2968 *Inorg. Chem.* **2000,** *39,* 2968−2969

Involvement of Multiply Bonded Dirhenium Complexes in Mixed-Metal Assemblies. Isolation and Characterization of a New Type of $\mathrm{Re_4Pd_2}$ Cluster

Shan-Ming Kuang, Phillip E. Fanwick, and Richard A. Walton*

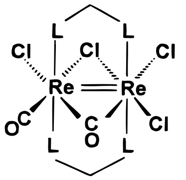
Department of Chemistry, Purdue University, 1393 Brown Building, West Lafayette, Indiana 47907-1393

Received March 7, 2000

More than any other multiply bonded dimetal core,[1] that of $[\mathrm{Mo}\overset{4}{-}\mathrm{Mo}]^{4+}$ has proven to be ideal for incorporation into small cluster assemblies. Examples include ligand-bridged chains[2] and cyclic quartets[3] containing two quadruply bonded units, as well as cyclic clusters containing three,[4] four,[5] or six[6] such dimolybdenum(II) units. Examples have also been encountered in dimolybdenum(III) chemistry, e.g., $[(\mathrm{Me_3CO})_2\mathrm{Mo}\overset{4}{-}\mathrm{Mo}-(\mathrm{OCMe_3})_2]_2(\mu\text{-F})_4$.[7] In addition, linear trinuclear and tetranuclear complexes that contain $\mathrm{M}\cdots\cdots\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ (M = Ru, Pd or Pt)[8] or $\mathrm{M}\cdots\mathrm{Mo}\overset{4}{-}\mathrm{Mo}\cdots\mathrm{M}$ arrays (M = Pd or Pt)[8(b),9] can be obtained through the use of a tridentate ligand that can bridge the $\mathrm{Mo_2}$ pair as well as M. In some instances, the [2 + 2] cycloaddition of two $\mathrm{M}\overset{4}{-}\mathrm{M}$ bonds (M = Mo or W) can occur to generate tetrametallocyclodiyne type clusters,[10−12] but these complexes have a chemistry quite different from that of the aforementioned species, which retain their localized $\mathrm{M}\overset{4}{-}\mathrm{M}$ bonding.

Surprisingly, despite the isoelectronic nature of $[\mathrm{Mo}\overset{4}{-}\mathrm{Mo}]^{4+}$ and $[\mathrm{Re}\overset{4}{-}\mathrm{Re}]^{6+}$,[1] the incorporation of this dirhenium core into clusters or extended arrays has not been reported, although polymers of the type $[cis\text{-}\mathrm{Re_2}(\mu\text{-}\mathrm{O_2CMe})_2\mathrm{Cl_4}(\mu\text{-LL})]_\infty$ (LL = bridging bidentate ligand) have recently been characterized[13] and the first tetrarhenium cyclodiyne type clusters have been reported.[14] Because of the rich redox chemistry of multiply bonded dirhenium(III,III), (III,II), and (II,II) complexes,[1] we have begun to examine the potential for these units to be incorporated into mixed-metal clusters. Preliminary results reported herein describe a novel $\mathrm{Re_4Pd_2}$ cluster that contains pairs of $[\mathrm{Re}{=}\mathrm{Re}]^{4+}$ units that are linked by thiocyanate bridges through a $[\mathrm{Pd_2}]^{4+}$ unit. These observations have no precedent in the aforementioned dimolybdenum chemistry that has been reported.

We have established previously that in dicarbonyl complexes of the type $\mathrm{Re_2Cl_4}(\mu\text{-LL})_2(\mathrm{CO})_2$ (**1**; LL = $\mathrm{Ph_2PCH_2PPh_2}$ (dppm) or $\mathrm{Ph_2PC}(=\mathrm{CH_2})\mathrm{PPh_2}$ (dppE)) the Cl ligand cis to the bridging CO ligand is labile toward substitution by neutral ligands such as CO, RNC, and RCN.[15−18] These substitutions proceed with retention of stereochemistry. The substitution of this Cl ligand in **1a** and **1b** by other *monoanionic* ligands has not previously been studied. In the present study we find that NaSCN (between 1 and 5 equiv) reacts with **1b** in methanol to afford red-brown crystals of the N-bound thiocyanate complex $\mathrm{Re_2Cl_3(NCS)}(\mu\text{-dppE})_2(\mathrm{CO})_2$ (**2**) in ca. 80% yield.[19] When this reaction is carried out in the presence of $\mathrm{Pd(1,5\text{-}COD)Cl_2}$ and an excess of NaSCN, the $\mathrm{Re_4Pd_2}$ cluster **3** is formed in high yield (>80%).[20] The structure of **3** was established by X-ray crystallography, and an ORTEP[21] representation is shown in Figure 1.[22] The uncoordinated sulfur of the N-bound thiocyanato ligand present in **2** is used to complex a Pd atom in the assembly of this cluster, the formation of which is represented in Scheme 1. The asymmetric unit comprises one-half of the molecule with an inversion center being coincident with the center of the $[\mathrm{Pd_2}(\mu\text{-SCN})_2]$ core. The Re−Re double bond that is present in **1b** (Re−Re = 2.5748(5)



1

LL = dppm (1a)
or dppE (1b)

---

* To whom correspondence should be addressed. E-mail: rawalton@purdue.edu.

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, 1993.

(2) Cayton, R. H.; Chisholm, M. H.; Huffman, J. C.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1991**, *113*, 8709.

(3) (a) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Lin, C.; Murillo, C. A. *Inorg. Chem. Commun.* **1998**, *1*, 109. (b) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1998**, *120*, 3398. (c) Cotton, F. A.; Daniels, L. M.; Guimet, I.; Henning, R. W.; Jordan, G. T., IV; Lin, C.; Murillo, C. A.; Schultz, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 12531.

(4) Suen, M.-C.; Tseng, G.-W.; Chen, J.-D.; Keng, T.-C.; Wang, J.-C. *Chem. Commun.* **1999**, 1185.

(5) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 4538.

(6) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *Chem. Commun.* **1999**, 841.

(7) Chisholm, M. H.; Clark, D. L.; Huffman, J. C. *Polyhedron* **1985**, *4*, 1203.

(8) (a) Mashima, K.; Kaneda, Y.; Fukumoto, A.; Tanaka, M.; Tani, K.; Nakano, H.; Nakamura, A. *Inorg. Chim. Acta* **1998**, *270*, 459. (b) Mashima, K.; Nakano, H.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 11632. (c) Nakano, H.; Nakamura, A.; Mashima, K. *Inorg. Chem.* **1996**, *35*, 4007.

(9) (a) Mashima, K.; Nakano, H.; Nakamura, A. *J. Am. Chem. Soc.* **1996**, *118*, 9083. (b) Mashima, K.; Fukumoto, A.; Nakano, H.; Kaneda, Y.; Tani, K.; Nakamura, A. *J. Am. Chem. Soc.* **1998**, *120*, 12151.

(10) McGinnis, R. N.; Ryan, T. R.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 7900.

(11) Reference 1, pp 554−558 and references therein.

(12) Beers, W. W.; McCarley, R. E.; Martin, D. S.; Miskowski, V. M.; Gray, H. B.; Hopkins, M. D. *Coord. Chem. Rev.* **1999**, *187*, 103.

(13) Ding, Y.; Lau, S. S.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta*, in press.

(14) (a) Lau, S. S.; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2273. (b) Cotton, F. A.; Dikarev, E. V. *J. Cluster Sci.* **1995**, *6*, 411. (c) Chen, J. D.; Cotton, F. A. *J. Am. Chem. Soc.* **1991**, *113*, 5857.

(15) Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 3524.

(16) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 4180.

(17) Fanwick, P. E.; Price, A. C.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3920.

(18) Kuang, S.-M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta*, in press.

(19) Synthesis of **2**. A sample of NaSCN (8.1 mg, 0.10 mmol) was dissolved in methanol (5 mL) and this solution added to one of **1b** (136 mg, 0.10 mmol) in 30 mL of dichloromethane. The mixture was stirred at room temperature for 4 h, during which time the reaction color changed from yellow to green to red-brown, and then filtered to remove insoluble materials. The solvent was evaporated under reduced pressure to give a red-brown solid, which was washed with methanol (2 × 3 mL) and diethyl ether (2 × 5 mL). Recrystallization from $\mathrm{CH_2Cl_2/Et_2O}$ afforded red-brown microcrystals; yield, 106 mg (77%). Anal. Calcd for $\mathrm{C_{56}H_{46}Cl_5NO_2P_4Re_2S}$ (i.e., $\mathbf{2}\cdot\mathrm{CH_2Cl_2}$): C, 45.74, H, 3.15. Found: C, 46.22; H, 3.17. IR spectrum (KBr disk): ν(NCS) 2081 vs, $\nu(\mathrm{CO})_t$ 1961 vs, br, $\nu(\mathrm{CO})_b$ 1729 m $\mathrm{cm^{-1}}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum ($\mathrm{CD_2Cl_2}$): $\delta = +12.7$ m, $\delta = +1.1$ m (centers of AA′BB′ multiplets). Cyclic voltammogram (0.1 M n-$\mathrm{Bu_4NPF_6}$−$\mathrm{CH_2Cl_2}$ solution, Pt-bead electrode, scan rate 200 mV $\mathrm{s^{-1}}$, potentials vs Ag/AgCl): $E_{1/2}(\mathrm{ox}) = +0.96$V, $E_{1/2}(\mathrm{red}) = -0.45$ V, $E_{1/2}(\mathrm{red}) = -1.33$ V.

10.1021/ic000250g CCC: $19.00

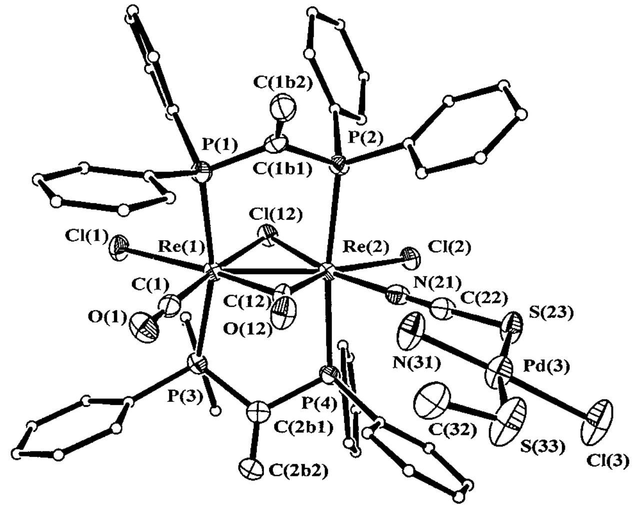
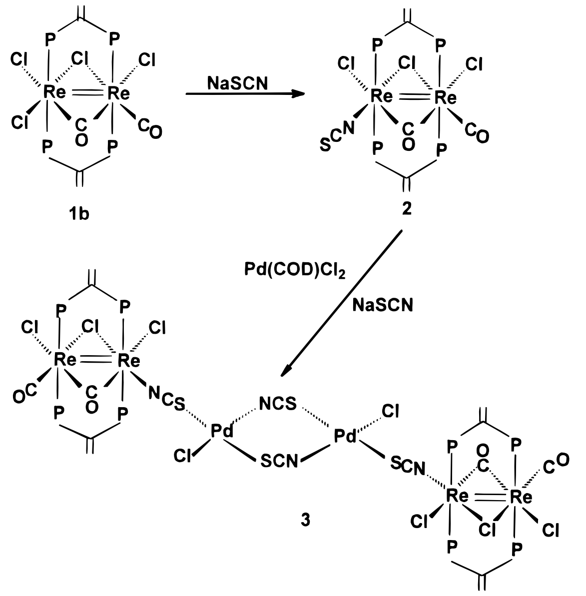


Figure 1. ORTEP[21] representation of the structure of the asymmetric unit Re_2Pd present in the Re_4Pd_2 cluster **3**. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands, which are circles of arbitrary radius. The molecule contains an inversion center that is coincident with the center of the [Pd(μ-SCN)(μ-NCS)Pd] ring (see the structural representation of **3** in Scheme 1) so that only one set of C, N, and S atoms is shown for these bridging thiocyanate ligands. Selected bond distances (Å) and bond angles (deg): Re(1)−Re(2) 2.5775(4), Re(1)−C(1) 1.915(10), Re(1)−C(12) 2.192(8), Re(1)−Cl(1) 2.427(2), Re(1)−Cl(12) 2.4739(19), Re(2)−C(12) 1.973(9), Re(2)−N(21) 2.064(7), Re(2)−Cl(2) 2.419(2), Re(2)−Cl(12) 2.4456(19), Pd(3)−N(31) 2.002(8), Pd(3)−Cl(3) 2.287(3), Pd(3)−S(33) 2.326(3), Pd(3)−S(23) 2.333(3), S(23)−C(22) 1.647(9), S(33)−C(32) 1.670(12), N(21)−C(22) 1.148(11), N(31)−C(32) 1.130(12), Re(2)−N(21)−C(22) 171.1(7), S(23)−C(22)−N(21) 175.2(8), Pd(3)−S(23)−C(22) 107.7(3), Pd(3)−S(33)−C(32) 104.0(4), S(33)−C(32)−N(31) 179.2(10).

Scheme 1. Reactions of **1b** with NaSCN and $Pd(COD)Cl_2$ (Ph Groups of dppE Ligands Omitted)



Å)[18] is retained in **3**, which has a Re−Re distance of 2.5775(4) Å. The structural parameters for the dirhenium units present in **3** are similar to those for **1b**.[18] Formally, the neutral Re_4Pd_2 unit can also be considered as arising from the combination of two $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2]^+$ cations and a $[Pd_2(\mu\text{-SCN})(\mu\text{-NCS})Cl_2(SCN)_2]^{2-}$ anion. The latter species has not previously been structurally characterized, although related ones that are of the type $[Pd_2(\mu\text{-SCN})(\mu\text{-NCS})X_4]^{2-}$ are known[25] and structurally resemble the dipalladium(II) unit present in **3**. Two types of bridging thiocyanato ligands are present in **3** that lead to two different Pd−S bonds; these have distances that are very similar (2.333(3) and 2.326(3) Å).

The regiospecificity of the substitution of the Cl ligand that is cis to the μ-CO ligand of **1b** by neutral and anionic ligands can be utilized to extend this new chemistry to the synthesis of other mixed-metal assemblies. Thus, the reactions of **1b** in dichloromethane with mixtures of $TlPF_6$ and *trans*-$Pt(CN)_2(CN\text{-}t\text{-}Bu)_2$[26,27] and with TlO_3SCF_3 and $Et_4N[W(CO)_5(CN)]$[28] afford the μ-CN-bridged complexes $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2\{NCPt(CN)(CN\text{-}t\text{-}Bu)_2\}]PF_6$ (**4**) and $Re_2Cl_3(\mu\text{-dppE})_2(CO)_2\{NCW(CO)_5\}$ (**5**), respectively.

The full scope of the chemistry that can be developed through the coordination of thiocyanato and cyano functionalities to various redox-active, multiply bonded dirhenium cores is under investigation, and full details will be presented in due course, including structural details for representative complexes.

Acknowledgment. We thank the John A. Leighty Endowment Fund for support of this work.

Supporting Information Available: X-ray crystallographic files in CIF format for $3\cdot10C_6H_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000250G

---

(20) Synthesis of **3**. A solution of NaSCN (4.0 mg, 0.05 mmol) in methanol (5 mL) was added to a mixture of **1b** (69 mg, 0.05 mmol) and Pd(1,5-COD)Cl_2 (14 mg, 0.05 mmol) in 30 mL of dichloromethane. The mixture was stirred at room temperature for 24 h and filtered, and the volume of the filtrate was reduced to ca. 3 mL. The addition of diethyl ether (20 mL) afforded a yellow-brown precipitate of **3**, which was filtered off, washed with diethyl ether (20 mL), and dried. Recrystallization from CH_2Cl_2/C_6H_6 gave brown crystals; yield, 66 mg (84%). Anal. Calcd for $C_{124}H_{100}Cl_8N_4O_4P_8Pd_2Re_4S_4$ (i.e., $3\cdot2C_6H_6$): C, 44.76; H, 3.03. Found: C, 44.92; H, 2.97. IR spectrum (KBr disk): ν(NCS) 2082 vs, $\nu(CO)_t$ 1964 vs, br, $\nu(CO)_b$ 1726 cm^{-1}. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2): $\delta = +12.5$, $\delta = +0.9$ (centers of AA′BB′ multiplets). Cyclic voltammogram (0.1 M $n\text{-}Bu_4NPF_6-CH_2Cl_2$ solution, Pt-bead electrode, scan rate 200 mV s^{-1}, potentials vs Ag/AgCl): $E_{1/2}(ox) = +0.93$V, $E_{1/2}(red) = -0.46$V, $E_{1/2}(red) = -1.34$ V.

(21) Johnson, C. K. ORTEP Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(22) Crystal data for $3\cdot10C_6H_6$ (193K): space group $P2_1/c$ (No. 14) with $a = 18.6374(5)$ Å, $b = 21.8098(5)$ Å, $c = 20.1559(6)$ Å, $\beta = 104.9915(13)°$, $V = 7914.1(7)$ Å^3, $Z = 2$, $d_{calcd} = 1.658$ g cm^{-3}, μ(Mo Kα) = 3.630 mm^{-1}. The data collection was performed on a Nonius Kappa CCD and the structure solved using the structure solution program PATTY in DIRDIF92.[23] The remaining atoms were located in succeeding difference Fourier syntheses. The structure was refined through the use of SHELX-97;[24] 62 018 reflections were measured of which 15 474 were unique. Hydrogen atoms were included but constrained to ride on the atom to which they are bonded. A cutoff $F_o^2 > 2\sigma(F_o^2)$ was used for R-factor calculations to give $R(F_o) = 0.064$, $R_w(F_o^2) = 0.116$, and GOF = 1.092. The asymmetric unit contains five benzene molecules, the carbon atoms of which were refined anisotropically.

(23) Beurskens, P. T.; Admirall, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF92 Program System*; Technical Report; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1992.

(24) Sheldrick, G. M. *SHELXL-97. A Program for Crystal Structure Refinement*; University of Gottingen: Gottingen, Germany, 1997.

(25) López, G.; Garcia, G.; Santana, M. D.; Sánchez, G.; Ruiz, J.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1621.

(26) Isir, H.; Mason, W. R. *Inorg. Chem.*, **1975**, *14*, 913.

(27) Conder, H. L.; Cotton, F. A.; Falvello, L. R.; Han, S.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1887.

(28) Buchner, W.; Schenk, W. A. *Inorg. Chem.* **1984**, *23*, 132.