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Reactions of the Electronically Unsaturated Polyhydride $[Re_2(\mu\text{-}H)H_4(\mu\text{-dmpm})_3]PF_6$ (dmpm = $Me_2PCH_2PMe_2$) with Carbon Monoxide and Isocyanide Ligands. Isolation and Structural Characterization of Complexes of Composition $[Re_2H_{5-n}L_n(\mu\text{-dmpm})_3]PF_6$ (n = 2 or 4; L = CO or RNC)

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The electronically unsaturated dirhenium polyhydride complex $[Re_2(\mu\text{-}H)H_4(\mu\text{-dmpm})_3]PF_6$ (dmpm = $Me_2PCH_2PMe_2$) reacts with xylyl isocyanide, *tert*-butyl isocyanide and carbon monoxide to produce the complexes $[Re_2H_3L_2(\mu\text{-dmpm})_3]PF_6$ (L = xylNC (**1a**), *t*-Bu (**1b**)) and $[Re_2HL_4(\mu\text{-dmpm})_3]PF_6$ (L = xylNC (**2a**), *t*-Bu (**2b**), and CO (**2c**)) in which the electronic unsaturation of the dirhenium unit is eliminated in two, two-electron reduction steps. In all cases, the $[Re_2(\mu\text{-}H)(\mu\text{-dmpm})_3]$ unit is retained. The coordination of the first two ligand molecules occurs at one of the metal centers, with the concomitant reductive elimination of H_2; the second pair of ligands then bind to the remaining unreduced metal center. The X-ray structures of crystals of compositions $[Re_2H_3(CNxyl)_2(dmpm)_3](PF_6)_{0.79}(ReO_4)_{0.21}$ (**1a**), $[Re_2H(CNxyl)_4(dmpm)_3]PF_6$ (**2a**), and $[Re_2H(CO)_4(dmpm)_3]PF_6\cdot(CH_3)_2CO$ (**2c**), along with NMR spectral measurements, have confirmed that the dirhenium monocations in **1a**, **2a**, and **2c** can be represented as $[(xylNC)_2Re(\mu\text{-}H)(\mu\text{-dmpm})_3ReH_2]^+$, $[(xylNC)_2Re(\mu\text{-}H)(\mu\text{-dmpm})_3Re(CNxyl)_2]^+$, and $[(OC)_2Re(\mu\text{-}H)(\mu\text{-dmpm})_3Re(CO)_2]^+$, respectively. The only Re···Re interactions are through three-center, two-electron bonds; the Re···Re distances are 3.448 (1), 3.446 (1), and 3.3625 (4) Å, respectively. Crystal data for **1a** (+20 °C): orthorhombic space group $Pna2_1$ (No. 33), a = 13.874 (2) Å, b = 30.362 (3) Å, c = 10.731 (1) Å, V = 4520 (2) Å^3, and Z = 4. The structure was refined to R = 0.046 (R_w = 0.058) for 2686 data with $I > 3.0\sigma(I)$. Crystal data for **2a** (+20 °C): monoclinic space group $P2_1/n$ (No. 14), a = 11.969 (4) Å, b = 20.397 (4) Å, c = 25.845 (5) Å, β = 92.97 (2)°, V = 6301 (5) Å^3, and Z = 4. The structure was refined to R = 0.043 (R_w = 0.049) for 4490 data with $I > 3.0\sigma(I)$. Crystal data for **2c** (–62 °C): monoclinic space group $C2/c$ (No. 15), a = 34.987 (5) Å, b = 10.980 (1) Å, c = 19.232 (3) Å, β = 91.020 (7)°, V = 7386 (3) Å^3, and Z = 8. The structure was refined to R = 0.041 (R_w = 0.060) for 4329 data with $I > 3.0\sigma(I)$.

Introduction

The chemistry of dirhenium octahydride complexes of the type $Re_2H_8(PR_3)_4$, where PR_3 represents a monodentate phosphine ligand, have been of considerable interest to several groups.[1] One particularly important feature of these complexes is the ease with which they can be converted into other dirhenium polyhydrides that contain nine, seven, five, or four hydride ligands, a demonstration of their rich and varied reaction chemistry.

More recently, attention has been focused upon dirhenium polyhydrides that contain bidentate or tridentate phosphine ligands. In the course of these studies,[1g,1h,2–6] several unusual features in the structural and reaction chemistry of these complexes have been uncovered. Among these was the isolation of the unexpectedly stable salt $[Re_2H_5(dmpm)_3]PF_6$ (dmpm = $Me_2PCH_2PMe_2$), the structural characterization of which revealed[3,6] that the cation has the symmetrical structure $[H_2Re(\mu\text{-}H)(\mu\text{-dmpm})_3ReH_2]^+$ and an exceptionally long Re–Re distance. The only Re–Re interaction is via a three-center, two-electron bond, which leaves the metal centers with a degree of electronic unsaturation unprecedented for a polyhydride complex of the heavier transition elements. This is especially remarkable in the case of rhenium, an element which shows a strong propensity to form metal–metal multiple bonds.[7] Accordingly, we had anticipated that this complex would be exceedingly reactive but to our surprise found[3,6] it to be quite resistant to attack by air and water; indeed, aqueous salts of this cation are stable for extended periods. In a study of the reactivity of $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$, we have found that it reacts with π-acceptor CO and isocyanide ligands to produce in a stepwise fashion a new series of lower-valent dirhenium complexes of stoichiometry $[Re_2H_{5-n}L_n(\mu\text{-dmpm})_3]PF_6$, where n = 2 or 4, in which the electronic unsaturation is eventually relieved and the $[Re(\mu\text{-}H)(\mu\text{-dmpm})_3Re]$ unit is retained. The synthetic details and

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spectroscopic and structural properties of this class of new complexes are now reported.

Experimental Section

Starting Materials. The polyhydride complex $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$ was prepared by the usual method.[3,6] Bis(dimethylphosphino)methane (dmpm) was purchased from Quantum Design, Inc. and Strem Chemicals. *tert*-Butyl isocyanide was prepared by the method of Weber et al.,[8] while xylyl isocyanide (2,6-Me_2-C_6H_3NC;xylNC) was purchased from Fluka AG (Switzerland). The remaining reagents and solvents were obtained from commercial sources and used as received. Solvents were deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dinitrogen gas with standard Schlenk techniques.

A. Reactions with Isocyanides. (i) Synthesis of $[Re_2H_3(CNxyl)_2(dmpm)_3]PF_6$ (1a). A mixture of the reactants $[Re_2H_5(dmpm)_3]PF_6$ (0.039 g, 0.042 mmol) and xylyl isocyanide (0.017 g, 0.13 mmol) was placed in a round bottom flask equipped with a sidearm and a reflux column. The system was purged with gaseous N_2, 10 mL of methanol solvent was added to the flask, and the mixture was heated to reflux. As the system was heated, the color of the solution changed from yellow to red-brown, and after 4 h, the mixture was cooled to room temperature and the solvent removed under vacuum. The residue was recrystallized from $CHCl_3$/diethyl ether to afford yellow microcrystals which were filtered off and dried under vacuum; yield 0.033 g (66%). Anal. Calcd for $C_{34}H_{64}Cl_3F_6N_2P_7Re_2$ (i.e. $[Re_2H_3(C_9H_9N)_2(C_5H_{14}P_2)_3]PF_6\cdot CHCl_3$): C, 30.24; H, 5.34. Found: C, 29.61; H, 5.12. The ^1H NMR spectrum of the complex (recorded in $(CD_3)_2CO$) displayed a peak at δ +7.27 in accord with the presence of approximately one molecule of lattice $CHCl_3$.

(ii) Synthesis of $[Re_2H(CNxyl)_4(dmpm)_3]PF_6$ (2a). With the use of a procedure similar to that given in section A(i), 0.040 g of $[Re_2H_5(dmpm)_3]PF_6$ (0.043 mmol) and 0.030 g of xylyl isocyanide (0.24 mmol) were heated together at reflux in 15 mL of *n*-propanol. After 24 h, the reaction mixture was cooled, the solvent was removed under vacuum, and the residue was recrystallized from $CHCl_3$/diethyl ether. The yellow crystals were filtered off and dried under vacuum; yield 0.043 g (69%). Anal. Calcd for $C_{51}H_{79}F_6N_4P_7Re_2$: C, 42.20; H, 5.50. Found: C, 41.44; H, 5.24.

(iii) Synthesis of $[Re_2H_3(CN\text{-}t\text{-}Bu)_2(dmpm)_3]PF_6$ (1b). A mixture of $[Re_2H_5(dmpm)_3]PF_6$ (0.034 g, 0.037 mmol), 0.2 mL of *t*-BuNC, and 20 mL of methanol was heated at reflux for 2 h, the system then cooled to room temperature, and the solvent removed under vacuum. The residue was recrystallized from $CHCl_3$/diethyl ether, and the yellow solid was filtered off and dried under vacuum; yield 0.017 g (42%). Anal. Calcd for $C_{25}H_{63}F_6N_2P_7Re_2$: C, 27.43; H, 5.76. Found: C, 27.16; H, 5.75.

(iv) Synthesis of $[Re_2H(CN\text{-}t\text{-}Bu)_4(dmpm)_3]PF_6$ (2b). The reaction of 0.039 g of $[Re_2H_5(dmpm)_3]PF_6$ (0.042 mmol) with 0.5 mL of *t*-BuNC in 20 mL of *n*-propanol was carried out as described in section A(i). The mixture was heated to reflux for 24 h, and the solvent was then removed under vacuum. A pale yellow product was isolated by recrystallization of the residue from $CHCl_3$/diethyl ether. The product was collected by filtration and dried under vacuum; yield 0.020 g (39%). Anal. Calcd for $C_{35}H_{79}F_6N_4P_7Re_2$: C, 33.38; H, 6.34. Found: C, 32.62; H, 6.35.

B. Reactions with Carbon Monoxide. (i) Synthesis of $[Re_2H(CO)_4(dmpm)_3]PF_6$ (2c). A solution of $[Re_2H_5(dmpm)_3]PF_6$ (0.055 g, 0.059 mmol) in 25 mL of *n*-propanol was prepared in a round bottom flask equipped with a sidearm and a reflux column that was in turn attached to a mercury bubbler system. A steady stream of CO gas was passed through the solution while the reaction mixture was heated at reflux. After 8 h, the reaction mixture was cooled to room temperature, during which time a white solid precipitated from solution. The solvent volume was reduced under vacuum, and the insoluble product was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.045 g (61%). Anal. Calcd for $C_{19}H_{43}F_6O_4P_7Re_2$: C, 21.97; H, 4.18. Found: C, 20.99; H, 4.16.

(ii) Attempted Synthesis of $[Re_2H_3(CO)_2(dmpm)_3]PF_6$ (1c). Following the procedure outlined in section B(i), a stream of CO gas was bubbled through a solution of $[Re_2H_5(dmpm)_3]PF_6$ (0.032 g, 0.034 mmol) in 25 mL of ethanol that was heated at reflux. After 4 h, the reaction mixture was cooled to room temperature, and the insoluble product was collected by filtration. The pale yellow solid was washed with diethyl ether and dried under vacuum. The product was concluded to be a mixture of $[Re_2H_3(CO)_2(dmpm)_3]PF_6$ (1c) and $[Re_2H(CO)_4(dmpm)_3]PF_6$ (2c) based upon its ^1H NMR spectrum. In addition to the resonances arising from the presence of 2c (see Results Section), the spectrum (recorded in $CDCl_3$) contained an additional Re–*H* resonance at δ −9.02 (multiplet) and extra dmpm resonances at δ +3.23, and +2.58 (–CH_2–), and δ +1.75 and +1.57 (–CH_3).

Table I. Crystallographic Data for $[Re_2H_3(CNxyl)_2(dmpm)_3](PF_6)_{0.79}(ReO_4)_{0.21}$ (**1a**), $[Re_2H(CNxyl)_4(dmpm)_3]PF_6$ (**2a**), and $[Re_2H(CO)_4(dmpm)_3]PF_6\cdot(CH_3)_2CO$ (**2c**)

	1a	**2a**	**2c**
chem formula	$Re_{2.21}P_{6.79}F_{4.73}$-$O_{0.84}N_2C_{33}H_{63}$	$Re_2P_7F_6N_4$-$C_{51}H_{79}$	$Re_2P_7F_6O_5$-$C_{22}H_{49}$
fw	1213.31	1451.43	1096.84
space group	*Pna*2_1 (No. 33)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a, Å	13.874 (2)	11.969 (4)	34.987 (5)
b, Å	30.362 (3)	20.397 (4)	10.980 (1)
c, Å	10.731 (1)	25.845 (5)	19.232 (3)
β, deg		92.97 (2)	91.020 (7)
V, $Å^3$	4520 (2)	6301 (5)	7386 (3)
Z	4	4	8
T, °C	20	20	−62
λ, Å (MoKα)	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.783	1.530	1.972
μ(Mo Kα), cm^{-1}	58.38	41.17	69.98
transm coeff	1.00–0.48	1.00–0.63	1.00–0.68
R^a	0.046	0.043	0.041
$R_w{}^b$	0.058	0.049	0.060

^{a} $R = \Sigma||F_o| - |F_c||\Sigma|F_o|$. ^{b} $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

C. Oxidation of $[Re_2H(CNxyl)_4(dmpm)_3]PF_6$. A mixture of $[Re_2H(CNxyl)_4(dmpm)_3]PF_6$ (0.032 g, 0.022 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.008 g, 0.024 mmol) was placed in a round bottom flask that was sealed with a septum and purged with gaseous N_2. Following the addition of 5 mL of CH_2Cl_2, the mixture was stirred for 5 min. This reaction afforded a red solution, and addition of 10 mL of diethyl ether precipitated the paramagnetic complex $[Re_2H(CNR)_4(dmpm)_3](PF_6)_2$; yield 0.028 g (80%). The identity of this product was established on the basis of its electrochemical and spectroscopic properties.

Preparation of Single Crystals for X-ray Structure Analyses. Crystals of $[Re_2H_3(CNxyl)_2(dmpm)_3]PF_6$ (**1a**), $[Re_2H(CNxyl)_4(dmpm)_3]PF_6$ (**2a**) and $[Re_2H(CO)_4(dmpm)_3]PF_6$ (**2c**) were obtained by the slow diffusion of isopropyl ether into a solution of each complex in acetone.

X-ray Structure Analyses. The structures of crystals of composition $[Re_2H_3(CNxyl)_2(dmpm)_3](PF_6)_{0.79}(ReO_4)_{0.21}$,$[Re_2H(CNxyl)_4(dmpm)_3]PF_6$, and $[Re_2H(CO)_4(dmpm)_3]PF_6\cdot(CH_3)_2CO$ were determined by the application of standard procedures. For convenience we will retain the labels **1a**, **2a**, and **2c**, respectively, for these complexes even though in two instances the composition of the crystals varied slightly from those of the bulk complex, although not in a chemically significant way. Data for **1a** and **2a** were collected at room temperature and for **2c** at −62 °C. The basic crystallographic parameters for all three complexes are listed in Table I. The cell constants are based on 25 reflections with $17° < \theta < 20°$, $13° < \theta < 17°$ and $22° < \theta < 23°$ for **1a**, **2a**, and **2c**, respectively. Three standard reflections were measured after every 5000 s of beam exposure during data collection but we observed no systemmatic variations in decay of these standards. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystal of **1a** was found to belong to the orthorhombic space group *Pna*2_1 (No. 33), those of **2a** and **2c** were found to belong to the monoclinic space groups $P2_1/n$ (No. 14) and $C2/c$ (No. 15), respectively. Lorentz and polarization corrections were applied to all three sets of data. An empirical absorption correction[9] was applied in all cases. The linear absorption coefficient used was 58.38 cm^{-1} for **1a**, 41.17 cm^{-1} for **2a** and 69.98 cm^{-1} for **2c**. No corrections for extinction were applied.

The structures were solved by the use of the Patterson heavy-atom method which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The structures were refined by full-matrix least-squares methods where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where *w* is the weighting factor defined as $w = 1/\sigma^2(F_o)$.

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During the course of the structure refinement of **1a** it became clear that the $[PF_6]^-$ anion, which is located on a general position, would not refine satisfactorily when this site was assigned a full occupancy. This was reflected by a negative isotropic thermal parameter for P and very large thermal parameters for the F atoms. This problem was resolved by modeling the anion as a mixture of $[PF_6]^-$ and $[ReO_4]^-$ with occupancies of approximately 0.8 and 0.2, respectively. Convergence was achieved with multiplicities of 79% for $[PF_6]^-$ and 21% for $[ReO_4]^-$; the fluorine atoms had rather large temperature factors, and the oxygen atoms associated with the $[ReO_4]^-$ anion could not be identified. It is uncertain whether this is a consequence of the large thermal motion of the rhenium atom or whether it reflects a disorder of this anion. This structure solution satisfied the charge requirements for the complex. Also, it is chemically reasonable in view of the propensity for rhenium polyhydride complexes to decompose to form perrhenate;[5,6] presumably a small amount of decomposition occurred during the slow crystal growing procedure. Furthermore, the spectroscopic and electrochemical properties of this batch of crystals were in accord with the presence of the $[Re_2H_3(CNxyl)_2(dmpm)_3]^+$ cation, the $[PF_6]^-$ anion, and a small amount of $[ReO_4]^-$, the latter species being identified by a ν(Re–O) mode at 904(m) cm^{-1} in the IR spectrum. The hydrido ligands were not located in the structure of **1a**, their presence being inferred from the spectroscopic properties of this complex. Hydrogen atoms of the dmpm and xylNC ligands were included at fixed positions which were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. We assumed that the value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. All non-hydrogen atoms of **1a** were refined anisotropically, except for carbon atom C(221) of one of the dmpm ligands and atoms P(1000) and Re(3) of the anions. Corrections for anomalous scattering were applied to these atoms.[10]

The structure refinements of **2a** and **2c** were relatively routine. Only in the case of **2a** was the bridging hydride ligand located following anisotropic refinement of all non-hydrogen atoms. A disordered molecule of lattice acetone was located about a general position in **2c**. Hydrogen atoms of the dmpm ligands of **2a** and **2c** and the xylylNC ligand of **2a** were included at fixed positions which were calculated by assuming idealized geometry and a C-H bond distance of 0.95 Å. The value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, was taken as $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. These hydrogen atoms were used in the calculation of F_c, but their positions were not refined. All non-hydrogen atoms, except those of the lattice acetone molecule of **2c**, were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[10]

Positional parameters and their errors for the important atoms of the dirhenium cations of **1a**, **2a**, and **2c** are listed in Tables II–IV. The most important intramolecular bond distances and angles for these structures are given in Tables V and VI. Tables giving full details of the crystal data and data collection parameters, the positional parameters for all non-hydrogen and hydrogen atoms, the anisotropic thermal parameters, and complete listings of bond distances and bond angles are available as supplementary material.

Physical Measurements. A Perkin-Elmer 1800 FTIR spectrometer was used to record the IR spectra of compounds as Nujol mulls supported on KBr plates in the region 4800–400 cm^{-1}. Electrochemical measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and were uncorrected for junction potentials. Under our experimental conditions the ferrocenium/ferrocene couple is at $E_{1/2} = +0.47$ V vs Ag/AgCl. Bulk electrolyses were carried out with the use of a Pt-gauze working electrode and a Bioanalytical Systems Inc. Model SP-2 potentiostat. ^{1}H and ^{31}P NMR spectra were recorded on a Varian XL-200A spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuterated solvent (δ +7.27 in $CDCl_3$). Phosphorous resonances were referenced externally to 85% H_3PO_4. X-Band ESR spectra were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer.

Elemental microanalyses were carried out by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Xylyl Group Atoms of the Dirhenium Cation of **1a** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.69796 (5)	0.33483 (2)	0.00350	2.20 (1)
Re(2)	0.67738 (6)	0.44763 (3)	0.0294 (1)	3.27 (2)
P(11)	0.7856 (4)	0.3371 (2)	0.2018 (6)	2.9 (1)
P(12)	0.8339 (4)	0.3474 (2)	−0.1266 (6)	2.8 (1)
P(13)	0.5366 (4)	0.3301 (2)	0.0762 (7)	3.9 (1)
P(21)	0.7684 (5)	0.4403 (2)	0.2198 (8)	4.4 (2)
P(22)	0.8056 (5)	0.4490 (2)	−0.1158 (7)	4.0 (2)
P(23)	0.5147 (4)	0.4324 (2)	0.0832 (7)	3.9 (2)
N(30)	0.588 (1)	0.3401 (7)	−0.250 (2)	3.8 (5)
N(40)	0.717 (1)	0.2330 (5)	−0.017 (2)	3.4 (4)
C(30)	0.625 (1)	0.3387 (7)	−0.148 (3)	2.8 (5)
C(40)	0.709 (1)	0.2710 (6)	−0.010 (2)	2.7 (4)
C(111)	0.725 (2)	0.327 (1)	0.351 (3)	5.8 (8)
C(112)	0.889 (2)	0.301 (1)	0.217 (3)	4.7 (6)
C(121)	0.843 (2)	0.3099 (9)	−0.254 (3)	4.7 (6)
C(122)	0.962 (2)	0.345 (1)	−0.067 (3)	5.9 (7)
C(131)	0.467 (2)	0.2883 (9)	−0.009 (3)	5.3 (7)
C(132)	0.496 (2)	0.318 (1)	0.237 (3)	4.9 (7)
C(211)	0.704 (2)	0.439 (1)	0.370 (3)	6.6 (9)
C(212)	0.855 (3)	0.483 (1)	0.254 (4)	8.7 (9)
C(221)	0.933 (2)	0.460 (1)	−0.052 (3)	6.7 (8)*
C(222)	0.791 (2)	0.489 (1)	−0.237 (4)	7.7 (9)
C(231)	0.430 (2)	0.4686 (7)	0.012 (3)	4.6 (5)
C(232)	0.471 (2)	0.4355 (9)	0.246 (3)	5.4 (7)
C(1B)	0.841 (2)	0.3907 (9)	0.231 (3)	4.9 (7)
C(2B)	0.825 (2)	0.3997 (9)	−0.209 (3)	4.6 (6)
C(3B)	0.467 (1)	0.3774 (7)	0.032 (3)	4.7 (6)

[a] The starred value indicates an atom was refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the xylyl group atoms are available as supplementary material.

Results

The dirhenium polyhydride complex $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$ reacts with 2,6-dimethylphenyl isocyanide (xylNC), *tert*-butyl isocyanide (*t*-BuNC), and CO in refluxing alcohol solvents according to the reactions shown in eqs 1 and 2 to give complexes

$$[Re_2H_5(\mu\text{-dmpm})_3]PF_6 + 2L \rightarrow [Re_2H_3L_2(\mu\text{-dmpm})_3]PF_6 + H_2 \quad (1)$$

1a (L = xylNC)
1b (L = *t*-BuNC)

$$[Re_2H_3L_2(\mu\text{-dmpm})_3]PF_6 + 2L \rightarrow [Re_2HL_4(\mu\text{-dmpm})_3]PF_6 + H_2 \quad (2)$$

2a (L = xylNC)
2b (L = *t*-BuNC)
2c (L = CO)

of types **1** and **2**. We were unable to control the reaction conditions to obtain a pure sample of the bis(carbonyl) complex **1c**. The yields of the 1:2 complexes **1a** and **1b** were maximized by the use of the lower boiling methanol solvent, controlling the quantity of isocyanide ligand used, and short reaction times. The structural identities of these complexes were established by single-crystal X-ray structure analyses on crystals of compositions $[Re_2H_3(CNxyl)_2(dmpm)_3](PF_6)_{0.79}(ReO_4)_{0.21}$, $[Re_2H(CNxyl)_4(dmpm)_3]PF_6$, and $[Re_2H(CO)_4(dmpm)_3]PF_6\cdot(CH_3)_2CO$. These revealed that the structures of the dirhenium monocations in **1a**, **2a**, and **2c** can be represented as $[(xylNC)_2Re(\mu\text{-H})(\mu\text{-dmpm})_3ReH_2]^+$, $[(xylNC)_2Re(\mu\text{-H})(\mu\text{-dmpm})_3Re(CNxyl)_2]^+$, and $[(OC)_2Re(\mu\text{-H})(\mu\text{-dmpm})_3Re$-

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(10) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Xylyl Group Atoms of the Dirhenium Cation of **2a** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.18266 (5)	0.18649 (3)	0.18234 (2)	3.45 (1)
Re(2)	0.17888 (6)	0.20617 (3)	0.31475 (2)	4.20 (1)
P(11)	0.2841 (3)	0.2869 (2)	0.1791 (2)	4.7 (1)
P(12)	0.1061 (4)	0.0823 (2)	0.2016 (2)	4.5 (1)
P(13)	0.0055 (3)	0.2435 (2)	0.1798 (2)	4.6 (1)
P(21)	0.3189 (4)	0.2855 (2)	0.2993 (2)	5.2 (1)
P(22)	0.0646 (4)	0.1103 (2)	0.3177 (2)	5.4 (1)
P(23)	0.0301 (4)	0.2841 (2)	0.2942 (2)	5.8 (1)
N(10)	0.410 (1)	0.1143 (7)	0.1721 (5)	6.1 (4)
N(20)	0.148 (1)	0.2457 (8)	0.4285 (5)	8.2 (4)
N(100)	0.152 (1)	0.1750 (9)	0.0653 (5)	8.4 (4)
N(200)	0.382 (1)	0.1198 (6)	0.3577 (5)	6.4 (4)
C(10)	0.326 (1)	0.1421 (8)	0.1768 (6)	5.2 (4)
C(20)	0.159 (1)	0.2283 (8)	0.3860 (6)	6.2 (4)
C(100)	0.163 (1)	0.1796 (8)	0.1084 (5)	5.0 (4)
C(200)	0.305 (1)	0.1510 (8)	0.3409 (6)	5.7 (4)
C(111)	0.239 (2)	0.3546 (9)	0.1366 (7)	7.1 (5)
C(112)	0.425 (1)	0.2791 (9)	0.1582 (6)	6.5 (5)
C(121)	0.022 (2)	0.0387 (9)	0.1521 (6)	6.9 (5)
C(122)	0.210 (1)	0.0201 (8)	0.2192 (8)	7.2 (5)
C(131)	–0.033 (2)	0.2866 (9)	0.1201 (7)	7.3 (5)
C(132)	–0.126 (1)	0.203 (1)	0.1867 (8)	7.7 (5)
C(211)	0.458 (1)	0.252 (1)	0.2920 (8)	7.6 (5)
C(212)	0.348 (2)	0.3501 (9)	0.3462 (7)	8.2 (6)
C(221)	–0.066 (2)	0.108 (1)	0.3523 (7)	9.3 (6)
C(222)	0.131 (2)	0.0397 (8)	0.3485 (7)	7.3 (5)
C(231)	0.048 (2)	0.364 (1)	0.3237 (9)	11.1 (7)
C(232)	–0.106 (2)	0.267 (1)	0.3173 (9)	13.6 (8)
C(B1)	0.304 (1)	0.3339 (7)	0.2396 (6)	5.2 (4)
C(B2)	0.014 (1)	0.0756 (8)	0.2555 (6)	5.7 (4)
C(B3)	–0.002 (1)	0.3091 (8)	0.2275 (6)	6.0 (4)
H	0.24 (1)	0.177 (6)	0.256 (4)	5 (3)*

[a] The starred value indicates an atom was refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the xylyl group atoms are available as supplementary material.

$(CO)_2]^+$, respectively. ORTEP representations of these structures are shown in Figures 1–3 while the crystallographic data and important structural parameters are given in Tables I–VI. Some spectroscopic properties are presented in Table VII.

In spite of the very unsymmetrical nature of the bis(xylyl isocyanide) complex **1a**, the ^1H and $^{31}P\{^1H\}$ NMR spectra (Table VII) are deceptively simple and indicate the occurrence of some type of fluxional process. The spectrum for the xylNC ligands accords with the solid-state structure in which these two ligands are inequivalent (assuming equivalent methyl groups on each due to free rotation about the Re–C bonds). However, the ^1H spectrum of the dmpm ligands is quite simple, as is the $^{31}P\{^1H\}$ NMR spectrum which shows a single resonance (fwhm ≈ 36 Hz) exhibiting some poorly resolved structure. Note that the structure of **1a**, as represented in Figure 1, possesses at least four sets of chemically distinct phosphorus atoms. The Re–H resonances consists of a broad resonance at δ –9.35 which shows no resolvable P–H coupling. A temperature range study (+20 to –80 °C) on a CD_2Cl_2 solution of this complex showed that this resonance broadened slowly and then collapsed (with coalescence occurring at ca. –50 °C), followed by the appearance of a very broad resonance at δ –8.30 at the low temperature limit; this change was fully reversible upon rewarming the solution to +20 °C. The 1:2 *tert*-butyl isocyanide complex **1b** has NMR spectral properties very similar to those of **1a** and is therefore assumed to have a very similar structure. The IR spectrum of **1a** (recorded as a Nujol mull) exhibits ν(CN) modes at 1982 (vs) and 1924 (vs) cm^{-1}, with shoulders at ≈2010 and ≈1864 cm^{-1}, and a ν(P–F) mode at 840 (vs) cm^{-1}.

Table IV. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Atoms of the Dirhenium Cation of **2c** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.41732 (1)	–0.04623 (4)	0.10631 (2)	1.511 (8)
Re(2)	0.32484 (1)	–0.01127 (4)	0.06006 (2)	1.494 (8)
P(11)	0.42725 (8)	0.1601 (3)	0.0701 (1)	2.08 (6)
P(12)	0.39910 (8)	0.0087 (3)	0.2253 (1)	1.99 (6)
P(13)	0.40377 (8)	–0.2591 (3)	0.1186 (1)	2.06 (6)
P(21)	0.34121 (8)	0.1921 (3)	0.0259 (1)	1.98 (6)
P(22)	0.31184 (8)	0.0404 (3)	0.1821 (1)	2.06 (6)
P(23)	0.31794 (8)	–0.2277 (3)	0.0772 (1)	1.94 (6)
O(11)	0.4333 (2)	–0.0972 (9)	–0.0471 (4)	3.6 (2)
O(12)	0.5004 (2)	–0.0860 (9)	0.1515 (5)	4.1 (2)
O(21)	0.3448 (3)	–0.0690 (8)	–0.0901 (4)	4.0 (2)
O(22)	0.2428 (2)	0.0366 (8)	0.0118 (5)	4.1 (2)
C(11)	0.4274 (3)	–0.078 (1)	0.0094 (5)	2.1 (2)
C(12)	0.4694 (3)	–0.069 (1)	0.1329 (6)	2.2 (2)
C(21)	0.3384 (3)	–0.0468 (9)	–0.0331 (6)	2.0 (2)
C(22)	0.2735 (3)	0.016 (1)	0.0307 (6)	2.3 (2)
C(111)	0.4714 (3)	0.180 (1)	0.0232 (7)	3.3 (3)
C(112)	0.4303 (4)	0.293 (1)	0.1259 (6)	3.2 (3)
C(121)	0.4317 (4)	0.106 (1)	0.2738 (6)	3.5 (3)
C(122)	0.3926 (3)	–0.108 (1)	0.2910 (6)	3.0 (3)
C(131)	0.4170 (4)	–0.352 (1)	0.0442 (7)	3.4 (3)
C(132)	0.4282 (3)	–0.344 (1)	0.1866 (7)	3.5 (3)
C(211)	0.3182 (4)	0.236 (1)	–0.0559 (6)	3.4 (3)
C(212)	0.3331 (3)	0.329 (1)	0.0769 (6)	2.6 (2)
C(221)	0.2931 (3)	–0.070 (1)	0.2410 (6)	2.9 (3)
C(222)	0.2771 (3)	0.160 (1)	0.1964 (6)	2.9 (3)
C(231)	0.3207 (4)	–0.314 (1)	–0.0032 (6)	3.2 (3)
C(232)	0.2746 (3)	–0.288 (1)	0.1139 (7)	3.8 (3)
C(1B)	0.3922 (3)	0.208 (1)	0.0035 (6)	2.3 (2)
C(2B)	0.3554 (3)	0.095 (1)	0.2283 (5)	2.4 (2)
C(3B)	0.3541 (3)	–0.3015 (9)	0.1321 (5)	2.0 (2)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table V. Important Distances (Å) and Angles (deg) for the Cation of **1a**[a]

	Bond Distances		
Re(1)–Re(2)	3.448 (1)	Re(2)–P(22)	2.365 (8)
Re(1)–P(11)	2.452 (7)	Re(2)–P(23)	2.375 (7)
Re(1)–P(12)	2.378 (6)	N(30)–C(30)	1.21 (3)
Re(1)–P(13)	2.376 (6)	N(30)–C(31)	1.36 (3)
Re(1)–C(30)	1.92 (3)	N(40)–C(40)	1.16 (3)
Re(1)–C(40)	1.95 (2)	N(40)–C(41)	1.41 (3)
Re(1)–P(21)	2.413 (8)		
	Bond Angles		
Re(2)–Re(1)–P(11)	86.7 (2)	P(13)–Re(1)–C(40)	92.3 (6)
Re(2)–Re(1)–P(12)	87.3 (2)	C(30)–Re(1)–C(40)	92(1)
Re(2)–Re(1)–P(13)	87.5 (2)	Re(1)–Re(2)–P(21)	86.1 (2)
Re(2)–Re(1)–C(30)	87.9 (7)	Re(1)–Re(2)–P(22)	84.4 (2)
Re(2)–Re(1)–C(40)	179.6 (7)	Re(1)–Re(2)–P(23)	84.5 (2)
P(11)–Re(1)–P(12)	96.4 (3)	P(21)–Re(2)–P(22)	99.6 (3)
P(11)–Re(1)–P(13)	100.6 (3)	P(21)–Re(2)–P(23)	105.9 (3)
P(11)–Re(1)–C(30)	174.4 (7)	P(22)–Re(2)–P(23)	151.4 (3)
P(11)–Re(1)–C(40)	93.0 (7)	C(30)–N(30)–C(31)	158(2)
P(12)–Re(1)–P(13)	161.9 (3)	C(40)–N(40)–C(41)	163(3)
P(12)–Re(1)–C(30)	84.9 (7)	Re(1)–C(30)–N(30)	173(2)
P(12)–Re(1)–C(40)	93.0 (7)	Re(1)–C(40)–N(40)	179(2)
P(13)–Re(1)–C(30)	77.5 (7)		

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

Each of the complexes **2a**–**2c** shows a single Re–H resonance in their ^1H NMR spectra, which in the case of **2c** is a well-resolved multiplet that can be treated as a triplet of pentets. This pattern arises from P–H coupling involving the phosphorus atoms of the cis and trans dmpm phosphine ligands, and can be satisfactorily simulated with J_{PH} coupling constants of 20.4 and 9.1 Hz. The CH_3- resonances of the dmpm ligands appear as two broad singlets in a 2:1 intensity ratio, while the $-CH_2-$ resonances consist of an ABX_4 pattern for the pair of trans dmpm ligands and a triplet for the dmpm ligand that is cis to this pair. These properties accord with the essentially rigid structures as repre-

Table VI. Comparison of the Important Distances (Å) and Angles (deg) for **2a** and **2c**[a]

2a		2c	
	Bond Distances[b]		
Re(1)-Re(2)	3.446 (1)	Re(1)-Re(2)	3.3625 (4)
Re(1)-P(11)	2.384 (4)	Re(1)-P(11)	2.397 (2)
Re(1)-P(12)	2.377 (4)	Re(1)-P(13)	2.398 (2)
Re(1)-P(13)	2.416 (4)	Re(1)-P(12)	2.461 (2)
Re(1)-C(10)	1.95 (2)	Re(1)-C(11)	1.934 (8)
Re(1)-C(100)	1.92 (2)	Re(1)-C(12)	1.900 (8)
Re(1)-H	2.0 (1)		
Re(2)-P(21)	2.379 (5)	Re(2)-P(21)	2.400 (2)
Re(2)-P(22)	2.390 (5)	Re(2)-P(23)	2.412 (2)
Re(2)-P(23)	2.425 (5)	Re(2)-P(22)	2.466 (2)
Re(2)-C(20)	1.92 (2)	Re(2)-C(21)	1.903 (8)
Re(2)-C(200)	1.97 (2)	Re(2)-C(22)	1.895 (9)
Re(2)-H	1.8 (1)		
N(10)-C(10)	1.17 (2)	O(11)-C(11)	1.130 (9)
N(100)-C(100)	1.12 (2)	O(12)-C(12)	1.15 (1)
N(200)-C(200)	1.18 (2)	O(21)-C(21)	1.15 (1)
N(20)-C(20)	1.17 (2)	O(22)-C(22)	1.15 (1)
	Bond Angles		
P(11)-Re(1)-P(12)	167.8 (2)	P(11)-Re(1)-P(13)	168.48 (7)
P(11)-Re(1)-P(13)	91.9 (2)	P(11)-Re(1)-P(12)	94.58 (7)
P(11)-Re(1)-C(10)	86.9 (5)	P(11)-Re(1)-C(11)	82.1 (3)
P(11)-Re(1)-C(100)	93.8 (5)	P(11)-Re(1)-C(12)	93.4 (3)
P(12)-Re(1)-P(13)	95.1 (2)	P(12)-Re(1)-P(13)	95.30 (7)
P(12)-Re(1)-C(10)	87.1 (5)	P(13)-Re(1)-C(11)	87.6 (3)
P(12)-Re(1)-C(100)	96.6 (5)	P(13)-Re(1)-C(12)	92.0 (3)
P(13)-Re(1)-C(10)	174.2 (5)	P(12)-Re(1)-C(11)	174.0 (2)
P(13)-Re(1)-C(100)	86.9 (5)	P(12)-Re(1)-C(12)	92.6 (2)
C(10)-Re(1)-C(100)	87.5 (7)	C(11)-Re(1)-C(12)	92.6 (3)
P(21)-Re(2)-P(22)	166.3 (2)	P(21)-Re(2)-P(23)	168.29 (7)
P(21)-Re(2)-P(23)	91.9 (2)	P(21)-Re(2)-P(22)	95.48 (7)
P(21)-Re(2)-C(200)	85.0 (5)	P(21)-Re(2)-C(21)	82.4 (2)
P(21)-Re(2)-C(20)	97.1 (6)	P(21)-Re(2)-C(22)	90.2 (3)
P(22)-Re(2)-P(23)	97.4 (2)	P(22)-Re(2)-P(23)	94.35 (7)
P(22)-Re(2)-C(200)	87.2 (5)	P(23)-Re(2)-C(21)	87.4 (2)
P(22)-Re(2)-C(20)	93.6 (6)	P(23)-Re(2)-C(22)	95.6 (3)
P(23)-Re(2)-C(200)	171.3 (5)	P(22)-Re(2)-C(21)	176.0 (2)
P(23)-Re(2)-C(20)	86.0 (6)	P(22)-Re(2)-C(22)	93.3 (2)
C(20)-Re(2)-C(200)	86.3 (7)	C(21)-Re(2)-C(22)	90.1 (3)
Re(1)-C(10)-N(10)	178 (2)	Re(1)-C(11)-O(11)	180 (1)
Re(1)-C(100)-N(100)	179 (2)	Re(1)-C(12)-O(12)	176.9 (7)
Re(2)-C(200)-N(200)	178 (2)	Re(2)-C(21)-O(21)	176.8 (7)
Re(2)-C(20)-N(20)	176 (2)	Re(2)-C(22)-O(22)	177.2 (7)
Re(1)-H-Re(2)	128 (7)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] The data are arranged so that corresponding distances and angles in these two closely related structures (Figures 2 and 3) are compared.

sented in Figures 2 and 3. The $^{31}P\{^1H\}$ NMR spectra of **2a**–**2c** display two multiplets in an intensity ratio 1:2, an observation which is consistent with this same structure.

The Nujol mull IR spectra of **2a** and **2b** show two strong, broad ν(CN) bands (2026 and 1992 cm^{-1} for **2a** and 2042 and 1880 cm^{-1} for **2b**), while the carbonyl complex **2c** displays four ν(CO) bands at 1956, 1930, 1892, and 1860 cm^{-1} (these are at 1961, 1930, 1890, and 1857 cm^{-1} in the CH_2Cl_2 solution spectrum). All three complexes show an intense ν(P–F) mode at 842 (±2) cm^{-1} in their IR spectra.

While cyclic voltammetric (CV) measurements on 0.1 M TBAH in CH_2Cl_2 solutions of **1a** and **1b** revealed only irreversible oxidation processes at $E_{p,a}$ = +0.54 and +0.84 V vs Ag/AgCl for **1a** and $E_{p,a}$ = +0.26 and +0.45 V vs Ag/AgCl for **1b** when a sweep rate of 200 mV s^{-1} was used, the tetrakis(isocyanide) complexes **2a** and **2b** show more reversible redox behavior. Complex **2a** has a reversible oxidation at $E_{1/2}$ = +0.33 V (with $E_{p,a} - E_{p,c}$ = 80 mV) and an irreversible oxidation at $E_{p,a}$ = +0.76 V; for **2b** these processes are at +0.01 V ($E_{p,a} - E_{p,c}$ = 60 mV) and +0.49 V vs Ag/AgCl. The CV of the carbonyl complex **2c** has only an irreversible oxidation at $E_{p,c}$ = +1.30 V vs Ag/AgCl (v = 200 mV s^{-1}). The reversibility of the first oxidation of **2a** has been demonstrated both by bulk electrolysis at ca. +0.5 V and by use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ as a chemical one-electron oxidant. Solutions of the red dication $[Re_2H(CNxyl)_4(\mu\text{-dmpm})_3]^{2+}$ give a CV that is identical to that for the monocation parent, with the exception that the reversible process at $E_{1/2}$ = +0.33 now corresponds to a reduction. Rereduction of the dication

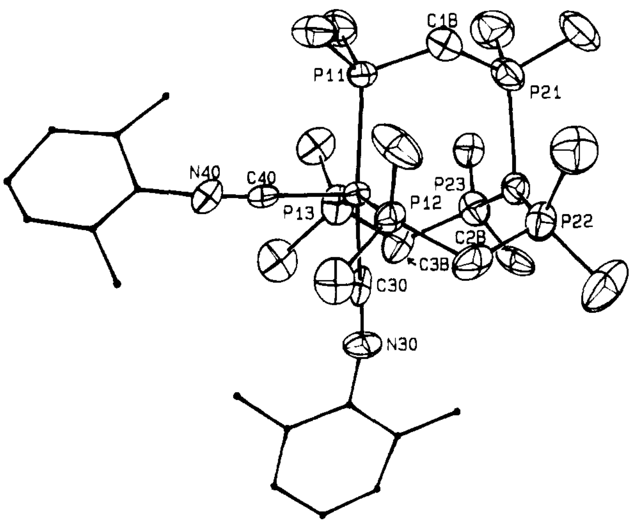

Figure 1. ORTEP view of the dirhenium-containing cation $[Re_2H_3(CNxyl)_2(\mu\text{-dmpm})_3]^+$ of **1a**. The thermal ellipsoids are drawn at the 50% probability level. The positions of the bridging and terminal hydride ligands were not determined. The labelling of the rhenium atoms Re(1) (left-hand side) and Re(2) (right-hand side) has been omitted for clarity.

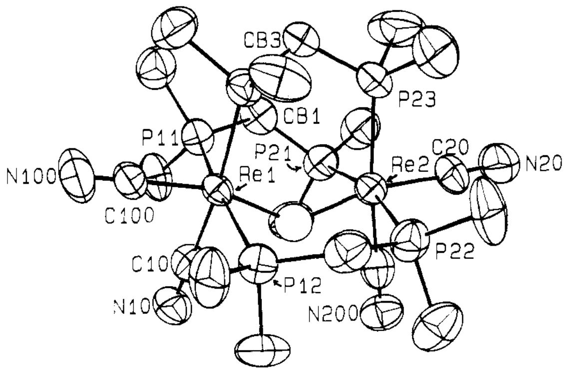

Figure 2. ORTEP view of the dirhenium-containing cation $[Re_2H(CNxyl)_4(\mu\text{-dmpm})_3]^+$ of **2a** with the xylyl groups omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. The unlabelled bridging hydride ligand, which is shown as an open circle, partially obscures one of the methyl carbons of a dmpm ligand.

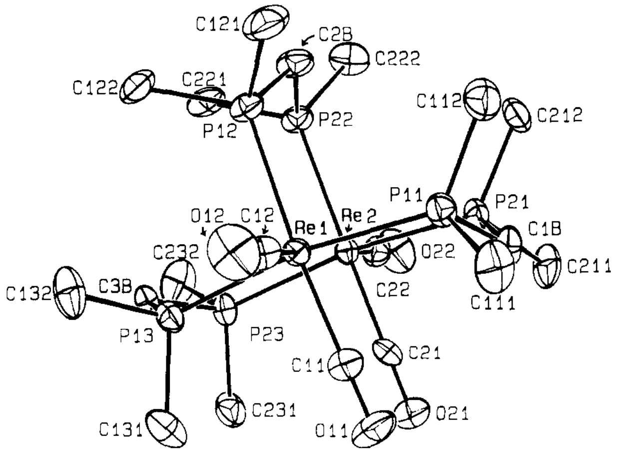

Figure 3. ORTEP view of the dirhenium-containing cation $[Re_2H(CO)_4(\mu\text{-dmpm})_3]^+$ of **2c**. The thermal ellipsoids are drawn at the 50% probability level. The position of the bridging hydride ligand was not determined.

Table VII. NMR Spectral Data for the Complexes $[Re_2H_{5-n}L_n(\mu\text{-dmpm})_3]PF_6$ (n = 2 or 4; L = RNC or CO)[a]

	^1H NMR, δ				
complex	RNC	dmpm ($-CH_2-$)[b]	dmpm ($-CH_3$)[b]	Re–H	$^{31}P\{^1H\}$NMR, δ[b,c]
$[Re_2H_3(CNxyl)_2(\mu\text{-dmpm})_3]PF_6$	+7.07 m, +2.48 s, +2.41 s	+3.08 br (2), +2.61 t (1)	+1.81 s (1), +1.69 s (1)	−9.35 br	−29.3 m
$[Re_2H_3(CN\text{-}t\text{-}Bu)_2(\mu\text{-dmpm})_3]PF_6$	+1.49 s, +1.33 s	+3.07 br (1), +2.87 b (1), + 2.59 t (1)	≈+1.7[d]	−9.49 br	−29.4 m
$[Re_2H(CNxyl)_4(\mu\text{-dmpm})_3]PF_6$	+7.01 m, +2.32 s, +2.22 s	+3.80 br (1), +3.23 t (1), +2.55 br (1)	+1.86 s (1), +1.74 s (2)	−17.07 m	−34.2 m (2), −39.5 m (1)[e]
$[Re_2H(CN\text{-}t\text{-}Bu)_4(\mu\text{-dmpm})_3]PF_6$	+1.48 s, +1.33 s	+3.48 br (1), +2.91 t (1), +2.30 br (1)	+1.77 s (1), +1.59 s (2)	−18.01 br	−35.0 m (2), −39.6 m (1)
$[Re_2H(CO)_4(\mu\text{-dmpm})_3]PF_6$		+3.59 m (1), +3.10 m (1), +2.94 t (1)	+2.01 s (1), +1.90 s (2)	−16.09 t of p[f]	−30.7 m (1), −33.5 m (2)

[a] Spectra recorded at room temperature in $CDCl_3$. Abbreviations are as follows: br = broad, s = singlet, t = triplet, m = multiplet, t of p = triplet of pentets. [b] Numbers in parentheses signify the relative intensities within each set of resonances. [c] For each complex an additional resonance (a binomial septet) is present close to δ −144 which is due to the $[PF_6]^-$ anion. [d] This resonance consists of several closely overlapping singlets. [e] $^2J_{P-H}$ = 11.5 Hz. [f] $^2J_{P-H}$ = 20.4 and 9.1 Hz (based upon a computer simulation).

to the monocation occurs quite readily. Characterization of a CH_2Cl_2 glass of the complex dication $[Re_2H(CNxyl)_4(\mu\text{-dmpm})_3]^{2+}$ at −160 °C by ESR spectroscopy shows that this species is paramagnetic. A broad signal is located at 3275 G ($g \approx 1.99$).

Discussion

The conversion of the electronically unsaturated complex $[Re_2(\mu\text{-H})H_4(\mu\text{-dmpm})_3]PF_6$ to $[Re_2H_3L_2(\mu\text{-dmpm})_3]PF_6$ (**1**) and $[Re_2HL_4(\mu\text{-dmpm})_3]PF_6$ (**2**), where L = RNC or CO, occurs in a stepwise fashion such that the $Re^{III}Re^{III}$ precursor (treating all hydride ligands as being hydridic in nature) is reduced in two, two-electron steps, with concomitant reductive elimination of H_2, to give Re^IRe^{III} and Re^IRe^I species. In this series of complexes the $[Re_2(\mu\text{-H})(\mu\text{-dmpm})_3]$ unit is preserved, and the only metal-to-metal interaction is via a three-center, two-electron Re–H–Re bond. In the products of type **2**, the electronic unsaturation that is present in the $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$ precursor is fully relieved, with the individual 17-electron Re fragments in **2** achieving an 18-electron count through formation of the Re–H–Re interaction.

The single-crystal X-ray structure determinations of **1a**, **2a**, and **2c** show that the $[Re_2(\mu\text{-dmpm})_3]$ unit which is present in $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$[3,6] is preserved; two dmpm ligands assume a trans bridging disposition to one another, while the other is cis to this pair. For the more symmetrical complexes **2a** and **2c**, the Re–P bond distances for the dmpm ligands that are trans to one another span the range 2.377–2.412 Å, and are shorter than those Re–P distances which are trans to the xylNC or CO ligands (range 2.416–2.466 Å). A similar disparity is found for the Re–P distances in $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$,[3,6] as well as **1a**. The coordination geometry about each Re atom in these three structures can be considered to be approximately octahedral, the bond angles about the Re atoms being fairly close to 90°. The xylNC and CO ligands can be classified as being axially or equatorially bound; axial being defined as colinear (or approximately colinear) with the Re–H–Re unit. However, within the limits of 3σ, the structural parameters for the different sets of xylNC and CO ligands are not significantly different. This includes the Re–C, C–N and CO distances, as well as the associated bond angles (see Tables V and VI). In all instances the Re–C–O and Re–C–N angles are essentially linear (range 173 (2)–180 (1)°).

For **1a** and **2c** the Re_2P_6 skeletons are essentially eclipsed, with the torsional angles being close to zero; this is clearly seen in Figure 3 for the tetrakis(carbonyl) complex, where it is apparent that the two equatorial CO ligands are also eclipsed. The tetrakis(xylyl isocyanide) complex **2a** is more distorted, presumably as a consequence of nonbonding repulsions between the pair of equatorial xylNC ligands. This is reflected by a staggering between the halves of the molecule and a considerable bending of the Re–H–Re bridge unit (128 (7)°). Only in the case of **2a** did we find evidence for a hydride ligand in the structure refinement. However, in all instances the ^1H NMR spectra provide confirmatory evidence for the presence of one or more of these ligands (see Results Section), and for these three structures the Re···Re distances spanned the narrow range 3.36–3.45 Å and are very similar to the Re···Re distance in $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$ (3.5150 (4) Å).[3,6] This accords with a similar type of interaction being present in each. Note that the absence of a bridging hydride ligand would render these molecules paramagnetic since a diamagnetic ground state through a three-center, two-electron Re–H–Re interaction would no longer be possible. Also, in the absence of a Re–H–Re unit such electronically unsaturated species would be expected to have much shorter Re–Re contacts, especially when bridging ligands are present which are of a type that can favor strong metal–metal bonding. In the case of **1a**, it would be reasonable to place one of the terminal hydride ligands essentially trans to the Re(2)–P(21) bond since the angle between the P atoms that would be cis to this Re–H bond (i.e. P(22)–Re(2)–P(23) = 151.4 (3)° is the largest P–Re–P angle about Re(2) and similar to the analogous P–Re–P angles found in the structure of $[Re_2H_5(\mu\text{-dmpm})_3]PF_6$ (151.07 (6) and 151.56 (7)°).[6] The corresponding angle about Re(1) in **1a** (i.e. P(12)–Re–P(13) = 161.9 (3)°), where an xylNC ligand is present instead of a hydride, is significantly larger. The other terminal Re–H bond would presumably lie approximately colinear with the Re–Re vector in the empty axial position at Re(2) (see Figure 1).

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters for **1a**, **2a**, and **2c** (Tables S1, S7, and S13), atomic positional parameters (Tables S2, S3, S8, S9, S14, and S15), anisotropic thermal parameters (Tables S4, S10, and S16), and complete bond distances (Tables S5, S11, and S17) and bond angles (Tables S6, S12, and S18) (52 pages). Ordering information is given on any current masthead page.