mensions of the crystallographically characterized Co(HB(3-*t*-Bupz)₃)(NCS) complex. Because the sharpness of the *tert*-butyl peak in the NMR spectrum of the analogous Zn(II) complex indicated free rotation of that group, we chose for calculations the cone angle of the conformation that brings one of the methyl hydrogen atoms closest to the Co atom. Then, the same calculations were repeated with a methyl group in place of the *tert*-butyl group, and finally with a hydrogen atom in place of the methyl group. Values of cone angles are 244, 224, and 184° for the *tert*-butyl group, the methyl group, and the hydrogen atom, respectively. Clearly, the *tert*-butyl group generates the largest cone angle known for polypyrazolylborate ligands.

Conclusion

The introduction of these new ligands broadens significantly

the scope of polypyrazolylborate chemistry. The reaction between [BH₄]⁻ and 3-R-pyrazole is regiospecific. This property allows the preparation of a wide variety of unsymmetrically substituted polypyrazolylborates. The bulky groups in the 3-position of the pyrazole ring prevent dimerization and bis-chelate formation, two properties that severely limit the usefulness of the parent ligands. This property coupled with the ability to construct custom-sized pockets around the metals ions, allowing access to molecules of predetermined size and/or shape, makes this new series of polypyrazolylborate ligands potentially very useful.

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

Low-Valent Molybdenum Carbonyl Complexes as an Entry to Octahedral MoI₃L₃ Complexes. Synthesis and X-ray Molecular Structure of MoI₃(THF)₃

F. Albert Cotton* and Rinaldo Poli

MoI₃(THF)₃ has been synthesized by iodination at room temperature of either Mo(CO)₃(η⁶-C₆H₅CH₃) or Mo₂I₄(CO)₈ in tetrahydrofuran (THF) as solvent. Crystals are orthorhombic, space group *Pbcn*, with *a* = 9.252 (3) Å, *b* = 14.541 (5) Å, *c* = 14.273 (3) Å, *V* = 1920 (2) Å³, *Z* = 4, d_{calcd} = 2.397 g cm⁻³, and *R* = 0.0501 for 926 data having $F_o^2 > 3\sigma(F_o^2)$. The molecule is octahedral, in the meridional configuration. Substitution reactions have been carried out with PR₃ (R = Me, Et) to produce MoI₃(PR₃)₃. The direct interaction between MoX₃ (X = Cl, I) and PR₃ (R = Me, Et) in toluene has been studied. Reduction competes with coordinative addition to produce mixtures of MoX₃(PR₃)₃ and Mo₂X₄(PR₃)₃ for X = Cl, I and R = Me and mixtures of [PHR₃][MoI₄(PR₃)₂] and Mo₂X₄(PR₃)₄ for X = I and R = Et. A possible mechanism for these reactions is discussed.

Introduction

In relation to our recent work on the synthesis of Mo₂I₄L₄ and Mo₂I₄(LL)₂ (L = phosphine; LL = diphosphine) complexes by decarbonylation of molybdenum(II) carbonyl derivatives,[1–4] where molybdenum(III) iodide complexes were also sometimes obtained as a result of a competitive disproportionation reaction, we became interested in finding alternative and better routes to derivatives of molybdenum(III) iodide. This interest was reinforced upon realizing that such derivatives were not known, although the chemistry of the corresponding chlorides and bromides had been developed. The [MoX₆]³⁻ and [Mo₂X₉]³⁻ (X = Cl, Br)[5,6] anions are well-known. MoX₃L₃ (X = Cl, Br) compounds with L = pyridine were prepared for the first time[7] by high-temperature reaction of MoX₃ and the ligand and later[8,9] from (NH₄)₂MoX₅·H₂O. Compounds with other hard-donor-based ligands were obtained[10] by disproportionation reactions from Mo₂X₄(CO)₈; the unavailability of a good preparative method for

Mo₂I₄(CO)₈[11a] may have prevented such chemistry from being performed on the iodide system.[11b] San Filippo and Schaefer King were able to prepare the MoX₃(py)₃ (X = Cl, Br; py = pyridine) compounds by interaction of the Mo₂X₄(py)₄ dimers of Mo(II) with pyridine at high temperatures.[12]

The cleanest route to MoX₃L₃ complexes, which also has the advantage of being applicable to the preparation of derivatives containing soft-donor-based ligands,[13] seems to be the substitution reaction on preformed MoX₃(THF)₃ (THF = tetrahydrofuran). Such a method has been applied so far only to the chloride system, the corresponding bromide and iodide being unknown. MoCl₃(THF)₃ has been conveniently obtained by reduction of MoCl₄(THF)₂ with zinc[14] or tin[15] or more recently via MoCl₃(MeCN)₃, which in turn had been obtained from MoCl₄(MeCN)₂.[16] The

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unavailability of molybdenum(IV) bromide and iodide starting materials may have prevented the development of such a chemistry for the heavier halides. We therefore tried to find alternative strategies for the preparation of MoI₃(THF)₃. The direct interaction between MoI₃[17] and THF is not a good one: no reaction occurs at room temperature, while at the reflux temperature I–(CH₂)₄–I and a highly insoluble material, presumably a molybdenum oxide or oxo-iodide, are obtained.[18] This is presumably due to the inertness of the MoX₃ material. MoCl₃ has two polymorphs, both of which contain extended networks of chloride ions with molybdenum ions embedded in adjacent octahedral cavities with strong metal–metal interactions.[19] On the other hand, at higher temperatures the oxophilicity of Mo(III) becomes the dominant feature and extraction of oxygen from the solvent occurs.

Since reduction (because of unavailability of starting materials) and direct interaction of MoI₃ and THF (because of inertness) are not feasible routes, we decided to try the oxidation of lower-valent molybdenum derivatives.

We wish to report here the successful synthesis of MoI₃(THF)₃ by iodination of two different complexes, i.e. Mo(CO)₃(η⁶-C₆H₅CH₃) and Mo₂I₄(CO)₈, and its conversion to MoI₃(PR₃)₃ (R = Me, Et). The direct interaction between MoX₃ (X = Cl, I) and PR₃ (R = Me, Et) will also be discussed.

Experimental Section

All operations were performed under an atmosphere of prepurified argon by using standard Schlenk tube techniques. Solvents were carefully dried and distilled under dinitrogen prior to use. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer. Elemental analyses were by Galbraith Laboratories Inc., Knoxville, TN. MoCl₃,[20] MoI₃,[17] Mo(CO)₃(η⁶-C₆H₅CH₃)[21] and Mo₂I₄(CO)₈[11c] were prepared as described elsewhere. PMe₃ (Strem Chemicals) and PEt₃ (Aldrich) were used as received.

Synthesis of MoI₃(THF)₃. A. From Mo(CO)₃(η⁶-C₆H₅CH₃) and I₂ in THF. Mo(CO)₃(η⁶-C₆H₅CH₃) (3.18 g, 11.7 mmol) was dissolved in THF (50 mL) and stirred for a few minutes. The IR bands at 1917 s and ca. 1775 vs (br) cm⁻¹ of the resulting solution indicated that conversion to Mo(CO)₃(THF)₃ had occurred. This solution was then slowly added to a well-stirred solution of I₂ (4.46 g, 17.6 mmol) in THF (50 mL). At the end of the addition the clear dark red solution showed IR bands at 2066 s, 2006 vs, ca. 1970 w, and 1932 s cm⁻¹. Stirring was continued at room temperature for 48 h, during which time the pale brown microcrystalline product precipitated out of the solution. The material was recovered by filtration, washed with THF, and dried in vacuo; yield 5.18 g (64%). This material had spectroscopic properties (IR in Nujol mull) identical with those of the analytically pure material, and it was used directly for the subsequent substitution reactions (vide infra).

B. From Mo₂I₄(CO)₈ and I₂ in THF. Mo₂I₄(CO)₈ (0.67 g, 0.72 mmol) was dissolved in 20 mL of THF. Gas evolution occurred, and the complete conversion[11c] to MoI₂(CO)₃(THF)₂ was confirmed by IR (bands at 2023 s, ca. 1945 sh, and 1929 vs cm⁻¹). I₂ (0.19 g, 0.76 mmol) was added and the resulting mixture stirred at room temperature for about 20 h. IR monitoring showed the intensity of the bands of MoI₂(CO)₃(THF)₂ to decrease and new bands at 2066, 2006, and 1932 cm⁻¹ first to emerge and then decrease again while the pale brown product precipitated out of the solution. The solid was collected and characterized as described above in procedure A; yield 0.56 g (56%).

Analytically pure material in a crystalline form that was also suitable for the X-ray diffractometric analysis was obtained by simply setting aside without stirring a solution of MoI₂(CO)₃(THF)₂ and I₂ in equimolar amounts prepared as described above. Anal. Calcd for C₁₂H₂₄I₃MoO₃: C, 20.8; H, 3.5. Found: C, 21.1; H, 3.8. IR (Nujol mull, cm⁻¹): 1340 m, 1295 w, 1245 w, 1180 w, 1045 m, 1005 s, 955 w, 925 sh, 915 m, 865 m, 840 vs, 685 w, 590 w.

Reaction between MoI₃(THF)₃ and PR₃ (R = Me, Et). Synthesis of MoI₃(PR₃)₃. A. R = Me. MoI₃(THF)₃ (0.49 g, 0.71 mmol) was suspended in THF (10 mL) and treated with PMe₃ (0.25 mL, 2.5 mmol). The resulting mixture was stirred at room temperature for ca. 2 h, during

which time all the solid dissolved to produce a clean bright red solution. The solvent was removed under reduced pressure and the residue crystallized by dissolution in toluene (2 mL) and reprecipitation by addition of 10 mL of *n*-hexane. After it was cooled to ca. –20 °C overnight, the brick red product was filtered off, washed with *n*-hexane, and dried in vacuo; yield 0.26 g (52%). Anal. Calcd for C₉H₂₇I₃MoP₃: C, 15.3; H, 3.9. Found: C, 15.7; H, 3.9. IR (Nujol mull, cm⁻¹): 1420 m, 1300 m, 1280 m, 1120 m (br), 950 s, 850 w, 730 m, 670 w.

B. R = Et. By a procedure identical with that described above for R = Me, from 0.80 g of MoI₃(THF)₃ and 0.6 mL of PEt₃ in 15 mL of THF, 0.70 g of the compound MoI₃(PEt₃)₃ was obtained (yield 73%). Anal. Calcd for C₁₈H₄₅I₃MoP₃: C, 26.0; H, 5.5. Found: C, 25.6; H, 5.3. IR (Nujol mull, cm⁻¹): 1415 m, 1250 w, 1110 w (br), 1035 s, 995 w, 975 w, 760 s, 745 s, 730 m–s, 710 m, 685 w–m, 675 w.

Reaction between MoX₃ and PR₃ in Toluene. A. MoI₃ and PMe₃. MoI₃ (0.52 g, 1.09 mmol) was suspended in 15 mL of toluene and treated with 0.45 mL of PMe₃ (4.5 mmol). Stirring at room temperature slowly developed a pale green color in the solution. The mixture was warmed to about 80 °C for 48 h to produce a deep emerald green solution and a pale solid. The latter was filtered off, washed with toluene, and dried in vacuo. It exhibited an IR band (Nujol mull) at 2405 cm⁻¹. Anal. Calcd for C₃H₁₀IP: C, 17.7; H, 5.0. Found: C, 17.7; H, 4.9. The volume of the filtered solution was reduced to ca. 5 mL, and 20 mL of *n*-hexane was added to cause the precipitation of brick red microcrystalline material. After it was cooled to ca. 5 °C overnight, the solid was filtered off, washed with *n*-hexane, and dried in vacuo. It was shown to be MoI₃(PMe₃)₃ by comparison of its spectroscopic properties with those of the material obtained from MoI₃(THF)₃ as described above; yield 0.31 g (41%). From the mother solution, now having a blue color, 0.17 g of blue crystals were obtained after evaporation to dryness and recrystallization of the residue from 15 mL of hot *n*-hexane. The spectroscopic properties of this sample (IR and UV/vis) are in accord with its formulation as the known[1] quadruply bonded Mo(II) dimer Mo₂I₄(PMe₃)₄.

B. MoCl₃ and PMe₃. MoCl₃ (0.50 g, 2.47 mmol) was treated in toluene (20 mL) with PMe₃ (0.80 mL, 8.0 mmol). The mixture was briefly (ca. 15 min) refluxed and then filtered. The red solution was concentrated to about 5 mL under reduced pressure and then treated with *n*-hexane (10 mL). The resulting yellow solid was filtered off, washed with *n*-hexane, and dried in vacuo. Analytical and spectroscopic properties indicated this compound to be the known[16] MoCl₃(PMe₃)₃, yield 0.52 g (48%). The mother solution of this solid was dichroic red/blue; its UV/visible properties confirmed the presence of Mo₂Cl₄(PMe₃)₄.[22]

C. MoI₃ and PEt₃. MoI₃ (0.47 g, 0.98 mmol) was suspended in 20 mL of toluene and treated with 0.45 mL of PMe₃ (3.0 mmol). A pale blue-green color slowly developed upon stirring at room temperature. The mixture was refluxed for about 5 h, after which time it consisted of a blue-green solution and some yellow solid. Following the filtration of the hot mixture, a yellow solid crystallized upon cooling to room temperature; yield 0.13 g. Anal. Calcd for C₁₈H₄₆I₄MoP₂: C, 22.5; H, 4.8. Found: C, 22.9; H, 5.2. IR (Nujol mull, cm⁻¹): 2395 w, 1415 m, 1260 m, 1245 w, 1050 m, 1035 s, 995 w, 970 w, 885 w, 870 m, 755 s, 740 w, 715 s, 700 w, 660 w, 620 w. The mother solution was evaporated to dryness and the blue residue recrystallized from 5 mL of hot *n*-hexane. A 0.08-g amount of blue crystals was recovered from the solution after cooling to –20 °C. Anal. Calcd for C₂₄H₆₀I₄Mo₂P₄: C, 24.6, H, 5.2. Found: C, 24.8; H, 5.1. IR (Nujol mull, cm⁻¹): 1410 m, ca. 1260 m (br), ca. 1100 m (br, with shoulder at ca. 1140), 1040 s, 985 w, 780 sh, 765 s, 750 s, 730 sh, 685 w, 670 w, 610 w, 490 w, 450 w. UV/vis (CH₂Cl₂; λ_max, nm (ε, mol L⁻¹ cm⁻¹)): 640 (1.2 × 10³), 383 (2.6 × 10³).

Thermal Treatment of MoI₃(PR₃)₃ (R = Me, Et) in Toluene. A. R = Me. A toluene solution of MoI₃(PMe₃)₃ (ca. 1.4 × 10⁻² M) was refluxed overnight. No significant change was observed during the treatment.

B. R = Et. MoI₃(PEt₃)₃ (0.24 g, 0.29 mmol) was refluxed in toluene (10 mL) for ca. 5 h. The resulting mixture contained some yellow solid in a green solution. From the filtered solution yellow crystals deposited upon cooling to room temperature. They were decanted, washed with *n*-hexane, and dried in vacuo. They were shown to be of [PHEt₃]-[MoI₄(PEt₃)₂] by comparison of their spectroscopic properties with those of the material obtained from MoI₃ and PEt₃ (vide supra). UV/vis spectroscopy on the mother solution confirmed the presence of Mo₂I₄-(PEt₃)₄.

X-ray Crystallography for MoI₃(THF)₃. A parallelepiped-shaped single crystal was glued to the inside of a thin-walled glass capillary, which was then sealed under nitrogen and mounted on a Nicolet P1 diffractometer with its longest dimension nearly parallel to the φ axis. The cell dimensions were determined by a least-squares calculation on

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Table I. Crystal Data for MoI₃(THF)₃

formula	$C_{12}H_{24}I_3MoO_3$
fw	692.88
space group	$Pbcn$
systematic absences	$0kl, k \neq 2n; h0l, l \neq 2n;$ $hk0, h + k \neq 2n$
a, Å	9.252 (3)
b, Å	14.541 (5)
c, Å	14.273 (3)
α, deg	90
β, deg	90
γ, deg	90
V, Å³	1920 (2)
Z	4
d_{calcd}, g cm⁻³	2.397
cryst size, mm	0.25 × 0.40 × 0.50
μ(Mo Kα), cm⁻¹	54.44
data collecn instrument	Nicolet P$\bar{1}$
radiation (monochromated in inciden beam)	Mo Kα (λ_α = 0.710 73 Å)
orientation reflecns: no.; range (2θ), deg	15; 20–30
temp, °C	20
scan method	ω
data collecn range, 2θ, deg	3–50.7
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1429, 926
no. of parameters refined	88
transmission factors: max, min	1.000, 0.769
R^a	0.0501
$R_w{}^b$	0.0642
quality-of-fit indicator^c	1.336
largest shift/esd, final cycle	0.24
largest peak, e Å⁻³	1.346

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

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å²) and Their Estimated Standard Deviations for MoI₃(THF)₃^a

atom	x	y	z	B
Mo	0.500	0.37167 (7)	0.250	2.17 (3)
I1	0.500	0.18281 (8)	0.250	4.06 (4)
I2	0.3162 (1)	0.37131 (7)	0.09507 (8)	3.76 (2)
O1	0.500	0.5238 (8)	0.250	3.1 (2)
O2	0.3103 (8)	0.3830 (9)	0.3414 (6)	3.3 (2)
C1	0.491 (2)	0.5820 (8)	0.334 (1)	8.7 (9)
C2	0.478 (2)	0.671 (1)	0.303 (2)	7.2 (6)
C3	0.303 (2)	0.338 (2)	0.430 (1)	6.1 (4)
C4	0.141 (2)	0.371 (1)	0.469 (1)	5.7 (5)
C5	0.109 (2)	0.454 (1)	0.408 (1)	5.6 (5)
C6	0.198 (2)	0.441 (1)	0.319 (2)	5.7 (3)

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

the setting angles of 15 reflections with 20° < 2θ < 30° and were subsequently confirmed by axial photographs. Data collection was performed with a scan rate of 3.0° min⁻¹ for reflections having 3.0° < 2θ < 39.7° and 2.0° min⁻¹ for those having 39.7° < 2θ < 50.7°. The periodic monitoring of six standard reflections showed no significant variation of intensity. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction[23] based on azimuthal (ψ) scans of five reflections having an Eulerian angle χ near 90° was also applied.

The structure was solved by SHELX-76 direct methods and then refined by subsequent least-squares full-matrix cycles and difference Fourier maps with the Enraf-Nonius SDP software. Anisotropic refinement converged at $R = 0.0501$ ($R_w = 0.0642$). The highest peak in the last difference Fourier map (1.336 e Å⁻³) was located at 0.88 Å from I(2), and it was considered to be the result of series termination errors. Pertinent crystal data are reported in Table I. Fractional atomic coordinates

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Table III. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations

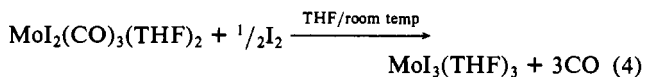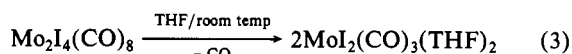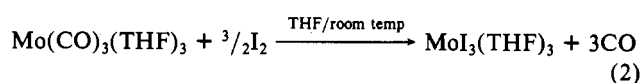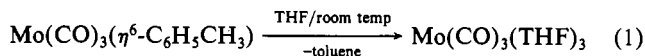|			
Mo–I1	2.746 (2)	Mo–O1	2.212 (12)
Mo–I2	2.790 (1)	Mo–O2	2.193 (8)
I1–Mo–I2	89.89 (3)	I2–Mo–O2	89.1 (2)
I1–Mo–O1	180.00 (0)	I2–Mo–O2'	90.9 (2)
I1–Mo–O2	94.3 (3)	O1–Mo–O2	85.7 (3)
I2–Mo–I2	180.00 (0)	O2–Mo–O2'	171.4 (5)
I2–Mo–O1	90.11 (3)		

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.
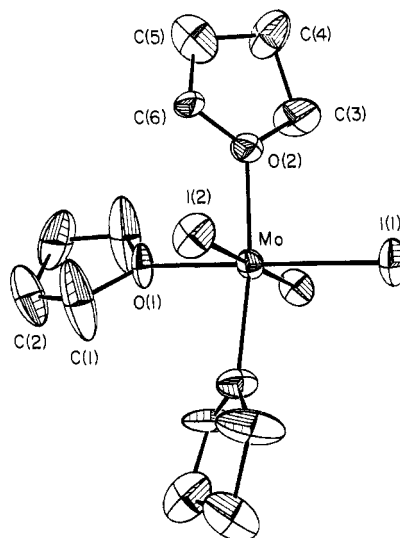
**Figure 1.** ORTEP view of MoI₃(THF)₃ with the atomic numbering scheme employed.

and equivalent isotropic displacement parameters are listed in Table II, while Table III contains selected bond distances and angles. Full tables of bond distances and angles, as well as anisotropic displacement parameters and a listing of observed and calculated structure factors, have been deposited as supplementary material.

Results and Discussion

Interaction of THF adducts of low-valent molybdenum carbonyl derivatives proves to be a convenient method for the synthesis of MoI₃(THF)₃. Mo(CO)₃(THF)₃, obtained in situ from Mo(CO)₃(η^6-C₆H₅CH₃) (eq 1), and MoI₂(CO)₃(THF)₂, obtained in situ from Mo₂I₄(CO)₈ (eq 3), were employed. The stoichiometries of the iodination reactions are outlined in eq 2 and 4.

$$Mo(CO)_3(\eta^6\text{-}C_6H_5CH_3) \xrightarrow[-\text{toluene}]{\text{THF/room temp}} Mo(CO)_3(THF)_3 \quad (1)$$

$$Mo(CO)_3(THF)_3 + \,^3/_2I_2 \xrightarrow{\text{THF/room temp}} MoI_3(THF)_3 + 3CO \quad (2)$$

$$Mo_2I_4(CO)_8 \xrightarrow[-\text{CO}]{\text{THF/room temp}} 2MoI_2(CO)_3(THF)_2 \quad (3)$$

$$MoI_2(CO)_3(THF)_2 + \,^1/_2I_2 \xrightarrow{\text{THF/room temp}}$$
$$MoI_3(THF)_3 + 3CO \quad (4)$$

It is important to perform reaction 2 by adding the molybdenum complex to the iodine solution so that an excess of iodine will always be present. This will minimize the side reaction of carbonylation of the starting material according to eq 5.

$$Mo(CO)_3(THF)_3 + 3CO \rightarrow Mo(CO)_6 + 3THF \quad (5)$$
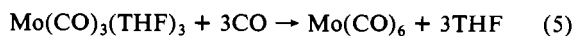
IR monitoring of reactions 2 and 4 shows the intermediacy of a carbonyl complex whose IR spectrum exhibits CO stretching vibrations at 2066, 2006, and 1932 cm⁻¹. Such a spectrum is strikingly similar to that of the [MoI₃(CO)₄]⁻ ion (bands at 2072 s, 2010 s, and 1945 m cm⁻¹ in CH₂Cl₂ solution for the *n*-Bu₄N⁺

salt)[24] and would therefore suggest such an intermediate to contain a $MoI_3(CO)_4$ moiety of a molybdenum(II) center, possibly bridged by one or more iodide ligands to one or more molybdenum(III) centers. This is, however, pure speculation based only on this IR evidence. We have been so far unsuccessful in isolating this intermediate.

We attribute the success of these syntheses of $MoI_3(THF)_3$ to the mild conditions employed. When we performed the iodination directly on $Mo(CO)_6$, which required higher temperatures for the labilization of the CO ligands, only oxygenated molybdenum products and $I-(CH_2)_4-I$ were obtained.[18]

The structure of the $MoI_3(THF)_3$ molecule is shown in Figure 1. The molecule resides on a crystallographic twofold axis, this passing through the Mo, I(1), and O(1) atoms. The coordination geometry is octahedral, the ligands having the meridional arrangement. The same geometry has been observed in other $MCl_3(THF)_3$ complexes of different metals (M = Sc,[25] Ti,[26] V,[27] Cr[27]) and in other Mo(III) complexes, such as $MoCl_3(py)_3$,[8] $MoBr_3(4\text{-pic})_3$[9] (4-pic = 4-picoline), and $MoI_3(PMe_2Ph)_2$-$(POMe_2Ph)$.[4] The Mo–I distance compares well with those found[4] in $MoI_3(PMe_2Ph)_2(POMe_2Ph)$ (ax, 2.746 (2) vs. 2.756 (2) Å; eq, 2.790 (1) vs. 2.762 (2) and 2.768 (2) Å; ax refers to the iodine atoms trans to the THF ligand, whereas eq refers to the iodine atoms trans to each other) and with those in the *trans*-[MoI_4-$(PEt_2Ph)_2$]⁻ anion (2.784 (1), 2.789 (1), 2.754 (1), and 2.797 (1) Å).[4] In particular, the Mo–I_{ax} bond length is shorter than the Mo–I_{eq} one, a feature that is observed also in all the other MX_3L_3 compounds so far structurally characterized and that is in agreement with the accepted order of trans influence (I⁻ > Cl⁻ > OR₂).[28] The observed trend in the Mo–O distances is also expected on trans-influence grounds: the Mo–O_{ax} (trans to iodide) distance is longer (2.21 (1) Å) than the Mo–O_{eq} one (2.193 (8) Å). Again, this is also observed in the $MCl_3(THF)_3$ complexes (M = Sc, Ti, V, Cr).[27] The thermal ellipsoids of the THF carbon atoms, particularly those attached to the oxygen atoms, are strongly elongated perpendicularly to the ideal THF plane. This indicates a high thermal motion. The bond distances and angles related to the THF molecules are therefore a time-averaged result over all the possible conformations assumed in the crystal and are not particularly meaningful from the chemical point of view.

Interaction of $MoI_3(THF)_3$ with 3 equiv of PR_3 (R = Me, Et) cleanly and rapidly affords solutions of $MoI_3(PR_3)_3$ (eq 6).

$$MoI_3(THF)_3 + 3PR_3 \xrightarrow[\text{R = Me, Et}]{\text{THF/room temp}} MoI_3(PR_3)_3 + 3THF \quad (6)$$
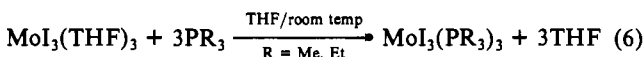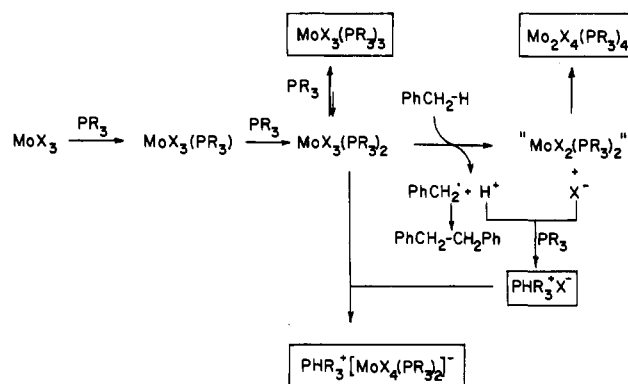
This represents the first clean synthetic route to octahedral MoI_3 derivatives.

The direct interaction between MoI_3 and PR_3 has been carried out in toluene as solvent. In the case of the trimethylphosphine reaction, $MoI_3(PMe_3)_3$ has been obtained, but a considerable amount of reduction to $Mo_2I_4(PMe_3)_4$ simultaneously takes place. $PHMe_3^+I^-$ is also produced under those conditions (see eq 7).

$$MoI_3 + 3PMe_3 \xrightarrow[\text{48 h}]{\text{toluene/80 °C}}$$
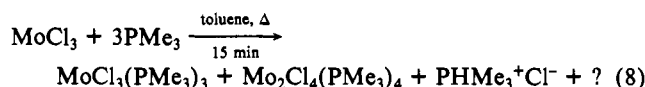$$MoI_3(PMe_3)_3 + Mo_2I_4(PMe_3)_4 + PHMe_3^+I^- + ? \quad (7)$$
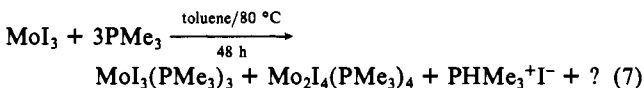
The reduction process to the quadruply bonded Mo(II) dimer, with concomitant protonation of PMe_3, presumably involves oxidative C–C coupling of solvent molecules. Since toluene has unusually reactive (benzylic) C–H bonds, the reaction might proceed differently (or not at all) in other solvents. The corresponding reaction starting from the molybdenum(III) chloride

(24) Barbati, A.; Calderazzo, F.; Poli, R.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1986**, 2569.
(25) Atwood, J. L.; Smith, K. D. *J. Chem. Soc., Dalton Trans.* **1974**, 921.
(26) Handlowic, M.; Miklos, D.; Zikmund, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *37*, 811.
(27) Cotton, F. A.; Duraj, S. A.; Powell, G. L.; Roth, W. J. *Inorg. Chim. Acta* **1986**, *113*, 81.
(28) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

Scheme I

gives similar results. The only noticeable difference was the reaction time necessary to consume the starting material completely (eq 8).

$$MoCl_3 + 3PMe_3 \xrightarrow[\text{15 min}]{\text{toluene, }\Delta}$$
$$MoCl_3(PMe_3)_3 + Mo_2Cl_4(PMe_3)_4 + PHMe_3^+Cl^- + ? \quad (8)$$

Another point concerning both these reactions in toluene is that bibenzyl might well be a byproduct. We have not attempted to detect it, however, so this aspect of the overall process remains uncertain. It is not impossible, however, that adventitious H_2O is the source of protons, with the oxygen atom being captured by PMe_3. Again, we do not have any evidence to rule this in, or out.

It is worth mentioning that the reaction between $MoCl_3$ and phosphine had been already reported by Edwards, Walton, and co-workers.[29] They performed the reaction in ethanol and were able to obtain only dinuclear derivatives of molybdenum(II). While we still obtain some amounts of Mo(II) materials, our main products are the complexes of Mo(III), indicating that the reducing power of the solvent plays an important role in this reaction.

Interaction of MoI_3 with PEt_3 again gave rise to some reduction process, affording $Mo_2I_4(PEt_3)_4$, but the Mo(III) product this time was the anionic [$MoI_4(PEt_3)_2$]⁻ complex, isolated as its $PHEt_3^+$ salt (eq 9). This exhibits the characteristic P–H stretching

$$MoI_3 + PEt_3 \xrightarrow[\text{5 h}]{\text{toluene/}\Delta}$$
$$[PHEt_3][MoI_4(PEt_3)_2] + Mo_2I_4(PEt_3)_4 + ? \quad (9)$$
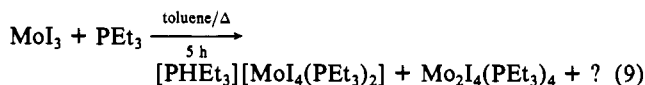
vibration at 2395 cm⁻¹ in the IR spectrum. We suggest for the anion a trans configuration, since this was found for the very similar [$MoI_4(PEt_2Ph)_2$]⁻ anion.[4]

We propose Scheme I to rationalize these results. The interaction between MoX_3 and PR_3 would presumably proceed stepwise through the intermediates $MoX_3(PR_3)$ and $MoX_3(PR_3)_2$. The latter can then take up the last PR_3 molecule to produce $MoX_3(PR_3)_3$. If, however, the intermediate $MoX_3(PR_3)_2$ undergoes a one-electron reduction at the expense of one electron of the solvent, we can then generate the molybdenum(II) product, along with some HX that would then be trapped by the phosphine to form $PHR_3^+X^-$. We have then rationalized the formation of all the products observed in the PMe_3 reaction. The formation of the Mo(III) compound observed in the PEt_3 reaction, i.e. [$PHEt_3$][$MoI_4(PEt_3)_2$], can also be rationalized if we suppose the reaction between intermediate $MoX_3(PR_3)_2$ and PR_3 to be reversible and to be more so for PEt_3 than for PMe_3. The intermediate $MoX_3(PR_3)_2$ would therefore be present in solution in substantial amounts to react with the $PHR_3^+X^-$ species generated in the reductive pathway to eventually produce the observed Mo(III) anion. Independent observations that are in agreement with this view are the following: (i) $MoI_3(PMe_3)_3$ is stable in refluxing toluene for at least several hours, giving no indication of reduction to $Mo_2I_4(PMe_3)_4$; (ii) $MoCl_3(PMe_3)_3$ is also rather

(29) Armstrong, J. E.; Edwards, D. A.; Maguire, J. J.; Walton, R. A. *Inorg. Chem.* **1979**, *18*, 1172.

stable in refluxing toluene, but to a lesser extent than its iodide analogue, since slow appearance of the typical $\delta \rightarrow \delta^*$ electronic transition of $Mo_2Cl_4(PMe_3)_4$ can be detected in the visible spectrum; (iii) thermal treatment of $MoI_3(PEt_3)_3$ as obtained from $MoI_3(THF)_3$ by the procedure described in eq 6 gives rise to a mixture of $Mo_2I_4(PEt_3)_4$ and $[PHEt_3][MoI_4(PEt_3)_2]$.

It would therefore seem that dissociation of a phosphine molecule from $MoI_3(PR_3)_3$ is a much more facile process for PEt_3 than for PMe_3. This is in agreement with the relative basicity of the two ligands and also with their steric requirements. A similar trend was found for the Mo(II) quadruply bonded dimers $Mo_2Cl_4(PR_3)_3$ in their reaction with CO: kinetic studies indicated that the dissociation of a phosphine is the necessary primary step, and the dimer with PMe_3 was found to be much less reactive than those containing phosphines with longer alkyl substituents.[30]

Finally, we would like to remark that the chemistry depicted in Scheme I may be related to other phosphine–molybdenum carbonyl reactions that were found to lead to salts of phosphonium cations.[4,11a,31]

Conclusions

A convenient route to $MoI_3(THF)_3$ has been developed by diiodine oxidation of molybdenum(0) and molybdenum(II) carbonyl starting materials. This route represents a new strategy for the preparation of THF adducts of transition-metal halides, the commonly used ones being direct interaction of the metal(III) halide with THF or reduction of higher valent starting materials. We anticipate that other unknown $MX_3(THF)_3$ complexes, particularly $MoBr_3(THF)_3$ and $WX_3(THF)_3$ (X = Br, I), could possibly be obtained in the same way.

(30) (a) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Organomet. Chem.* **1981**, *217*, C14. (b) Daniels, L. M. Ph.D. Dissertation, Texas A&M University, 1984.

(31) (a) Lewis, J.; Whyman, R. *J. Chem. Soc. A* **1967**, 77. (b) Tsang, W.-S.; Meek, D. W.; Wojcicki, A. *Inorg. Chem.* **1968**, *7*, 1263. (c) Baker, P. K.; Fraser, S. G. *Inorg. Chim. Acta* **1986**, *116*, L1.

Contribution from the Department of Chemistry,
University of Missouri—St. Louis, St. Louis, Missouri 63121

Reactions of Dichloro(diphosphine)platinum(II) Complexes with Tertiary Phosphines: 31P{1H} NMR Studies of [PtCl(PR3)(P⌢P)]+ and [Pt(PR3)2(P⌢P)]2+ (P⌢P = 1,2-Bis(diphenylphosphino)ethane (dppe), 1,2-Bis(dimethylphosphino)ethane (dmpe), or Bis(diphenylphosphino)methane (dppm))

Gordon K. Anderson* and Gregg J. Lumetta

[PtCl₂(dppe)] reacts with L (L = PBu₃, PEt₃, PMePh₂, PPh₃) to yield [PtCl(L)(dppe)]Cl. Likewise, [PtCl₂(dppm)] reacts with L (L = PBu₃, PMePh₂) to give [PtCl(L)(dppm)]Cl. When [PtCl₂(dppe)] is treated with 2 equiv of L, [PtCl(L)(dppe)]⁺ is the only platinum-containing species observed. In contrast, when [PtCl₂(dppm)] is treated with 2 equiv of PMePh₂, both chloride ligands are displaced to yield [Pt(PMePh₂)₂(dppm)]Cl₂. [Pt(PMePh₂)₂(dppe)]²⁺ can be generated, although not quantitatively, by treatment of [PtCl₂(dppe)] with 2 equiv of PMePh₂ in the presence of silver perchlorate. [PtCl₂(dppe)] reacts with dppm to give the unsymmetrical cation [Pt(dppm)(dppe)]²⁺, which has been isolated as both its chloride and tetraphenylborate salts. [PtCl₂(dmpe)] can be treated with dppe to form [Pt(dmpe)(dppe)]Cl₂. These unsymmetrical dipositive cations [PtL₂(P⌢P)]²⁺ display second-order ³¹P{¹H} NMR spectra that have been analyzed in terms of a four-spin system, and the analyses have been confirmed by spin simulation.

Introduction

We have recently been investigating the reaction chemistry of platinum(II) carboxylate complexes containing chelating diphosphine ligands. During the course of this work we have found that reactions of such complexes with tertiary phosphines are complicated by subsequent reactions with chlorinated solvents.[1] For example, when [Pt(OBz)₂(dppe)] (OBz = benzoate) is treated with PBu₃ in dichloromethane, the initial substitution product, [Pt(OBz)(PBu₃)(dppe)]⁺, is ultimately converted to [PtCl(PBu₃)(dppe)]⁺. A detailed account of the substitution chemistry of platinum(II) carboxylate complexes will be presented elsewhere, but in order to fully characterize the products of these reactions in chlorinated solvents, a study of the substitution reactions of the corresponding platinum(II) chloride complexes was undertaken. The results of this latter study are presented here.

Although ligand substitution reactions of square-planar platinum(II) complexes are well documented in general,[2] surprisingly

little has appeared in the literature regarding the substitution chemistry of [PtCl₂(P⌢P)] complexes. Davies et al. have reported the formation of [PtCl(PR₃)(dppe)]⁺ (R = Ph, *n*-Pr) complexes upon treatment of [PtCl₂(dppe)] with 1 equiv of PR₃ in the presence of silver perchlorate.[3] The compounds [PtCl(PR₃)(dppe)][ClO₄] were characterized by ³¹P{¹H} NMR, infrared, and UV–visible spectroscopies, solution conductivity experiments, and elemental analyses. We have found that the presence of a silver salt is not necessary for the formation of [PtCl(PR₃)(P⌢P)]⁺ complexes from the corresponding [PtCl₂(P⌢P)]. One chloride ligand can be displaced readily from [PtCl₂(dppe)] or [PtCl₂(dppm)] by the treatment of such complexes with 1 equiv of a tertiary phosphine ligand. Furthermore, in the case of [PtCl₂(dppm)], both chloride ligands can be displaced by tertiary phosphine ligands in the absence of a silver salt. On the other hand, it is much more difficult to remove the second chloride ligand

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(2) Cross, R. J. *Chem. Soc. Rev.* **1985**, *14*, 197 and references therein.
(3) Davies, J. A.; Hartley, F. R.; Murray, S. G. *Inorg. Chem.* **1980**, *19*, 2299.