one more conducive to equal Mo–O bond lengths.

Discussion

Reactions demonstrated in the current work are summarized in Scheme I. The two branches depicted differ only in the sequence of the exchange by RCO_2^- or $Ph_2PC_2H_4PPh_2$. It remains interesting that no kinetic connection was observed beween dimers **2** and **4** in the presence of excess diphos or dithiophosphate, despite the otherwise facile displacement of the latter by the former.

The vast majority (but not all) of $[Mo_2Z_2(\mu\text{-}S)_2L_2]$ complexes in recent years have involved an L = anionic (−1 or −2) sulfur donor. Two significant consequences of replacing one or both ligands L with phosphines are reduction of the overall charge on the complex and substitution of a potential π-donor by a potential π-acceptor. The π-acceptor properties per se, however, are not expected to be of great significance for d^1 Mo(V), which is itself π-accepting, particularly with regard to the terminal Z group. Reduced overall negative charge would be expected to reduce somewhat the nucleophilic reactivity at bridge sulfur positions. Initial results for the dithiophosphate–diphos–μ-carboxylate dimer **2** indeed show sulfur-based nucleophilic reactions, but these are much slower than those of dimer anion **1**. Steric effects may also be operative.

Acknowledgment. This work was supported by research awards from the Graduate School and from the College of Arts and Sciences of the University of Louisville and with funds from the National Science Foundation (Grant No. RII-8610671) and the Kentucky EPSCoR Program.

Supplementary Material Available: Tables of full crystallographic parameters, bond lengths and angles excluded from text, hydrogen atom parameters, displacement parameters, and least-squares planes (11 pages); a table of structure factors (24 pages). Ordering information is given on any current masthead page.

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Conformational Preferences in Six-Coordinate, Octahedral Complexes of Molybdenum(III). Synthesis and Structure of $MoX_3(dppe)L$ [X = Cl, Br, I; dppe = Bis(diphenylphosphino)ethane; L = Tetrahydrofuran, Acetonitrile, Trimethylphosphine]

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Received October 27, 1988

$MoBr_3(THF)_3$ can be obtained in large scale and high yields by bromination of $Mo_2Br_4(CO)_8$ in tetrahydrofuran (THF). The ligand replacement reaction of $MoX_3(THF)_3$ with bis(diphenylphosphino)ethane (dppe) in THF as solvent affords the mononuclear $MoX_3(dppe)(THF)$ compounds. An X-ray crystal structure investigation of the iodide derivative shows an octahedral structure with a *meridional* arrangement of the three iodo ligands. Crystal data: monoclinic, space group $P2_1/n$, a = 24.049 (4) Å, b = 12.283 (2) Å, c = 12.985 (2) Å, β = 99.94 (2)°, V = 3778.1 (2) Å^3, Z = 4, d_c = 1.79 g cm^{-3}, μ(Mo Kα) = 29.34 cm^{-1}, R = 0.0361, R_w = 0.0517 for 354 parameters and 3589 observations with $F_o^2 > 3\sigma(F_o^2)$. The remaining THF ligand in $MoX_3(dppe)(THF)$ can be replaced with MeCN or PMe_3 but not with $P(n\text{-}Bu)_3$, PPh_3, or dppe. The X-ray crystal structure of $MoI_3(dppe)(PMe_3)$ shows an octahedral geometry with a *facial* arrangement of the three iodo ligands. Crystal data: orthorhombic, space group *Pnma*, a = 15.413 (4) Å, b = 21.786 (4) Å, c = 9.787 (1) Å, V = 3286 (2) Å^3, Z = 4, d_c = 1.92 g cm^{-3}, μ(Cu Kα) = 274.81 cm^{-1}, R = 0.080, R_w = 0.080 for 154 parameters and 1091 observations with $F_o^2 > 3\sigma(F_o^2)$. For comparison purposes, a crystallographic study of *mer*-$MoI_3(PMe_3)_3$ has also been carried out. Crystal data: tetragonal, space group $I4_1/a$, a = 18.379 (5) Å, c = 26.257 (5) Å, V = 8896 (4) Å^3, Z = 16, d_c = 2.11 g cm^{-3}, μ(Mo Kα) = 47.62 cm^{-1}, R = 0.064, R_w = 0.074 for 145 parameters and 1854 observations with $F_o^2 > 2.5\sigma(F_o^2)$. The conformational preference in these octahedral Mo(III) complexes is discussed in terms of the steric interactions between the neutral ligands.

Introduction

Mononuclear molybdenum(III) compounds of general formula MoX_3L_3 or $MoX_3(L\text{-}L)L'$ (X = halogen; L, L′ = neutral monodentate ligand; L-L = neutral bidentate ligand) have been relatively well studied.[2] The neutral monodentate or bidentate ligands can be either hard[3] [tetrahydrofuran (THF), nitriles] or soft[4] (phosphines), always giving rise to high-spin stable compounds. Most of the studies, however, have been carried out on the chloride systems, primarily because the easiest route to these products is through the $MoX_3(THF)_3$ starting material (eq 1 and 2), which can be easily prepared for X = Cl.[3g,h,5]

$$MoX_3(THF)_3 + nL \rightarrow MoX_3L_n(THF)_{3-n} \qquad (1)$$

$$MoX_3(THF)_3 + L\text{-}L \rightarrow MoX_3(L\text{-}L)(THF) \qquad (2)$$

Other synthetic routes employed include interaction of MoX_3 or $[MoX_5(H_2O)]^-$ with L[3d,e,6] and, in the case of hard donor ligands, disproportionation of Mo(II) carbonyl compounds.[3b,c] $MoX_3(py)_3$ (X = Cl, Br; py = pyridine) was also prepared by interaction of the Mo(II) dimer $Mo_2X_4(py)_4$ with pyridine at high temperatures.[7] These alternative methods, however, do not offer the generality and facilitation of the THF replacement reactions described in eq 1 and 2.

The large-scale synthesis and THF replacement reactions of $MoI_3(THF)_3$ have been reported recently,[8] and we have successfully employed the same strategy in the large-scale preparation of the bromide system. The reactions described in eq 1 and 2 can now be applied to the extended series of Mo(III) halide derivatives, where X = Cl, Br, I. We report here studies on mononuclear

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Mo(III) compounds containing bis(diphenylphosphino)ethane as a bidentate ligand. Part of this work has been previously communicated.[9]

Our interest includes the steric interactions in the coordination sphere. Notably, it is experimentally established that MoX_3L_3 type compounds prefer to exist in the meridional configuration.[3d,e,i,4f,8,10] Indeed, most of the MX_3L_3 type complexes containing any M^{3+} transition metal have a meridional configuration.[11] Compounds with facial geometry are selectively obtained when a tripodal ligand or others with similar steric requirements force the metal to use three mutually cis coordination sites for bonding.[12] These exceptions include a compound of molybdenum(III).[12d] In the course of our research, we have found an example of facial geometry for a MoI_3L_3 type compound where the neutral donors are not part of the same polydentate unit.

Experimental Section

All operations were carried out under an atmosphere of dinitrogen. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. $MoCl_3(THF)_3$,[5] $MoI_3(THF)_3$,[8] and $MoI_3(PMe_3)_3$[8] were prepared according to published methods. dppe, PPh_3, PMe_3, and $P(n\text{-}Bu)_3$ were purchased from Strem. PPh_3 was recrystallized from absolute ethanol. PMe_3 and $P(n\text{-}Bu)_3$ were purified by distillation, whereas dppe was used as received. Instruments used were as follows: FTIR, Nicolet 5DXC; ESR, Bruker ER200; magnetic susceptibility balance (modified Gouy method), Johnson-Matthey; UV/vis, Shimadzu UV-240. Listings of the Nujol mull FTIR absorptions for all new compounds are located in the supplementary material. Elemental analyses were by Dr. F. Kasler, Department of Chemistry and Biochemistry, University of Maryland, and by Galbraith Laboratories, Knoxville, TN.

Synthesis of $MoBr_3(THF)_3$. $Mo_2Br_4(CO)_8$ was prepared in situ from $Mo(CO)_6$ (2.232 g, 8.454 mmol) and Br_2 (0.40 mL, 7.8 mmol) in CH_2Cl_2 at −78 °C according to the published procedure.[13] The solvent was removed under reduced pressure, and the residue was treated with THF (50 mL) with the evolution of gas to afford a red solution. After the solution was cooled to 0 °C, additional Br_2 (0.20 mL, 3.9 mmol) was introduced. Additional gas evolution occurred. The mixture was stirred at 0 °C for a few hours. Stirring was continued overnight at room temperature. The salmon pink product was filtered, washed with THF, and dried in vacuo; yield 3.268 g (75.8%). Anal. Calcd for $C_{12}H_{24}Br_3MoO_3$: C, 26.11; H, 4.38; Br, 43.43. Found: C, 26.15; H, 4.62; Br, 43.84.

Synthesis of MoX_3(dppe)(THF) (X = Cl, Br, I). The preparation of the iodide compound is described in detail. The other two products are prepared in a similar fashion. $MoI_3(THF)_3$ (1.013 g, 1.46 mmol) and dppe (0.588 g, 1.48 mmol) were placed in THF (50 mL), and the mixture was stirred until all the solid dissolved (ca. 48 h) to produce a red solution (bromide, orange; chloride, orange-yellow). Et_2O (140 mL) was added to the solution, followed by cooling to −20 °C. The resulting mixture of powder and crystalline material was recovered by filtration, washed with Et_2O, and dried in vacuo; yield 0.732 g, 49.1% (Br, 70.9%; Cl, 67.4%). In the chloride reaction, small amounts of pink insoluble material were deposited when the reaction was carried out over a long period of time. This was filtered off before precipitation of the product.

A single crystal obtained as described above from the iodide reaction was used for an X-ray crystallographic study. This proved to be *mer*-MoI_3(dppe)(THF)·THF. The three halide derivatives showed similar IR spectra. Magnetic susceptibility: $\mu = 3.13\ \mu_B$ (X = Cl), $3.78\ \mu_B$ (X = Br), $3.81\ \mu_B$ (X = I); diamagnetic correction $\chi_M = 356.26 \times 10^{-6}$ cgsu (X = Cl), 387.7×10^{-6} cgsu (X = Br), 429.76×10^{-6} cgsu (X = I). UV/visible [THF; λ_{max}, nm (ϵ, mol L^{-1} cm^{-1})]: Cl, 416 (540), 350 sh (1700), 288 (7000), 273 sh (7500), 266 sh (8100), 225 (36 000), 213 (38 000); Br, 440 (500), 362 sh (1800), 317 (8900), 222 sh (39 000), 213 (46 000); I, 401 (7100), 295 (7700), 220 sh (38 000), 212 (46 000). Anal. Calcd for $C_{30}H_{32}Br_3MoOP_2$: C, 44.70; H, 4.00; Br, 29.73. Found: C, 44.45; H, 3.77; Br, 30.58. An accurate elemental analysis for the iodide compound could not be obtained. The appearance of this product as a mixture of microcrystalline material and larger crystals suggests that the compound crystallizes in two different forms: the crystallographically characterized species contains an interstitial THF molecule (see Results and Discussion) whereas the microcrystals probably do not contain solvent of crystallization. The bromide species, obtained in microcrystalline form selectively, gives the correct analysis for $MoBr_3$(dppe)(THF).

Reaction of MoX_3(dppe)(THF) with MeCN. Synthesis of MoX_3(dppe)(MeCN). The preparation of the iodide compound is described in detail. MoI_3(dppe)(THF) was prepared in situ as described above from 0.297 g (0.429 mmol) of $MoI_3(THF)_3$ and 0.171 g (0.429 mmol) of dppe. After removal of the solvent under reduced pressure, the residue was treated with MeCN (30 mL), producing a cloudy reddish orange solution. After this solution was stirred at room temperature overnight, the orange product was filtered, washed with MeCN, and dried in vacuo; yield 0.192 g (48.9%). Anal. Calcd for $C_{28}H_{27}I_3MoNP_2$: C, 36.71; H, 2.97; I, 41.56; N, 1.53. Found: C, 36.26; H, 2.77; I, 40.14; N, 1.59. The other two halide derivatives were obtained in a similar fashion (Br, 65.4%; Cl, 40.8%). Anal. Calcd for $C_{28}H_{27}Br_3MoNP_2$: C, 43.39; H, 3.51; Br, 30.93; N, 1.81. Found: C, 43.27; H, 3.30; Br, 30.59; N, 1.80. Calcd for $C_{28}H_{27}Cl_3MoNP_2$: C, 52.40; H, 4.24; Cl, 16.57; N, 2.18. Found: C, 52.57; H, 4.26; I, 17.20; N, 1.80.

Reaction of MoX_3(dppe)(THF) with PMe_3. Synthesis of MoX_3(dppe)(PMe_3). (a) X = I. MoI_3(dppe)(THF) (0.282 g, 0.407 mmol) was placed in THF (30 mL), the mixture was stirred at room temperature until completely dissolved (ca. 10 min), and then PMe_3 (0.1 mL, 1 mmol) was added. A red precipitate immediately formed. The mixture was stirred at room temperature overnight and then filtered. The solid was washed with THF and dried in vacuo; yield 0.050 g (13%). An elemental analysis of the products fits that of a 50/50 mixture of MoI_3(dppe)(PMe_3) (of which a crystal structure has been obtained, see below) and MoI_3(dppe)(PMe_3)·THF. Anal. Calcd for $C_{31}H_{37}I_3MoO_{0.5}P_3$: C, 37.68; H, 3.77; I, 38.62. Found: C, 37.38; H, 3.82; I, 38.83.

The crystal growth process for MoI_3(dppe)(PMe_3) presented problems. The insolubility of the compound made recrystallization procedures impractical. We finally obtained a crystalline material by vapor diffusion of PMe_3 over a THF solution of MoI_3(dppe)(THF), with the entire apparatus being kept at 0 °C in order to achieve a slower diffusion process. Microscopic examination of the isolated crystals showed heterogeneity. The elemental analysis and IR spectroscopic properties compare with those of the material obtained as described above. Anal. Found: C, 37.47; H, 3.70; I, 38.04.

(b) X = Br. $MoBr_3$(dppe)(THF) (0.379 g, 0.470 mmol) was added to THF (15 mL) and treated with PMe_3 (0.1 mL, 1 mmol) at room temperature with stirring. The solution turned to golden yellow, and a yellow solid precipitated out. After the solid was filtered off, (65 mg), the mother solution was evaporated to dryness. The residue was redissolved in toluene (20 mL) to yield an orange solution. Within 30 min the color changed to yellow, during which a yellow product precipitated out. This was filtered, washed with toluene, and dried in vacuo; yield 0.152 g (40%). The IR spectrum of this material parallels that of the iodide derivative. Elemental analysis indicates that the product contains a molecule of interstitial toluene. Anal. Calcd for $C_{36}H_{41}Br_3MoP_3$: C, 47.92; H, 4.45; Br, 26.57. Found: C, 47.58; H, 4.37; Br, 26.45.

X-ray Crystallography. (a) *mer*-MoI_3(dppe)(THF)·THF. A single crystal was sealed under nitrogen in a thin-walled glass capillary and mounted on the diffractometer. The cell indexing, data collection, and reduction were routine. Crystal data are assembled in Table I. An absorption correction[14] was applied to the data. The structure was solved by direct methods and refined by alternate cycles of full-matrix least-squares and difference Fourier maps with the TEXSAN package. All atoms, except those of the interstitial THF molecule, were refined anisotropically. Hydrogen atoms were not included in the refinement. Positional and equivalent isotropic thermal parameters are listed in Table II, and selected bond distances and angles are in Table III.

(b) *fac*-MoI_3(dppe)(PMe_3). The crystals formed in bunches, and no isolated, nicely shaped crystal could be found. The specimen used for the X-ray analysis was obtained, after careful examination, by cutting the desired crystal from a large agglomerate. It was glued on the tip of a glass fiber and mounted on the diffractometer. After indexing, the axial photographs showed weak satellites around a few of the main peaks, indicating that the main crystal was contaminated by another small specimen. No better specimen could be found. The crystal data are

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Table I. Crystal Data for All Compounds

compd	$MoI_3(dppe)(THF){\cdot}THF$	$MoI_3(dppe)(PMe_3)$	$MoI_3(PMe_3)_3$
formula	$C_{34}H_{40}I_3MoO_2P_2$	$C_{29}H_{33}I_3MoP_3$	$C_9H_{27}I_3MoP_3$
fw	1019.29	951.15	704.86
space group	$P2_1/n$	*Pnma*	$I4_1/a$
a, Å	24.049 (4)	15.413 (4)	18.379 (5)
b, Å	12.283 (2)	21.786 (4)	18.379 (5)
c, Å	12.985 (2)	9.787 (1)	26.257 (4)
α, deg	90	90	90
β, deg	99.94 (2)	90	90
γ, deg	90	90	90
V, $Å^3$	3778.1 (2)	3286 (2)	8896 (4)
Z	4	4	16
d_c, g cm^{-3}	1.79	1.92	2.11
μ, cm^{-1}	29.34 (Mo Kα)	274.81 (Cu Kα)	47.62 (Mo Kα)
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	Cu Kα (λ = 1.54178 Å)	Mo Kα (λ = 0.71073 Å)
temp, °C	20	20	20
transmissn factors: max, min	1.000, 0.877	1.000, 0.315	1.000, 0.819
R^a	0.0361	0.080	0.0638
R_w^b	0.0517	0.080	0.0736

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

Table II. Positional Parameters and *B*(eq) Values for $MoI_3(dppe)(THF){\cdot}THF^a$

atom	*x*	*y*	*z*	*B*(eq), $Å^2$
Mo	0.40600 (3)	0.09235 (6)	0.75107 (6)	3.31 (3)
I(1)	0.38857 (3)	0.02248 (6)	0.54633 (5)	4.94 (3)
I(2)	0.41459 (3)	0.19274 (5)	0.94283 (5)	4.60 (3)
I(3)	0.39543 (3)	−0.11365 (5)	0.83205 (6)	5.38 (3)
P(1)	0.3018 (1)	0.1398 (2)	0.7278 (2)	3.5 (1)
P(2)	0.4102 (1)	0.2827 (2)	0.6708 (2)	3.5 (1)
C	0.4983 (3)	0.0645 (6)	0.7674 (6)	5.1 (3)
C(1)	0.2988 (4)	0.2890 (7)	0.7008 (8)	4.0 (4)
C(2)	0.3370 (4)	0.3162 (7)	0.6201 (7)	3.9 (4)
C(3)	0.5377 (5)	0.092 (1)	0.866 (1)	7.7 (7)
C(4)	0.5945 (5)	0.061 (2)	0.831 (1)	11 (1)
C(5)	0.5826 (7)	−0.036 (2)	0.756 (1)	12 (1)
C(6)	0.5225 (6)	−0.025 (1)	0.710 (1)	8.2 (8)
C(10)	0.2608 (4)	0.1250 (8)	0.8362 (7)	3.9 (4)
C(11)	0.2110 (4)	0.1833 (8)	0.8285 (8)	4.8 (5)
C(12)	0.1769 (5)	0.177 (1)	0.903 (1)	6.3 (6)
C(13)	0.1943 (6)	0.111 (1)	0.983 (1)	7.0 (7)
C(14)	0.2452 (6)	0.049 (1)	0.995 (1)	6.3 (6)
C(15)	0.2794 (5)	0.0576 (9)	0.9182 (8)	5.2 (5)
C(20)	0.2529 (4)	0.0789 (8)	0.6207 (7)	4.1 (5)
C(21)	0.2520 (4)	−0.0335 (9)	0.6147 (7)	4.6 (5)
C(22)	0.2135 (5)	−0.089 (1)	0.539 (1)	5.9 (6)
C(23)	0.1761 (5)	−0.026 (1)	0.472 (1)	7.2 (7)
C(24)	0.1756 (5)	0.088 (1)	0.477 (1)	8.2 (8)
C(25)	0.2155 (5)	0.141 (1)	0.5503 (9)	5.9 (6)
C(30)	0.4372 (4)	0.3972 (7)	0.7526 (7)	3.9 (4)
C(31)	0.4023 (5)	0.4793 (8)	0.7784 (9)	5.4 (5)
C(32)	0.4250 (7)	0.569 (1)	0.844 (1)	7.2 (7)
C(33)	0.4825 (7)	0.571 (1)	0.881 (1)	7.5 (8)
C(34)	0.5172 (6)	0.487 (1)	0.858 (1)	7.9 (8)
C(35)	0.4951 (5)	0.400 (1)	0.788 (1)	6.2 (6)
C(40)	0.4475 (4)	0.3042 (8)	0.5642 (8)	4.6 (5)
C(41)	0.4949 (5)	0.244 (1)	0.558 (1)	6.8 (7)
C(42)	0.5236 (6)	0.267 (1)	0.469 (1)	8.3 (8)
C(43)	0.5055 (7)	0.346 (1)	0.396 (1)	9 (1)
C(44)	0.4574 (7)	0.405 (2)	0.401 (1)	11 (1)
C(45)	0.4288 (6)	0.384 (1)	0.490 (1)	8.3 (8)
C(1)	0.789 (1)	0.137 (2)	0.793 (2)	24.1 (9)*
C(1L)	0.734 (1)	0.132 (3)	0.747 (2)	18 (1)*
C(2L)	0.721 (1)	0.241 (3)	0.735 (2)	20 (1)*
C(3L)	0.771 (2)	0.301 (3)	0.762 (2)	20 (1)*
C(4L)	0.819 (1)	0.238 (3)	0.770 (3)	21 (1)*

^{a}Numbers in parentheses are estimated standard deviations in the least significant digit. Starred values indicate atoms refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameters 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 Intramolecular Distances (Å) and Angles (deg) for $MoI_3(dppe)(THF){\cdot}THF^a$

Mo–I(1)	2.756 (1)	P(1)–C(10)	1.86 (1)
Mo–I(2)	2.754 (1)	P(1)–C(20)	1.82 (1)
Mo–I(3)	2.769 (1)	P(2)–C(2)	1.819 (9)
Mo–O	2.220 (7)	P(2)–C(30)	1.81 (1)
Mo–P(1)	2.539 (3)	P(2)–C(40)	1.79 (1)
Mo–P(2)	2.569 (2)	C(1)–C(2)	1.54 (1)
P(1)–C(1)	1.865 (9)		

O–Mo–P(1)	175.4 (2)	C(20)–P(1)–C(10)	100.4 (4)
O–Mo–P(2)	94.0 (2)	C(20)–P(1)–C(1)	105.1 (5)
O–Mo–I(2)	93.7 (2)	C(20)–P(1)–Mo	119.4 (3)
O–Mo–I(1)	91.6 (2)	C(10)–P(1)–C(1)	103.3 (4)
O–Mo–I(3)	88.8 (2)	C(10)–P(1)–Mo	121.9 (3)
P(1)–Mo–P(2)	81.38 (8)	C(1)–P(1)–Mo	104.7 (3)
P(1)–Mo–I(2)	85.59 (7)	C(40)–P(2)–C(30)	99.3 (4)
P(1)–Mo–I(1)	88.52 (7)	C(40)–P(2)–C(2)	105.6 (5)
P(1)–Mo–I(3)	95.85 (6)	C(40)–P(2)–Mo	120.5 (3)
P(2)–Mo–I(2)	87.55 (6)	C(30)–P(2)–C(2)	105.2 (4)
P(2)–Mo–I(1)	84.38 (6)	C(30)–P(2)–Mo	120.2 (3)
P(2)–Mo–I(3)	176.90 (7)	C(2)–P(2)–Mo	104.4 (3)
I(2)–Mo–I(1)	170.65 (4)	C(2)–C(1)–P(1)	109.4 (6)
I(2)–Mo–I(3)	93.63 (3)	C(1)–C(2)–P(2)	111.0 (6)
I(1)–Mo–I(3)	94.19 (3)		

^{a}Estimated standard deviations in the least significant figure are given in parentheses.

assembled in Table I. No decay of the intensity standards was observed during data collection. The systematic absences from the data indicated that the space group could be either *Pnma* or $Pn2_1a$. Volume considerations and the expectation of a meridional structure (for which no molecular symmetry element is possible) led us to choose the noncentrosymmetric space group. Direct methods gave a solution consisting of a facial arrangement of three heavy atoms around a fourth one (angles close to 90°). The mode was interpreted as a *fac*-MoI_3 moiety. Refinement of this moiety converged to 28%. A subsequent difference Fourier map revealed the three phosphorus atoms and a few of the dppe carbon atoms. Refinement of this new model lowered the *R* factor to 21% but at the same time showed high correlation between parameters related by a mirror plane passing through the molybdenum and one iodine atom and bisecting the angle formed at the molybdenum atom by the other two iodine atoms. Since the *fac*-$MoI_3(dppe)(PMe_3)$ molecule, in contrast to the meriodional isomer, can have a mirror plane as a symmetry element, such a mirror plane was imposed crystallographically by changing the space group to *Pnma*. This led to successful refinement of the entire structure. At the end of the isotropic refinement an additional absorption correction[15] was applied. All non-hydrogen atoms were refined anisotropically, except C(3), C(22), and C(23), which converged with nonpositive-definite thermal tensors and were therefore left isotropic. The hydrogen atoms were included at calculated positions but not refined. The agreement factor *R* = 0.080 was obtained. A few reasons for such a high *R* factor can be identified. The high absorption of the crystal, especially with the copper radiation used, and its platelike shape made an accurate absorption correction difficult. In addition, the satellites seen in the axial photographs (see above) indicate that some of the intensity data may have been measured inaccurately. The high residual electron

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[15] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

Table IV. Positional Parameters and *B*(eq) Values and Their Estimated Standard Deviations for $MoI_3(dppe)(PMe_3)$[a,b]

atom	*x*	*y*	*z*	*B*(eq), Å²
Mo	0.2124 (2)	$^1/_4$	0.0508 (3)	3.7 (2)
I(1)	0.2636 (1)	$^1/_4$	0.3227 (3)	5.2 (1)
I(2)	0.3288 (1)	0.3413 (1)	−0.0194 (2)	6.3 (1)
P(1)	0.1519 (6)	$^1/_4$	−0.197 (1)	4.7 (6)
P(2)	0.0966 (4)	0.1744 (3)	0.138 (1)	5.6 (4)
C(1)	0.039 (3)	$^1/_4$	−0.226 (5)	10 (4)
C(2)	0.185 (2)	0.187 (2)	−0.294 (4)	8 (2)
C(3)	0.011 (1)	0.224 (1)	0.207 (3)	7.6 (8)*
C(10)	0.119 (2)	0.119 (1)	0.276 (3)	5 (2)
C(11)	0.057 (2)	0.114 (2)	0.371 (4)	8 (2)
C(12)	0.078 (3)	0.067 (2)	0.476 (5)	9 (3)
C(13)	0.152 (3)	0.034 (2)	0.479 (4)	8 (3)
C(14)	0.207 (2)	0.045 (2)	0.379 (4)	9 (3)
C(15)	0.196 (2)	0.089 (2)	0.267 (3)	6 (2)
C(20)	0.042 (2)	0.126 (1)	0.013 (3)	5 (2)
C(21)	−0.048 (2)	0.128 (2)	−0.001 (5)	10 (3)
C(22)	−0.085 (2)	0.088 (2)	−0.087 (5)	9 (1)*
C(23)	−0.042 (3)	0.053 (2)	−0.160 (4)	10 (1)*
C(24)	0.047 (2)	0.040 (2)	−0.150 (4)	8 (3)
C(25)	0.086 (2)	0.081 (2)	−0.056 (5)	8 (3)
H(1)	0.0135	0.2845	−0.1886	11.0
H(2)	0.0305	$^1/_4$	−0.3273	11.0
H(3)	0.1582	0.1514	−0.2614	9.6
H(4)	0.1687	0.1940	−0.3873	9.6
H(5)	0.2463	0.1837	−0.2889	9.6
H(6)	−0.0401	0.2115	0.1630	15.0
H(7)	0.0077	0.2115	0.3025	15.0
H(11)	0.0050	0.1365	0.3706	9.2
H(12)	0.0387	0.0596	0.5486	11.2
H(13)	0.1648	0.0056	0.5485	9.2
H(14)	0.2576	0.0200	0.3808	10.7
H(15)	0.2379	0.0943	0.1964	7.7
H(21)	−0.0825	0.1542	0.0462	12.0
H(22)	−0.1473	0.0907	−0.1094	18.6
H(23)	−0.0687	0.0231	−0.2193	17.5
H(24)	0.0803	0.0127	−0.1973	10.1
H(25)	0.1463	0.0776	−0.0378	10.1

[a] See footnote *a* of Table II.

Table V. Intramolecular Distances (Å) and Angles (deg) for $MoI_3(dppe)(PMe_3)$[a]

Mo–I(1)	2.775 (4)	P(1)–C(2)	1.74 (3)
Mo–I(2)	2.765 (2)	P(2)–C(3)	1.83 (3)
Mo–P(1)	2.60 (1)	P(2)–C(10)	1.84 (3)
Mo–P(2)	2.574 (7)	P(2)–C(20)	1.82 (3)
P(1)–C(1)	1.77 (4)	C(3)–C(3′)	1.14 (6)
I(1)–Mo–I(2)	93.08 (9)	Mo–P(1)–C(2)	114 (1)
I(1)–Mo–P(1)	175.5 (2)	C(1)–P(1)–C(2)	102 (2)
I(1)–Mo–P(2)	83.1 (2)	C(2)–P(1)–C(2′)	103 (2)
I(2)–Mo–I(2′)	92.0 (1)	Mo–P(2)–C(3)	104 (1)
I(2)–Mo–P(1)	90.0 (2)	Mo–P(2)–C(10)	122 (1)
I(2)–Mo–P(2)	172.9 (2)	Mo–P(2)–C(20)	118 (1)
I(2)–Mo–P(2′)	94.1 (2)	C(3)–P(2)–C(20)	105 (1)
P(1)–Mo–P(2)	93.5 (3)	C(3)–P(2)–C(10)	104 (1)
P(2)–Mo–P(2′)	79.5 (3)	C(10)–P(2)–C(20)	102 (1)
Mo–P(1)–C(1)	120 (2)	P(2)–C(3)–C(3′)	126.1 (9)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

density in the last difference Fourier map is probably associated with this problem. All the peaks with density higher than 1 e Å^{-3} were closer than 1 Å to heavy atoms. No peak indicating the presence of interstitial solvent molecules or showing positional disorder was observed.

Positional and equivalent isotropic thermal parameters for the $MoI_3(dppe)(PMe_3)$ molecule are listed in Table IV, and selected bond distances and angles are reported in Table V.

(c) *mer*-$MoI_3(PMe_3)_3$. A crystal that was suitable for X-ray analysis was obtained by slow diffusion of *n*-heptane into a toluene solution of the compound. It was mounted on a glass fiber with epoxy cement, which also served as an atmospheric barrier. Systematic absences in the diffraction data and diffraction symmetry uniquely determined the tetragonal space gorup $I4_1/a$. No decay was observed in the three standard reflections monitored every 97 data. An empirical absorption correction was applied to the data, two forms of the data merged (R_{int} = 3.1%), and independent data with $F_o \geq 5\sigma(F_o)$ were retained.

Table VI. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for *mer*-$MoI_3(PMe_3)_3$

	x	*y*	*z*	*U*[a]
I(1)	7170 (1)	2464.5 (9)	1064.1 (5)	110.2 (7)
I(2)	8593 (1)	3413 (1)	140.2 (8)	148 (1)
I(3)	6539.8 (8)	1270.5 (8)	−156.9 (5)	94.1 (6)
Mo	7583.0 (8)	2328.6 (8)	47.4 (6)	63.1 (5)
P(1)	8038 (3)	2197 (5)	−862 (2)	144 (4)
P(2)	8501 (3)	1325 (4)	387 (3)	106 (3)
P(3)	6554 (6)	3236 (5)	−144 (3)	178 (5)
C(1)	9022 (7)	2301 (17)	−970 (12)	158 (15)
C(2)	7673 (21)	2838 (29)	−1331 (14)	409 (42)
C(3)	7882 (18)	1306 (14)	−1157 (14)	322 (33)
C(4)	8093 (13)	604 (14)	775 (11)	166 (16)
C(5)	9297 (12)	1679 (14)	732 (12)	169 (16)
C(6)	8953 (28)	724 (20)	−71 (14)	301 (34)
C(7)	6847 (20)	4191 (9)	−118 (26)	408 (46)
C(8)	6037 (19)	3146 (18)	−743 (9)	204 (20)
C(9)	5724 (14)	3143 (27)	249 (15)	499 (53)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VII. Selected Bond Distances (Å) and Angles (deg) for *mer*-$MoI_3(PMe_3)_3$

Mo–I(1)	2.786 (2)	P(1)–C(3)	1.83 (3)
Mo–I(2)	2.735 (3)	P(2)–C(4)	1.83 (3)
Mo–I(3)	2.783 (2)	P(2)–C(5)	1.84 (3)
Mo–P(1)	2.542 (7)	P(2)–C(6)	1.83 (4)
Mo–P(2)	2.655 (6)	P(3)–C(7)	1.84 (2)
Mo–P(3)	2.571 (10)	P(3)–C(8)	1.85 (3)
P(1)–C(1)	1.84 (1)	P(3)–C(9)	1.85 (3)
P(1)–C(2)	1.83 (4)		
I(1)–Mo–I(2)	92.0 (1)	P(2)–Mo–I(3)	91.0 (1)
I(1)–Mo–I(3)	93.4 (1)	P(3)–Mo–I(1)	85.9 (2)
I(2)–Mo–I(3)	173.8 (1)	P(3)–Mo–I(2)	92.5 (2)
P(1)–Mo–I(1)	176.6 (2)	P(3)–Mo–I(3)	84.8 (2)
P(1)–Mo–I(2)	85.9 (2)	P(1)–Mo–P(2)	92.3 (2)
P(1)–Mo–I(3)	88.8 (2)	P(1)–Mo–P(3)	96.9 (3)
P(2)–Mo–I(1)	85.0 (2)	P(2)–Mo–P(3)	169.7 (3)
P(2)–Mo–I(2)	92.6 (1)		

The structure was solved by direct methods and completed by subsequent difference Fourier syntheses. The methyl groups showed high thermal activity and/or disorder; consequently, no attempt was made to include H atom contributions. All non-hydrogen atoms were refined anisotropically. SHELXTL(5.1) software was used for all calculations (G. Sheldrick, Nicolet XRD Corp., Madison, WI).

Atomic coordinates are given in Table VI, and selected bond distances and angles are in Table VII.

Results

(a) Syntheses. The compound $MoBr_3(THF)_3$, previously obtained by ligand exchange from $MoBr_3(MeCN)_3$[3a] or by disproportionation of $Mo_2Br_4(CO)_8$ in THF,[3b] has now been obtained in large scale and yields as high as 75% by the sequence of reactions

$$2Mo(CO)_6 + 2Br_2 \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} Mo_2Br_4(CO)_8 + 4CO \qquad (3)$$

$$Mo_2Br_4(CO)_8 + Br_2 + 6THF \rightarrow 2MoBr_3(THF)_3 + 8CO \qquad (4)$$

This procedure differs from the reported[3b] disproportionation of $Mo_2Br_4(CO)_8$ in THF simply in that an extra 1 equiv of bromine is added.

The entire synthetic procedure can be conveniently carried out in the same flask without isolation of intermediates. The preparation of $Mo_2Br_4(CO)_8$ by this route has been previously described.[13] This synthetic strategy, that is, oxidation of lower valent molybdenum carbonyl derivatives, has been recently employed for the preparation of the analogous iodide system $MoI_3(THF)_3$.[8]

The compounds $MoX_3(THF)_3$ (X = Cl, Br, I) react smoothly at room temperature in THF with an equimolar amount of dppe (see eq 5).

$$\mathrm{MoX_3(THF)_3 + dppe \rightarrow MoX_3(dppe)(THF) + 2THF} \qquad (5)$$

$$\mathrm{X = Cl, Br, I}$$

The products can be precipitated by addition of ether. They are mononuclear, high-spin (as shown by magnetic susceptibility measurements), octahedral compounds [see structure of MoI_3(dppe)(THF) below], soluble in THF. The lower magnetic moment of the chloride compound might be the result of partial loss of THF in the solid with production of diamagnetic oligonuclear materials. The similarity of the IR spectra of the three compounds suggests that they have identical structures.

The remaining THF ligand can be easily replaced by MeCN and by PMe_3 (eq 6).

$$\mathrm{MoX_3(dppe)(THF) + L \rightarrow MoX_3(dppe)L + THF} \qquad (6)$$

$$\mathrm{X = Cl, Br, I; L = MeCN, PMe_3}$$

The products of these reactions are crystalline materials, sparingly soluble in toluene, THF, and CH_2Cl_2. The reactions with MeCN are best carried out in MeCN as solvent, but they also take place in THF when an excess of MeCN is added. Elemental analyses are in agreement with the formulation of the compounds *without* interstitial solvent molecules. However, solid-state IR spectra of these materials consistently showed two CN stretching vibrations instead of the expected single band. Possible explanations are as follows: (i) there is a solid-state effect (this would require two independent molecules to be present in the crystallographic asymmetric unit); (ii) the material is not a pure isomer but a mixture of meridional and facial isomers for a mononuclear Mo(III) center (a different electronic influence of the trans iodo ligand in the facial structure with respect to that of the trans phosphine ligand in the meridional structure would be sufficient to cause the appearance of two distinct bands for the nitrile CN stretch); (iii) the compound is a more or less strongly associated dimer with a low symmetry, thereby generating two CN stretching vibrations through electronic coupling of the two MeCN ligands. The small solubility of the compound in most solvents would seem to be in best agreement with the third hypothesis. Attempts to obtain a single crystal for an X-ray analysis proved unsuccessful. The low solubility also prevented a solution IR spectrum from being taken, which would have given evidence either in favor of hypothesis i or against it [though it could not have distinguished between (ii) and (iii)].

The compounds $MoX_3(dppe)(PMe_3)$ (X = I, Br) form very rapidly when THF solutions of MoX_3(dppe)(THF) are treated with stoichiometric amounts of PMe_3. These derivatives are stable in THF and acetonitrile. These observations indicate an affinity of donor elements for molybdenum(III) in the order P > N > O. Elemental analyses of the $MoX_3(dppe)(PMe_3)$ compounds show the presence of variable amounts of crystallization solvent (THF, X = I; toluene, X = Br; see Experimental Section). This is in agreement with the observation that two different types of crystals were obtained from the iodide system. The crystallographically characterized one (vide infra) exhibits a mononuclear *facial* octahedral structure without interstitial solvent molecules. We therefore infer that the other crystalline material contains solvent of crystallization. Whether this second crystalline form corresponds to a meridional or to a facial isomer remains to be established. In contrast to the case for the MeCN compound, we do not suggest the presence of dinuclear species for the PMe_3 derivatives in view of the higher steric demand of the PMe_3 ligand (see discussion of the *fac*-$MoI_3(dppe)(PMe_3)$ crystal structure below).

When the MoX_3(dppe)(THF) compounds are treated in noncoordinating solvents (e.g. toluene, CH_2Cl_2) without the presence of additional ligands, they produce diamagnetic oligonuclear species.[9] We do not observe (by UV–vis monitoring) any interaction between MoX_3(dppe)(THF) and more bulky phosphines such as $P(n\text{-}Bu)_3$, PPh_3, and dppe. The reason for this lack of reactivity toward PPh_3 or dppe could be both electronic and steric in nature. On the other hand, $P(n\text{-}Bu)_3$ is electronically similar to PMe_3, whereas its cone angle is about 14° higher than that of PMe_3.[16] According to our observation, PMe_3 is about as large a ligand as this system can accommodate. For this reason we have carried out a crystal structure study of $MoI_3(dppe)(PMe_3)$, with the hope of obtaining useful information on the steric interactions in this complex.

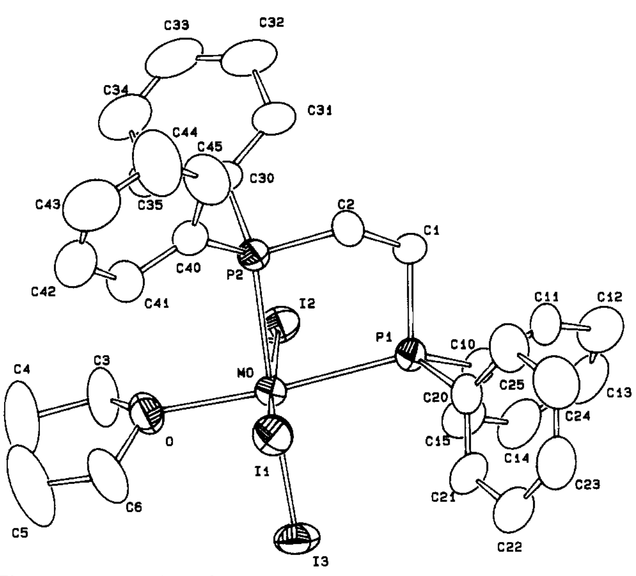

Figure 1. ORTEP view of the *mer*-MoI_3(dppe)(THF) molecule with the atomic numbering scheme employed.

(b) Crystallographic Studies. The compound MoI_3(dppe)(THF) crystallizes with one molecule of interstitial THF in the monoclinic space group $P2_1/n$. The molecule shows a distorted-octahedral configuration with a *meridional* arrangement of the three iodo ligands (see Figure 1), which is typical of six-coordinate transition-metal trihalide derivatives.[11] The conformation of the five-membered ring formed by the dppe phosphorus and methylene carbon atoms with the molybdenum atom is twisted [P(1)–C(1)–C(2)–P(2) torsion angle −62.0 (8)°], as most often found for complexes with chelating dppe. The molybdenum–iodine distances compare well with those of the few iodide derivatives of Mo(III) reported to date in the literature.[8,17] The Mo–I(3) (trans to phosphorus) distance [2.769 (1) Å] is slightly longer than the Mo–I(1) and Mo–I(2) (trans to iodine) distances [average 2.755 (1) Å], consistent with a higher trans influence of the phosphine ligand. The Mo–phosphorus distances also fall within the expected range[17a,b] with the bond trans to iodine [2.569 (2) Å] being longer than the one trans to THF [2.539 (3) Å], again in accord with the known trans influence trend ($I^- > OR_2$). Trans-influence arguments may also explain why the Mo–O(THF) distance [2.220 (7) Å] is longer than the analogous distances found[8] in $MoI_3(THF)_3$ [average 2.199 (12) Å].

The structure of $MoI_3(dppe)(PMe_3)$ is shown in Figure 2. The molecule crystallizes in the orthorhombic space group *Pnma* and sits on a crystallographically imposed mirror plane, which passes through the Mo, P(1), I(1), and C(1) atoms. The main difference with respect to the structure of the THF adduct shown in Figure 1 is the *facial* arrangement of the iodo ligands. The conformation of the chelating dppe ligand is also different, generating a five-membered ring with the molybdenum atom in a "folded envelope" conformation and a P(2)–C(3)–C(3′)–P(2′) torsion angle strictly equal to zero, as required by the presence of the crystallographic mirror plane. The Mo–I and Mo–P distances (see Table V) agree well with those of MoI_3(dppe)(THF) discussed above and with the others reported in the literature.[8,17]

The structure of *mer*-$MoI_3(PMe_3)_3$ is shown in Figure 3. The coordination geometry is only slightly distorted from octahedral, with all angles between bonds to cis ligands being within 5° of

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(16) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(17) (a) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1986**, *25*, 3624. (b) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 3310. (c) Cotton, F. A.; Poli, R. *J. Am. Chem. Soc.* **1988**, *110*, 830.

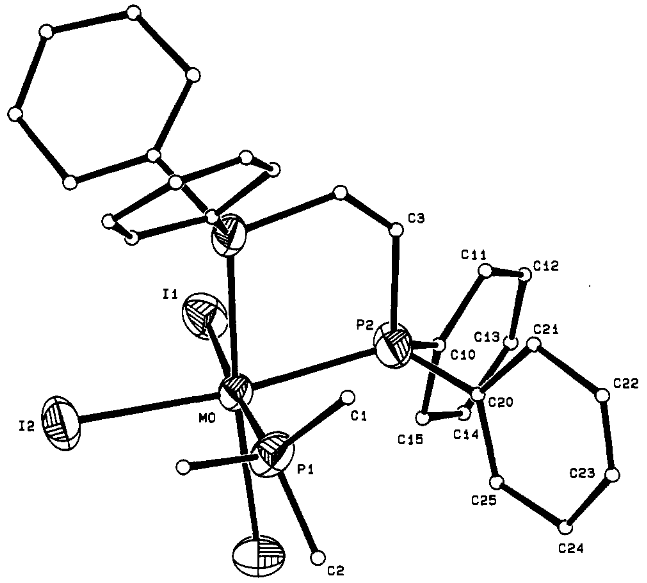

Figure 2. ORTEP view of the *fac*-MoI$_3$(dppe)(PMe$_3$) molecule with the atomic numbering scheme employed. For the sake of clarity, hydrogen atoms are not included and carbon atoms are drawn with arbitrary radii.

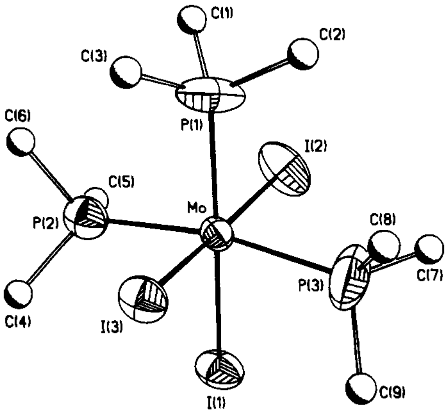

Figure 3. ORTEP view of the *mer*-MoI$_3$(PMe$_3$)$_3$ molecule with the atomic numbering scheme employed. The carbon atoms are shown as spheres of arbitrary radii due to high thermal activity.

the predicted 90° angle. The Mo–I (2.735–2.786 Å) and Mo–P (2.542–2.655 Å) bond distances vary over a wider range than found for the other complexes described above, in a fashion that cannot be explained on the basis of known trans-influence trends nor by the presence of long-range, intermolecular associations, which are all found to be long and to be without correlation to the intramolecular distances.

Discussion

We have reported a useful approach to the synthesis of mononuclear octahedral compounds of Mo(III) of formula MoX$_3$(dppe)L (X = Cl, Br, I; L = monodentate neutral ligand). This procedure should be easily extended to the preparation of derivatives with different phosphines. We have also determined the molecular structure of two of these derivatives, *mer*-MoI$_3$(dppe)(THF) and *fac*-MoI$_3$(dppe)(PMe$_3$).

The main question to be addressed is as follows: Why is the geometry different in these two similar compounds? It seems safe to conclude, from the data available in the literature, that the meridional geometry is electronically preferred for these types of compounds.[3,4,8,10,11] In this respect, it is important to observe that MX$_3$L$_3$ compounds prefer the meridional configuration regardless of the d-electron count or principal quantum number of the transition-metal valence shell. Cases where the facial isomer has also been observed together with the meridional isomer are few and are limited to transition metals with a high electron count. Examples include RuCl$_3$(H$_2$O)$_3$,[18] IrCl$_3$(H$_2$O)$_3$,[19] RhCl$_3$(MeCN)$_3$,[20] Co(NO$_3$)$_3$(NH$_3$)$_3$,[21] and IrCl$_3$(PMe$_2$Ph)$_3$.[22] To the best of our knowledge, the last compound is the only one that has been crystallographically characterized in both the *fac* and *mer* arrangements.[22] VCl$_3$(MeCN)$_3$ has been claimed to be facial in the solid state solely on the basis of IR spectroscopy,[23] but it has been shown that the meridional isomer is present in solution.[24]

Facial geometries are observed when tripodal ligands are employed. The steric rigidity of these ligands makes the choice of a meridional geometry impossible. Compounds where the situation occurs include CrCl$_3$[MeC(CH$_2$PMe$_2$)$_3$][12c] and {MoCl$_3$[HB(3,5-Me$_2$N$_2$C$_3$H)$_3$]}.[12d] Ligands with similar steric requirements are H$_2$NCH$_2$CH$_2$XCH$_2$CH$_2$NH$_2$ [X = NH (dien), S (daes)], found in the facial configuration in CrCl$_3$(dien)[12a] and CoCl$_3$(daes).[12b] CrCl$_3$(dien) has also been obtained in a different crystalline geometry, believed to have a meridional configuration.[12a]

Assuming that the meridonal geometry is preferred electronically for Mo(III) octahedral compounds, a steric effect must be responsible for the facial geometry of MoI$_3$(dppe)(PMe$_3$). Figure 2 suggests that no major steric interactions are present in MoI$_3$(dppe)(PMe$_3$). One PMe$_3$ methyl group lies in the pocket between the two PPh$_2$ moieties, whereas the other two methyl groups are directed away from the dppe ligand. On the other hand, in the hypothetical *mer*-MoI$_3$(dppe)(PMe$_3$) structure (either with a twisted conformation of the five-membered Mo–dppe ring, which can be visualized by replacing the THF ligand with a PMe$_3$ ligand in Figure 1, or with a "folded envelope" conformation of the same ring, which can be visualized by exchanging the PMe$_3$ and I(2) ligands in Figure 2), at least one of the PMe$_3$ methyl groups would come in close contact with the phenyl groups on one end of the dppe ligand, resulting in an increased steric interaction.

To prove that the choice of a facial geometry in MoI$_3$(dppe)(PMe$_3$) is not electronic in origin (one might argue that the strong trans-directing PMe$_3$ ligand would prefer to bind trans to an iodo ligand rather than to another phosphorus donor atom), we have determined the crystal structure of the known[8] MoI$_3$(PMe$_3$)$_3$. This compound is electronically similar to MoI$_3$(dppe)(PMe$_3$), but the steric interactions are alleviated by the replacement of the dppe ligand with two additional PMe$_3$ ligands. As expected, the MoI$_3$(PMe$_3$)$_3$ molecule, like MoI$_3$(THF)$_3$[8] and MoI$_3$(dppe)(THF), but unlike MoI$_3$(dppe)(PMe$_3$), crystallizes in the meridional configuration.

Conclusions

We reported an improved synthesis of the MoBr$_3$(THF)$_3$ compound. This material, together with the readily available MoX$_3$(THF)$_3$ congeners (X = Cl,[2g,h,4] I[7]), is anticipated to be a useful starting material for the synthesis of a wide variety of molybdenum–halide derivatives in the +III and other oxidation states. We described in this paper the MoX$_3$(dppe)(THF) (X = Cl, Br, I) compounds and the MoX$_3$(dppe)L (L = MeCN, PMe$_3$) derivatives that can be obtained from them. An investigation of the steric requirements around an octahedral Mo(III) center has been carried out by crystallographic characterization of the MoI$_3$(dppe)L (L = THF, PMe$_3$) and MoI$_3$(PMe$_3$)$_3$ compounds. These analyses revealed a rare example of facial ligand arrangement for MX$_3$L$_3$ type compounds. A steric interaction between the neutral monodentate ligands has been advanced as a plausible explanation.

An open question remains as to what causes the meridional geometry to be electronically preferred over the facial ones in this

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type of structure. As far as we are aware of, this question has not been addressed before. We can advance a simple interpretation on the basis of the formal ionic charge on the halide atoms. For the less electronegative early transition metals, the M–X bonds will have more ionic character and the halogen atoms will be more negatively charged. This will result in a decreased electrostatic repulsion in the meridional structure, where these ligands are further apart from each other. For the more electronegative middle and late transition metals, the M–X bonds will become more covalent and the electrostatic destabilization will not be as important, therefore allowing both *mer* and *fac* isomers to be obtained. The examples mentioned above illustrate this point.[18-22] Even in these cases, however, the meridional structure is expected to be thermodynamically more stable in the absence of additional electronic (e.g. π bonding) or steric factors. This has proven to be the case for RhCl$_3$(MeCN)$_3$, where the *fac* isomer has been shown to convert to the *mer* isomer under thermal conditions.[20]

Acknowledgment. We are grateful to the University of Maryland College Park (UMCP) Department of Chemistry and Biochemistry, the UMCP General Research Board, the Camille and Henry Dreyfus Foundation (through the Distinguished New Faculty program), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The X-ray diffractometer and MicroVax computer system at the University of Maryland were purchased in part with NSF funds (Grant No. CHE-84-02155). We thank Prof. H. Ammon for technical assistance and S. T. Krueger for obtaining single crystals of MoI$_3$(PMe$_3$)$_3$.

Registry No. MoCl$_3$(THF)$_3$, 39210-30-5; MoI$_3$(THF)$_3$, 107680-52-4; *mer*-MoI$_3$(PMe$_3$)$_3$, 107680-53-5; MoBr$_3$(THF)$_3$, 39210-32-7; Mo$_2$Br$_4$(CO)$_8$, 80594-72-5; Br$_2$, 7726-95-6; MoCl$_3$(dppe)(THF), 119455-61-7; MoBr$_3$(dppe)(THF), 119455-62-8; MoI$_3$(dppe)(THF), 119455-63-9; *mer*-MoI$_3$(dppe)(THF)$\cdot$THF, 119455-64-0; MoI$_3$(dppe)(MeCN), 119455-65-1; MoCl$_3$(dppe)(MeCN), 119455-66-2; MoBr$_3$(dppe)(MeCN), 119455-67-3; *fac*-MoI$_3$(dppe)(PMe$_3$), 119455-68-4; MoBr$_3$(dppe)(PMe$_3$), 119455-69-5.

Supplementary Material Available: Listings of the Nujol mull FTIR absorptions for all new compounds and full tables of crystal data, bond distances and angles, and anisotropic displacement parameters for the compounds MoI$_3$(dppe)(THF), MoI$_3$(dppe)(PMe$_3$), and MoI$_3$(PMe$_3$)$_3$ (15 pages); listings of observed and calculated structure factors for MoI$_3$(dppe)(THF), MoI$_3$(dppe)(PMe$_3$), and MoI$_3$(PMe$_3$)$_3$ (57 pages). Ordering information is given on any current masthead page.

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Solid-State ^{31}P NMR, Far-IR, and Structural Studies on Two-Coordinate (Tris(2,4,6-trimethoxyphenyl)phosphine)copper(I) Chloride and Bromide

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Received September 29, 1988

The reactions of acetonitrile solutions of copper(I) chloride, CuCl, and copper(I) bromide, CuBr, with the sterically hindered, highly basic tertiary phosphine ligand tris(2,4,6-trimethoxyphenyl)phosphine [≡P(2,4,6)$_3$] have been shown to form 1:1 monomeric adducts, [P(2,4,6)$_3$CuX]. The two compounds are isomorphous, crystallizing in the tetragonal space group $P4_3$. For the chloride, a = 15.237 (4) Å, c = 12.373 (3) Å, Z = 4, and R = 0.029 for 2339 "observed" ($I \geq 3\sigma(I)$) reflections, while for the bromide, a = 15.312 (8) Å, c = 12.457 (6) Å, Z = 4, and R = 0.052 for 2148 "observed" reflections. Cu–P is 2.177 (1) Å and Cu–Cl is 2.118 (2) Å in the chloro compound; for the bromide, Cu–P is 2.197 (3) Å and Cu–Br is 2.259 (2) Å. In both complexes, the copper atom is displaced toward the nearest *o*-methoxy oxygen with Cu···O = 2.629 (4) (Cl) and 2.628 (7) Å (Br); P–Cu–X angles are 172.97 (6) (Cl) and 172.00 (9)° (Br). Far-infrared spectra show expected strong ν(Cu–Cl) and ν(Cu–Br) bands at 355 and 262 cm^{-1}, respectively. Strong bands in the range 90–100 cm^{-1} are assigned to δ(P–Cu–X) bending modes. No bands assignable to ν(Cu–P) modes were observable. The solid-state ^{31}P NMR spectrum of the ligand is characterized by a single line at −73 ppm (with respect to 85% H$_3$PO$_4$). The spectrum for each complex shows an asymmetric quartet centered at −65 ppm with highly asymmetric line spacings of 1.40, 2.21, and 2.50 kHz and 1.48, 2.17, and 2.43 kHz, respectively. These data have been used to estimate copper nuclear quadrupole coupling constants for the two compounds.

Introduction

The solid-state ^{31}P NMR spectra of [(PR$_3$)$_m$CuX]$_n$ complexes have shown that each crystallographically independent phosphorus atom gives rise to a quartet of lines with asymmetric spacings due to Cu–P quadrupole coupling effects. For example, in the four-coordinate tetrahedral complex [(PPh$_3$)$_3$CuBr],[2] the line spacings are 0.93, 0.94, and 0.93 kHz, whereas for the three-coordinate, trigonal-planar complex [(PPh$_3$)$_2$CuBr],[3] these are 0.88, 1.28, and 1.44 kHz. We were interested to extend our NMR studies on this class of compound to two-coordinate linear complexes [(PR$_3$)CuX] where the quadrupole coupling effects might be expected to be considerably greater. The tertiary phosphine ligand, tris(2,4,6-trimethoxyphenyl)phosphine [≡P(2,4,6)$_3$] is a highly basic, bulky ligand that would be expected to form metal complexes with low coordination numbers.[4] We have now isolated reasonably air-stable crystalline material of the complexes [P(2,4,6)$_3$CuCl] and [P(2,4,6)$_3$CuBr] and characterized these as monomeric, two-coordinate species by X-ray diffraction and far-infrared spectroscopic techniques and have recorded the solid-state ^{31}P NMR spectra of each compound. From these NMR data, we have estimated values for the copper quadrupole coupling constants. We report this work here.

Experimental Section

Preparation of Compounds. The ligand P(2,4,6)$_3$ was prepared according to the procedures outlined in the literature[4] by the reaction of P(OPh)$_3$ and (2,4,6-trimethoxyphenyl)lithium in diethyl ether, followed by recrystallization from ethanol of the solid product formed. [P-

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