Mg_2CoD_5 is presumably nonmetallic, and it shows no detectable homogeneity range within experimental resolution. In view of its structural and electronic similarities to the related hydrides Mg_2NiD_4 and Mg_2FeD_6, it is reasonable to rationalize its bonding in terms of divalent magnesium cations and tetravalent hydrido–transition-metal anions that satisfy the 18-electron rule. Its relatively low magnetic susceptibility ($\chi_g = 3\ (2) \times 10^{-6}$ emu/g) favors a low-spin state for the Co(I) ions. It does not favor a high-spin state because square-pyramidal d^8 high-spin systems show relatively strong paramagnetic behavior ($\chi_g > 10 \times 10^{-6}$ emu/g as reported for compounds containing high-spin Ni^{2+}.[16] The thermal stability of Mg_2CoH_5 (86 (5) kJ/mol of H_2) is higher than that of Mg_2NiH_4 (64 kJ/mol of H_2) but lower than that of Mg_2FeH_6 (98 (3) kJ/mol of H_2). Its volume and weight efficiency for hydrogen storage (4.5 wt %, 7.5 × 10^{22} H atoms/cm^3) are intermediate between those of Mg_2NiH_4 (3.6 wt %, 5.8 × 10^{22} H atoms/cm^3) and Mg_2FeH_6 (5.4 wt %, 9.0 × 10^{22} H atoms/cm^3).

Acknowledgment. This work was supported financially by the Swiss Energy Research Foundation (NEFF). The help of A. F. Williams (chemical purification), B. Seeber (electrical conductivity measurements), A. Bezinge (magnetic susceptibility measurements), and L. Schlapbach and P. Brack (desorption measurements) is gratefully acknowledged.

Registry No. Mg_2CoH_5, 98586-77-7; Mg_2CoD_5, 98586-78-8; Mg, 7439-95-4; Co, 7440-48-4; H_2, 1333-74-0; D_2, 7782-39-0.

Supplementary Material Available: Tables of raw neutron diffraction data (298 K) and the results of the structure refinement including structural data for Mg_2CoD_5 and MgD_2, profile parameters, *R* factors, and background values (7 pages). Ordering information is given on any current masthead page.

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(16) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Reactions of the Dicarbonyl Complex $Re_2Cl_4(dppm)_2(CO)_2$ with Nitriles and Isocyanides. Synthesis of $[Re_2Cl_3(dppm)_2(CO)_2L]^{n+}$ (n = 0, 1; L = RCN, RNC) and the Structural Characterization of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$

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The dicarbonyl complex $Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)$ (dppm = bis(diphenylphosphino)methane) reacts with nitriles (RCN) and isocyanides (RNC) in the presence of $TlPF_6$ to generate cations of stoichiometry $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = CH_3CN, C_2H_5CN, C_6H_5CN, Me_2CHNC, Me_3CNC). These complexes exhibit a well-defined electrochemistry including a chemically accessible reduction ($E_{1/2} \simeq -0.1$ V vs. Ag/AgCl). The reactions of cobaltocene with these salts produce the paramagnetic neutral complexes $Re_2Cl_3(dppm)_2(CO)_2L$, the first examples of multiply bonded dirhenium complexes that possess the Re_2^{3+} core. The nitrile compound $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6\cdot CH_2Cl_2\cdot {}^1/_2(C_2H_5)_2O$ has been characterized by X-ray crystallography. It forms crystals in space group $P\bar{1}$ with $Z = 2$ and the following unit cell dimensions: a = 16.574 (5) Å, b = 17.617 (6) Å, c = 12.238 (3) Å, α = 101.94 (2)°, β = 107.64 (2)°, γ = 65.54 (2)°, V = 3086 (2) Å^3. The cation is an edge-sharing bioctahedron with one bridging CO and one bridging Cl. The central plane containing the shared edge has the EtCN, μ-CO, and CO ligands along one side and three Cl atoms along the other. The bridging bidentate dppm ligands occupy the positions above and below this plane. The Re–Re distance is 2.586 (1) Å, the average Re–P distance is 2.472 [5] Å, the Re–CO(terminal) distance is 1.92 (2) Å, and the two Re–CO(bridge) distances are 2.00 (2) and 2.13 (2) Å. The Re–Cl(bridge) distances, 2.473 (5) and 2.448 (4) Å, are longer than the Re–Cl(terminal) distances, 2.407 (5) and 2.419 (5) Å, as expected. This structure provides further insight into the structure of the $Re_2Cl_4(dppm)_2(CO)_2$ molecule, which forms systematically disordered crystals.

Introduction

Studies involving the reactions of the electron-rich triply bonded complex $Cl_2Re(\mu\text{-}dppm)_2ReCl_2$ (dppm = bis(diphenylphosphino)methane) are presently being conducted in our laboratory. This compound displays a surprising reactivity toward nitriles and pyridine,[2] as well as toward isocyanide ligands[3] and carbon monoxide.[4] The carbonylation reactions of $Re_2Cl_4(dppm)_2$ led to the discovery of the fluxional molecules $Re_2Cl_4(dppm)_2(CO)_n$ (n = 1, 2), the first examples of dinuclear carbonyl derivatives of this type in which a M–M bond is retained.[4] The green dicarbonyl species was shown by X-ray crystallography to possess the edge-shared bioctahedral structure $Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)$. However, due to a disorder problem it was not possible to distinguish between a cis and trans disposition of the bridging and terminal carbonyl groups.[4]

As part of our efforts to develop the chemistry of this unusual dicarbonyl complex, we investigated its reactivity with the intent of preparing derivatives that could be readily characterized and that would in turn allow us to ascertain the stereochemistry of the carbonyl ligands. Although this molecule is relatively unreactive under ordinary conditions, it can be induced to undergo substitution reactions with a variety of ligands in the presence of $TlPF_6$. In the present report we describe the synthesis and characterization of the diamagnetic salts $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = RCN, RNC) together with some details of the analogous paramagnetic neutral complexes, which are prepared by the cobaltocene reductions of the monocations. The latter species constitute the first examples of dirhenium complexes that possess the Re_2^{3+} core. The results of a single-crystal X-ray diffraction study of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$ are also described.

Experimental Section

Starting Materials. The complex $Re_2Cl_4(dppm)_2(CO)_2$ was prepared as previously described from the reaction of $Re_2Cl_4(dppm)_2$ with carbon monoxide in dichloromethane.[4] Nitriles and other common solvents were obtained from commercial sources and were stored over molecular sieves. The *tert*-butyl and isopropyl isocyanide ligands were prepared according to a standard literature procedure.[5] Bis(diphenylphosphino)methane

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(1) (a) Texas A&M University. (b) Purdue University.

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0020-1669/85/1324-4180$01.50/0

(dppm) and cobaltocene were obtained from Strem Chemicals and were used without further purification.

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

A. Reactions of $Re_2Cl_4(dppm)_2(CO)_2$ with Nitriles. (i) $[Re_2Cl_3(dppm)_2(CO)_2(NCCH_3)]PF_6$. A solution containing $Re_2Cl_4(dppm)_2(CO)_2$ (0.18 g, 0.13 mmol) and $TlPF_6$ (0.06 g, 0.17 mmol) in 10 mL of acetone–acetonitrile (1:1) was stirred at room temperature for 24 h. The resulting green solution was filtered to remove the precipitated TlCl, and the filtrate was evaporated to dryness. The residue was extracted with dichloromethane, to give a green solution plus a small amount of insoluble unreacted $TlPF_6$. Diethyl ether was added to the filtrate to initiate precipitation, and the yellow-green crystals were filtered off and recrystallized from acetone–hexane mixtures; yield 0.19 g (95%). Anal. Calcd for $C_{54}H_{47}Cl_3F_6NO_2P_5Re_2$: C, 43.54; H, 3.18. Found: C, 43.31; H, 3.08.

(ii) $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$. A quantity of $Re_2Cl_4(dppm)_2(CO)_2$ (0.30 g, 0.224 mmol) was added to a solution of $TlPF_6$ (0.11 g, 0.34 mmol) in 10 mL of neat propionitrile. The reaction mixture was stirred for 14 h at room temperature and then treated with copious amounts of diethyl ether to precipitate the product. The resulting crude solid was washed with dichloromethane to separate the desired product from the insoluble impurities. Evaporation of the dichloromethane washings yielded a green residue, which was recrystallized from acetone–diethyl ether; yield 0.30 g (89%). Anal. Calcd for $C_{55}H_{49}Cl_3F_6NO_2P_5Re_2$: C, 43.93; H, 3.28. Found: C, 43.63; H, 3.66.

(iii) $[Re_2Cl_3(dppm)_2(CO)_2(NCC_6H_5)]PF_6$. A mixture of $Re_2Cl_4(dppm)_2(CO)_2$ (0.13 g, 0.098 mmol) and $TlPF_6$ (0.05 g, 0.143 mmol) in acetone (10 mL) and benzonitrile (5 mL) was allowed to react for 10 h. The yellow-green reaction mixture was then filtered to remove insoluble TlCl and the filtrate reduced in volume under a stream of gaseous nitrogen. When the acetone solvent was evaporated, the product began to form an oil. Accordingly, an excess of KPF_6 was added to aid the precipitation of the PF_6^- salt. The mixture was stirred for a period of 1 h, and the solution was treated with an excess of diethyl ether to yield an impure solid, which was filtered off and washed with several portions of dichloromethane. The dark gold colored product was precipitated from the dichloromethane washings by the addition of diethyl ether and recrystallized from acetone–diethyl ether; yield 0.123 g (82%). Anal. Calcd for $C_{59}H_{49}Cl_3F_6NO_2P_5Re_2$: C, 45.67; H, 3.18. Found: C, 45.50; H, 3.22.

B. Reactions of $Re_2Cl_4(dppm)_2(CO)_2$ with Isocyanides. (i) $[Re_2Cl_3(dppm)_2(CO)_2(CNCHMe_2)]PF_6$. A mixture comprising $Re_2Cl_4(dppm)_2(CO)_2$ (0.15 g, 0.112 mmol), $TlPF_6$ (0.05 g, 0.143 mmol) and 1 equiv of Me_2CHNC (11 μL, 0.12 mmol) in dichloromethane (15 mL) was stirred for 12 h at room temperature. The resulting green solution was filtered to remove insoluble impurities, and the bright green filtrate was treated with diethyl ether (10 mL) and chilled to 0 °C for 5 h. The yellow-green crystals were filtered off, washed with diethyl ether, and dried under reduced pressure; yield 0.12 g (78%). Anal. Calcd for $C_{56}H_{51}Cl_3F_6NO_2P_5Re_2$: C, 44.32; H, 3.39; Cl, 7.01. Found: C, 43.88; H, 3.62; Cl, 7.64.

The filtrate from the above reaction yielded a small amount of an emerald green solid, but IR spectroscopy and electrochemical measurements revealed it to be a mixture of products.

(ii) $[Re_2Cl_3(dppm)_2(CO)_2(CNCMe_3)]PF_6$. A dichloromethane solution (15 mL) containing $Re_2Cl_4(dppm)_2(CO)_2$ (0.20 g, 0.15 mmol), $TlPF_6$ (0.07 g, 0.20 mmol), and 20 μL (0.19 mmol) of Me_3CNC was stirred for 15 h. This yielded a crop of yellow-green crystals following a workup procedure identical with that described in part B(i); yield 0.18 g (79%). Anal. Calcd for $C_{57}H_{53}Cl_3F_6NO_2P_5Re_2$: C, 44.70; H, 3.49. Found: C, 44.58; H, 3.89.

C. Reactions of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$. (i) Reaction with Isocyanide. In a typical reaction, $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$ (0.10 g, 0.067 mmol) and Me_3CNC (8 μL, 0.076 mmol) were stirred in dichloromethane (10 mL) for 12 h at room temperature. The yellow-green solution was evaporated to dryness, and the residue was recrystallized from acetone–diethyl ether; yield 0.08 g (80%). The product was identified as $[Re_2Cl_3(dppm)_2(CO)_2(CNCMe_3)]PF_6$ by a comparison of its electrochemical and IR spectral properties with those obtained for samples of the authentic fully characterized complex (see part B(ii)).

(ii) Reaction with Carbon Monoxide. A dichloromethane solution of the propionitrile complex did not react with CO under reaction conditions that were similar to those employed in part C(i). The recovered starting material was identified on the basis of its IR spectral properties.

D. Reactions of $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ with Cobaltocene. (i) L = CH_3CN. A quantity of $[Re_2Cl_3(dppm)_2(CO)_2(NCCH_3)]PF_6$ (0.10 g, 0.067 mmol) was added to a solution of cobaltocene (0.15 g, 0.079 mmol) in acetone (10 mL). A green to blue color change ensued, with the precipitation of a bright blue product within 0.5 h. The solid was filtered off under nitrogen and washed with small amounts of acetone to remove unreacted cobaltocene as well as any $[Cp_2Co]PF_6$ that had been formed; yield 0.085 g (95%). Anal. Calcd for $C_{54}H_{47}Cl_3NO_2P_4Re_2$: C, 48.24; H, 3.52. Found: C, 48.15; H, 3.64.

(ii) L = C_2H_5CN. A procedure analogous to that described in part D(i) was used; viz. 0.12 g (0.080 mmol) of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$ and cobaltocene (0.20 g, 0.10 mmol) were stirred in 10 mL of acetone for 15 min; yield 0.10 g (90%). This complex was recrystallized from dichloromethane–diethyl ether mixtures and identified by IR and ESR spectroscopy and by cyclic voltammetry.

(iii) L = C_6H_5CN. The reaction between $[Re_2Cl_3(dppm)_2(CO)_2(NCC_6H_5)]PF_6$ (0.10 g, 0.064 mmol) and cobaltocene (0.016 g, 0.08 mmol) in 5 mL of acetone produced a blue solid; yield 0.080 g (89%). The identity of this product was established by IR and ESR spectroscopy and by cyclic voltammetry.

(iv) L = Me_2CHNC. A mixture of $[Re_2Cl_3(dppm)_2(CO)_2(CNCHMe_2)]PF_6$ (0.10 g, 0.066 mmol) and cobaltocene (0.013 g, 0.07 mmol) in 10 mL of acetone was stirred for 0.5 h. The resulting blue product was filtered off, washed with acetone, and dried in vacuo; yield 0.075 g (83%). This product, unlike the analogous nitrile complexes, appears to be quite stable in solution and was recrystallized from dichloromethane–diethyl ether. Anal. Calcd for $C_{56}H_{51}Cl_3NO_2P_4Re_2$: C, 48.99; H, 3.75. Found: C, 46.72; H, 4.16. We were unable to prepare an analytically pure sample of this complex although it had spectroscopic and electrochemical properties that were essentially identical with those of its *tert*-butyl isocyanide analogue. We have been unable to identify the nature of the minor contaminant that is present.

(v) L = Me_3CNC. The neutral *tert*-butyl isocyanide complex was obtained by a procedure similar to that described in part D(iv) but with the use of $[Re_2Cl_3(dppm)_2(CO)_2(CNCMe_3)]PF_6$ (0.083 g, 0.054 mmol) and 0.011 g (0.058 mmol) of cobaltocene in 7 mL of acetone; yield 0.07 g (93%). Anal. Calcd for $C_{57}H_{53}Cl_3NO_2P_4Re_2$: C, 49.37; H, 3.85. Found: C, 48.67; H, 4.04.

Preparation of Single Crystals of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$. Crystals of $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$ that were suitable for X-ray crystallographic studies could be grown by dissolving a sample of the complex in dichloromethane and carefully layering diethyl ether on top of this solution. Well-faceted crystals were deposited at the bottom of the flask after several days. These crystals were found to lose solvent molecules rapidly, with concomitant degeneration of the single-crystal diffraction pattern into one resembling a powder pattern. The sample was redissolved in a 1:1 mixture of dichloromethane and diethyl ether, and the solvent was allowed to evaporate over a period of several hours. Smaller, less regular crystals were formed, and several of these were mounted immediately on glass fibers and covered with coats of epoxy.

X-ray Structure Analysis. Geometric and intensity data were measured by an automated four-circle diffractometer (Nicolet P3/F) from a crystal of dimensions 0.28 × 0.22 × 0.13mm, which was prepared and mounted as described above. The procedures employed for data collection have been described previously.[6] The crystal was found to be triclinic. The unit-cell parameters (Table I) and orientation matrix were refined by a least-squares fit to the positions of 23 reflections in the range $20 < 2\theta < 30°$. The lattice dimensions were verified by axial photography.

The ω-scan technique was used to scan 9806 possible data points in the range $4.0 \leq 2\theta \leq 47.0°$. Three standard reflections, measured after every 97 data points, lost an average of 8.3% of their initial intensities during the 304 hours of X-ray exposure time.

The X-ray data were reduced by routine methods.[7] Azimuthal scans of nine reflections were used as the basis of an empirical absorption correction.[7b] After equivalent data were averaged, there remained 7590 unique structure factors, of which 4557 with $F_o^2 \geq 3\sigma(F_o^2)$ were used in the development and refinement of the structure.

The positions of the two unique rhenium atoms were derived from a Patterson map. The structure was developed and refined in a series of alternating least-squares analyses and difference Fourier maps. All of

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(5) Weber, W. D.; Gobel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

(6) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(7) (a) Data processing was done on a PDP-11/60 (RSX-11M V4.1) computer with PDP-11 simulated VAXSDP, and on a VAX-11/780 (VMS V3.6) computer, with programs from the package VAXSDP. (b) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

Table I. Crystal Data for $[Cl(EtCN)Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)]PF_6\cdot CH_2Cl_2\cdot 0.5Et_2O$

formula	$Re_2Cl_5P_5F_6O_{2.5}NC_{58}H_{56}$
fw	1625.6
space group	$P\bar{1}$
a, Å	16.574 (5)
b, Å	17.617 (6)
c, Å	12.238 (3)
α, deg	101.94 (2)
β, deg	107.64 (2)
γ, deg	65.54 (2)
V, Å^3	3086 (2)
Z	2
d_{calcd}, g/cm^3	1.749
cryst size, mm	0.28 × 0.22 × 0.13
μ(Mo Kα), cm^{-1}	45.5
data collecn instrument	Nicolet P3/F
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientation reflecns: no., range (2θ)	23, 20–30
temp, °C	22 ± 1
scan method	ω scans
data collecn range, 2θ, deg	4–47
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	7590, 4557
no. of parameters refined	647
transmission factors: max, min	calcd 0.55, 0.18; obsd 1.00, 0.78
R^a	0.0566
$R_w^{\ b}$	0.0693
quality-of-fit indicator^c	1.261
largest shift/esd, final cycle	0.19
largest peak, e/Å^3	1.28

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

the remaining atoms of the complex cation $[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]^+$ were located and refined, with the exception of the β-carbon atom of the propionitrile group (vide infra); all of the atoms located in the cation were refined anisotropically, as was the phosphorus atom of the PF_6^- counterion. In addition, one CH_2Cl_2 molecule on a general position was located and refined, and a molecule of diethyl ether was found in a position disordered about a crystallographic inversion center. The atoms of the last two groups, as well as the fluorine atoms of the PF_6^- anion, were refined isotropically.

In each of the lattice molecules, two of the three crystallographically unique atoms were refined with thermal parameters in good agreement with the values expected for this type of site. The third atom in each case converged with a somewhat larger thermal parameter. (See Table II.) We attribute this to static rather than dynamic effects—that is, to slight differences in the positions of the respective atoms in different unit cells. The "thermal" parameters of atom Cl(5) of the CH_2Cl_2 molecule and atom C(56) of the disordered Et_2O molecule represent root-mean-square displacements of ca. 0.5 Å; such values are common in lattice molecules.

In the final refinement, then, 4557 data were used to fit 647 variable parameters (data:parameter ratio 7.0), giving covergence with residuals (defined and summarized in Table I) of $R = 0.0566$, $R_w = 0.0693$, and quality of fit 1.261. The final least-squares cycle did not shift any parameter by more than 0.19 times its estimated standard deviation.

A difference Fourier map, following convergence of the refinement, had a peak of density 1.28 e/Å^3 located within 1 Å of the phosphorus atom of the PF_6^- anion. Several disordered models were developed and refined for this group; however, none gave results that were chemically acceptable. We report the coordinates of the PF_6^- group refined in the original model, without disorder, since the evident disorder is not of sufficient proportion to allow construction and refinement of a reasonable model. The coordinates reported give acceptable, although not ideal, derived parameters.

The β-carbon atom of the propionitrile group was neither refined nor included in the calculation of structure factors. This atom is free to move in a circular path about an extension of the vector from (N)C to Cα (i.e., from C(3) to C(4); see Figure 1). A section of the final difference map, taken in the plane in which the β-carbon atom can lie, shows a semiannular region of electron density characteristic of a dynamic disorder. Although three areas of slightly greater electron density opened the possibility of refining a disordered model, we found that, as expected, any combination of positional and displacement parameters for the disordered congeners of the β-carbon atom was highly covariant. This result, coupled with the strong indication of dynamic disorder, leaves open only one valid, practicable option—to omit the β-carbon atom from the calculations. (This is not a common occurrence in structural inorganic chemistry, but it is well-known in structural biochemistry.)

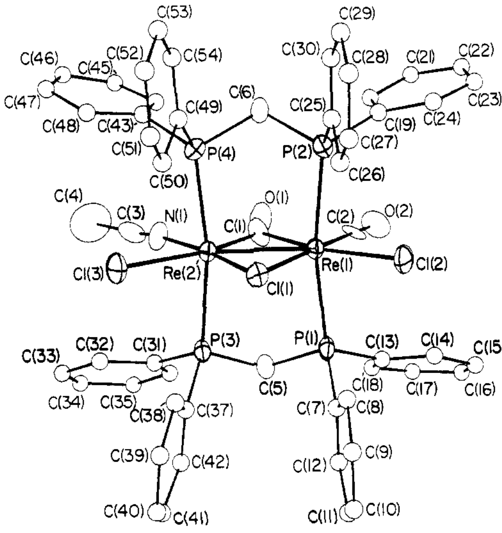

Figure 1. ORTEP plot of the complex cation $[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]^+$, showing the atom-labeling scheme. Phenyl-group carbon atoms are shown as small circles, for clarity. All other atoms are represented by their 40% probability ellipsoids.

Positional and equivalent isotropic displacement parameters are listed in Table II. Tables III and IV list the important distances and angles, respectively. A perspective drawing of the complex cation, $[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]^+$, is given in Figure 1.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates or as dichloromethane solutions with an IBM Instruments IR 32 Fourier transform (4000–400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 (900–300 nm) and Cary 17 (1800–900 nm) UV–visible spectrophotometers. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were 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. X-Band ESR spectra of frozen dichloromethane solutions were recorded at −160 °C with the use of a Varian E-109 spectrometer. Conductivity measurements were performed on 1 × 10^{-3} M acetone solutions with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz using an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on Varian XL-200 or Perkin-Elmer R-32 90-MHz spectrometers. Resonances were referenced internally to the impurity in the deuterated solvent.

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

Results and Discussion

(a) Synthesis and Preliminary Characterization of $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = CH_3CN, C_2H_5CN, C_6H_5CN, Me_2CHNC, or Me_3CNC). Dichloromethane solutions of the complex $Re_2Cl_4(dppm)_2(CO)_2$ do not undergo substitution reactions with isocyanide or nitrile ligands even under reflux conditions and with reaction times of up to 24 h. This presumably reflects the kinetic inertness of this very stable edge-shared bioctahedral structure. However, these reactions do proceed in the presence of $TlPF_6$ to generate, in high yield, the diamagnetic species $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$, in which a chloride ion has been replaced by a neutral isocyanide or nitrile ligand. The byproduct of the reaction, TlCl, precipitates from the reaction solution, thereby allowing for its easy separation from the soluble dirhenium cations.

IR and electronic absorption spectral data along with the molar conductance data are summarized in Table V. Conductivity

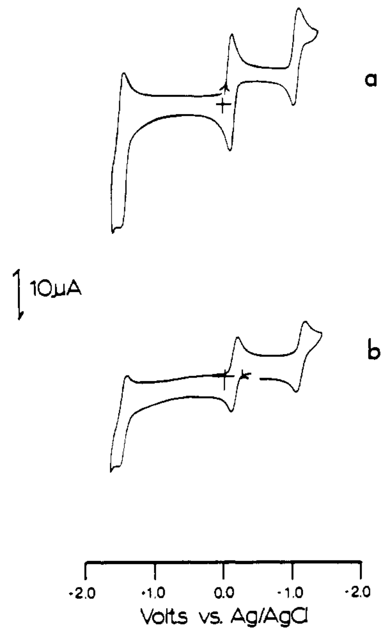

Figure 2. Cyclic voltammograms (scan rate 200 mV/s at a Pt-bead electrode) in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane: (a) $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$; (b) $Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)$.

measurements performed on 1×10^{-3} M acetone solutions confirm the formulation of these complexes as 1:1 electrolytes (Λ_m = 110–130 Ω^{-1} cm^2 mol^{-1}). In the case of the nitrile derivatives, a weak feature in their Nujol mull IR spectra (2260–2190 cm^{-1}) is assignable to the ν(CN) mode. The isocyanide complexes exhibit a single, sharp band in the region 2200–2185 cm^{-1}, which is attributed to ν(CN) of a terminally bound isocyanide ligand.

The IR spectra in the ν(CO) region show the presence of two bands located close to 2000 and 1700 cm^{-1}, which are assigned to terminal and bridging carbonyl ligands, respectively. These spectra resemble very closely that of the parent dicarbonyl complex $Cl_2Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)$ and suggest a similarity in structure between these complexes, a conclusion that has been substantiated by a single-crystal X-ray structure determination of the propionitrile derivative (see part b of Results and Discussion). In the case of the nitrile and isocyanide derivatives, this close structural relationship is further reflected in the ease of converting $[Re_2Cl_3(dppm)_2(CO)_2(NCC_2H_5)]PF_6$ to $[Re_2Cl_3(dppm)_2(CO)_2(CNCMe_3)]PF_6$ upon reaction of the former with 1 equiv of *tert*-butyl isocyanide.

The electronic absorption spectra of the nitrile complexes exhibit a broad band of moderate intensity at ca. 850 nm ($\epsilon_{max} \simeq 200$) and a much more intense transition at ca. 420 nm ($\epsilon_{max} \simeq 5500$) in the visible region. Two absorption maxima are also observed in the case of the isocyanide derivatives, although both these bands are shifted to lower energies (Table V).

Cyclic voltammetric data for the complexes $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ are given in Table VI. A representative cyclic voltammogram is shown in Figure 2. As reported earlier,[4] $Re_2Cl_4(dppm)_2(CO)_2$ exhibits two oxidations ($E_{1/2}$ = +1.75 and +0.91 V) and two reductions ($E_{1/2}$ = −0.57 V and $E_{p,c}$ = −1.6 V vs. SCE). In contrast, solutions of the nitrile complexes in 0.2 M TBAH–dichloromethane exhibit a reversible one-electron oxidation at $E_{1/2}$ = +1.45 V and two reversible one-electron reductions at $E_{1/2} \simeq$ −0.12 and −1.10 V vs. Ag/AgCl. These redox processes are, therefore, shifted to more positive potentials (by ~+0.5 V) compared to those of the parent complex. This leads to the disappearance of the second oxidation (it presumably shifts to a potential above that accessed by our measurements) and results in the first reduction becoming quite accessible chemically (vide infra). This result can be rationalized in terms of the replacement of a negatively charged chloride ligand by a neutral nitrile or isocyanide ligand, with the concomitant formation of a cationic complex. This can be expected to be more difficult to oxidize but much less difficult to reduce. The *tert*-butyl and isopropyl isocyanide complexes also possess one oxidation and two reductions (both reversible), but the potentials for all three couples are shifted to more positive potentials (by up to 0.2 V) relative to the nitrile-containing derivatives (Table VI). This reflects the effect of binding a moderate π-acceptor ligand such as RNC to the dimetal center compared to the σ-donor RCN ligands. The former are more likely to remove electron density, thereby leading to an increase in relative positive charge and increase in the difficulty of oxidizing such a species.

(b) Crystal Structure of $[Cl(EtCN)Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)]PF_6\cdot CH_2Cl_2\cdot 0.5Et_2O$. The structure of the complex cation, comprising an edge-sharing pair of octahedra, is similar in its general features to the structures of $Re_2Cl_4(dppm)_2(CO)_2$[4] and $Re_2Cl_6(dppm)_2$.[8] In the case of the dicarbonyl complex,[4] a crystallographic disorder prevented the determination of whether the carbonyl groups were cis or trans (or both) to each other. In the present case, in which the substitution of a propionitrile ligand for a chlorine atom evidently introduces space-filling properties sufficient to militate against disorder, we observe that both of the terminal π-bonding ligands are cis to the bridging carbonyl group (see Figure 1). The terminal –CO and –NCEt ligands are not swept back as far as the terminal chlorine atoms: The average Re–Re–Cl$_t$ angle[9] is 148.3 [9]°, while the angle Re(2)–Re(1)–C(2) is 120.9 (7)° and Re(1)–Re(2)–N(1) is 130.8 (5)°. These values are in line with those found in $Re_2Cl_6(dppm)_2$ (average Re–Re–Cl$_t$ = 138.8 [4]°) and its dicarbonyl derivative (average Re–Re–Cl$_t$ = 141.3 [7]°; average Re–Re–C$_t$ = 125 [2]°).

The Re–Re bond length of 2.586 (1) Å in the present complex is almost identical with the value of 2.584 (1) Å found in $Re_2Cl_4(dppm)_2(CO)_2$. Both of these complexes contain formal Re_2^{4+} cores, and yet the metal–metal bond distances are quite similar to the value of 2.616 (1) Å found in the doubly bonded complex $Re_2Cl_6(dppm)_2$, which has a Re_2^{6+} core. They are far removed from the values between 2.2 and 2.3 Å found[10] in the triply bonded, Re_2^{4+}-containing complexes of the type $Re_2X_4L_4$. These results can be understood, as previously suggested,[4] if the bridging carbonyl group is regarded as being divalent, thus giving a Re_2^{6+} core. In any event, it is clear that the bonding in these edge-sharing bioctahedral complexes containing π-acceptor ligands is quite different from that in other compounds with formal Re_2^{4+} cores.

The Re_2P_2C rings in the complex cation are in half-chair conformations. Both of the bridging methylene groups are folded to the same side of the complex, the side on which the π-bonding ligands are located. Since an anti folding pattern was observed in the complex $Re_2Cl_4(dppm)_2(CO)_2$, which has a metal–metal bond length nearly identical with that in the present case, we can conclude that the conformations of the Re_2P_2C rings do not cause, or reflect, any internal electronic effects. Thus, the patterns we observe result from crystal-packing requirements.

(c) NMR Spectroscopy. The ^{1}H and $^{31}P\{^1H\}$ NMR spectra were recorded for the diamagnetic complexes $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = RCN, RNC). The data are summarized in Table VI. The identity and stoichiometry of the products was confirmed by integration of the ^{1}H NMR resonances of the isocyanide or nitrile ligand to the methylene protons of the dppm ligands. The dppm methylene region for the acetonitrile and propionitrile derivatives consists of a second-order AB pattern with superimposed P–H coupling, corresponding to two different environments for the bridgehead protons. Analysis of the spectrum of the acetonitrile complex led[11] to chemical shifts δ_A = 4.16 and δ_B = 4.41 and coupling constants J(P–H) = 4.3 Hz and $J(H_A\text{–}H_B)$

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(8) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

(9) The deviation in brackets is calculated as $[(\sum_i \Delta_i^2/n(n-1))]^{1/2}$, in which Δ_i is the deviation of the *i*th value from the mean of the set of *n* elements.

(10) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982.

(11) Becker, E. D. "High Resolution NMR Theory and Chemical Applications"; Academic Press: New York, 1980; P 138.

Table II. Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) and Their Estimated Standard Deviations for $[Cl(EtCN)Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)]PF_6{\cdot}CH_2Cl_2{\cdot}0.5Et_2O$[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.34573 (5)	0.21095 (5)	0.18824 (6)	2.38 (2)
Re(2)	0.24795 (5)	0.31303 (5)	0.32592 (6)	2.34 (2)
Cl(1)	0.3186 (3)	0.1623 (3)	0.3445 (4)	2.6 (1)
Cl(2)	0.4406 (4)	0.0705 (3)	0.1323 (5)	4.5 (2)
Cl(3)	0.1849 (4)	0.3307 (3)	0.4879 (4)	4.4 (2)
P(1)	0.2180 (3)	0.1803 (3)	0.0470 (4)	2.6 (1)
P(2)	0.4919 (3)	0.2189 (3)	0.3101 (4)	3.0 (1)
P(3)	0.1019 (3)	0.3033 (3)	0.2055 (4)	2.5 (1)
P(4)	0.3768 (3)	0.3403 (3)	0.4694 (4)	3.0 (1)
C(1)	0.275 (1)	0.343 (1)	0.196 (1)	3.0 (5)
O(1)	0.2645 (9)	0.4006 (7)	0.148 (1)	4.2 (4)
C(2)	0.362 (1)	0.251 (1)	0.065 (2)	3.8 (5)
O(2)	0.3717 (9)	0.272 (1)	−0.007 (1)	6.6 (5)
N(1)	0.180 (1)	0.4395 (9)	0.333 (1)	3.8 (5)
C(3)	0.139 (1)	0.504 (1)	0.336 (2)	4.0 (6)
C(4)	0.082 (2)	0.603 (2)	0.354 (3)	10 (1)
C(5)	0.111 (1)	0.275 (1)	0.056 (1)	2.8 (5)
C(6)	0.467 (1)	0.322 (1)	0.395 (2)	3.5 (5)
C(7)	0.191 (1)	0.091 (1)	0.050 (1)	3.0 (5)
C(8)	0.251 (1)	0.028 (1)	0.125 (1)	2.9 (5)
C(9)	0.223 (1)	−0.037 (1)	0.127 (2)	3.9 (6)
C(10)	0.146 (1)	−0.046 (1)	0.049 (2)	3.9 (6)
C(11)	0.094 (1)	0.012 (1)	−0.029 (2)	5.0 (6)
C(12)	0.114 (1)	0.083 (1)	−0.029 (2)	3.2 (5)
C(13)	0.223 (1)	0.170 (1)	−0.105 (1)	2.4 (4)*
C(14)	0.290 (2)	0.098 (1)	−0.141 (2)	4.5 (7)
C(15)	0.294 (1)	0.087 (1)	−0.258 (2)	4.7 (6)
C(16)	0.237 (2)	0.150 (1)	−0.330 (2)	5.4 (7)
C(17)	0.177 (2)	0.223 (1)	−0.290 (2)	5.7 (7)
C(18)	0.166 (1)	0.231 (1)	−0.177 (2)	4.9 (6)
C(19)	0.564 (1)	0.220 (1)	0.225 (1)	3.1 (5)
C(20)	0.550 (1)	0.293 (1)	0.182 (2)	5.1 (7)
C(21)	0.605 (2)	0.293 (1)	0.112 (2)	5.2 (7)
C(22)	0.674 (1)	0.216 (1)	0.087 (2)	5.5 (7)
C(23)	0.688 (2)	0.140 (2)	0.129 (2)	6.5 (8)
C(24)	0.638 (2)	0.143 (1)	0.201 (2)	6.6 (8)
C(25)	0.569 (1)	0.141 (1)	0.416 (2)	3.4 (5)
C(26)	0.547 (1)	0.075 (1)	0.416 (1)	3.1 (5)
C(27)	0.610 (1)	0.014 (1)	0.498 (2)	4.4 (7)
C(28)	0.686 (2)	0.024 (1)	0.569 (2)	5.7 (8)
C(29)	0.706 (1)	0.091 (2)	0.564 (2)	5.7 (8)
C(30)	0.645 (1)	0.152 (1)	0.486 (2)	3.4 (6)
C(31)	0.003 (1)	0.404 (1)	0.193 (2)	3.1 (5)
C(32)	−0.029 (2)	0.435 (1)	0.293 (2)	5.5 (7)
C(33)	−0.111 (2)	0.512 (2)	0.287 (2)	8.5 (9)
C(34)	−0.153 (2)	0.554 (2)	0.188 (3)	8 (1)
C(35)	−0.120 (2)	0.520 (2)	0.086 (3)	11 (1)
C(36)	−0.037 (2)	0.442 (1)	0.097 (2)	5.7 (8)
C(37)	0.056 (1)	0.235 (1)	0.238 (1)	3.0 (5)
C(38)	0.103 (1)	0.183 (1)	0.333 (2)	4.7 (6)
C(39)	0.060 (2)	0.134 (1)	0.352 (2)	7.1 (7)
C(40)	−0.024 (2)	0.136 (1)	0.279 (3)	8.1 (9)
C(41)	−0.073 (2)	0.194 (2)	0.195 (3)	9 (1)
C(42)	−0.031 (1)	0.242 (2)	0.163 (2)	6.4 (8)
C(43)	0.349 (1)	0.452 (1)	0.526 (2)	4.0 (6)
C(44)	0.345 (1)	0.510 (1)	0.463 (2)	4.5 (6)
C(45)	0.312 (2)	0.598 (1)	0.503 (2)	6.4 (9)
C(46)	0.291 (2)	0.619 (2)	0.611 (2)	8 (1)
C(47)	0.292 (2)	0.559 (2)	0.673 (3)	8 (1)
C(48)	0.318 (2)	0.473 (1)	0.628 (2)	6.3 (9)
C(49)	0.440 (1)	0.283 (1)	0.599 (1)	3.3 (5)
C(50)	0.404 (2)	0.230 (1)	0.626 (2)	5.3 (7)
C(51)	0.457 (2)	0.184 (2)	0.723 (2)	6.2 (8)
C(52)	0.530 (2)	0.201 (2)	0.795 (2)	6.3 (9)
C(53)	0.561 (1)	0.257 (2)	0.769 (2)	6.8 (8)
C(54)	0.513 (1)	0.299 (1)	0.673 (2)	5.2 (7)
P(5)	0.1639 (3)	0.7405 (3)	0.1879 (5)	3.9 (1)
F(1)	0.236 (2)	0.736 (2)	0.255 (3)	20 (1)*
F(2)	0.077 (2)	0.735 (2)	0.148 (3)	21 (1)*
F(3)	0.194 (2)	0.728 (2)	0.109 (2)	19 (1)*
F(4)	0.131 (2)	0.822 (2)	0.205 (2)	19 (1)*
F(5)	0.136 (2)	0.748 (2)	0.306 (2)	20 (1)*
F(6)	0.195 (2)	0.652 (2)	0.207 (3)	22 (1)*
C(55)	0.331 (3)	0.528 (2)	0.076 (3)	14 (1)*
Cl(4)	0.4336 (8)	0.5151 (7)	0.194 (1)	14.3 (4)*
Cl(5)	0.386 (1)	0.476 (1)	−0.044 (2)	22.3 (7)*

Table II (Continued)

atom	x	y	z	B
O(3)	0.060 (3)	−0.044 (3)	0.501 (4)	12 (1)*
C(56)	−0.011 (4)	−0.067 (3)	0.394 (5)	20 (2)*
C(57)	0.100 (2)	0.002 (2)	0.599 (3)	11 (1)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Selected Bond Distances (Å) and Their Estimated Standard Deviations for $[Cl(EtCN)Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)]PF_6{\cdot}CH_2Cl_2{\cdot}0.5Et_2O$[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Re(1)	Re(2)	2.586 (1)	Re(2)	P(4)	2.470 (5)	P(3)	C(31)	1.84 (2)
Re(1)	Cl(1)	2.473 (5)	Re(2)	C(1)	2.00 (2)	P(3)	C(37)	1.82 (2)
Re(1)	Cl(2)	2.407 (5)	Re(2)	N(1)	2.03 (2)	P(4)	C(6)	1.85 (2)
Re(1)	P(1)	2.471 (5)	P(1)	C(5)	1.88 (2)	P(4)	C(43)	1.86 (2)
Re(1)	P(2)	2.473 (6)	P(1)	C(7)	1.82 (2)	P(4)	C(49)	1.84 (2)
Re(1)	C(1)	2.13 (2)	P(1)	C(13)	1.86 (2)	C(1)	O(1)	1.19 (2)
Re(1)	C(2)	1.92 (2)	P(2)	C(6)	1.84 (2)	C(2)	O(2)	1.10 (2)
Re(2)	Cl(1)	2.448 (4)	P(2)	C(19)	1.82 (2)	N(1)	C(3)	1.06 (2)
Re(2)	Cl(3)	2.419 (5)	P(2)	C(25)	1.86 (2)	C(3)	C(4)	1.61 (3)
Re(2)	P(3)	2.478 (5)	P(3)	C(5)	1.84 (2)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Angles (deg) and Their Estimated Standard Deviations for $[Cl(EtCN)Re(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)]PF_6{\cdot}CH_2Cl_2{\cdot}0.5Et_2O$[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Re(2)	Re(1)	Cl(1)	57.8 (1)	Re(1)	Re(2)	C(1)	53.5 (6)	Re(1)	P(2)	C(19)	112.0 (6)
Re(2)	Re(1)	Cl(2)	149.2 (2)	Re(1)	Re(2)	N(1)	130.8 (5)	Re(1)	P(2)	C(25)	121.4 (7)
Re(2)	Re(1)	P(1)	95.4 (1)	Cl(1)	Re(2)	Cl(3)	88.6 (2)	C(6)	P(2)	C(19)	103.6 (9)
Re(2)	Re(1)	P(2)	95.0 (1)	Cl(1)	Re(2)	P(3)	92.3 (2)	C(6)	P(2)	C(25)	105.2 (9)
Re(2)	Re(1)	C(1)	49.0 (5)	Cl(1)	Re(2)	P(4)	93.0 (2)	C(19)	P(2)	C(25)	104.9 (9)
Re(2)	Re(1)	C(2)	120.9 (7)	Cl(1)	Re(2)	C(1)	112.3 (6)	Re(2)	P(3)	C(5)	108.2 (6)
Cl(1)	Re(1)	Cl(2)	91.4 (2)	Cl(1)	Re(2)	N(1)	170.4 (5)	Re(2)	P(3)	C(31)	114.9 (6)
Cl(1)	Re(1)	P(1)	91.3 (2)	Cl(3)	Re(2)	P(3)	85.5 (2)	Re(2)	P(3)	C(37)	120.8 (7)
Cl(1)	Re(1)	P(2)	92.2 (2)	Cl(3)	Re(2)	P(4)	85.9 (2)	C(5)	P(3)	C(31)	101.2 (8)
Cl(1)	Re(1)	C(1)	106.8 (5)	Cl(3)	Re(2)	C(1)	159.1 (6)	C(5)	P(3)	C(37)	107.8 (8)
Cl(1)	Re(1)	C(2)	177.9 (7)	Cl(3)	Re(2)	N(1)	81.8 (5)	C(31)	P(3)	C(37)	102.0 (9)
Cl(2)	Re(1)	P(1)	85.8 (2)	P(3)	Re(2)	P(4)	169.7 (2)	Re(2)	P(4)	C(6)	108.3 (6)
Cl(2)	Re(1)	P(2)	84.0 (2)	P(3)	Re(2)	C(1)	93.3 (6)	Re(2)	P(4)	C(43)	113.6 (7)
Cl(2)	Re(1)	C(1)	161.8 (5)	P(3)	Re(2)	N(1)	86.6 (5)	Re(2)	P(4)	C(49)	123.2 (7)
Cl(2)	Re(1)	C(2)	90.0 (7)	P(4)	Re(2)	C(1)	92.8 (6)	C(6)	P(4)	C(43)	101.8 (9)
P(1)	Re(1)	P(2)	169.3 (2)	P(4)	Re(2)	N(1)	86.7 (5)	C(6)	P(4)	C(49)	103.5 (9)
P(1)	Re(1)	C(1)	95.0 (6)	C(1)	Re(2)	N(1)	77.3 (7)	C(43)	P(4)	C(49)	104 (1)
P(1)	Re(1)	C(2)	87.2 (6)	Re(1)	Cl(1)	Re(2)	63.4 (1)	Re(1)	C(1)	Re(2)	77.5 (7)
P(2)	Re(1)	C(1)	93.7 (6)	Re(1)	P(1)	C(5)	107.1 (6)	Re(1)	C(1)	O(1)	138 (2)
P(2)	Re(1)	C(2)	89.5 (6)	Re(1)	P(1)	C(7)	122.9 (7)	Re(2)	C(1)	O(1)	144 (2)
C(1)	Re(1)	C(2)	71.9 (8)	Re(1)	P(1)	C(13)	114.0 (6)	Re(1)	C(2)	O(2)	178 (2)
Re(1)	Re(2)	Cl(1)	58.8 (1)	C(5)	P(1)	C(7)	105.7 (9)	Re(2)	N(1)	C(3)	174 (2)
Re(1)	Re(2)	Cl(3)	147.4 (1)	C(5)	P(1)	C(13)	103.6 (8)	N(1)	C(3)	C(4)	174 (2)
Re(1)	Re(2)	P(3)	95.1 (1)	C(7)	P(1)	C(13)	101.8 (8)	P(1)	C(5)	P(3)	110 (1)
Re(1)	Re(2)	P(4)	95.2 (1)	Re(1)	P(2)	C(6)	108.2 (7)	P(2)	C(6)	P(4)	110 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Spectroscopic and Conductivity Data for the Dirhenium(II) Complexes $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$

L		IR spectra, cm^{-1}			electronic abs max λ_{max}, nm (ϵ)	molar conductivity,[d] Ω^{-1} cm^2 mol^{-1}
		$\nu(CN)_{terminal}$	$\nu(CO)_{terminal}$	$\nu(CO)_{bridging}$		
CH_3CN	*a*	2189 vw	1995 vs	1713 s	850 br (200), 425 (5000)[c]	110
	b		1998 vs	1707 ms		
C_2H_5CN	*a*		1993 vs	1709 s	850 br (200), 420 (5600)[c]	120
	b		2000 vs	1707 m		
C_6H_5CN	*a*	2259 vw	1997 vs	1701 ms	860 br (210), 410 (5500)[c]	120
	b		2000 vs	1705 s		
Me_2CHNC	*a*	2197 s	2002 vs	1709 ms	1025 br (200), 775 (290)[d]	130
	b	2199 s	2008 vs	1703 ms		
Me_3CNC	*a*	2184 vs	2002 vs	1705 ms	1070 br (180), 790 (220)[d]	125
	b	2189 vs	2008 vs	1705 s		

[a] Nujol mull on KBr plates. Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak. [b] Dichloromethane solution. [c] Dichloromethane solution, 5 × 10^{-4} M; br = broad. [d] Acetone solution, 1 × 10^{-3} M.

= 13.5 Hz. The data for the propionitrile complex are very similar, and the values are listed in Table VI. The $^{31}P\{^1H\}$ NMR spectra for the three nitrile complexes exhibited two complex multiplets in an AA′BB′ pattern (Table VI). This result is consistent with the presence of the unsymmetrical ligand set arrangement as determined by X-ray crystallographic studies on the molecule $[(C_2H_5CN)ClRe(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-}dppm)_2ReCl(CO)]^+$. Spin simulation studies were carried out, and the chemical shift and

Table VI. Electrochemical and NMR Chemical Shift Data for $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$

L	$^{31}P\{^1H\}$	^1H[c]				CV half-wave potentials[f]		
		P–CH_2–P			L			
	δ	δ	J(P–H), Hz	J(H–H), Hz	δ	$E_{1/2}$(ox(1))	$E_{1/2}$(red(1))	$E_{1/2}$(red(2))
CH_3CN	−10.61 −18.24 [b]	4.16 4.41 [d]	4.3	13.5	1.88 s	+1.46	−0.14	−1.12
C_2H_5CN	−13.04 −20.74 [b]	4.14 4.40 [d]	4.0	13.3	0.72 t 2.20 q	+1.47	−0.12	−1.09
C_6H_5CN	−13.07 −19.84 [b]					+1.45	−0.12	−1.07
Me_2CHNC	−11.48 −19.53 [b]	4.59 5.40 [e]	4.8 5.4	13.9	0.69 d 3.75 h	+1.68	−0.01	−1.01
Me_3CNC	−11.96 −23.31 [b]	4.53 5.51 [e]	4.6 5.0	13.7	0.79 s	+1.70	−0.04	−1.03

[a] Recorded on CH_2Cl_2/CD_2Cl_2 solutions vs 85% aqueous H_3PO_4. [b] ν_A, ν_B; AA′BB′ pattern. [c] Recorded on CD_2Cl_2 solutions. Abbreviations: s = singlet, t = triplet, q = quartet, h = heptet. [d] ν_A, ν_B; AB pattern with superimposed P–H coupling. [e] ν_A, ν_X; AX pattern with superimposed P–H coupling. [f] $E_{1/2}$ values in volts vs. Ag/AgCl in 0.2 M TBAH–CH_2Cl_2 solution at a Pt-bead electrode.

Table VII. Spectroscopic Data for $Re_2Cl_3(dppm)_2(CO)_2(L)$

L		IR spectra, cm^{-1}			electronic abs
		$\nu(CN)_{terminal}$	$\nu(CO)_{terminal}$	$\nu(CO)_{bridging}$	max λ_{max}, nm (ϵ)[c]
CH_3CN	*a*		1929 vs	1653 ms	948 (sh), 968 (700), 584 (3800)
	b	2284 vw	1929 vs	1653 wm	
C_2H_5CN	*a*	2271 vw	1931 vs	1659 ms	950 (sh), 970 (680), 585 (3700)
	b	2276 vw	1929 vs	1655 wm	
C_6H_5CN	*a*	2238 vw	1933 vs	1653 ms	960 (sh), 975 (700), 584 (3600)
	b	2242 vw	1931 vs	1651 wm	
Me_2CHNC	*a*	2140 s	1939 vs	1659 ms	930 (380), 590 (3600)
	b	2155 s	1937 vs	1657 m	
Me_3CNC	*a*	2135 s	1943 vs	1655 wm	925 (400), 595 (3400)
	b	2145 s	1937 vs	1657 m	

[a] Nujol mull on KBr plates. [b] Dichloromethane solution. [c] 5×10^{-4} M dichloromethane solution.

coupling constants were obtained from these results.[12] In the ^1H NMR spectra of the isopropyl and *tert*-butyl isocyanide complexes, an AX pattern is observed for the dppm methylene region, and it consists of the two eight-line patterns (1:4:6:5:5:6:4:1) resulting from the overlap of two pentets. The chemical shifts δ_a and δ_X and coupling constants $J(P-H_A)$, $J(P-H_X)$, and $J(H_A-H_X)$ are given in Table VI. The $^{31}P\{^1H\}$ NMR spectra for the isocyanide complexes are, like those of their nitrile analogues, characteristic of an AA′BB′ spin system. Spin simulations of these spectra gave parameters that were very similar to those obtained in the case of the nitrile derivatives of this type.[12]

(d) Preparation of the Neutral Complexes $Re_2Cl_3(dppm)_2(CO)_2L$ (L = RCN, RNC) Possessing the Re_2^{3+} Core. As mentioned earlier, the cationic complexes $[Re_2Cl_3(dppm)_2(CO)_2L]PF_6$ (L = RCN, RNC) exhibit a one-electron reduction at $E_{1/2} \simeq -0.10$ V vs. Ag/AgCl. The position of this couple suggested to us the feasibility of carrying out a chemical reduction. The choice of cobaltocene as the reducing agent in the reaction was based upon the effective use of this reagent in several recent studies involving other multiply bonded dimetal systems.[13-15] Solutions of the cations in acetone react quickly with 1 equiv of cobaltocene, as evidenced by an immediate color change from bright green to blue. The products are fairly insoluble in acetone, and they precipitate from the reaction mixture, leaving behind any unreacted cobaltocene and $[Cp_2Co]PF_6$. The nitrile derivatives of the $Re_2Cl_3(dppm)_2(CO)_2L$ type complexes are quite unstable in solution as well as in the solid state. In contrast, the neutral isopropyl and *tert*-butyl isocyanide complexes are fairly stable in air both in the solid state and in solution. This difference in behavior is not surprising in view of the fact that the π-accepting isocyanides are rather effective ligands for stabilizing low-valent transition-metal complexes whereas nitriles are typically σ-donor ligands.

The paramagnetism of these products was confirmed by measuring the X-band ESR spectra of frozen dichloromethane solutions (−160 °C). These spectra, which are essentially identical, display a very complex pattern between 1250 and 4250 G, revealing hyperfine coupling to the phosphorus and rhenium nuclei. The spectra are centered at ~2850 G ($g \approx 2.28$) and resemble those obtained for other paramagnetic dirhenium complexes that contain chloride and phosphine ligands.[16-18]

The electrochemistry of the $Re_2Cl_3(dppm)_2(CO)_2L$ complexes (in 0.2 M TBAH–CH_2Cl_2), as determined by cyclic voltammetry, are characterized by three couples. These processes correspond to two oxidations and one reduction, at the same potentials as those found for the parent 1:1 salts (see Figure 2 and Table VI). Solutions of the nitrile and isocyanide complexes in acetonitrile are essentially nonconducting ($\Lambda_m < 10\ \Omega^{-1}\ cm^2\ mol^{-1}$).

IR spectroscopic measurements of dichloromethane solutions are summarized in Table VII. The nitrile products exhibit a very weak feature in the region 2280–2240 cm^{-1}, while the isocyanide derivatives display a strong band in the range 2155–2135 cm^{-1}. In both cases, these are assignable to ν(CN) modes. The ν(CO) region of the solution IR spectra reveals two bands, one of which corresponds to a terminal ν(CO) mode (1940–1930 cm^{-1}) while the other is a bridging mode (1660–1650 cm^{-1}). These ν(CO) modes are ~50 cm^{-1} lower in energy than the corresponding bands in the spectra of the respective monocations (Table V). The one-electron reduction of the Re_2^{4+} core of $[Re_2Cl_3(dppm)_2$-

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(12) The following parameters were obtained from $^{31}P\{^1H\}$ NMR spin simulation studies of $[Re_2Cl_3(dppm)_2(CO)_2(NCR)]PF_6$: R = CH_3, $\delta_A = \delta_{A'} = 10.61$, $\delta_B = \delta_{B'} = -18.24$, $J_{AA'} = 228.0$ Hz, $J_{BB'} = 197.1$ Hz, $J_{AB} = J_{A'B'} = 58.8$ Hz, $J_{AB'} = J_{A'B} = 7.0$ Hz; R = C_2H_5, $\delta_A = \delta_{A'} = -13.04$, $\delta_B = \delta_{B'} = -20.74$, $J_{AA'} = 235.8$ Hz, $J_{BB'} = 205.4$ Hz, $J_{AB} = J_{A'B'} = 58.1$ Hz, $J_{AB'} = J_{A'B} = 7.8$ Hz; R = C_6H_5, $\delta_A = \delta_{A'} = -13.07$, $\delta_B = \delta_{B'} = -19.84$, $J_{AA'} = 235.8$ Hz, $J_{BB'} = 223.2$ Hz, $J_{AB} = J_{A'B'} = 58.2$ Hz, $J_{AB'} = J_{A'B} = 7.7$ Hz.

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$(CO)_2L]PF_6$ to yield the low-valent Re_2^{3+} core probably leads to increased π-back-donation from the metal centers to the carbonyl ligands and would be expected to result in a lowering in energy of the $\nu(CO)$ modes.

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Registry No. $[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]PF_6{\cdot}CH_2Cl_2{\cdot}0.5Et_2O$, 98919-87-0; $[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]PF_6$, 98838-38-1; $[Re_2Cl_3(dppm)_2(CO)_2(EtCN)]$, 98838-46-1; $[Re_2Cl_3(dppm)_2(CO)_2(CH_3CN)]PF_6$, 98838-36-9; $[Re_2Cl_3(dppm)_2(CO)_2(CH_3CN)]$, 98838-45-0; $[Re_2Cl_3(dppm)_2(CO)_2(C_6H_5CN)]PF_6$, 98838-40-5; $[Re_2Cl_3(dppm)_2(CO)_2(C_6H_5CN)]$, 98838-47-2; $[Re_2Cl_3(dppm)_2(CO)_2(Me_2CHNC)]PF_6$, 98838-42-7; $[Re_2Cl_3(dppm)_2(CO)_2(Me_2CHNC)]$, 98838-48-3; $[Re_2Cl_3(dppm)_2(CO)_2(Me_3CNC)]PF_6$, 98838-44-9; $[Re_2Cl_3(dppm)_2(CO)_2(Me_3CNC)]$, 98857-68-2; $Re_2Cl_4(dppm)_2(CO)_2$, 96306-80-0; cobaltocene, 1277-43-6.

Supplementary Material Available: Full tables of bond distances and bond angles, anisotropic displacement parameters, and structure factors (30 pages). Ordering information is given on any current masthead page.

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Disproportionation of Nickel(III) Bis(oxime imine) Complexes

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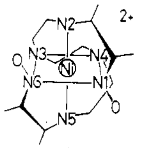
The kinetics of the redox equilibrium Ni(IV) + Ni(II) $\rightleftharpoons$ 2Ni(III) have been studied for nickel complexes of a bis(oxime imine) ligand system, LH_2, as a function of pH. Above pH 5, reductions of $Ni^{IV}L^{2+}$ by $Ni^{II}L$, $Ni^{II}LH^+$, and $Ni^{II}LH_2^{2+}$ take place with second-order rate constants 1.24×10^6, 3.8×10^3, and 3.5×10^2 M^{-1} s^{-1}, respectively. Below pH 5, disproportionation of nickel(III) is dominated by the reaction of $Ni^{III}L^+$ with $Ni^{III}LH^{2+}$, which has a second-order rate constant of 3.4×10^3 M^{-1} s^{-1}. At very low pH, where the concentration of $Ni^{III}L^+$ is very small, disproportionation of $Ni^{III}LH^{2+}$, though thermodynamically favored, is slow. This reflects the inability of $Ni^{IV}L^{2+}$ to support protonation. The electron-transfer reactions are outer-sphere in nature and are discussed in terms of Marcus theory.

Introduction

Over the past few years, interest has developed in the mechanistic chemistry of the nickel(IV) complexes[1,2] $Ni^{IV}L^{2+}$ (**1**), where LH_2 is the sexidentate ligand 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (**2**). This complex is readily and reversibly reduced to the nickel(II) complex $Ni^{II}LH_2^{2+}$, and the kinetics and mechanisms of reductions by a variety of one-[3-7] and two-electron[8-10] reagents have been examined. Oxidations of $Ni^{II}LH_2^{2+}$ have also been reported.[11-13]



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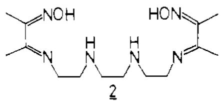

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A consistent feature of these studies is the participation of nickel(III) intermediates in the reactions. These intermediates are thermodynamically stable above pH 5 but below this value disproportionate to form nickel(IV) and nickel(II) complexes. A knowledge of the kinetics of these disproportionation–comproportionation processes is important in understanding the chemistry of the nickel(III) intermediates and their role in the nickel(IV)–nickel(II) redox interconversion.

In this paper, the kinetics and mechanisms of disproportionation of nickel(III) over the pH range 1–4 and the reduction of nickel(IV) by nickel(II) over the pH range 4–10 are investigated. The results are discussed in terms of Marcus theory,[14] and comparisons are made with other electron-transfer reactions of these nickel complexes.

Experimental Details

Materials. The compounds $Ni^{IV}L(ClO_4)_2$ and $Ni^{II}LH_2(ClO_4)_2$ were prepared as outlined previously.[1,3] Solutions of nickel(IV) were standardized spectrophotometrically with use of literature absorption coefficients (ϵ_{500} = 6300 M^{-1} cm^{-1}) while nickel(II) solutions were prepared by dissolving accurately weighed amounts of the crystalline solid. The nickel(III) complex $Ni^{III}L^+$ was generated by electrochemical means[3] or more simply by mixing equimolar amounts of $Ni^{IV}L^{2+}$ and $Ni^{II}L$ at pH >5. Samples of the complex $Ni^{II}((S)\text{-}Me_2LH_2)(ClO_4)_2$, where $(S)\text{-}Me_2LH_2$ is (5*S*,12*S*)-4,7,10,13-tetraaza-3,5,12,14-tetramethylhexadeca-3,13-diene-2,15-dione dioxime, were prepared as outlined previously.[4] The nickel(IV) complex $Ni^{IV}((S)\text{-}Me_2L)^{2+}$ was obtained by oxidation of $Ni^{II}((S)\text{-}Me_2LH_2)^{2+}$ in aqueous solution with a stoichiometric amount of Na_2IrCl_6 (Aldrich), followed by elution of the solution through an anion-exchange column (Amberlite CG-400, perchlorate form) to remove the $IrCl_3^{3-}$ formed.

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