

Redox Chemistry of a Pair of Complexes That Contain the Bridging Bis(diphenylphosphino)methane Ligand and the Re_2^{6+} and Re_2^{4+} Cores: $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4$ and $[\text{Re}_2(\mu\text{-dppm})_2\text{Cl}_3(\text{NCR})_2]\text{PF}_6$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$)

KIM R. DUNBAR, DOUGLAS POWELL, and RICHARD A. WALTON*

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The oxidant NOPF_6 has been used to prepare the new paramagnetic dirhenium complexes $[\text{Re}_2(\mu\text{-dppm})_2\text{Cl}_3(\text{NCR})_2](\text{PF}_6)_2$ (dppm = bis(diphenylphosphino)methane; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$) from the monocationic precursors. The compounds are derivatives of the Re_2^{5+} core. The doubly bonded dirhenium(III) complex $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ undergoes a one-electron oxidation with NOX ($\text{X} = \text{BF}_4^-, \text{PF}_6^-$), and a one-electron reduction with cobaltocene, to yield paramagnetic ions with bond orders of 1.5. The resulting monocation and monoanion provide examples of previously unknown types of metal-metal bonds of order 1.5 ($\sigma^2\pi^2\delta^*2\delta^1$ and $\sigma^2\pi^2\delta^*2\delta^2\pi^*1$, respectively). The structural identity of the monocation, a rare example of a Re_2^{7+} core complex, has been established through an X-ray crystal structure determination on the salt $[\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4]\text{H}_2\text{PO}_4\cdot\text{H}_3\text{PO}_4\cdot 4\text{H}_2\text{O}$. This compound crystallizes in the monoclinic space group $C2/c$ with cell dimensions $a = 23.524$ (4) Å, $b = 13.354$ (3) Å, $c = 19.717$ (5) Å, $\beta = 93.60$ (2)°, and $Z = 4$. The cation possesses crystallographic inversion symmetry. The phosphate groups (also related by inversion symmetry) and the waters are disordered. From 5418 unique data collected with use of $\text{Mo K}\alpha$ radiation on an Enraf-Nonius CAD-4 diffractometer ($2\theta < 50^\circ$; ω - 2θ scans), 3967 data were considered observed ($I > 2\sigma(I)$). The data were refined by block-diagonal least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$ to an R of 0.051. The Re-Re distance in this complex (2.6823 (6) Å) is appreciably longer than that in the parent neutral complex $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4$ (2.616 (1) Å).

Introduction

Recently, efforts in our laboratory have focused upon the reactivity of the triply bonded complex $\text{Re}_2\text{Cl}_4(\text{dppm})_2$, a compound that contains the bidentate bridging tertiary phosphine ligand bis(diphenylphosphino)methane (abbreviated dppm). The enhanced stability of this complex that is afforded by the trans bridging dppm ligands allows for the isolation of novel dinuclear complexes from reactions with isocyanides¹ and carbon monoxide,² products that may be viewed as intermediates in the pathway which eventually leads to M-M bond scission. The latter is the more usual reaction course when complexes that contain the Re_2^{4+} core are reacted with such π -acceptor ligands.³⁻⁷ During the course of other investigations into the chemistry of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$, we discovered that it displays a surprising reactivity toward nitriles to afford dirhenium(II) complexes of stoichiometry $[\text{Re}_2(\mu\text{-dppm})_2\text{Cl}_3(\text{NCR})_2]\text{X}$ ($\text{X} = \text{Cl}^-, \text{PF}_6^-$).⁸ This behavior has no counterpart in the chemistry of the analogous triply bonded dirhenium(II) complexes $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$,⁹ species that contain monodentate tertiary phosphine ligands. Finally, we have observed that oxidation of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ in the presence of chloride ion generates sequentially $\text{Re}_2\text{Cl}_5(\text{dppm})_2$ and then $\text{Re}_2\text{Cl}_6(\text{dppm})_2$.¹⁰ The latter complex has been structurally characterized as $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4$; i.e., it is an edge-shared bioctahedron and is believed to contain a Re-Re double bond.^{10,11}

The subsequent discovery that the complexes $[\text{Re}_2(\mu\text{-dppm})_2\text{Cl}_3(\text{NCR})_2]\text{PF}_6$ and $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4$ have a quite extensive redox chemistry has led us to explore this facet of their reactivity. We now report details of the synthesis and spectroscopic and magnetic properties of salts of the paramagnetic $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR})_2]^{2+}$, $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]^+$, and $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]^-$ ions, species that are formulated as possessing Re-Re bond orders of 3.5, 1.5, and 1.5, respectively. Some of these results have been

the subject of a preliminary communication.¹²

Experimental Section

Starting Materials. The complexes $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ and $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR})_2]\text{PF}_6$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$) were prepared according to the established literature procedures.^{10,13} The nitronium salts NOPF_6 and NOBF_4 were purchased from Alfa Products, and cobaltocene was supplied by Strem Chemicals. The nitriles and other common solvents were of commercial grade and used without further purification.

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen, and all solvents were deoxygenated thoroughly with N_2 prior to use.

A. Reactions of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR})_2]\text{PF}_6$ with NOPF_6 . (i) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_2\text{H}_5)_2](\text{PF}_6)_2$. In a typical reaction, $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_2\text{H}_5)_2]\text{PF}_6$ (0.15 g, 0.10 mmol) and NOPF_6 (0.02 g, 0.11 mmol) were stirred in 15 mL of dry, deoxygenated dichloromethane for 0.5 h. The resulting deep red-purple solution was filtered to remove any insoluble impurities, and diethyl ether was added to initiate precipitation of the product. The mixture was chilled to yield a crop of dark red-purple crystals, which were filtered off and recrystallized from acetone/diethyl ether; yield 0.145 g (90%). Anal. Calcd for $\text{C}_{54}\text{H}_{50}\text{Cl}_3\text{F}_{12}\text{N}_2\text{P}_6\text{Re}_2$: C, 40.04; H, 3.11; Cl, 6.57. Found: C, 40.08; H, 3.43; Cl, 7.03.

(ii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_2\text{H}_5)_2](\text{PF}_6)_2$. In a reaction procedure similar to (i) of part A, $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_2\text{H}_5)_2]\text{PF}_6$ (0.20 g, 0.13 mmol) and NOPF_6 (0.025 g, 0.14 mmol) were allowed to react for 1 h. The pale red-purple product was recrystallized from acetone/diethyl ether; yield 0.18 g (84%). Anal. Calcd for $\text{C}_{56}\text{H}_{54}\text{Cl}_3\text{F}_{12}\text{N}_2\text{P}_6\text{Re}_2$: C, 40.82; H, 3.30. Found: C, 39.84; H, 3.38.

(iii) $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_6\text{H}_5)_2](\text{PF}_6)_2$. The reaction of 0.14 g (0.09 mmol) of $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_6\text{H}_5)_2]\text{PF}_6$ and 0.016 g of NOPF_6 produced the dark purple complex; yield 0.13 g (87%). Anal. Calcd for $\text{C}_{64}\text{H}_{54}\text{Cl}_3\text{F}_{12}\text{N}_2\text{P}_6\text{Re}_2$: C, 44.08; H, 3.12. Found: C, 44.67; H, 3.36.

B. Reactions of $\text{Re}_2\text{Cl}_6(\text{dppm})_2$. (i) $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{PF}_6$. A solution containing $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ (0.20 g, 0.148 mmol) and NOPF_6 (0.026 g, 0.15 mmol) in 10 mL of acetonitrile was stirred at room temperature for 15 min. The reaction solution was treated with diethyl ether (10 mL) and chilled to 0 °C for 5 h. The resulting purple crystals were filtered off, washed with diethyl ether, and dried in vacuo; yield 0.19 g (86%). Anal. Calcd for $\text{C}_{50}\text{H}_{44}\text{Cl}_6\text{F}_6\text{P}_3\text{Re}_2$: C, 40.06; H, 3.06. Found: C, 40.54; H, 3.46.

(ii) $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{BF}_4$. A procedure identical to (i) of part B, but with 1 equiv of NOBF_4 in place of NOPF_6 , produced a dark purple crystalline solid. Anal. Calcd for $\text{C}_{50}\text{H}_{44}\text{BF}_4\text{Cl}_6\text{P}_3\text{Re}_2$: C, 41.68; H, 3.08. Found: C, 41.16; H, 3.22.

(iii) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{Re}_2\text{Cl}_6(\text{dppm})_2]$. A suspension of $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ (0.19 g, 0.14 mmol) and cobaltocene (0.03 g, 0.16 mmol) in 10 mL of acetone was stirred at 0 °C for 0.5 h. At the end of this time, the light green insoluble product was filtered off, washed with acetone, and dried in vacuo; yield 0.20 g (92%). Anal. Calcd for $\text{C}_{60}\text{H}_{54}\text{Cl}_6\text{CoP}_3\text{Re}_2$: C, 46.70; H, 3.53. Found: C, 45.60; H, 3.55.

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Table I. Positional Parameters for Non-Hydrogen Atoms and Their Estimated Standard Deviations^{a,b}

atom	x	y	z	B, Å ²	occupancy
Re	0.22121 (2)	0.16390 (3)	0.50502 (2)	2.568 (9)	
Cl1	0.2897 (1)	0.1940 (2)	0.4257 (1)	3.16 (6)	
Cl2	0.1560 (1)	0.0926 (3)	0.5774 (2)	4.11 (8)	
Cl3	0.2092 (1)	0.0088 (2)	0.4493 (2)	3.86 (7)	
P1	0.1394 (1)	0.2191 (2)	0.4247 (2)	3.08 (7)	
P2	0.2007 (1)	0.4186 (2)	0.4212 (2)	3.00 (7)	
C1	0.1326 (5)	0.3552 (8)	0.4325 (5)	3.0 (3)	
C2	0.0700 (5)	0.1755 (9)	0.4443 (6)	3.8 (3)	
C3	0.0422 (6)	0.102 (1)	0.4045 (7)	5.0 (4)	
C4	-0.0131 (6)	0.071 (1)	0.4186 (8)	5.7 (4)	
C5	-0.0382 (6)	0.110 (1)	0.4741 (9)	6.6 (5)	
C6	-0.0113 (6)	0.181 (1)	0.5143 (9)	6.4 (5)	
C7	0.0439 (6)	0.214 (1)	0.5005 (7)	4.9 (4)	
C8	0.1402 (5)	0.1971 (9)	0.3332 (6)	3.5 (3)	
C9	0.1791 (5)	0.1349 (9)	0.3046 (6)	4.1 (3)	
C10	0.1766 (6)	0.117 (1)	0.2352 (6)	4.9 (4)	
C11	0.1366 (7)	0.161 (1)	0.1946 (7)	5.9 (4)	
C12	0.0980 (7)	0.225 (1)	0.2207 (7)	6.1 (4)	
C13	0.0998 (6)	0.243 (1)	0.2901 (7)	4.9 (4)	
C14	0.2949 (5)	0.0750 (9)	0.6699 (6)	3.5 (3)	
C15	0.3328 (6)	0.014 (1)	0.7087 (7)	5.3 (4)	
C16	0.3320 (7)	0.011 (1)	0.7769 (7)	6.7 (5)	
C17	0.2964 (7)	0.067 (1)	0.8114 (7)	7.0 (5)	
C18	0.2592 (7)	0.125 (1)	0.7739 (7)	6.1 (4)	
C19	0.2576 (6)	0.131 (1)	0.7050 (6)	4.6 (3)	
C20	0.3126 (5)	-0.0488 (9)	0.5538 (6)	3.3 (3)	
C21	0.3506 (6)	-0.0684 (9)	0.5037 (7)	4.4 (3)	
C22	0.3614 (6)	-0.167 (1)	0.4853 (8)	5.4 (4)	
C23	0.3335 (6)	-0.2425 (9)	0.5162 (8)	5.6 (4)	
C24	0.2959 (7)	-0.221 (1)	0.5642 (8)	5.9 (4)	
C25	0.2849 (6)	-0.126 (1)	0.5821 (7)	4.8 (3)	
P3	0.4893 (2)	0.0240 (4)	0.3857 (5)	12.8 (3)	
O1*	0.4394 (8)	0.073 (2)	0.3942 (9)	15.6 (6)	
O2*	0.530 (1)	0.087 (2)	0.370 (1)	21.4 (9)	
O3*	0.504 (1)	-0.012 (2)	0.433 (1)	23.0 (9)	
O4*	0.495 (1)	-0.045 (2)	0.339 (2)	25 (1)	
O5A*	0.6011 (6)	0.374 (1)	0.3257 (8)	4.6 (3)	0.55
O5B*	0.598 (2)	0.272 (4)	0.295 (2)	6 (1)	0.20
O5C*	0.552 (1)	0.429 (3)	0.244 (2)	5.1 (8)	0.25
O6A*	0.609 (1)	0.244 (2)	0.220 (2)	5.6 (7)	0.30
O6B*	0.582 (2)	0.288 (3)	0.210 (2)	6.4 (9)	0.25
O6C*	0.636 (1)	0.231 (2)	0.241 (1)	4.1 (6)	0.30
O6D*	0.590 (2)	0.391 (5)	0.250 (3)	5 (1)	0.15

^a Atoms marked with an asterisk were refined isotropically. ^b Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(8\pi^2/3)(U_{11} + U_{22} + U_{33} + 2U_{12} + U_{13} + U_{23})$.

Preparation of Single Crystals of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{H}_2\text{PO}_4\cdot\text{H}_3\text{PO}_4\cdot 4\text{H}_2\text{O}$.

Attempts to grow crystals of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{PF}_6$ from CH_2Cl_2 -ethyl acetate resulted in the rapid hydrolysis (due to the presence of adventitious water) of the PF_6^- anion to give $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{H}_2\text{PO}_4\cdot\text{H}_3\text{PO}_4\cdot 4\text{H}_2\text{O}$ (IR(Nujol): $\nu(\text{P}-\text{O}) = 1055 \text{ cm}^{-1}$). There is precedence for such a hydrolysis¹⁴ and for the existence of H_3PO_4 "solvates" of H_2PO_4^- salts.^{15,16} Spectroscopic characterizations (far-IR, ESR and electronic absorption) and electrochemical measurements confirmed that the cation $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]^+$ had remained intact during the hydrolysis. Furthermore, conductivity measurements in acetonitrile showed behavior typical of a 1:1 electrolyte.

X-ray Crystallography. Details of the solution and refinement of the structure of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{H}_2\text{PO}_4\cdot\text{H}_3\text{PO}_4\cdot 4\text{H}_2\text{O}$ are available as supplementary material. An ORTEP drawing of the $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]^+$ cation is shown in Figure 1. Positional parameters for non-hydrogen atoms are listed in Table I, while the more important bond distances and angles are given in Table II. Full tables of thermal parameters, bond distances, and bond angles are available as supplementary material.

Physical Measurements. Infrared spectra were recorded on KBr plates in the region 4800–400 cm^{-1} with an IBM Instruments IR/32 FTIR spectrometer and from 500–50 cm^{-1} on polyethylene plates with a Digilab FTS-20B spectrometer. Electronic absorption spectra were recorded as CH_2Cl_2 or CH_3CN solutions on Cary 17 (900–1800 nm) and IBM 9420 (300–900 nm) UV-visible spectrophotometers. X-band ESR spectra of

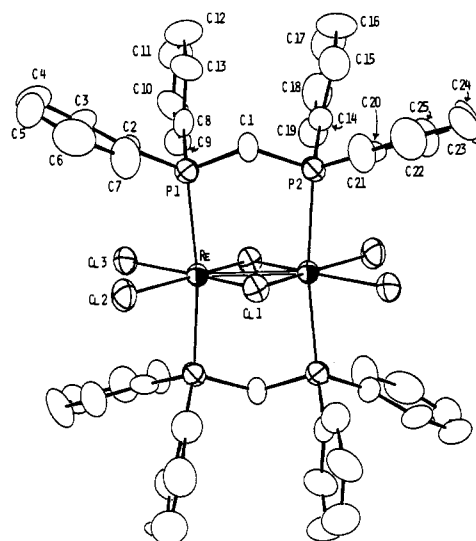


Figure 1. Molecular structure of the $[\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4]^+$ cation showing the atomic numbering. The atoms are represented by ellipsoids of thermal motion at the 50% probability level.

dichloromethane solutions were recorded at -170°C with the use of a Varian E-109 spectrometer. Conductivity measurements were performed on $1 \times 10^{-3} \text{ M}$ acetonitrile solutions with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. Electrochemical measurements

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Table II. Selected Distances (Å) and Angles (deg) with Estimated Standard Deviations

atom 1	atom 2	dist	atom 1	atom 2	dist
Re	Re	2.6823 (6)	P1	C1	1.84 (2)
Re	Cl1	2.349 (3)	P1	C2	1.80 (1)
Re	Cl1	2.363 (3)	P1	C8	1.83 (1)
Re	Cl2	2.360 (3)	P2	C1	1.84 (1)
Re	Cl3	2.353 (3)	P2	C14	1.81 (1)
Re	P1	2.524 (3)	P2	C20	1.85 (1)
Re	P2	2.523 (3)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Re	Re	Cl1	55.52 (7)	Cl3	Re	P1	84.3 (2)
Re	Re	Cl1	55.07 (7)	Cl3	Re	P2	86.9 (2)
Re	Re	Cl2	137.81 (8)	P1	Re	P2	171.0 (1)
Re	Re	Cl3	140.04 (8)	Re	Cl1	Re	69.40 (8)
Re	Re	P1	94.13 (7)	Re	P1	C1	107.7 (3)
Re	Re	P2	93.68 (8)	Re	P1	C2	116.0 (5)
Cl1	Re	Cl1	110.6 (1)	Re	P1	C8	121.1 (4)
Cl1	Re	Cl2	166.0 (2)	C1	P1	C2	102.7 (5)
Cl1	Re	Cl3	84.6 (2)	C1	P1	C8	104.5 (5)
Cl1	Re	P1	93.4 (1)	C2	P1	C8	103.0 (6)
Cl1	Re	P2	87.4 (1)	Re	P2	C1	109.7 (3)
Cl1	Re	Cl2	82.9 (2)	Re	P2	C14	120.6 (4)
Cl1	Re	Cl3	164.4 (2)	Re	P2	C20	112.9 (4)
Cl1	Re	P1	91.3 (1)	C1	P2	C14	104.3 (5)
Cl1	Re	P2	96.8 (1)	C1	P2	C20	103.8 (6)
Cl2	Re	Cl3	82.1 (1)	C14	P2	C20	104.0 (5)
Cl2	Re	P1	89.9 (2)	P1	C1	P2	111.4 (6)
Cl2	Re	P2	87.3 (2)				

were made in dichloromethane solvents that contained 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$ and referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Magnetic susceptibility measurements were done by the Evans method on dichloromethane solutions of the complexes with a 90-MHz Perkin-Elmer R32 spectrometer.

Analytical Procedure. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

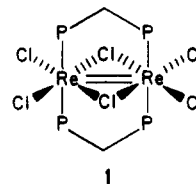
Results and Discussion

(a) The $[\text{Re}_2(\mu\text{-dppm})_2\text{Cl}_3(\text{NCR})_2]^{2+}$ Ions. The stable diamagnetic 1:1 salts $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR})_2]\text{PF}_6$,⁸ which are formally derivatives of the Re_2^{4+} dinuclear core, react cleanly with NOPF_6 to generate the paramagnetic dication $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR})_2](\text{PF}_6)_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$). The electrochemical properties of these products, as determined by cyclic voltammetry, are characterized by two couples (Table III); both processes correspond to reductions of the bulk complex. These couples occur at the same potentials as those found for the parent 1:1 salts⁸ and have properties in accord with them being quasi-reversible electron-transfer processes. They are characterized by i_{pc}/i_{pa} ratios approximately equal to unity (1.0 ± 0.1) and constant $i_p/\nu^{1/2}$ ratios for sweep rates between 50 and 400 mV/s. The potential separation between coupled anodic and cathodic peaks, ΔE_p , was 90–150 mV for a sweep rate of 200 mV/s and increased slightly with increasing sweep rate. Note that the high positive potential for the 2+/+ couple (at $\sim +0.6$ V) causes these species to be sensitive to spontaneous reduction in solution; therefore, it was necessary to use very pure, dry solvents for any solution characterizations. The conductivity of these salts in 1×10^{-3} M acetonitrile solutions confirms their identity as 1:2 electrolytes ($\Lambda_m = 240\text{--}250 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

IR spectroscopic measurements of Nujol mulls reveal a weak feature in the region 2285–2240 cm^{-1} , which can be assigned to the $\nu(\text{C}\equiv\text{N})$ modes (Table III). The electronic absorption spectra of the three complexes are very similar (Table III), and each exhibits a broad, intense band in the near-IR region at ~ 1140 nm ($\epsilon \approx 330$), a feature that is characteristic of paramagnetic complexes that possess the Re_2^{5+} core and a $\sigma^2\pi^4\delta^2\delta^*$ ground-state electronic configuration.^{9,17–19} This band has been assigned to

the $\delta \rightarrow \delta^*$ transition.²⁰ The expected paramagnetic nature of these complexes has been verified by X-band ESR spectral measurements of dichloromethane glasses (-170°C). These spectra, which are essentially identical, display a very complex pattern between 1200 and 5000 G that reflects the low symmetry of these molecules and hyperfine coupling to the phosphorus and rhenium nuclei. The spectra, which are centered at ~ 2500 G ($g \approx 2.4$), resemble those of other Re_2^{5+} complexes that contain chloride and phosphine ligands.^{21,22}

(b) The $[\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4]^{+}$ Ions. We have recently identified the complex $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4$ as possessing an edge-shared bioctahedral structure (**1**).¹⁰ A special interest in



this molecule was provoked because of its formulation as a derivative of the double-bonded $(\text{Re}=\text{Re})^{6+}$ core ($\sigma^2\pi^2\delta^2\delta^*$ electronic configuration).^{10,11} Cyclic voltammetric measurements on solutions of **1** in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane show the presence of four metal-based couples in the potential range +1.8 to -1.8 V (vs. Ag/AgCl). Those at $E_{1/2} = +1.63$ and $+0.81$ V correspond to one-electron oxidations, while those at $E_{1/2} = -0.54$ and -1.41 V are one-electron reductions.¹⁰ The position and degree of reversibility of the oxidation at $+0.81$ V and the reduction at -0.54 V indicated the feasibility of isolating the monocation (**2**) and the monoanion (**3**) by chemical means, an expectation that has been realized.

The addition of 1 equiv of NOPF_6 or NOBF_4 to a suspension of the red-purple complex **1** in CH_3CN results in the production of a deep blue-purple solution of the monocation **2** with concomitant loss of $\text{NO}(\text{g})$. The product may be precipitated as its PF_6^- or BF_4^- salt in very high yield by the addition of diethyl ether to the reaction solution. The monoanionic species **3** is prepared by the addition of an acetone solution of cobaltocene to an equimolar quantity of **1** suspended in this same solvent. This reaction affords the light green product $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{Re}_2\text{Cl}_6(\text{dppm})_2]$ in essentially quantitative yield. The use of cobaltocene as a reducing agent has proved most effective in other multiply bonded dimetal systems.^{23,24} The complexes behave as 1:1 electrolytes in acetonitrile ($\Lambda_m \approx 120 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$) and possess electrochemical properties that show them to be derivatives of the Re_2^{7+} (**2**) or Re_2^{5+} (**3**) cores and to bear a very close structural relationship to **1**. The four couples that characterize 0.2 M TBAH– CH_2Cl_2 solutions of **2** correspond to one oxidation and three reductions, while for **3** we have three oxidations and one reduction. In the case of the cobaltocenium salt of **3**, an additional couple at $E_{1/2} = -0.86$ V vs. Ag/AgCl is due to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}^+ / (\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$; this couple possesses the same current as that of the four one-electron dirhenium-based couples.

The close structural relationship between **1**, **2**, and **3** that is implied by the electrochemical results (vide supra) is further supported by the Nujol mull far-IR spectra of these species. The low-frequency spectra (below 400 cm^{-1}) are strikingly similar, with the three $\nu(\text{Re}-\text{Cl})$ modes of **1** at 355 m, 312 s, and 282 m cm^{-1}

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Table III. Electrochemical and Spectroscopic Data for $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR})_2](\text{PF}_6)_2$

R	IR spectra $\nu(\text{C}\equiv\text{N}), \text{cm}^{-1}$ ^a	electronic abs spectra $\lambda_{\text{max}}, \text{nm} (\epsilon)$ ^b	CV half-wave potentials ^c	
			$E_{1/2}(\text{red})(1), \text{V}$	$E_{1/2}(\text{red})(2), \text{V}$
CH ₃	2284	1140 (330), ~680 sh, 543 (1200), ~420 sh	+0.60 (100)	-1.41 (150)
C ₂ H ₅	2276	1135 (300), ~680 sh, 540 (1100), ~430 sh	+0.58 (100)	-1.43 (130)
C ₆ H ₅	2244	1150 (330), ~680 sh, 550 (1500), ~420 sh	+0.59 (90)	-1.39 (110)

^a Nujol mull on KBr plates. ^b Dichloromethane solutions (5×10^{-4} – 1×10^{-3} M). ^c Electrochemical measurements in 0.2 M TBAH–dichloromethane referenced to Ag/AgCl. Numbers in parentheses are values of ΔE_p at a sweep rate of 200 mV/s.

all undergoing a small increase in frequency to 360, 318, and 288 cm^{-1} in the case of **2** (PF_6^- salt) and a decrease to 335, 290, and 266 cm^{-1} in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{Re}_2\text{Cl}_6(\text{dppm})_2]$. These spectral shifts accord very nicely with the expected correlation between $\nu(\text{Re}-\text{Cl})$ and the order of metal oxidation states, viz., $\text{Re}_2^{7+} > \text{Re}_2^{6+} > \text{Re}_2^{5+}$. The electronic absorption spectra of all three species are, as expected, very different, but a detailed analysis is at present unwarranted.²⁵

Salts containing the ions **2** and **3** are paramagnetic as demonstrated by magnetic susceptibility and low-temperature ESR spectral measurements. The room-temperature magnetic moment of an acetonitrile solution of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{PF}_6$ was shown to be 1.82 μ_B as determined by the Evans method. The X-band ESR spectrum of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{PF}_6$ in dichloromethane (-170°C) shows a broad, complex, and poorly resolved signal centered at ~ 3750 G ($g \approx 1.6$). The cobaltocenium salt of the anion **3** displays a much less complex, narrow resonance at ~ 2300 G ($g \approx 2.88$) in both the solid state and in dichloromethane at $\sim -170^\circ\text{C}$. This signal actually comprises two closely spaced components separated by ~ 120 G, with additional weaker features in the wings that may reflect the presence of rhenium hyperfine splitting.

(c) Structural Results and Interpretation. When attempts were made to grow crystals of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{PF}_6$ from dichloromethane–ethyl acetate mixtures, hydrolysis of the PF_6^- anion occurred, and crystals of the salt $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{H}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4 \cdot 4\text{H}_2\text{O}$ were deposited (see Experimental Section). The structure of the cation was readily ascertained (see Figure 1 and supplementary material), although the identity of the anion remained, for a time, somewhat controversial. That hydrolysis of the hexafluorophosphate anion had indeed occurred to give phosphate (due, presumably, to the presence of adventitious water in the solvent system) was clearly ascertained by using IR spectroscopy (no $\nu(\text{P}-\text{F})$ modes but $\nu(\text{P}-\text{O})$ at 1055 cm^{-1}).

The phosphate oxygens of the anionic species were located with some difficulty in the refinement and were clearly disordered as indicated by their large isotropic thermal parameters and short P–O bond lengths. However, difference electron density maps revealed no other clear structural model. There are two (symmetry-related) phosphate groups per cation in the solid state. For charge neutrality to be maintained, we believe that one of these phosphates is H_2PO_4^- and that the other is H_3PO_4 . The dissimilarity of these groups may account for the disorder. There is precedence for the existence of H_3PO_4 solvates of H_2PO_4^- salts.^{15,16} In addition, a region of peaks about 3 Å in diameter was found in the difference maps. These peaks were low in density ($< 3 \text{ e}/\text{\AA}^3$) and formed no clear covalent bonding pattern. These peaks were assigned as water oxygens. However, because of their proximity to each other, these sites could not be fully occupied. The oc-

Table IV. Complexes of the Type $\text{M}_2(\mu\text{-L})_2\text{L}_8$ That Contain Metal–Metal Bonds of Order 1.5

complex	electronic config ^a	metal core
$[\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4]^-$	$\sigma^2\pi^2\delta^*2\delta^2\pi^*1$	Re_2^{5+}
$[\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4]^+$	$\sigma^2\pi^2\delta^*2\delta^1$	Re_2^{7+}
$[\text{W}_2(\mu\text{-OEt})_2\text{Cl}_4(\text{hp})_2]^{-b}$	$\sigma^2\pi^2\delta^*1$	W_2^{7+}
$[\text{W}_2(\mu\text{-OEt})_2\text{Cl}_4(\text{OEt})_2(\text{py})_2]^+$	$\sigma^2\pi^1$	W_2^{9+}

^a Based upon theoretical treatments as described in ref 11 and 26. ^b hp is the monoanion of 2-hydroxypyridine.

cupancies suggested by the map and refinement calculations are shown in the table of positional parameters (Table I).

In its essential features the structure of the cation **2** is very similar to that of its neutral precursor **1**, although the Re–Cl distances of the former are somewhat shorter and the Re–P distances slightly longer (Table II) than the comparable distances in the structure of **1**.¹⁰ These trends are not unexpected in view of the metal oxidation state change that occurs; comparable trends are seen in the metal–ligand distances for other dirhenium complexes that contain only chloride and phosphine ligands.¹⁹ The crystallographic data reveal that there is a significant increase in the metal–metal bond distance in going from $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ (2.616 (1) Å)¹⁰ to $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]^+$ (Re–Re = 2.6823 (6) Å). This bond lengthening may be a consequence of the decrease in Re–Re bond order as one removes a δ -bonding electron by oxidation or the increase in the charge at the metal centers, which results in less effective overlap of σ - and π -bonding orbitals, or a combination of these two factors. The increase in the oxidation state at the two metal centers has been found to play a key role in governing metal–metal bond distance changes, particularly as observed in the series $[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^{n+}$ ($n = 0, 1, \text{ or } 2$),¹⁹ where, unlike the present case, the effect of the metal oxidation state increase works in opposition to the formal bond order changes.

Our results provide good support for the prediction¹¹ that the metal–metal bonding in **1** and **2** can be represented by the $\sigma^2\pi^2\delta^*2\delta^2$ and $\sigma^2\pi^2\delta^*2\delta^1$ ground-state configurations, respectively. On the other hand, a one-electron cobaltocene reduction of **1** to paramagnetic **3** should lead to a $\sigma^2\pi^2\delta^*2\delta^2\pi^*1$ ground-state configuration, which is also representative of a metal–metal bond order of 1.5.

(d) Concluding Remarks. The coordination of two nitrile ligands and the dissociation of a chloride ligand have a marked effect on the redox properties of the $(\text{Re}\equiv\text{Re})^{4+}$ core as seen in the conversion of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ to cationic $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCR})_2]^+$ (R = CH₃, C₂H₅, C₆H₅). The greater degree of difficulty in oxidizing this cationic species is paralleled by its much greater ease of reduction, compared to the situation with $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and related derivatives that contain monodentate phosphines, viz., $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$.²² This suggests that, with appropriate modification of the ligand environment about the Re_2^{4+} core, chemical reduction to a stable authentic Re_2^{3+} derivative may be feasible. Such studies are currently in progress.

In our studies of the redox chemistry of $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-dppm})_2\text{Cl}_4$, we have encountered an unexpectedly rich, reversible redox chemistry for a complex that possesses an edge-shared bioctahedral structure. Our results hint that comparable chemistry may exist for other *halide-bridged* metal–metal-bonded compounds of this type. Furthermore, when these findings are considered in conjunction with some recent data for edge-shared bioctahedral tungsten complexes that contain the W_2^{9+} and W_2^{7+} cores,^{13,14} there is a strong inference that multiply bonded dimetal

(25) The spectrum of **1** in dichloromethane shows bands at 1435 nm ($\epsilon = 300$) and 516 nm ($\epsilon = 1700$).¹⁰ There are two prominent features present in the near-IR region of the spectrum of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{PF}_6$ (measured in CH_3CN), namely, a broad band at 2000 nm ($\epsilon \approx 560$) and a second absorption at a somewhat higher energy, 1045 nm ($\epsilon \approx 360$). An intense band in the visible region of this compound occurs at 660 nm ($\epsilon \approx 2800$) with a shoulder at ~ 580 nm. Due to the insolubility, as well as the solution instability, of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{Re}_2\text{Cl}_6(\text{dppm})_2]$, measurements on this complex were performed on Nujol mull samples: the most notable features are bands located at 800 and 530 nm.

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complexes of this structural type may be capable of existing in four different electronic configurations that correspond to formal metal-metal bond orders of 1.5 (see Table IV).

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Registry No. $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCCH}_3)_2](\text{PF}_6)_2$, 97391-38-3; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCCH}_3)_2](\text{PF}_6)$, 95345-98-5; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2-$

$(\text{NCC}_2\text{H}_5)_2](\text{PF}_6)_2$, 97391-40-7; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_2\text{H}_5)_2](\text{PF}_6)$, 95345-96-3; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_6\text{H}_5)_2](\text{PF}_6)_2$, 97391-42-9; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{NCC}_6\text{H}_5)_2](\text{PF}_6)$, 95345-94-1; $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{PF}_6$, 96438-01-6; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2]\text{BF}_4$, 96322-62-2; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}][\text{Re}_2\text{Cl}_6(\text{dppm})_2]$, 96343-32-7; $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{H}_3\text{PO}_4\cdot\text{H}_3\text{PO}_4\cdot 4\text{H}_2\text{O}$, 96322-64-4; $\text{Re}_2\text{Cl}_6(\text{dppm})_2$, 58312-74-6; Re, 7440-15-5; cobaltocene, 1277-43-6.

Supplementary Material Available: Details of the structure solution, listings of the experimental details (Table S1), positional parameters for the hydrogen atoms (Table S2), thermal parameters (Table S3), bond distances and bond angles (Table S4), torsional angles (Table S5), and observed and calculated structure factors, and a figure showing the full atomic numbering scheme (Figure S1) for the crystal structure of $[\text{Re}_2\text{Cl}_6(\text{dppm})_2]\text{H}_3\text{PO}_4\cdot\text{H}_3\text{PO}_4\cdot 4\text{H}_2\text{O}$ (39 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Kansas State University, Manhattan, Kansas 66506

Reactivity of Molybdenum Oxo-Imido Complexes with Organophosphines: Generation and Chemistry of $[\text{Mo}^{\text{V}}(\text{Ntol})(\text{S}_2\text{CNET}_2)_2]_2\text{O}$ and $\text{Mo}^{\text{IV}}(\text{Ntol})(\text{S}_2\text{CNET}_2)_2$

DAVID D. DEVORE and ERIC A. MAATTA*

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The oxo-imido molybdenum(VI) dithiocarbamate complex $\text{MoO}(\text{Ntol})\text{L}_2$ (tol = *p*-tolyl; L = S_2CNET_2) reacts with 0.5 equiv of Ph_2P or EtPh_2P to produce the dinuclear Mo(V) complex $[\text{Mo}(\text{Ntol})\text{L}_2]_2\text{O}$ and the corresponding phosphine oxide. An oxo-bridged structure for the dinuclear complex is indicated by IR and ^{17}O NMR studies. The visible spectrum of the dinuclear complex displays an intense absorption at 533 nm that does not obey the Lambert-Beer law; this observation is interpreted in terms of an equilibrium disproportionation reaction, whereby $\text{Mo}^{\text{IV}}(\text{Ntol})\text{L}_2$ and $\text{Mo}^{\text{VI}}\text{O}(\text{Ntol})\text{L}_2$ are produced via Mo-O bond scission in the dimer. Support for this proposition is provided by the fact that toluene solutions of $[\text{Mo}(\text{Ntol})\text{L}_2]_2\text{O}$ react with Ph_2P or EtPh_2P to produce the corresponding phosphine oxide and $\text{Mo}(\text{Ntol})\text{L}_2$, which has been trapped as its dimethyl acetylenedicarboxylate (DMAC) adduct, $\text{Mo}(\text{Ntol})(\text{DMAC})\text{L}_2$. Solutions of $\text{Mo}(\text{Ntol})\text{L}_2$ react with O_2 to regenerate $\text{MoO}(\text{Ntol})\text{L}_2$; this reaction, in combination with the above oxygen-abstraction reaction, thus completes a catalytic cycle for the oxidation of tertiary phosphines. Solutions containing $\text{Mo}(\text{Ntol})\text{L}_2$ react similarly with Me_2SO to afford Me_2S and $\text{MoO}(\text{Ntol})\text{L}_2$.

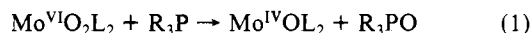
Introduction

An important aspect of the reactivity of *cis*-dioxo-molybdenum(VI) complexes is their ability to function as oxygen atom transfer reagents. By far, the most extensively studied class of such reactions involves oxygen atom transfer to tertiary-phosphine substrates.¹⁻²¹ In all cases, the initial products of these

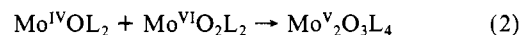
Table I. Molar Absorptivity ($\lambda = 533$ nm) vs. Concentration of $[\text{Mo}(\text{Ntol})(\text{S}_2\text{CNET}_2)_2]_2\text{O}$ in Toluene Solution

concn, M	molar abs	concn, M	molar abs
9.6×10^{-6}	9 120	3.86×10^{-5}	14 560
1.93×10^{-5}	14 040	1.11×10^{-4}	15 800

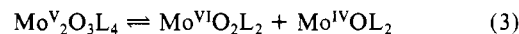
reactions are an oxomolybdenum(IV) species and a tertiary-phosphine oxide as depicted in eq 1. However, in most but not



all²² instances, the nascent $\text{Mo}^{\text{IV}}\text{OL}_2$ species is rapidly intercepted by unreacted $\text{Mo}^{\text{VI}}\text{O}_2\text{L}_2$, producing an oxo-bridged Mo(V) dimer, $\text{Mo}_2\text{O}_3\text{L}_4$ (eq 2). The ultimate isolation of $\text{Mo}^{\text{IV}}\text{OL}_2$ products



in these systems depends upon the reversibility of eq 2; that is, the $\text{Mo}_2\text{O}_3\text{L}_4$ species must participate in the disproportionation equilibrium depicted in eq 3.²³ Disproportionation of the



$\text{Mo}_2\text{O}_3\text{L}_4$ species is markedly dependent on the nature of the donor atoms provided by the ligands L. Thus, S,S chelates (dithiocarbamates,^{1,3,9} dithiophosphates,^{3,24} dithiophosphinates,³

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