored in this system.

The corresponding reactions of $\text{Re}_2\text{Cl}_4(\text{LL})_2$, where LL = dppe, arphos,^{18,19} with *t*-BuNC are very sluggish, due to the limited solubility of these complexes in the reaction solvents. However, their much more soluble oxidized congeners $[\text{Re}_2\text{X}_4(\text{LL})_2]\text{PF}_6$ (X = Cl, Br; LL = dppe, arphos)²⁰ react smoothly when treated with the isocyanide ligands *t*-BuNC and *t*-PrNC (2-4 equiv) in CH_2Cl_2 to give the dirhenium(II) complexes $[\text{Re}_2\text{X}_3(\text{LL})_2(\text{CNR})]\text{PF}_6$ in ca. 75% yield (based on starting complex).²¹ Each of these green to brown solids behaves as a 1:1 electrolyte in acetone and exhibits a single, sharp IR-active $\nu(\text{C}\equiv\text{N})$ mode (2141-2155 cm^{-1}). They possess similar electrochemical properties, with a reversible oxidation at $E_{1/2} = \text{ca. } +0.65 \text{ V}$ and an irreversible reduction at $E_{\text{pc}} = \text{ca. } -1.5 \text{ V}$ vs. SCE. The ¹H NMR spectra of these complexes are consistent with their formulation as diamagnetic, triply bonded Re_2^{4+} species containing a single isocyanide ligand. They most likely possess a staggered structure similar to that of the parent $\text{Re}_2\text{X}_4(\text{LL})_2$ complexes.¹⁹

While the complexes $[\text{Re}_2\text{X}_3(\text{LL})_2(\text{CNR})]\text{PF}_6$ (X = Cl, Br; R = *i*-Pr, *t*-Bu; LL = dppe, arphos) are quite inert to further reaction with RNC, the same is not true of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CN}-t\text{-Bu})$. In this instance, the treatment of **2** with 1 equiv of *t*-BuNC, or of **1** with 2 equiv of this same ligand, gives diamagnetic complexes of stoichiometry $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CN}-t\text{-Bu})_2]\text{PF}_6$ (**4** and **5**) as shown in Scheme I.²² The formation of **5** is favored by the presence of TlPF₆; this reagent apparently labilizes one of the Re-Cl bonds (leading to the precipitation of TlCl) prior to the attack of the second molecule of *t*-BuNC. While we believe that **4** and **5** may be structural isomers, we have not as yet been able to convert one to the other. Both complexes behave as 1:1 electrolytes in acetone ($\Delta_m = 100-120 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for $c_m = 1 \times 10^{-3} \text{ M}$), and they exhibit distinctly different spectral properties. Their IR spectra show only terminal $\nu(\text{C}\equiv\text{N})$ modes,²³ while in the ³¹P{¹H} NMR spectra an AA'BB' pattern is observed for **4**, whereas an AA'XX' pattern is found for complex **5**.²³ These data support the notion that in both **4** and **5** the two dppm ligands retain their trans-bridging disposition. The ¹H NMR spectrum of **4**

Scheme I. Reactions of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with *tert*-Butyl Isocyanide



(recorded in CD_2Cl_2) exhibits only one resonance for the isocyanide ligands ($\delta = +0.68$), indicating that both isocyanides are magnetically equivalent, and a pentet ($\delta = +6.00$, $J_{\text{PH}} = 5.3 \text{ Hz}$) associated with the methylene protons of the dppm ligands. This constitutes good evidence that **4** does not possess an A-frame type structure.⁷ Its structure is, we believe, closely akin to that of the recently characterized triply bonded nitrile derivatives $[(\text{RCN})_2\text{ClRe}(\mu\text{-dppm})_2\text{ReCl}_2]\text{X}$ (R = Me, Et, Ph, 4-Ph-C₆H₄; X = Cl⁻, PF₆⁻).²⁴ This is supported by the striking similarity of the electrochemical properties of **4** and the nitrile-containing complexes.²⁵ Complex **5** shows an AB pattern in the ¹H NMR spectrum ($\delta_{\text{A}} = +6.00$; $\delta_{\text{B}} = +5.42$), and as for complex **2**, an A-frame structure may be present. The ¹H NMR spectrum of **5** also exhibits two resonances for the isocyanide ligands ($\delta = +2.03$ and $+1.24$), thereby showing that the two isocyanide ligands are inequivalent.

Work is under way to expand the scope of these studies to include reactions of isocyanides with other complexes of the type $\text{M}_2\text{X}_4(\text{dppm})_2$ (M = Mo, W, Re; X = Cl, Br). Full details will be published following completion of structural studies.²⁶

(24) Barder, T. J.; Cotton, F. A.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.*, in press.

(25) Solutions of **4** in 0.2 M Bu₄NPF₆-CH₂Cl₂ are characterized by a one-electron oxidation at $E_{1/2} = +0.65 \text{ V}$ vs. SCE and an irreversible reduction process at ca. -1.6 V vs. SCE. The corresponding processes for **5** are an oxidation at $+1.04 \text{ V}$ and an irreversible reduction at $E_{\text{pc}} = -1.07 \text{ V}$ vs. SCE.

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Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Lori Beth Anderson
Timothy J. Barder
Richard A. Walton*

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(19) Cotton, F. A.; Stanley, G. G.; Walton, R. A. *Inorg. Chem.* 1978, 17, 2099.

(20) Brant, P.; Glicksman, H. D.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* 1978, 17, 3203.

(21) Satisfactory elemental microanalyses were obtained for all six complexes of this type. For example: Anal. Calcd for $[\text{Re}_2\text{Cl}_3(\text{dppe})_2(\text{CN}-t\text{-Bu})]\text{PF}_6$: C, 45.51; H, 3.83. Found: C, 45.12; H, 4.08.

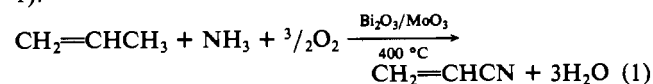
(22) Anal. Calcd for $\text{C}_{60}\text{H}_{62}\text{Cl}_3\text{F}_6\text{N}_2\text{P}_3\text{Re}_2$: C, 46.23; H, 4.01; Cl, 6.82. Found (**4**): C, 45.78; H, 3.94; Cl, 6.99. Found (**5**): C, 45.49; H, 3.83; Cl, 6.51.

(23) Complex **4**: IR (Nujol) $\nu(\text{C}\equiv\text{N})$ 2186 w, 2159 s, 2127 sh cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$ 2188 w, 2164 s, 2124 w cm^{-1} ; ³¹P{¹H} NMR (H_3PO_4 external, 3:1 CH_2Cl_2 -acetone-*d*₆) $\delta_{\text{A}} = -10.71$, $\delta_{\text{B}} = -15.15$, $J_{\text{AA}'} = 198.8 \text{ Hz}$, $J_{\text{BB}'} = 178.5 \text{ Hz}$, $J_{\text{AB}} = 78.5 \text{ Hz}$, $J_{\text{AB}'} = 2.6 \text{ Hz}$. Complex **5**: IR (Nujol) $\nu(\text{C}\equiv\text{N})$ 2138 sh, 2124 s cm^{-1} ; IR (CH_2Cl_2) $\nu(\text{C}\equiv\text{N})$ 2140 sh, 2125 s cm^{-1} ; ³¹P{¹H} NMR (H_3PO_4 external, 3:1 CH_2Cl_2 -acetone-*d*₆) $\delta_{\text{A}} = +5.08$, $\delta_{\text{B}} = -13.35$, $J_{\text{AA}'} = 162.2 \text{ Hz}$, $J_{\text{BB}'} = 130.4 \text{ Hz}$, $J_{\text{AB}} = 61.7 \text{ Hz}$, $J_{\text{AB}'} = 7.7 \text{ Hz}$.

Homogeneous Models for Propylene Ammoxidation. 2. The Carbon-Nitrogen Bond-Forming Step¹

Sir:

The ammoxidation of propylene is a major industrial process by which 8 billion pounds of acrylonitrile are produced annually. In this process, a mixture of propylene, ammonia, and air is passed over a heterogeneous bismuth molybdate-containing catalyst (eq 1).



The rate-limiting step for eq 1 is C-H bond cleavage to produce

(1) Part 1: Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* 1985, 107, 251-252.