for added $PMePh_2$ suggests that exchange of free and coordinated phosphine is slow on the NMR time scale. This contrasts with the situation for *mer*-$VCl_3(CN\text{-}t\text{-}Bu)_3$[13] exchanging with CN-*t*-Bu. Indeed the finding here (and for $VCl_3(NMe_3)_2$) of five-coordination, while octahedral six-coordination is found for ligands THF and CN-*t*-Bu, indicates that steric factors are dominant in determining both thermodynamics and kinetics of VCl_3L_n complexes (see Figure 2). Note also that PEt_3 gives only a five-coordinate complex.[5] For comparison, the sum of van der Waals radii of P and Cl is 3.7 Å, while $VCl_3(PMePh_2)_2$ has Cl–P separations of 3.4 Å.

The curious adoption of a C_{2v} structure, rather than D_{3h}, by both independent molecules of $VCl_3(PMePh_2)_2$ remains unexplained. $VCl_3(NMe_3)_2$ exhibits neither inequivalent V–Cl bond lengths (2.241 (4) (twice) and 2.236 (5) Å) nor bending of the N–V–N axis (179.0 (5)°).[4] The C_{2v} structure cannot originate in a Jahn–Teller effect, since the ground state of a D_{3h} structure should be nondegenerate ($^3A_2'$). In any event, the good agreement between the electronic spectrum of $VCl_3(PMePh_2)_2$ in toluene and the theoretical model[8] (as well as the observed spectrum of $VCl_3(NMe_3)_2$[8]) suggests that the phosphine complex shows no significant symmetry reduction *in solution*. Moreover, the detection of two unpaired electrons in benzene solutions of $VCl_3(PMePh_2)_2$ confirms that there is no splitting of the $(e'')^2$ electronic configuration sufficient to yield the diamagnetism that would characterize a low-spin C_{2v} molecule.

The V–Cl distances in $VCl_3(PMePh_2)_2$ are 0.15–0.20 Å shorter than those in $CpVCl_2(PMe_3)_2$ and $(CpVClPEt_3)_2$,[3] evidence for chlorine π donation into the half-occupied e'' (d_{xz}, d_{yz}; *z* axis along the P–V–P line) orbitals of the trichloride. The V–P distances are essentially the same in all three compounds.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank the Stauffer Chemical Co. for material support, Scott Horn for skilled technical assistance, and Jan Teuben for assistance with analytical problems.

Supplementary Material Available: Listings of hydrogen positional and isotropic thermal parameters, anisotropic thermal parameters, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Molybdenum(IV) Cyclopentadienyl Phosphine Halide Complexes

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Slow addition of a solution of $CpMo(CO)_3Cl$ (Cp = η^5-C_5H_5) to $Ph_2PCH_2CH_2PPh_2$ (dppe) in boiling toluene gives CpMo(dppe)(CO)Cl (**2**) as red crystals in 85% yield. Oxidation of **2** with Cl_2 or Br_2 at 0 °C results in the formation of the formally eight-coordinate complexes $CpMo(dppe)X_2Cl$ (X = Cl (**4**), Br (**5**), respectively). The solid-state structure of **4** shows the molecule adopts a pseudooctahedral structure (counting Cp as occupying one coordination site) with *mer*-Cl_3 groups and one P atom trans to the Cp centroid. ^1H and ^{31}P NMR and conductivity studies show that, in solution, this isomer is in equilibrium with the *fac* isomer (**4a**) and with an ionic form, $[CpMo(dppe)Cl_2]Cl$ (**4c**), formed by dissociation of one chloride ligand. The structure of **4** was obtained on a solvate, **4**·CH_2Cl_2: triclinic, $P\bar{1}$, $Z = 4$ with cell constants *a*, *b*, *c* (Å) = 12.329 (2), 15.778 (4), 17.448 (4), α, β, γ (deg) = 91.59 (2), 99.89 (2), 101.14 (2), and $V = 3274$ (1) Å^3. The structure was solved by direct methods and Fourier syntheses to agreement indices $R_1 = 0.052$ and $R_2 = 0.059$ on 4963 reflections with $I > 3\sigma(I)$. Some relevant molecular dimensions are as follows: Mo–C(Cp) = 2.32 (6) Å; Mo–Cl = 2.456 (2), 2.481 (3), 2.491 (3) Å; Mo–P(1)(ax) = 2.688 [4] Å; Mo–P(2)(eq) = 2.521 [2] Å; P(1)–Mo–Cl = 70.6 [2]–77.7 [1]°; P(1)–Mo–P(2) = 77.2 [1]°.

Introduction

The trihalides $CpMo(LL)X_3$ are potentially useful starting materials for the synthesis of alkyl and hydride complexes of Mo(IV). These complexes may show unusual behavior. For example, $CpMo(dmpe)H_3$ (dmpe = 1,2-bis(dimethylphosphino)ethane) has been reported to show photoinduced catalysis of H/D exchange with various aliphatic and aromatic hydrocarbons.[1] However, existing syntheses of $CpMo(LL)X_3$ complexes either have inconvenient precursors or suffer from the formation of mixtures and low yields of the desired products (see Discussion).

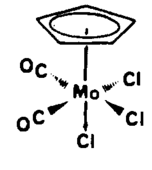
Furthermore, little is known about the stereochemistry and solution behavior of these compounds. Green et al.[2,3] have shown that the trihydrides of the type $CpMo(PP)H_3$ exhibited a 1:2:1 triplet for the ^1H NMR signal, which suggests the compounds undergo a fluxional process in solution wherein the respective magnetic environments of the two phosphorus donors and the three hydrides are equalized.

The dicarbonyl–trihalogeno derivatives $CpMo(CO)_2X_3$ (X = Cl, Br, I), which are available as air-sensitive brown solids from oxidation of $Cp_2Mo_2(CO)_6$ (eq 1) or $CpMo(CO)_3X$ (eq 2), have been described previously:[4,5]

$$[CpMo(CO)_3]_2 + 3X_2 \rightarrow 2CpMo(CO)_2X_3 \tag{1}$$

$$CpMo(CO)_3X + X_2 \rightarrow CpMo(CO)_2X_3 + CO \tag{2}$$

A pseudooctahedral structure with the two neutral ligands in the equatorial positions was suggested by Green et al.:[5]



In connection with our work on C–H activation with (organosilyl)transition-metal complexes,[6,7] we desired to investigate some

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Table I. Summary of Crystal and Collection Data

formula	$C_{32}H_{31}Cl_5MoP_2$, CpMo(dppe)Cl_3·CH_2Cl_2
color	black-violet
fw	750.75
a, *b*, *c*, Å	12.329 (2), 15.778 (4), 17.448 (4)
α, *β*, *γ*, deg	91.59 (2), 99.89 (2), 101.14 (2)
V, Å^3	3274 (1)
ρ_{calcd}, g cm^{-3}	1.468
space group	$P\bar{1}$
Z	4
crystal dimens, mm	0.195 × 0.331 × 0.232
radiation	Mo Kα (monochromatized from graphite)
abs coeff (μ), cm^{-1}	7.596
scan speed, deg min^{-1}	2.5–12 (variable)
scan range	0.8–0.9
bkgd ratio	0.8
2θ limit, deg	40
reflcns collected	6530 (4963 with $I > 3\sigma(I)$)
R_1	0.0520
R_2	0.0590
weight	$K/[\sigma^2(F) + 0.001(F^2)]$
octants collected	$+h,\pm k,\pm l$
temp, °C	20

reactions of CpMo(dppe)X_3 complexes (X = halide, H). We here report a high-yield, convenient synthesis of these halides, discuss some equilibria that must be taken into account in their syntheses, and give the structure of CpMo(dppe)Cl_3 and the ^1H and ^{31}P NMR spectra of CpMo(dppe)X_2Cl (X = Br, Cl).

Experimental Section

All operations were carried out under N_2 with use of Schlenk techniques. Solvents were dried by standard procedures and degassed prior to use. ^1H and $^{31}P\{H\}$ NMR spectra were recorded on a Bruker WM-360 instrument. IR spectra were obtained on a Perkin-Elmer 257 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. CpMo(CO)$_3$Cl (**1**) was prepared by the method of Piper and Wilkinson.[8]

CpMo(CO)(dppe)Cl (2). A hot solution of 9.6 g (34.2 mmol) of **1** in 400 mL of toluene was added dropwise over a period of 5 h to a boiling solution of 14.6 g (36.6 mmol) of dppe in 75 mL of toluene. Compound **2** crystallized during the reaction. The solution was filtered while still warm, and the solid was washed with methanol; yield 18.2 g (85%). Anal. Calcd for $C_{32}H_{29}ClMoOP_2$: C, 61.70; H, 4.69; Cl, 5.69; P, 9.94. Found: C, 61.68; H, 4.90; Cl, 5.90; P, 10.01. IR ($CHCl_3$ or KBr): ν_{CO} 1845 (s) cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$, 25 °C) δ 7.25–7.79 (m, 20 H, C_6H_5), 4.50 (s, 5 H, Cp), 2.72 (m, 2 H, CH_2), 1.66 (m, 2 H, CH_2).

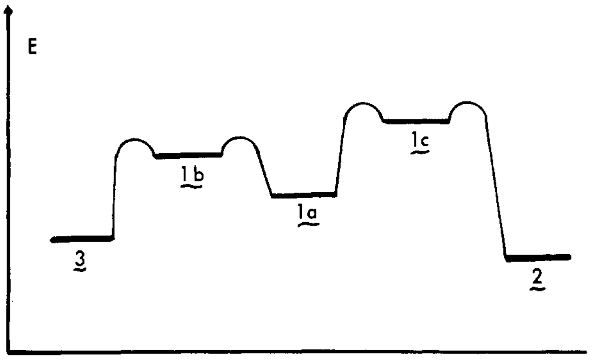
The color of crystalline **2** depends on crystal size. Small crystals are orange; large ones are cherry red.

CpMo(dppe)Cl_3·$(CH_3)_2CO$ (4·$(CH_3)_2CO$). Compound **2**, 1.0 g (1.6 mmol), was dissolved in 50 mL of CH_2Cl_2 and cooled in an ice bath. While the solution was stirred, 50 mL (2.2 mmol) of dry Cl_2 gas was slowly added with a syringe. The color of the solution turned from orange red to dark red-brown. After complete reaction (monitored by IR spectroscopy) the solvent was removed in vacuo and the residue was stirred with 100 mL of acetone overnight. The light violet, fine crystalline product was filtered and then washed several times with acetone. For further purification it was dissolved in as little CH_2Cl_2 as possible and slowly precipitated with acetone at low temperatures: yield 0.61 g (53%); black-violet crystals. Anal. Calcd for $C_{34}H_{35}Cl_3MoOP_2$: C, 56.41; H, 4.87; Cl, 14.69; P, 8.56. Found: C, 56.16; H, 4.62; Cl, 14.43; P, 8.65.

CpMo(dppe)Br_2Cl·$(CH_3)_2CO$ (5·$(CH_3)_2CO$). A solution of 1.0 g (1.6 mmol) of **2**, dissolved in 50 mL of CH_2Cl_2 and cooled in an ice bath, was treated dropwise with a solution of 0.3 g (1.9 mmol) of Br_2 in 10 mL of CH_2Cl_2. Isolation and purification of the product was as described for **4**: yield 0.56 g (43%); dark violet crystals. Anal. Calcd for $C_{34}H_{35}Br_2ClMoOP_2$: C, 50.24; H, 4.34; Br, 19.66; Cl, 4.36; P, 7.62. Found: C, 49.27; H, 4.22; Br, 23.48; Cl, 2.66; P, 7.51.

Reaction of 4 with $AgBF_4$. Compound **4**, 0.2 g (0.28 mmol), and 0.054 g (0.28 mmol) of $AgBF_4$ were stirred in 25 mL of $CHCl_3$ at room temperature overnight. During this period the originally dark violet solution became brown. The $CHCl_3$ solvent was pumped off under vacuum, and the residue taken up in CH_3CN and filtered, giving a white solid (AgCl) and a brown filtrate, which gave a brown solid (0.18 g, 91%) upon removal of the solvent. Anal. Calcd for $C_{31}H_{29}BCl_2F_4MoP_2$: C, 51.92; H, 4.08; Cl, 9.89; P, 8.64. Found: C, 53.03; H, 4.54; Cl, 8.35; P, 8.55.

Scheme I



Structure Determination of 4·CH_2Cl_2. Crystals of **4** were grown by diffusion of hexane into a solution of **4** in CH_2Cl_2. The complex so obtained is a solvate, **4**·CH_2Cl_2. A plate-shaped crystal was affixed to a glass fiber and mounted on a Syntex P2$_1$ four-circle diffractometer. Centering on 16 reflections yielded cell parameters of the triclinic system. The structure was refined well in the space group $P\bar{1}$ ($Z = 4$). A summary of the crystal data is given in Table I. The Mo was located by direct methods, and the remaining non-hydrogen atoms were located by subsequent difference Fourier maps. A regular hexagon with C–C = 1.395 Å was fitted to all benzene rings, which were then refined as rigid groups. Refinement of positional and thermal parameters of all other non-hydrogen atoms led to isotropic convergence with $R_1 = 0.0753$, $R_2 = 0.0753$. Anisotropic refinement yielded final agreement indices of $R_1 = 0.0520$, $R_2 = 0.0590$. During refinement, the function minimized with $\sum w(|F_o| - |F_c|)^2$ and the weight, *w*, is given by $w = k/[\sigma^2(F_o) - 0.001(F_o)^2]$. Computer programs used were from the SHELX package by G. Sheldrick, ORTEP by C. K. Johnson, and MULTAN 78 by P. Main. Scattering factors[9] for neutral atoms were used. No absorption correction was applied. Check reflections recorded after every 50 data points, showed no decay. Table II lists the fractional atomic coordinates, Table III (supplementary material (SM)) gives the temperature factors, and Table IV has selected bond distances and angles. Tables V and VI (SM) contain a complete table of bond distances and angles and F_o vs. F_c, respectively.

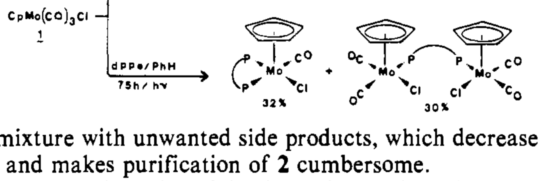
Results and Discussion

CpMo(dppe)(CO)Cl is a convenient precursor to the trihalides according to eq 3. Compound **2** has been prepared previously

$$\underset{\mathbf{2}}{\text{CpMo(dppe)(CO)Cl}} + X_2 \xrightarrow{-CO} \text{CpMo(dppe)}X_2\text{Cl} \qquad (3)$$

$$X = Cl, Br$$

by Treichel[10] and by Haines[11] using two different reaction paths as shown in eq 4. In both paths, the desired product, **2**, is formed



(4a)

(4b)

in a mixture with unwanted side products, which decreases the yield and makes purification of **2** cumbersome.

A simple modification of the thermal route (eq 4a) gives a high yield of **2** in pure form. The modification consists of slowly adding a solution of **1** in hot toluene *to* a solution of dppe in boiling toluene. Complex **2** precipitates during the course of the reaction and is isolated in 85% yield as beautiful red crystals that require no further purification.

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Table II. Fractional Atomic Coordinates

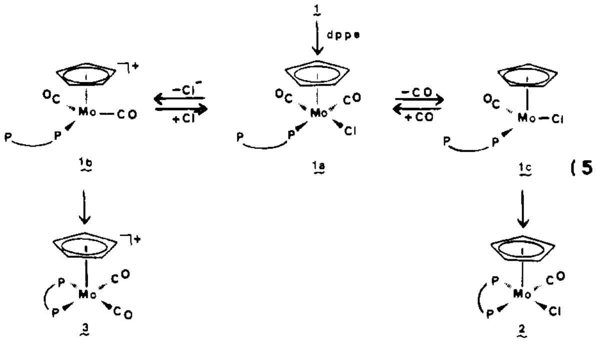
atom	*x*	*y*	*z*	U, Å^2
Mo1	0.7270 (01)	0.3924 (00)	0.5768 (00)	0.0282
C11	0.8671 (08)	0.4318 (07)	0.5095 (06)	0.0469
C12	0.7671 (09)	0.4441 (07)	0.4594 (06)	0.0550
C13	0.7250 (10)	0.5114 (07)	0.4943 (07)	0.0600
C14	0.7975 (09)	0.5400 (06)	0.5649 (06)	0.0494
C15	0.8865 (08)	0.4920 (06)	0.5757 (06)	0.0468
Cl1	0.5280 (02)	0.4014 (01)	0.5423 (01)	0.0366
Cl2	0.8709 (02)	0.3186 (01)	0.6473 (01)	0.0396
Cl3	0.6727 (02)	0.2614 (02)	0.4850 (01)	0.0421
P1	0.6035 (02)	0.2721 (01)	0.6496 (01)	0.0271
C1A	0.4655 (04)	0.2155 (04)	0.5987 (04)	0.0113
C1B	0.3682 (04)	0.2432 (04)	0.6100 (04)	0.0160
C1C	0.2635 (04)	0.1999 (04)	0.5697 (04)	0.0191
C1D	0.2562 (04)	0.1290 (04)	0.5181 (04)	0.0228
C1E	0.3534 (04)	0.1014 (04)	0.5068 (04)	0.0224
C1F	0.4581 (04)	0.1446 (04)	0.5471 (04)	0.0169
C1G	0.6587 (05)	0.1806 (03)	0.6925 (03)	0.0100
C1H	0.6363 (05)	0.1541 (03)	0.7648 (03)	0.0149
C1I	0.6711 (05)	0.0806 (03)	0.7946 (03)	0.0180
C1K	0.7282 (05)	0.0336 (03)	0.7520 (03)	0.0190
C1L	0.7505 (05)	0.0602 (03)	0.6797 (03)	0.0174
C1M	0.7157 (05)	0.1336 (03)	0.6500 (03)	0.0136
C1	0.5753 (07)	0.3336 (06)	0.7333 (05)	0.0339
C2	0.6903 (08)	0.3850 (05)	0.7752 (05)	0.0361
P2	0.7386 (02)	0.4671 (01)	0.7084 (01)	0.0295
C2A	0.6530 (05)	0.5491 (03)	0.7214 (03)	0.0103
C2B	0.6516 (05)	0.5788 (03)	0.7972 (03)	0.0128
C2C	0.5905 (05)	0.6421 (03)	0.8097 (03)	0.0166
C2D	0.5310 (05)	0.6757 (03)	0.7464 (03)	0.0157
C2E	0.5325 (05)	0.6461 (03)	0.6706 (03)	0.0141
C2F	0.5935 (05)	0.5827 (03)	0.6581 (03)	0.0122
C2G	0.8789 (04)	0.5227 (04)	0.7568 (04)	0.0125
C2H	0.9584 (04)	0.4760 (04)	0.7901 (04)	0.0145
C2I	1.0690 (04)	0.5185 (04)	0.8179 (04)	0.0198
C2K	1.1001 (04)	0.6077 (04)	0.8124 (04)	0.0227
C2L	1.0206 (04)	0.6543 (04)	0.7791 (04)	0.0252
C2M	0.9100 (04)	0.6118 (04)	0.7513 (04)	0.0180
Mo2	0.2434 (01)	0.1044 (00)	0.9196 (00)	0.0284
C21	0.3182 (10)	0.0575 (07)	1.0384 (06)	0.0571
C22	0.3977 (09)	0.0699 (07)	0.9870 (07)	0.0537
C23	0.3566 (09)	0.0065 (06)	0.9225 (06)	0.0493
C24	0.2523 (09)	−0.0425 (06)	0.9363 (07)	0.0495
C25	0.2285 (10)	−0.0110 (07)	1.0078 (06)	0.0564
Cl4	0.2998 (02)	0.2392 (02)	1.0070 (01)	0.0415
Cl5	0.0580 (02)	0.0938 (01)	0.9562 (01)	0.0394
Cl6	0.3847 (02)	0.1776 (02)	0.8448 (01)	0.0414
P3	0.1524 (02)	0.0239 (01)	0.7908 (01)	0.0299
C3A	0.0211 (04)	−0.0584 (03)	0.7810 (03)	0.0106
C3B	−0.0359 (04)	−0.0888 (03)	0.7063 (03)	0.0131
C3C	−0.1349 (04)	−0.1513 (03)	0.6965 (03)	0.0147
C3D	−0.1770 (04)	−0.1834 (03)	0.7616 (03)	0.0162
C3E	−0.1200 (04)	−0.1530 (03)	0.8364 (03)	0.0151
C3F	−0.0210 (04)	−0.0906 (03)	0.8461 (03)	0.0125
C3G	0.2416 (05)	−0.0336 (04)	0.7430 (04)	0.0119
C3H	0.3265 (05)	0.0124 (04)	0.7080 (04)	0.0139
C3I	0.3993 (05)	−0.0311 (04)	0.6773 (04)	0.0183
C3K	0.3872 (05)	−0.1205 (04)	0.6816 (04)	0.0193
C3L	0.3023 (05)	−0.1665 (04)	0.7166 (04)	0.0208
C3M	0.2294 (05)	−0.1230 (04)	0.7473 (04)	0.0164
C3	0.0411 (07)	0.1553 (05)	0.7622 (05)	0.0339
C4	0.1106 (07)	0.1025 (06)	0.7216 (05)	0.0349
P4	0.1368 (02)	0.2199 (01)	0.8444 (01)	0.0283
C4A	0.0476 (04)	0.2737 (04)	0.8951 (03)	0.0110
C4B	−0.0683 (04)	0.2429 (04)	0.8831 (03)	0.0152
C4C	−0.1347 (04)	0.2819 (04)	0.9246 (03)	0.0204
C4D	−0.0851 (04)	0.3516 (04)	0.9782 (03)	0.0233
C4E	0.0308 (04)	0.3824 (04)	0.9903 (03)	0.0226
C4F	0.0972 (04)	0.3434 (04)	0.9487 (03)	0.0158
C4G	0.2132 (05)	0.3117 (03)	0.8001 (03)	0.0104
C4H	0.3111 (05)	0.3628 (03)	0.8428 (03)	0.0142
C4I	0.3661 (05)	0.4354 (03)	0.8110 (03)	0.0187
C4K	0.3233 (05)	0.4568 (03)	0.7363 (03)	0.0198
C4L	0.2254 (05)	0.4057 (03)	0.6936 (03)	0.0200
C4M	0.1703 (05)	0.3331 (03)	0.7254 (03)	0.0142
Cl01	−0.0585 (04)	0.0916 (03)	0.5054 (03)	0.1172
Cl02	0.0060 (04)	0.2557 (03)	0.4425 (03)	0.1270
C01	−0.0984 (12)	0.1849 (10)	0.4758 (10)	0.1067
Cl03	0.6359 (04)	0.2646 (04)	0.0606 (04)	0.1585
Cl04	0.6359 (05)	0.4326 (04)	0.0007 (04)	0.1761
C02	0.5742 (13)	0.3251 (14)	−0.0095 (1)	0.1325

Table IV. Selected Bond Distances (Å) and Angles[a] (deg)

C–C(Cp)	1.43 [1]	Mo–Cl(2)	2.481 [3]
Mo–C(Cp)	2.32 [6]	Mo–Cl(3)	2.491 [3]
Mo–P(1)	2.688 [4]	P(1)–C(1)	1.842 [9]
Mo–P(2)	2.521 [2]	P(2)–C(2)	1.843 [9]
Mo–Cl(1)	2.456 [2]	C(1)–C(2)	1.541 [3]
P(1)–Mo–P(2)	77.2 [1]	P(2)–Mo–Cl(3)	151.6 [1]
P(1)–Mo–Cl(1)	70.6 [2]	Mo–P(1)–C(1)	103.9 [3]
P(1)–Mo–Cl(2)	77.7 [1]	P(1)–C(1)–C(2)	106.8 [9]
P(1)–Mo–Cl(3)	74.8 [1]	C(1)–C(2)–P(2)	106.4 [6]
P(2)–Mo–Cl(1)	90.1 [1]	C(2)–P(2)–Mo	108.5 [3]
P(2)–Mo–Cl(2)	84.2 [1]		

[a] Standard deviations in brackets calculated as in ref 12.

On the basis of our observations of the reaction, we believe there is a simple explanation for the effect of temperature and mode of addition on the course of the substitution (see eq 5 and Scheme I). We assume the first substitution proceeds to give complex **1a**. This intermediate dissociates either a chloride to give **1b** or a carbonyl to give **1c**. Closure of the chelate ring in **1c** leads to the ionic product **3**, whereas closure in **1c** gives the desired product **2** (eq 5).



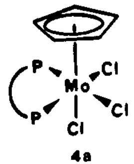
(5)

Scheme I shows a qualitative energy diagram for these substitutions. If *E* for Cl^- loss from **1a** is lower than for CO loss, low temperatures will give predominately the ionic complex **3**. Increasing the temperature favors the reaction with the higher activation energy, i.e. formation of **1c** and ultimately product **2**. We believe that **2** is the thermodynamic product since **3** can be converted to **2** by heating solutions of **3**. In benzene (nonpolar), **3** is insoluble so that conversion of **3** to **2** occurs only very slowly. The *reverse* addition (**1** *to* dppe) is necessary to prevent **1a** from reacting with excess **1** to give the bis(phosphine)-bridged dimer (eq 4b).

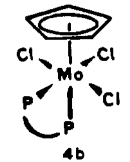
Oxidation of **2** in CH_2Cl_2 with a slight excess of Cl_2 or Br_2 at 0 °C for 30 min gives the trihalides **4** or **5** in yields of 53% and 43%, respectively (eq 3). These compounds crystalize from acetone with one acetone of crystallization per complex molecule. Similar solvates are obtained from alcohols, Me_2SO, or CH_2Cl_2. These molecules of solvation are not coordinated to the metal (see below) but stabilize the crystals by filling voids between the irregularly shaped molecules of the complexes.

Green et al.[2] have described a four-step synthesis of **4** in 14% overall yield from Cp_2MoBr_2, which is itself not as readily available as $CpMo(CO)_3Cl$.

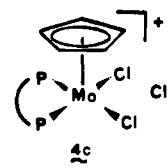
Molecular Structure of $CpMo(dppe)Cl_3{\cdot}CH_2Cl_2$. There are three possible structures for $CpMo(dppe)Cl_3$ that must be considered. Two nonionic complexes, **4a** and **4b**, differ in having the phosphorus donors equatorial–equatorial (ee) or equatorial–axial (ea) (or in having the chlorides *fac* or *mer*, respectively). These descriptions assume a pseudooctahedral geometry in which the Cp group is assigned only one coordination site even though elec-



4a



4b



4c

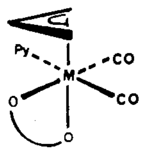
tronically it probably occupies three sites (formally eight-coordinate). In addition, an ionic, four-legged piano stool isomer (**4c**) is a distinct possibility.

The X-ray structure determination shows that **4** crystallizes as the isomer, **4b**. An ORTEP drawing of the molecule appears in Figure 1. There are no unusual intermolecular contacts between the molecules of **4** or between **4** and the CH_2Cl_2 of crystallization (omitted from Figure 1). Selected bond distances and angles averaged over chemically equivalent bonds in the two independent molecules found in the crystal are given in Table IV.[12]

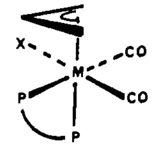
The coordination sphere about the molybdenum may be described as a distorted octahedron with the Cp ligand occupying one site. The Mo–C(Cp) average distance is 2.32 [6] Å and does not differ significantly from Mo–Cp distances in related compounds.[13-15] The two Mo–P bonds have significantly different lengths. The axial Mo–P_1 bond trans to Cp is considerably elongated (Mo–P_1 = 2.688 [4] Å) with respect to the equatorial Mo–P_2 = 2.521 [2] Å. Both Mo–P bonds are longer than those observed in "piano stool" complexes (Mo–P ≈ 2.44–2.50 Å). Conversely, the Mo–Cl bonds in **4** (overall average 2.476 [16] Å) are somewhat shorter than Mo–Cl bond lengths in compounds, e.g., $CpMo(CO)_3Cl$ and CpMo(dppe)(CO)Cl (Mo–Cl = 2.54 Å). These observations may be rationalized if it is assumed that the lengthening of the Mo–P bonds results primarily from steric effects. As the Mo–P bonds become longer, their trans influence[16] is weakened and the Mo–Cl bonds contract accordingly. In addition to steric effects, the Mo–P_1 (axial) bond is weakened further by the strong trans influence of the Cp group. Thus, the effect of the increased coordination member on the bond lengths in **4** is not isotropic. Some bonds lengthen while others contract.

The Mo atom is displaced out of the center of the pseudooctahedron toward the Cp ligand (Figure 1). Thus, the angles between P_1 and the P and 3 Cl groups in the equatorial plane lie between 71 and 78°. The structure found here is similar to those of $CpNb(dppe)X_3$ (X = Cl,[17] Br[18]).

Magnetic Resonance Studies. NMR studies of the pseudooctahedral π-allyl complexes **6** and **7** have been described.[19,20] These compounds are fluxional at room temperature and show simplified spectra indicative of equivalent magnetic environments for the carbonyls and both ends of the bidentate ligands. Only at low temperatures are the NMR spectra consistent with the solid-state structures shown above.



6



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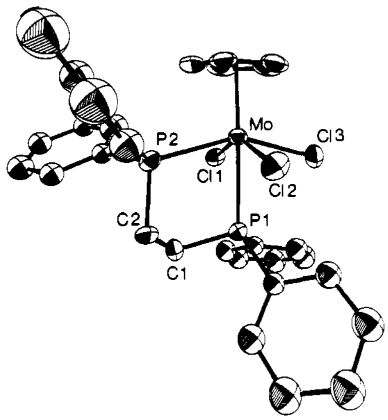

Figure 1. ORTEP drawing of one of the independent molecules of $CpMo(dppe)Cl_3$ (**4b**). Thermal ellipsoids are drawn at the 50% probability level.

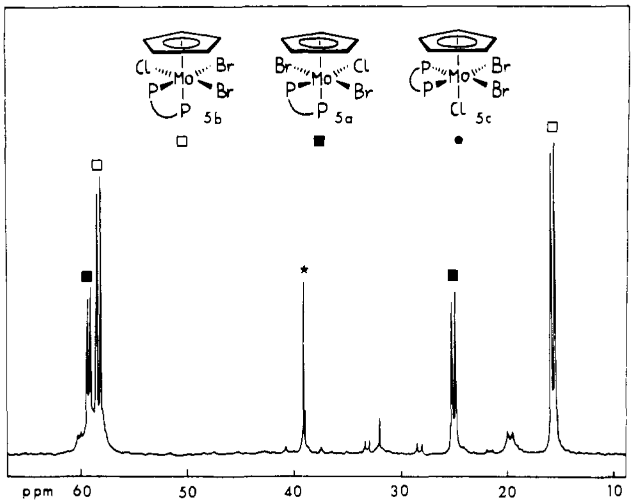

Figure 2. ^{31}P NMR spectrum of **5** in CD_2Cl_2 (mixture of isomers).

In contrast, the room-temperature ^1H and ^{31}P NMR spectra of **4** and **5** are *more* complex than expected from the solid-state structure. (NMR data are summarized in Table VII.) Thus, the $^{31}P\{H\}$ NMR spectrum of **4** consists of two doublets at δ 35.5 and 60.2 with $^2J_{PP}$ = 49.2 Hz and a singlet at δ 38.6. The two doublets are assigned to the ae isomer, **4b**, and the singlet to the ee isomer, **4a**, in which both P atoms are equivalent. The ratio of **4b**:**4a** determined from the ^{31}P NMR spectrum is ca. 8:2.

The ^1H NMR spectrum of **4** is consistent with this interpretation. Two signals for the Cp protons are observed: a doublet at δ 5.07 (J_{PH} = 2.4 Hz) and a singlet at δ 5.32. The doublet arises from coupling of the Cp protons with the axial phosphorus. Coupling to the equatorial phosphorus is not observed. A strong dependence of the magnitude of the P–Cp coupling constant on geometry is well-known in compounds of this type.[21-26] Thus, a lack of observable coupling between the Cp protons and the

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(12) The standard deviation [σ] in bond distances and angles is given as the larger of the two quantities $\sigma = (\sigma_1\sigma_2)^{1/2}$ and $[\sum(x - \bar{x})^2/(n - 1)]^{1/2}$, where σ_1 and σ_2 are the standard deviations of the individual determinations obtained from the variance–covariance matrix.

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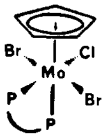
Table VII. ^{31}P and ^{1}H NMR Data for **4** and **5**

compd	$\delta(^{31}P)$ [J_{PP}, Hz][a]	$\delta(^{1}H)$ [J_{PH}, Hz][b]
CpMo(dppe)$Cl_3\cdot(CH_3)_2CO$[c]	35.5, 60.2 [d, 49.2] (**4b**); 38.6 (s) (**4a**)	2.14 (s, 6 H, acetone); 2.96 (m, 2 H, CH_2); 3.35 (m, 2 H, CH_2); 5.07 (**4b**) [2.4] and 5.32 (**4a**) (5 H combined, Cp);[c] 7.71 (m, 20 H, C_6H_5)
CpMo(dppe)$Br_2Cl\cdot(CH_3)_2CO$[d]	15.8, 58.3 [d, 46.5] (**5b**); 25.1, 59.2 [d, 47.4] (**5a**); 39.1 (s) (**5c**)	2.17 (s, 6 H, acetone); 3.02 (m, 2 H, CH_2); 3.31 (m, 2 H, CH_2); 5.19 (**5a**) [2.36], 5.24 (**5b**) [2.14], and 5.28 (**5c**) (s) (5 H combined, Cp);[d] 7.70 (m, 20 H, C_6H_5)

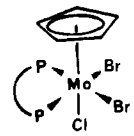
[a] In CD_2Cl_2, external H_3PO_4 referenced to deuterium lock. [b] In $CDCl_3$, internal Me_4Si. [c] Ratio of **4b**:**4a** = 4:1 from integration of ^{31}P and ^{1}H NMR (Cp) signals. [d] Ratio of **5b**:**5a**:**5c** = 6:3:2 from integration of ^{31}P and ^{1}H NMR (Cp) signals.

e-phosphorus atoms in **4a,b** is not unexpected.

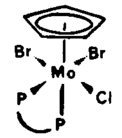
In addition to the ae–ee isomers displayed by **4**, there is the possibility of cis–trans isomers for the Cl and Br ligands in the mixed-halide complex **5**. This doubles the number of possible isomers as shown in **5** and is reflected in the rich ^{31}P NMR spectrum of **5** (Figure 2). The major peaks include two doublets at δ 15.8 and 58.3 ($^2J_{PP}$ = 46.5 Hz), assigned to the ae-cis isomer **5b**, and the doublets at δ 25.1 and 59.2 ($^2J_{PP}$ = 47.4 Hz) assigned to the ae-trans isomer **5a**. This assignment is based on the 2:1 ratio of the sets of signals, which is the ratio expected for a statistical distribution of the Cl_2Br ligands among three sites. The other major line is a singlet at δ 39.1, assigned to the ee isomer **5c**. The low-field resonances near δ 60 are assigned to the axial P atom of the ae isomers since this resonance should be less affected by positional interchange of the halides. The higher field doublet is then assigned to the equatorial phosphorus.



5a



5c



5b

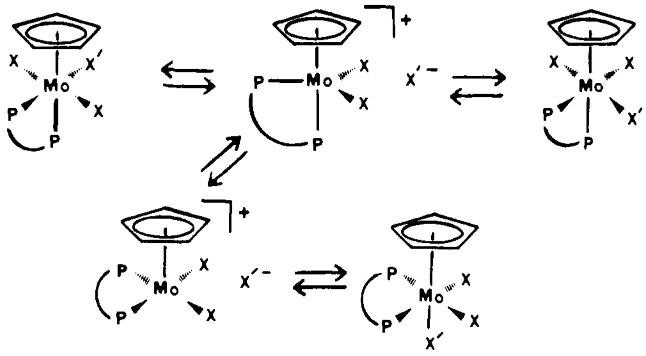
The Cp region of the ^{1}H NMR spectrum (Table VII) of **5** is also consistent with the presence of the three isomers **5a–c**. The singlet at δ 5.28 is assigned to the ee isomer, **5c**, and the doublets to **5a** (δ 5.19) and **5b** (δ 5.24). The assignments are made on the basis of the relative intensities (**5b**:**5a** $\approx$ 2:1).

The various isomers of **4** and **5** could possibly interconvert via an intramolecular trigonal twist mechanism,[27-29] but a dissociative intermolecular mechanism is considered to be more likely in the present instance. The molar conductivity of a freshly prepared solution of **4b** rises from a low initial value to a steady-state value of approximately 70 cm^2 Ω^{-1} mol^{-1}, which suggests that the equilibrium shown in eq 6 is established.

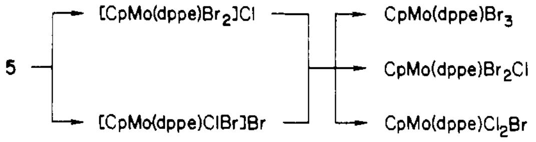
$$CpMo(dppe)Cl_3 + CH_3CN \rightleftarrows [CpMo(dppe)Cl_2(CH_3CN)]^+Cl^- \quad (6)$$

A solution of **4** in $CHCl_3$ slowly deposits a brown solid, soluble in polar solvents, e.g. CH_3OH or CH_3CN. The brown solid is believed to be the ionic isomer, **4c**. Brown $[CpMo(dppe)Cl_2]BF_4$ is obtained by adding $AgBF_4$ to $CHCl_3$ solutions of **4**. Thus, the lability of the halide is established. A dissociative mechanism, shown in Scheme II, easily accounts for the isomerizations observed in the NMR spectra.

Scheme II



Furthermore, the weak lines shown in the ^{31}P NMR spectrum of **5** can now be assigned to ionic species and/or to disproportionation products formed according to eq 7. These disproportionation reactions also account for the high bromine content in the analytical sample of **5**. As Figure 3 shows, the fresh sample is predominately **5** (three isomers), but the analytical results (see Experimental Section) on the recrystallized sample indicated that it contains nearly equal proportions of CpMo(dppe)Br_3 and CpMo(dppe)Br_2Cl.



(7)

CpMo(dppe)Cl_3 reacts readily with good nucleophiles, e.g. acetate, MeO^-, etc., to give red, crystalline substitution products. However, the NMR spectra of these solutions are quite complex owing to the formation of isomers and disproportionation products. Isolation and characterization of the individual compounds were not pursued.

Acknowledgment. The support of the Office of Naval Research is gratefully acknowledged.

Supplementary Material Available: Table III (temperature factors), Table V (complete table of bond distances and angles), and Table VI (F_o vs. F_c) (23 pages). Ordering information is given on any current masthead page.

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