potential was chemically irreversible (as judged by bulk electrolysis at −0.65 V). An attempt to generate a solution of the monoanion using cobaltocene as the reducing agent failed to yield a pure product. The redox behavior observed for $Re_2(OR)_2X_4(PPh_3)_2$ differs considerably from that reported for $Re_2X_6(PR_3)_2$ compounds,[25] for which two one-electron reductions occur at potentials more negative than +0.1 V.

(e) Concluding Remarks. In our examination of the reactions of $Re_2(O_2CR)_2X_4L_2$ (X = Cl or Br; R = CH_3 or C_2H_5) toward monodentate tertiary phosphines, we have discovered a novel type of disproportionation reaction in which a Re(III)–Re(III) core is transformed into Re(IV)–Re(II), namely, in the complexes of stoichiometry $Re_2(OR)_2X_4(PPh_3)_2$. This constitutes an important development in the field of multiple-bond chemistry and may presage the discovery of other examples of this kind. The only previous example of this type of reaction was encountered many years ago; the $Re_2Cl_8^{2-}$ ion was found to react with the 2,5-dithiahexane ligand ($CH_3SCH_2CH_2SCH_3$, dth) to afford the triply bonded paramagnetic complex $Cl_4ReRe(dth)_2Cl$.[26] The present discovery is much more significant in terms of its potential scope. Furthermore, these reactions are of additional significance, for they provide a route to a new class of rarely encountered alkoxide complexes of rhenium.[27] Our studies are continuing into the reactivity patterns of the dirhenium(III) carboxylates $Re_2(O_2CR)_2X_4L_2$.

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Supplementary Material Available: Tables of complete bond distances and angles, anisotropic thermal parameters, and root-mean-square amplitudes of thermal vibration (9 pages); a table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(24) This solution possessed a cyclic voltammogram with couples at $E_{1/2}$ = +0.81 and −0.60 V vs. Ag/AgCl, both of which correspond to one-electron reductions. The X-band ESR spectrum (CH_2Cl_2 solution at −160 °C) gave a broad complex signal between 2000 and 5500 G. We have not yet analyzed this spectrum in detail.

(25) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

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(27) The only previous example of a multiply bonded dirhenium complex that also contains a Re–OR bond is $Re_2(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2Cl_3(OR)$ (R = Me, Et, or *n*-Pr); see: Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

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Thermal Reaction of $Mo_2I_4(CO)_8$ with PMe_2Ph, PEt_2Ph, and Pyridine. Formation of Metal–Metal Quadruple Bonds vs. Disproportionation. X-ray Crystal Structures of $MoI_3(PMe_2Ph)_2(POMe_2Ph)$ and $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$

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The thermal reactions of $Mo_2I_4(CO)_8$ with PMe_2Ph, PEt_2Ph, and pyridine (py) have been studied. The reaction with pyridine leads to disproportionation with formation of $Mo(CO)_3(py)_3$ and $MoI_3(py)_3$. The reactions with the two phosphines in toluene as solvent lead to disproportionation as well as to the formation of the $Mo_2I_4L_4$ (L = PMe_2Ph, PEt_2Ph) dimers with metal–metal quadruple bonds. The use of THF as solvent in the PEt_2Ph reaction suppresses the formation of the molybdenum(II) dimer in favor of disproportionation. Compounds $Mo_2I_4(PMe_2Ph)_4$ (**1**) and $MoI_3(PMe_2Ph)_2(POMe_2Ph)$ (**2**) have been isolated from the PMe_2Ph reaction in toluene, while the compound $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$ (**3**) has been obtained from the PEt_2Ph reaction in THF. Compounds **2** and **3** have been structually characterized by X-ray diffraction methods. Compound **2**: space group $Pmn2_1$, a = 13.801 (3) Å, b = 12.303 (3) Å, c = 9.298 (1) Å, V = 1578.7 (8) Å^3, Z = 2, R = 0.0516 (R_w = 0.0622) for 1038 data with $F_o^2 > 3\sigma(F_o^2)$. Compound **3**: space group $P2_1/c$, a = 20.144 (6) Å, b = 10.368 (2) Å, c = 19.822 (3) Å, β = 109.37°, V = 3904 (3) Å^3, Z = 4, R = 0.0371 (R_w = 0.0540) for 3902 data with $F_o^2 > 3\sigma(F_o^2)$. A possible mechanism that interrelates the two different pathways is discussed.

Introduction

The recent development[1] of a convenient synthesis of $Mo_2I_4(CO)_8$[2] has permitted more reactivity studies to be carried out on this molecule. As a result, a new route to the quadruply bonded dimolybdenum(II) tetraiodide complexes has been recently found in this laboratory.[3] In particular, $Mo_2I_4(PMe_3)_4$,[3a] $Mo_2I_4(dppm)_2$,[3a,b] and $Mo_2I_4(dmpm)_2$[3c] could be produced upon reaction of $Mo_2I_4(CO)_8$ with the appropriate phosphine in refluxing toluene. To probe the possible application of this method to the preparation of a wider variety of dimolybdenum(II) molecules, we have investigated the same reaction with different systems. We report here the results obtained by using PMe_2Ph, PEt_2Ph, and pyridine (py) as ligands, which show this reaction to be far more complicated than expected.

Experimental Section

All operations were carried out under an atmosphere of prepurfied argon. Solvents were dried by conventional methods and distilled under dinitrogen. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer; the solution spectra were recorded on expanded abscissa and calibrated with both CO(g) and water vapor. Elemental analyses were by Galbraith Laboratories, Knoxville, TN. PMe_2Ph and PEt_2Ph were purchased from Strem Chemicals and used without further purification. $Mo_2I_4(CO)_8$ was prepared as previously described.[1]

Reaction of $Mo_2I_4(CO)_8$ with PMe_2Ph. $Mo_2I_4(CO)_8$ (0.38 g, 0.41 mmol) was treated at room temperature with PMe_2Ph (0.23 mL, 1.6 mmol) in 20 mL of toluene as solvent. Vigorous gas evolution occurred,

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(1) (a) Poli, R. "Tesi di perfezionamento", Scuola Normale Superiore, Pisa, Italy, 1985. (b) Calderazzo, F.; Poli, R.; Zanazzi, P. F., manuscript in preparation.

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and the resulting yellow solution had IR bands at 2026 s, 1957 s, and 1919 s cm^{-1}. After filtration, the solution was refluxed overnight to produce a blue-green solution from which, upon cooling to room temperature, 0.25 g of dark blue crystals of $Mo_2I_4(PMe_2Ph)_4$ (**1**) was obtained (yield 49%). Anal. Calcd for $C_{32}H_{44}I_4Mo_2P_4$: C, 30.7; H, 3.5. Found: C, 30.6; H, 3.5. UV-visible spectroscopic properties [CH_2Cl_2; λ_{max}, cm^{-1} (ϵ, cm^{-1} L mol^{-1})]: 15 300 (5080), 24 800 (7350), 25 200 (7440). The mother solution of this solid had IR bands at 2017 m, 1937 m, 1915 m, 1897 s, 1888 sh, and 1842 s cm^{-1}. This was evaporated to dryness and the residue recrystallized from CH_2Cl_2/*n*-hexane. A mixture of red crystals and more crystals of compound **1** was obtained over a few days. A red crystal from this crop (compound **2**) was used for the X-ray diffractometric study.

Reaction of $Mo_2I_4(CO)_8$ with PEt_2Ph. (A) In Toluene as Solvent. $Mo_2I_4(CO)_8$ and PEt_2Ph in a 1:4 molar ratio were mixed in toluene. Gas evolution occurred, and a red-orange solution having IR bands at 2021 s, 1949 s, and 1922 s cm^{-1} was obtained. Subsequent overnight reflux afforded a dark emerald green solution that exhibited weak IR bands at 2020, 1955, 1915, 1895, and 1840 cm^{-1} and a band in the visible spectrum at 15 400 cm^{-1}. No pure crystalline material could be isolated during the subsequent workup of the mixture.

(B) In THF as Solvent. $Mo_2I_4(CO)_8$ (0.23 g, 0.25 mmol) was treated with 15 mL of THF. Gas evolution occurred, and the resulting orange solution was treated with 0.17 mL of PEt_2Ph (0.97 mmol). The resulting solution, which showed IR bands at 2021 s, 1952 s, and 1923 s cm^{-1}, was refluxed overnight. At this point the solution was golden yellow and showed IR bands at 2017 m, 1947 w, 1911 m, 1892 s, ca. 1875 sh, and 1836 cm^{-1}. These properties did not change upon further reflux for 2 days more. The final mixture was filtered, concentrated under reduced pressure, and finally layered with *n*-hexane. Orange-red crystals formed over a period of several days at room temperature (compound **3**). IR (Nujol mull): 2370 w, 2350 w, 1590 w, 1570 w, 1435 m, 1415 m, 1160 m, 1120 m, 1105 m, 1075 w, 1050 m, 1035 m, 1020 w, 1000 w, 770 m, 750 ms, 730 s, 710 m, 700 ms, 635 w, 530 w, 500 m, 480 w, and 440 m cm^{-1}. A single crystal from this crop was used for the X-ray diffractometric study.

Reaction of $Mo_2I_4(CO)_8$ with Pyridine. $Mo_2I_4(CO)_8$ (0.37 g, 0.40 mmol) was treated with 20 mL of pyridine; profuse gas evolution was observed. The resulting red solution was immediately used for an IR spectroscopic study in the carbonyl stretching region: it exhibited bands at 2022 s, 1942 s, 1926 s, 1904 s, 1832 w, and 1778 s cm^{-1}. The spectrum was recorded a second time within a few minutes, the result being that the bands at 2022, 1942, and 1926 cm^{-1} had decreased in intensity, while those at 1904, 1832, and 1778 cm^{-1} had increased. The solution was then refluxed overnight. The color did not change, but the final IR spectrum of the solution showed only two bands at 1904 s and 1778 s cm^{-1}. Cooling to −20 °C afforded a microcrystalline yellow-orange solid, which was filtered off, washed with toluene, and dried (compound **4**); yield 0.11 g. IR (Nujol mull): 1605 s, 1480 s, 1440 s, 1360 m, 1220 s, 1150 m, 1070 s, 1050 ms, 1010 ms, 980 w, 875 w, 760 s, 730 w, 695 s, 655 w, 645 m, 450 w, and 435 w cm^{-1}. Anal. Calcd for $C_{15}H_{15}I_3MoN_3$: C, 25.2; H, 2.2; N, 5.9. Found: C, 25.5; H, 2.2; N, 5.9.

X-ray Crystallography. $MoI_3(PMe_2Ph)_2(POMe_2Ph)$ (2). A single crystal protected in a thin-wall glass capillary was mounted on a computer-controlled CAD-4 diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The lattice was found to be orthorhombic, and the lattice parameters were determined by a least-squares calculation based on the setting angles of 25 reflections. The intensities were collected up to $2\theta = 45°$ with the ω–2θ scan technique, the scan range being $\Delta\omega = A + B \tan \omega$, with $A = 1.1°$ and $B = 0.35°$, and the speed ranging between 0.037 and 0.158 deg s^{-1}. A total of 1105 reflections were measured, of which 67, having $I < 3\sigma(I)$, were considered as unobserved and excluded from the refinement. Three standard reflections, measured periodically, showed no significant variation of intensity. The data were corrected for Lorentz and polarization factors. A semiempirical absorption correction based on the variation in intensity during azimuthal scans of eight reflections, according to the method of North, Phillips, and Mathews,[4] was also applied. Systematic absences from the data ($h + l \neq 2n$ for $h0l$) indicated that the space group could be either *Pmnm* or $Pmn2_1$. The centrosymmetric space group was initially chosen, but it proved later to be incorrect. Direct methods on the $Pmn2_1$ space group revealed the positions of the heavy atoms, which were then refined by the full-matrix least-squares method with the Enraf-Nonius Structure Determination Package of programs. A difference Fourier map revealed the positions of the other non-hydrogen atoms. Final anisotropic refinement converged to $R = 0.0516$ (R_w = 0.0622). At this stage, four peaks with heights of 1.9–1.4 e Å^{-3} were still present in the difference Fourier map and were located at about 1.15 Å from the molybdenum and the three iodine atoms, perpendicular to the symmetry plane. They were considered to be the result of series termination errors. The highest peak after these had a height of 1.1 e Å^{-3}. No attempt was made to locate and refine the hydrogen atoms.

Table I. Crystal Data for Compounds **2** and **3**

	2	**3**
formula	$C_{24}H_{33}I_3MoOP_3$	$C_{30}H_{46}I_4MoP_3$
fw	907.10	1103.18
space group	$Pmn2_1$	$P2_1/c$
systematic absences	$h0l$, $h + l \neq 2n$	$h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$
a, Å	13.801 (3)	20.144 (6)
b, Å	12.303 (3)	10.368 (2)
c, Å	9.298 (1)	19.822 (3)
α, deg	90	90
β, deg	90	109.37 (3)
γ, deg	90	90
V, Å^3	1578.7 (8)	3904 (3)
Z	2	4
d_{calcd}, g/cm^3	1.908	1.877
cryst size, mm	0.2 × 0.3 × 0.5	0.1 × 0.3 × 0.8
μ(Mo Kα), cm^{-1}	34.74	35.98
data colln instrument	CAD-4	CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.710 73 Å)	^{d}
orientation reflecns: no., range (2θ)	25, 17–37	25, 22–36
temp, °C	20	20
scan method	ω–2θ	ω
data collecn range, 2θ, deg	4–45	4–45
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1038	3902
no. of parameters refined	163	297
transmission factors: max, min	99.84, 47.72%	99.80, 63.62%
R^a	0.0516	0.0371
$R_w{}^b$	0.0622	0.0540
quality-of-fit indicator^c	1.954	1.559
largest shift/esd, final cycle	0.01	0.66
largest peak, e/Å^3	1.963	1.246

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$. [d] As for compound **2**.

$[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$ (3). A single crystal was put on the tip of a glass fiber and mounted on a computer-controlled CAD-4 diffractometer, as previously described for compound **2**. The lattice was found to be monoclinic primitive. The ω-scan technique was employed, the scan range being $\Delta\omega = A + B \tan \omega$, with $A = 0.8°$ and $B = 0.35°$ and the scan speed ranging between 0.018 and 0.167 deg s^{-1}. A total of 5697 reflections were measured, of which 1795, having $I < 3\sigma(I)$, were considered as unobserved and excluded from the refinement. No significant change was observed in the intensity of three periodically measured standard reflections. Corrections for Lorentz, polarization, and absorption were applied as for compound **2** (see above). Systematic absences from the data ($l \neq 2n$ for $h0l$ and $k \neq 2n$ for $0k0$) uniquely determined the space group as $P2_1/c$. The structure was solved by direct methods and refined as previously described for compound **2**. The final refinement converged to $R = 0.0371$ ($R_w = 0.0540$). The carbon atoms of the ethyl groups in the phosphonium cation showed somewhat high thermal parameters. This may be due to high thermal motion and/or to some sort of disorder. The latter possibility was also suggested by the presence of peaks of about 1–1.2 e Å^{-3} in the final Fourier map which are at bonding distance from P(3) and from the ethyl carbons attached to it. An attempt to model this disorder was unsuccessful.

Significant crystallographic data for compounds **2** and **3** are collected in Table I. Fractional atomic coordinates are in Table II for compound **2** and in Table III for compound **3**. Relevant bond distances and angles are collected in Tables IV (compound **2**) and V (compound **3**).

Results

Reaction of $Mo_2I_4(CO)_8$ with PMe_2Ph in toluene proceeds at room temperature to produce $MoI_2(CO)_3(PMe_2Ph)_2$ and CO. This is evidenced by the solution IR spectrum, which shows three bands whose positions and relative intensities (see Experimental Section) are typical of $MX_2(CO)_3L_2$ complexes (M = Mo, W; X = halogen; L = phosphine).[5] Subsequent reflux affords a

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[4] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $MoI_3(PMe_2Ph)_2(POMe_2Ph)$[a]

atom	*x*	*y*	*z*	*B*
I1	0.500	0.3540 (1)	0.953	3.52 (3)
I2	0.500	−0.0062 (2)	0.5984 (3)	5.76 (5)
I3	0.500	0.0383 (1)	1.0288 (3)	4.10 (3)
Mo	0.500	0.1679 (2)	0.7871 (3)	2.80 (4)
P1	0.3121 (3)	0.1640 (4)	0.8062 (6)	3.7 (1)
P2	0.500	0.3064 (5)	0.4548 (9)	3.7 (1)
O	0.500	0.272 (1)	0.609 (2)	4.4 (4)
C1	0.262 (1)	0.213 (2)	0.980 (2)	5.2 (5)
C2	0.257 (1)	0.027 (1)	0.790 (4)	6.1 (6)
C3	0.247 (1)	0.247 (1)	0.680 (2)	4.0 (4)
C4	0.184 (1)	0.206 (2)	0.577 (3)	4.9 (5)
C5	0.137 (1)	0.268 (2)	0.475 (3)	5.5 (5)
C6	0.154 (1)	0.381 (2)	0.472 (4)	7.2 (7)
C7	0.219 (2)	0.426 (2)	0.574 (3)	7.5 (7)
C8	0.268 (1)	0.358 (2))	0.676 (3)	5.5 (5)
C9	0.396 (1)	0.262 (2)	0.359 (2)	5.0 (4)
C10	0.500	0.456 (2)	0.454 (3)	3.2 (5)
C11	0.500	0.512 (2)	0.578 (3)	5.0 (7)
C12	0.500	0.626 (3)	0.572 (4)	7 (1)
C13	0.500	0.682 (2)	0.439 (4)	5.2 (7)
C14	0.500	0.626 (3)	0.321 (4)	8 (1)
C15	0.500	0.510 (3)	0.325 (4)	6.3 (8)

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

Table III. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$[a]

atom	*x*	*y*	*z*	*B*
Mo1	1.000	0.000	1.000	4.21 (2)
I1	0.89383 (3)	0.18349 (6)	0.97665 (3)	5.64 (2)
I2	0.94221 (3)	−0.08401 (7)	0.85886 (3)	5.72 (2)
P1	1.0754 (1)	0.1624 (3)	0.9554 (1)	5.09 (6)
C1	1.1209 (5)	0.087 (1)	0.8985 (5)	7.0 (3)
C2	1.1643 (5)	0.180 (1)	0.8686 (6)	10.2 (4)
C3	1.1448 (5)	0.248 (1)	1.0274 (6)	7.2 (3)
C4	1.2034 (7)	0.160 (2)	1.064 (1)	14.6 (6)
C5	1.0305 (4)	0.3006 (9)	0.9027 (4)	5.2 (2)
C6	0.9946 (5)	0.284 (1)	0.8281 (5)	6.6 (3)
C7	0.9611 (5)	0.391 (1)	0.7863 (5)	7.5 (3)
C8	0.9642 (6)	0.512 (1)	0.8181 (6)	8.5 (3)
C9	0.9966 (6)	0.527 (1)	0.8895 (6)	7.3 (3)
C10	1.0313 (5)	0.4199 (9)	0.9333 (5)	6.4 (3)
Mo2	0.500	0.000	0.500	3.39 (2)
I3	0.55528 (3)	0.19880 (6)	0.59411 (3)	4.92 (1)
I4	0.62100 (3)	−0.14454 (6)	0.56785 (3)	5.21 (1)
P2	0.5566 (1)	0.0866 (2)	0.4091 (1)	4.26 (5)
C11	0.6341 (4)	0.0016 (9)	0.4013 (5)	6.2 (2)
C12	0.6139 (6)	−0.133 (1)	0.3647 (6)	7.9 (3)
C13	0.4949 (5)	0.093 (1)	0.3154 (4)	6.4 (3)
C14	0.5288 (6)	0.145 (1)	0.2610 (5)	8.4 (3)
C15	0.5885 (4)	0.2514 (8)	0.4281 (4)	4.9 (2)
C16	0.5402 (5)	0.350 (1)	0.4168 (6)	7.0 (3)
C17	0.5654 (6)	0.480 (1)	0.4376 (6)	8.6 (3)
C18	0.6407 (6)	0.503 (1)	0.4723 (6)	8.7 (3)
C19	0.6877 (7)	0.406 (1)	0.4840 (7)	9.5 (4)
C20	0.6602 (5)	0.274 (1)	0.4605 (5)	6.8 (3)
P3	0.7832 (3)	0.3221 (4)	0.2459 (3)	11.7 (2)
C21	0.726 (1)	0.445 (3)	0.254 (1)	19.8 (8)*
C22	0.6977 (7)	0.397 (2)	0.2984 (8)	10.6 (4)*
C23	0.788 (1)	0.397 (3)	0.163 (1)	23 (1)*
C24	0.8329 (8)	0.351 (2)	0.147 (1)	14.8 (6)*
C25	0.7590 (5)	0.159 (1)	0.2416 (5)	6.8 (2)*
C26	0.7913 (6)	0.082 (1)	0.3036 (7)	8.7 (3)*
C27	0.7689 (6)	−0.045 (1)	0.3021 (7)	9.4 (3)*
C28	0.7201 (6)	−0.091 (1)	0.2405 (7)	9.0 (3)*
C29	0.6916 (6)	−0.025 (1)	0.1816 (6)	8.5 (3)*
C30	0.7100 (6)	0.105 (1)	0.1806 (6)	7.7 (3)*

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

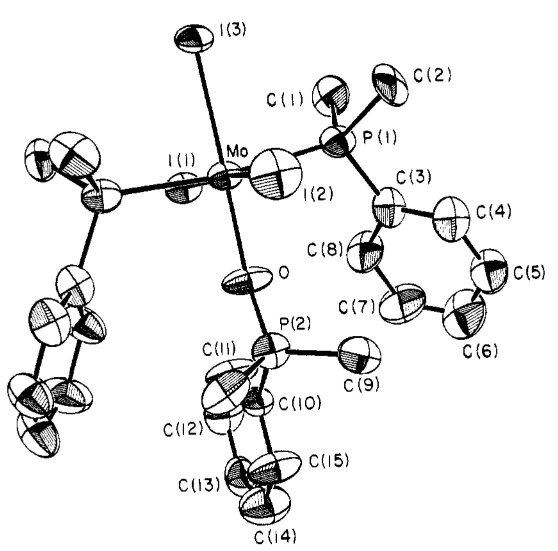

Figure 1. ORTEP view of compound **2**.

solution containing a mixture of several products, among which $Mo_2I_4(PMe_2Ph)_4$ (**1**), isolated in 49% yield, is the most abundant. This compound exhibits a visible absorption at 15 300 cm^{-1} in CH_2Cl_2, which is typical for the $\delta \rightarrow \delta^*$ transition of the quadrupole bond. Infrared spectroscopy on the mother solution indicates the presence of molybdenum(0) carbonyl derivatives. The bands at 2017 m, 1915 m, 1897 s, and 1888 sh cm^{-1} are assigned to *cis*-$Mo(CO)_4(PMe_2Ph)_2$ (cf. 2011 s, 1912 sh, 1895 vs, and 1878 sh cm^{-1} in chloroform solution[6]) while those at 1937 m and 1842 s cm^{-1} are assigned to *fac*-$Mo(CO)_3(PMe_2Ph)_3$ (cf. 1939 s, 1832 vs, and 1824 sh cm^{-1} in chloroform solution[6]). The compound $MoI_3(PMe_2Ph)_2(POMe_2Ph)$ (**2**) was also isolated from this solution. Its X-ray crystal structure has been determined and a view of the molecule is shown in Figure 1. The molecule exhibits an octahedral arrangement of the ligands around the metal, the three iodine atoms being in a *mer* arrangement with the phosphine oxide ligand trans to the central iodine atom. The three iodine atoms, the molybdenum atom, and the oxygen, phosphorus, and phenyl ring carbon atoms of the phosphine oxide ligand lie on a crystallographic mirror plane. The molybdenum–iodine distances are around 2.7 Å, a value that is in the same range found for Mo–I bonds in quadruply bonded molybdenum(II) dimers[3a,b] but is shorter than those commonly found for molybdenum(II) 18-electron complexes.[7] No other molybdenum(III)–iodine distances, to the best of our knowledge, are reported in the literature. The Mo–P distance is 2.600 (4) Å and is a little longer than those commonly found in molybdenum(II) phosphine derivatives.

The reaction of $Mo_2I_4(CO)_8$ with PEt_2Ph in toluene follows a course similar to that of PMe_2Ph. From the room-temperature reaction a solution containing $MoI_2(CO)_3(PEt_2Ph)_2$ is obtained and the final solution after reflux shows weak IR bands attributable to molybdenum(0) carbonyl complexes, while the visible spectrum denotes the presence of the quadruply bonded molybdenum(II) dimer, $Mo_2I_4(PEt_2Ph)_4$ (band at 15 400 cm^{-1}, compared to that at 15 300 cm^{-1} in CH_2Cl_2 for compound **1**). Since several attempts to crystallize materials out of this solution were unfruitful, the reaction was repeated in a different solvent, namely tetrahydrofuran. $Mo_2I_4(CO)_8$ is known[1] to react with THF to produce the reactive intermediate $MoI_2(CO)_3(THF)_2$; this bis(tetrahydrofuran) adduct reacts with PEt_2Ph at room temperature to form the molybdenum(II) tricarbonyl bis(phosphine) derivative, $MoI_2(CO)_3(PEt_2Ph)_2$, as evidenced by IR. Reflux of this solution, in contrast to the same reaction carried out in toluene, does not lead to the formation of any quadruply bonded molybdenum(II) dimer. The final solution shows no visible band in the region expected for the $\delta \rightarrow \delta^*$ transition of the Mo–Mo quadruple bond,

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Table IV. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $MoI_3(PMe_2Ph)_2(POMe_2Ph)$[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
I1	Mo	2.762 (2)	Mo	O	2.093 (14)	P2	O	1.49 (2)
I2	Mo	2.768 (2)	P1	C1	1.86 (2)	P2	C9	1.77 (2)
I3	Mo	2.756 (2)	P1	C2	1.852 (12)	P2	C10	1.84 (2)
Mo	P1	2.600 (4)	P1	C3	1.79 (2)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
I1	Mo	I2	174.69 (8)	I3	Mo	O	177.7 (4)	C2	P1	C3	105.2 (8)
I1	Mo	I3	91.36 (7)	P1	Mo	P1	171.9 (2)	O	P2	C9	113.2 (6)
I1	Mo	P1	88.69 (9)	P1	Mo	O	93.75 (9)	O	P2	C10	107 (1)
I1	Mo	O	86.3 (4)	Mo	P1	C1	115.1 (5)	C9	P2	C9	108 (1)
I2	Mo	I3	93.95 (7)	Mo	P1	C2	114.7 (5)	C9	P2	C10	107.6 (7)
I2	Mo	P1	91.66 (9)	Mo	P1	C3	116.2 (5)	Mo	O	P2	158.8 (9)
I2	Mo	O	88.4 (4)	C1	P1	C2	102 (1)				
I3	Mo	P1	86.19 (9)	C1	P1	C3	101.6 (8)				

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

Table V. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Mo1	I1	2.784 (1)	C1	C2	1.55 (2)	P2	C13	1.861 (8)
Mo1	I2	2.789 (1)	C3	C4	1.48 (2)	P2	C15	1.819 (9)
Mo1	P1	2.610 (3)	Mo2	I3	2.754 (1)	C11	C12	1.563 (14)
P1	C1	1.845 (12)	Mo2	I4	2.797 (1)	C13	C14	1.55 (2)
P1	C3	1.861 (10)	Mo2	P2	2.592 (2)			
P1	C5	1.826 (9)	P2	C11	1.843 (10)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
I1	Mo1	I1	180.00 (0)	C1	P1	C3	105.7 (5)	I4	Mo2	P2	89.68 (5)
I1	Mo1	I2	90.23 (2)	C1	P1	C5	103.6 (5)	P2	Mo2	P2	180.00 (0)
I1	Mo1	I2	89.77 (2)	C3	P1	C5	99.6 (4)	Mo2	P2	C11	118.2 (3)
I1	Mo1	P1	90.27 (6)	P1	C1	C2	115.4 (8)	Mo2	P2	C13	113.8 (4)
I1	Mo1	P1	89.73 (6)	P1	C3	C4	110.8 (9)	Mo2	P2	C15	112.8 (3)
I2	Mo1	I2	180.00 (0)	I3	Mo2	I3	180.00 (0)	C11	P2	C13	103.8 (5)
I2	Mo1	P1	87.57 (5)	I3	Mo2	I4	89.00 (2)	C11	P2	C15	102.4 (4)
I2	Mo1	P1	92.43 (5)	I3	Mo2	I4	91.00 (2)	C13	P2	C15	104.3 (4)
P1	Mo1	P1	180.00 (0)	I3	Mo2	P2	92.27 (5)	P2	C11	C12	111.6 (6)
Mo1	P1	C1	113.4 (4)	I3	Mo2	P2	87.73 (5)	P2	C13	C14	113.8 (7)
Mo1	P1	C3	115.0 (4)	I4	Mo2	I4	180.00 (0)				
Mo1	P1	C5	117.8 (3)	I4	Mo2	P2	90.32 (5)				

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

while strong IR bands are present in the carbonyl stretching region. Those at 2017 m, 1911 m, 1892 s, and ca. 1875 sh cm^{-1} are assigned to *cis*-$Mo(CO)_4(PEt_2Ph)_2$ (cf. 2012 s, 1907 sh, 1895 vs, and 1866 s cm^{-1} in 1,2-dichloroethane[8] and the corresponding PMe_2Ph derivative bands reported above), while those at 1947 w and 1836 w cm^{-1} are assigned to small amounts of *fac*-$Mo(CO)_3(PEt_2Ph)_3$. From this solution the salt $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$ (**3**) was isolated. Its Nujol mull IR spectrum clearly shows the P–H stretching vibration, which appears as a doublet at 2370 and 2350 cm^{-1}. This is in the same region as other P–H stretching vibrations in phosphonium cations and may be compared, for instance, with 2350 cm^{-1} for $[PHPh_3][MoI_3(CO)_3(PPh_3)]$.[2,9]

The molecular structure of compound **3** has been determined by X-ray diffraction methods. The lattice contains two independent and geometrically equivalent anions with the molybdenum atoms sitting in the inversion centers at (1, 0, 1) and (0.5, 0, 0.5), respectively; the phosphonium cation is on a general position. Figure 2 shows a view of one of the anions with the atomic numbering scheme employed. The geometry around the molybdenum atom is octahedral with the four iodine atoms in the equatorial plane and the phosphines in the axial positions. The lengths of corresponding bonds are comparable in the two independent anions and similar to those found in compound **2**: the Mo–I distances are 2.75–2.80 Å, and the Mo–P distances are around 2.6 Å.

The reaction of $Mo_2I_4(CO)_8$ with pyridine proceeds initially in a way similar to the reactions with the phosphine ligands, giving rise to $MoI_2(CO)_3(py)_2$, as evidenced by the IR bands at 2022 s, 1942 s, and 1926 s cm^{-1}. In contrast to the reactions with the phosphines, however, further reaction occurs at room temperature as shown by the increasing intensity of IR bands at 1904, 1832, and 1778 cm^{-1} at the expense of those of $MoI_2(CO)_3(py)_2$. The bands at 1904 and 1778 cm^{-1} were the only one detectable after reflux and were assigned to *fac*-$Mo(CO)_3(py)_3$, on the basis of the observation that the same IR spectrum was obtained by dissolving $Mo(CO)_3(\eta^6\text{-toluene})$ in pyridine. The band at 1832 cm^{-1} that initially grows but that is not present in the final solution is presumably due to an uncharacterized intermediate in the conversion process of $MoI_2(CO)_3(py)_2$ to $Mo(CO)_3(py)_3$. No formation of the quadruply bonded $Mo_2I_4(py)_4$ occurs, although such a species is known in the literature.[10] $MoI_3(py)_3$ (**4**) is the only other compound obtained from this reaction. We are tempted to suggest for it a *mer* configuration, in view of the fact that such an arrangement of the ligands has been found in the crystallographically characterized $MoCl_3(py)_3$[11] and in compound **2** reported in this paper. $MoBr_3(py)_3$ was also reported to be isostructural with its chlorine analogue.[11]

Discussion

The reactions of $Mo_2X_4(CO)_8$ complexes (X = Cl, Br, I) with a variety of ligands have been the subject of numerous studies.[2,5,12] Room-temperature interaction with the ligand in a 1:4 ratio gives rise to the corresponding $MoX_2(CO)_3L_2$ complexes.[2,5] These compounds are generally stable when L is a soft donor ligand such

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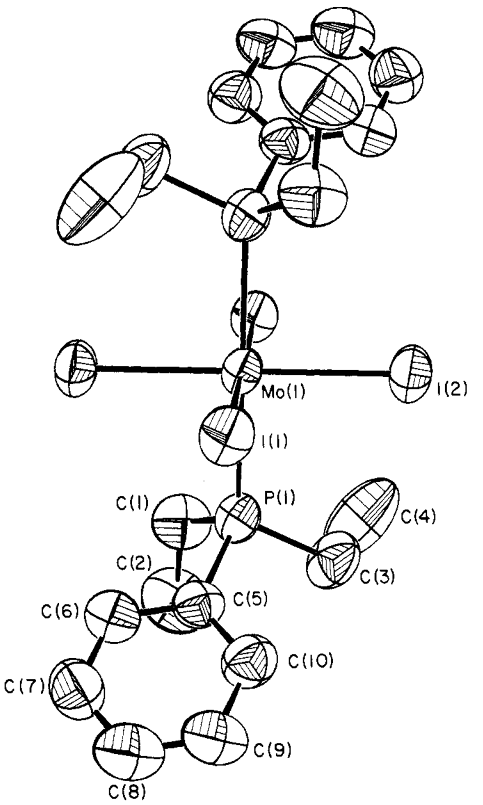


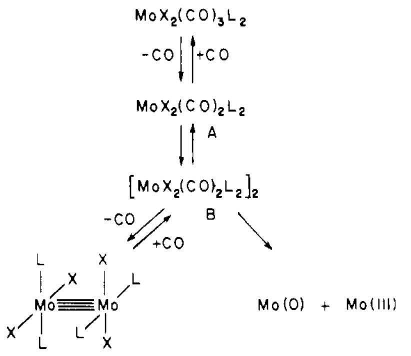
Figure 2. ORTEP view of one of the two crystallographically independent anions of compound **3**.

as a phosphine or arsine. Some of these compounds have been subjected to thermal treatment, and the dicarbonyl complexes $MoX_2(CO)_2L_2$ or $[MoX_2(CO)_2L_2]_2$ were the only reported products.[13] When L, on the other hand, is a ligand such as pyridine, a nitrile, THF, or even tetrahydrothiophene, the $MoX_2(CO)_3L_2$ species react further, at room temperature or above, by disproportionation to form molybdenum(0) and molybdenum(III) derivatives.[12] We have recently shown[3] that thermal treatment of $MoI_2(CO)_3L_2$ (L = phosphine) complexes can also be performed in such a way as to completely remove carbon monoxide and produce $Mo_2I_4L_4$ compounds with a metal-metal quadruple bond. The results we report here prove that the disproportionation reaction is also possible for these complexes and that the route followed depends upon the nature of both the phosphine and the solvent. Thus, $MoI_2(CO)_3(PMe_3)_2$ affords $Mo_2I_4(PMe_3)_4$ free of disproportionation products in toluene;[3a] $MoI_2(CO)_3L_2$ complexes (L = PMe_2Ph, PEt_2Ph), while similarly affording the corresponding $Mo_2I_4L_4$ compounds when the reaction is conducted in the same solvent, also show some accompanying disproportionation. When $MoI_2(CO)_3(PEt_2Ph)_2$ is refluxed in THF, on the other hand, no dimer is formed and only products of disproportionation can be detected.

The nature of the disproportionation products varies depending upon the conditions employed, but in all cases they are derivatives of molybdenum(0) and molybdenum(III). In the pyridine reaction, owing to the excess of the ligand that is used as solvent, $Mo(CO)_3(py)_3$ and $MoI_3(py)_3$ are formed, according to the stoichiometry of reaction 1. In the other cases, where the L/Mo ratio is close to 2, only small amounts of $Mo(CO)_3L_3$ were produced, the $Mo(CO)_4L_2$ complexes being the most abundant ones for molybdenum(0).

$$3MoI_2(CO)_3(py)_2 + 3py \rightarrow Mo(CO)_3(py)_3 + 2MoI_3(py)_3 + 6CO \quad (1)$$

Scheme I



Compound **2** is the isolated molybdenum(III) material in the PMe_2Ph reaction conducted in toluene. The origin of the oxygen atom found in the phosphine oxide ligand is uncertain, although the participation of adventitious air seems probable. Regarding the PEt_2Ph reaction conducted in THF, compound **3** is the only molybdenum(III) isolated product. The polar nature of the solvente might be the factor determining the formation of a salt, although it is not clear what is the source of the hydrogen atom in the phosphonium ion. As compound **2** can be envisaged to be produced by interaction of a hypothetical $MoI_3(PMe_2Ph)_3$ species with oxygen, compound **3** can be envisaged to arise from the interaction of $MoI_3(PEt_2Ph)_3$ with HI. Similar behavior has been observed in other systems. For instance, $[PHPh_3][MoI_3(CO)_3(PPh_3)]$ is obtained instead of the expected $MoI_2(CO)_3(PPh_3)_2$ either upon interaction of $Mo_2I_4(CO)_8$ with PPh_3[2] or by diiodine oxidation of $Mo(CO)_3(PPh_3)_3$.[9]

All reported disproportionation reactions for molybdenum(II) $MX_2(CO)_3L_2$ complexes lead to Mo(0) and Mo(III) products. When M is tungsten, similar reactions lead to W(0) and W(IV) under mild conditions, while W(0) and W(III) are obtained at higher temperatures.[12] If, as seems probable, these reactions follow the same mechanism for the two different metals, M(0) and Mo(IV) compounds are the expected primary products but, due to the higher oxidizing power of Mo(IV) with respect to that of W(IV), it is likely that further reaction occurs between Mo(IV) and Mo(0) or unreacted Mo(II) compounds to produce the observed species of molybdenum(III).

The different observed behaviors of the $MoX_2(CO)_3L_2$ complexes toward thermal conditions can possibly be rationalized by the paths reported in Scheme I. The reaction would in any case go through the dicarbonyl species A and the corresponding dimer B that have been actually isolated in a few cases.[13] At this point, depending upon the nature of the ligand L and upon the nature of the solvent, disproportionation may be the preferred pathway, or compound B may be stable enough to undergo further decarbonylation at higher temperature to produce the molybdenum(II) quadruply bonded dimers. As we have shown in this paper, when L is PMe_2Ph or PEt_2Ph, X is iodine, and toluene is used as solvent, both paths are simultaneously followed, while the change of the solvent to the more polar THF strongly favors disproportionation. The intimate mechanism of the conversion of B to $M_2X_4L_4$ and to the disproportionation products is, however, still obscure, and a rationale of the factor favoring one path over the other is lacking.

It is pertinent to remark that the reaction of $Mo_2X_4L_4$ with CO has been studied and found to lead to the formation of molybdenum(II) and molybdenum(0) carbonyl derivatives.[14,15] The reduction to molybdenum(0) was tentatively associated with the simultaneous oxidation of CO to $COCl_2$, although no oxidation products were detected in the final mixtures. In view of Scheme I we are now tempted to suggest that the reaction of $Mo_2X_4L_4$ with CO proceeds with initial formation of species B that can then uptake more CO to produce $MoX_2(CO)_3L_2$ or disproportionate.

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This would mean that the formation of molybdenum(0) carbonyl complexes would be accompanied by the production of compounds with the metal in a higher oxidation state.

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Supplementary Material Available: Full tables of bond lengths and angles and tables of anisotropic displacement parameters for compounds **2** and **3** and a stereoscopic ORTEP view of the unit cell for compound **3** (8 pages); listings of observed and calculated structure factors for **2** and **3** (26 pages). Ordering information is given on any current masthead page.

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Reactions of the Dirhenium(II) Complexes $Re_2X_4(dppm)_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) with Isocyanides. 3.[1] Dinuclear Species Containing Two or Three Isocyanide Ligands

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The triply bonded dirhenium(II) compound $Re_2Cl_4(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$) reacts with 2 equiv of *t*-BuNC to yield the bis(isocyanide) species $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)_2]^+$ (isolated as its PF_6^- salt) in two isomeric forms (green and yellow). The reaction between the monoisocyanide complexes $Re_2Cl_4(dppm)_2(CNR)$ (R = *t*-Bu or xylyl) and an excess of a nitrile R′CN (R′ = Me, Et, or Ph) in the presence of KPF_6 produces the mixed isocyanide–nitrile complexes $[Re_2Cl_3(dppm)_2(CNR)(NCR')]PF_6$. The probable structures of these new products are discussed in light of structural data for the previously characterized bis(nitrile) derivatives. Complexes containing three RNC ligands $[Re_2Cl_3(dppm)_2(CNR)_3]^+$ (R = *t*-Bu or xylyl) have been isolated by the reaction of $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)(NCEt)]PF_6$ or $Re_2Cl_4(dppm)_2$ with ca. 4 equiv of *t*-BuNC and of $[Re_2Cl_3(dppm)_2(CNxyl)(NCPh)]PF_6$ with 2.5 equiv of xylNC. These products provide further examples of structural isomerism in compounds with edge-shared bioctahedral geometries. A novel complex that contains a μ-iminyl ligand, $[Re_2(\mu\text{-}Cl)(\mu\text{-}C{=}NH\text{-}t\text{-}Bu)(\mu\text{-}dppm)_2Cl_2(CN\text{-}t\text{-}Bu)_2]PF_6$, has been isolated as a byproduct in the synthesis of the green isomer of stoichiometry $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)_2]PF_6$. This complex, which has been characterized by X-ray crystallography, forms monoclinic crystals in space group $P2_1/a$, with the following unit cell dimensions: a = 22.841 (4) Å, b = 25.949 (5) Å, c = 24.076 (4) Å; β = 93.34 (1)°. With Z = 8, the asymmetric unit is defined by two independent molecules of the complex cation **5** and two hexafluorophosphate anions, all of which reside on general positions. The dirhenium molecules **5a** and **5b** are structurally identical, and their corresponding bond distances and angles are very similar. Some average values: Re–Re = 2.704 [1] Å, Re–Cl(terminal) = 2.437 [4] Å, Re–Cl(bridge) = 2.434 [1] Å, Re–C(terminal) = 1.98 [1] Å, Re–C(bridge) = 1.98 [2] Å, Re–P = 2.455 [3] Å; Re–Cl–Re = 67.45 [5]°, Re–C–Re = 85.9 [5]°, C(bridge)–N–CMe_3 = 131 [1]°. All new products have been fully characterized by electrochemical and spectroscopic measurements. In addition, the redox chemistry of some of the complexes has been explored. Of special note is the chemical oxidation and reduction of $[Re_2Cl_3(dppm)_2(CNxyl)_3]PF_6$ to give paramagnetic $[Re_2Cl_3(dppm)_2(CNxyl)_3](PF_6)_2$ and $Re_2Cl_3(dppm)_2(CNxyl)_3$, respectively.

Introduction

In contrast to the facile cleavage of the Re–Re triple bond of $Re_2X_4(PR_3)_4$ (X = Cl or Br; PR_3 representing a monodentate phosphine ligand) by CO and RNC ligands,[3,4] the analogous phosphine-bridged species $Re_2(\mu\text{-}dppm)_2X_4$ (dppm = $Ph_2PCH_2PPh_2$) react to give products in which a Re–Re bond is preserved.[1,5–8] In previous studies, we have examined the chemistry of the novel 1:1 isocyanide complexes $Re_2(\mu\text{-}X)(\mu\text{-}dppm)_2X_3(CNR)$, which possess an A-frame-like structure.[1,7] The present report describes the nature of the species that are found in the reactions between $Re_2Cl_4(dppm)_2$ and an excess of RNC, including the isolation and structural characterization of the μ-iminyl complex $[Re_2(\mu\text{-}Cl)(\mu\text{-}C{=}NH\text{-}t\text{-}Bu)(\mu\text{-}dppm)_2Cl_2(CN\text{-}t\text{-}Bu)_2]PF_6$. Some of this chemistry has been the subject of two preliminary communications.[7,9]

Experimental Section

Starting Materials. The dirhenium complexes $Re_2Cl_4(dppm)_2$ and $Re_2Cl_4(dppm)_2(CNR)$, where R = *t*-Bu or xylyl (xyl), were prepared according to the literature methods.[1,7,10] The *t*-BuNC ligand was prepared by using the reported procedure,[11] while the xylNC ligand was purchased from Fluka Chemicals and used without further purification. The nitriles, along with other solvents, were thoroughly deoxygenated prior to use. The $NOPF_6$ was purchased from Alfa Products, cobaltocene was obtained from Strem Chemicals, and HBF_4 was obtained from Aldrich Chemical Co. as a 1.5 M solution in water.

Reaction Procedures. All reactions were performed in a nitrogen atmosphere using standard vacuum line techniques.

A. Bis(isocyanide) Complexes. (i) $[Re_2Cl_3(dppm)_2(CN\text{-}t\text{-}Bu)_2]PF_6$ (1, Green Isomer). A solution of $Re_2Cl_4(dppm)_2$ (0.20 g, 0.16 mmol) and *t*-BuNC (16.5 μL, 0.16 mmol) in 5 mL of dichloromethane was stirred for 2 min. An additional 16.5 μL of *t*-BuNC was then added, and the green-brown solution was stirred for 30 min. Addition of diethyl ether (30 mL) precipitated the crude product. The resulting green solid was collected and then redissolved in 15 mL of an acetone solution saturated with KPF_6. Diethyl ether (~100 mL) was added and the mixture al-

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