Conversion of η^6-Arylphosphine to η^6-Benzene Complexes of Molybdenum by Use of Strong Acids To Cleave the Phosphorus–Carbon Bonds. The Crystal and Molecular Structure of $[Mo(H)(\eta^6\text{-}C_6H_6)(PPh_2CH_2CH_2PPh_2)(PPh_2F)]BF_4$

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The major products (~60%) in solution from the reaction between aqueous HBF_4 or HF and $Mo(\eta^6\text{-}PhPPh_2)\{PPh_2(CH_2)_nPPh_2\}(PPh_3)$ [$n = 1$ (dppm, **1a**), $n = 2$ (dppe, **1b**), or $n = 3$ (dppp, **1c**)] are the fluxional cations $[Mo(H)(\eta^6\text{-}C_6H_6)\{PPh_2(CH_2)_nPPh_2\}(PPh_2OH)]^+$ (**2a–c**, respectively) and $HPPh_3^+$ (or $[PPh_3CMe_2CH_2C(O)Me]BF_4$ (**4**) if acetone is present). $[MoO(F)(dppe)_2]BF_4$ was identified in some reaction mixtures. Similar reactions of $Mo(\eta^6\text{-}PhPMePh)\{PPh_2(CH_2)_nPPh_2\}(PMePh_2)$ [$n = 1$, **1d**; $n = 2$, **1e**; $n = 3$, **1f**] give $[Mo(H)(\eta^6\text{-}C_6H_6)\{PPh_2(CH_2)_nPPh_2\}(PMePhOH)]^+$ (**2d–f**, respectively) and $HPMePh_2^+$. The reaction of **1b** or **1e** with $HBF_4\cdot Et_2O$ under anhydrous conditions yields $[Mo(H)(\eta^6\text{-}C_6H_6)(dppe)(PRPhF)]BF_4$ (R = Ph, **3b**, or R = Me, **3e**) mixed with **2b** or **2e**. The structures are based on ^{31}P, ^1H, and ^{19}F NMR spectra and spectral similarities to **3b** whose structure has been determined by single-crystal X-ray diffraction [monoclinic, $P2_1/c$, $a = 18.603$ (5) Å, $b = 15.774$ (2) Å, $c = 28.011$ (8) Å, $\beta = 100.41$ (2)°, $V = 8084$ Å^3, $D_{calcd} = 1.42$ g cm^{-3} for $Z = 8$, $R = 0.081$ for 3266 reflections with $I \geq 3\sigma(I)$]. Also reported is a preliminary structure of **4** [triclinic, $P\bar{1}$, $a = 10.122$ (2) Å, $b = 13.186$ (3) Å, $c = 18.889$ (3) Å, $\alpha = 83.75$ (1)°, $\beta = 82.65$ (1)°, $\gamma = 76.99$ (2)°, $V = 2428$ Å^3, $D_{calcd} = 1.24$ g cm^{-3} for $Z = 4$, $R = 0.085$ for 2416 reflections with $I \geq 3\sigma(I)$] and some structural data for $[MoO(F)(dppe)_2]BF_4$ [monoclinic Cc, $a = 9.921$ (1) Å, $b = 22.618$ (4) Å, $c = 21.313$ (3) Å, $\beta = 92.69$ (2)°, $V = 4777$ Å^3] which is isomorphous with $[MoO(OH)(dppe)_2]BF_4$. The reactions involve facile P–C bond cleavage and likely proceed by release of a $PRPhXH^+$ group (X = F or OH) in an exo fashion from the ring since a crossover of PPh_2 and PMePh fragments occurs when mixtures of complexes are treated with HBF_4(aq); reaction with **1d** and $Mo(\eta^6\text{-}PhPPh_2)(dppe)(PMePh_2)$ produces **2a**, **2b**, **2d**, and **2e**; reaction with **1b** and **1f** gives **2b**, **2c**, **2e**, and **2f**; reaction of **1b** and $Mo(\eta^6\text{-}PhPMePh)(PR_2CH_2CH_2PR_2)(PMePh_2)$ (R = *p*-tol, **1g**) also gave the four crossover products. The crossover products do not exchange PPh_2OH and PPhMeOH ligands.

Introduction

Protonation of organometallic compounds is a well-established means of generating metal-bound hydrides.[1] Complexes of the type $Mo(\eta^6\text{-}arene)(PR_3)_3$ or $\{Mo(\eta^6\text{-}Me_3C_6H_3)(dmpe)\}_2N_2$ react with strong acids to give monohydride complexes[2-4] while reaction of $Mo(\eta^6\text{-}benzene)(PEt_3)_3$ with HCl gives $[Mo(H)_2(\eta^6\text{-}benzene)(PEt_3)_3]^{2+}$.[2] Thus we expected that our η^6-phenylphosphine complexes of molybdenum[5] which have similar structures to these would protonate at the metal. Protonation of the uncoordinated phosphorus of the η^6-phenylphosphine group was also expected based on its known reactivity toward boron-based[5b] or transition-metal-based Lewis acids.[5c-g] A third site of reactivity that was not anticipated was the P–C bond of the η^6-arene. We report here the proton-induced cleavage of this bond under mild conditions. The reactions of protons with other η^6-arene or η^5-cyclopentadienyl ligands have been reviewed.[6] Reactions that result in the cleavage of phosphorus–carbon bonds in tertiary phosphines[7] are currently of interest because of their role in the deactivation of homogeneous transition-metal catalysts.[7,8]

Experimental Section

All reactions and manipulations were carried out under argon or nitrogen, using standard drybox or Schlenk techniques. All solvents were dried and degassed before use. Acetone was distilled from Linde type 4A molecular sieves. All other solvents were distilled from purple sodium benzophenone ketyl. Starting materials were obtained from commerical sources and used without further purification. Phosphines were purchased from the Strem Chemical Co.

NMR spectra were recorded on Varian XL-400 or XL-200 (200 MHz ^1H, 81 MHz ^{31}P, and 196 MHz ^{19}F) and Bruker WP-80 (80 MHz ^1H, 32.3 MHz ^{31}P) spectrometers. ^1H and ^2H NMR spectra were calibrated by using residual solvent peaks as internal standards but are reported relative to tetramethylsilane. ^{19}F spectra were calibrated relative to external $CFCl_3$ in acetone. ^{31}P chemical shifts were measured relative to 1% $P(OMe)_3$ in C_6D_6 sealed in coaxial capillaries. They are reported relative to 85% H_3PO_4 using the known chemical shift difference, δ −140.4. In all cases high-frequency shifts are reported as positive.

The syntheses of compounds **1b**[5a] and **1e**[5d] have been reported. The preparations of **1a** and **1c**[9] are identical with that of **1b** although the preparation of **1c** is very difficult to reproduce (twice out of 18 attempts). The preparation of **1a** starting from $MoCl_4$(dppm) is given below. Complexes **1d** and **1f**[9] were prepared like **1e** by reacting $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$[5f] with dppm and dppp, respectively; their purity was verified by NMR. ^{31}P NMR spectra of these complexes are given in Table I.

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[1] Schunn, R. A. *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York 1971; p 218.

[2] Green, M. L. H.; Mitchard, L. C.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1361–1364.

[3] Canestrari, M.; Green, M. L. H.; Izquierdo, A. *J. Chem. Soc., Dalton Trans.* **1984**, 2795–2801.

[4] Green, M. L. H.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2164–2166.

[5] (a) Frizzell, J. J.; Luck, R. L.; Morris, R. H.; Peng, S. H. *J. Organomet. Chem.* **1985**, *284*, 243–255. (b) Luck, R. L.; Morris, R. H. *Inorg. Chem.* **1984**, *23*, 1489–1491. (c) Luck, R. L.; Morris, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 7978–7980. (d) Luck, R. L.; Morris, R. H. *J. Organomet. Chem.* **1983**, *255*, 221–230. (e) Luck, R. L.; Morris, R. H.; Sawyer, J. F. *Organometallics* **1984**, *3*, 1009–1014. (f) *Ibid.* **1984**, *3*, 247–255. (g) Luck, R. L.; Morris, R. H. *J. Organomet. Chem.* **1988**, *347*, 349–364.

[6] Watts, W. E. *Compr. Organomet. Chem.* **1982**, *3*, 1019.

[7] Montachemi, R.; Kannert, G.; Schumann, H.; Chowon, S.; Michman, M. *J. Organomet. Chem.* **1986**, *310*, 107–114.

[8] Garrou, P. *Chem. Rev.* **1985**, *85*, 171–185.

[9] Sella, A. MSc. Thesis, University of Toronto, 1986.

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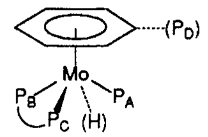
Table I. ^{31}P NMR Data for the Complexes 1, 2, and 3 in CD_3COCD_3



	chemical shifts (ppm)			coupling, Hz
	P_A	P_B, P_C	P_D	J_{AB}, J_{AC}
$Mo(\eta^6\text{-}C_6H_5PPh_2)(dppm)(PPh_3)$ (**1a**)	63.1	20.1	−7.2	32
$Mo(\eta^6\text{-}C_6H_5PPh_2)(dppe)(PPh_3)$ (**1b**)	57.2	83.9	−8.3	27
$Mo(\eta^6\text{-}C_6H_5PPh_2)(dppp)(PPh_3)$ (**1c**)	61.5	36.3	−10.9	27
$Mo(\eta^6\text{-}C_6H_5PMePh)(dppm)(PMePh_2)$ (**1d**)	34.2	22.1, 21.5^a	−22.9	33, 33
$Mo(\eta^6\text{-}C_6H_5PMePh)(dppe)(PMePh_2)$ (**1e**)	31.0	85.8, 83.2^b	−28.0	25, 28
$Mo(\eta^6\text{-}C_6H_5PMePh)(dppp)(PMePh_2)$ (**1f**)	33.5	37.7, 35.7^c	−30.3	29, 29
$Mo(\eta^6\text{-}C_6H_5PMePh)(dptpe)(PMePh_2)$ (**1g**)	30.6	83.8, 80.8^d	−27.6	25, 28
$Mo(\eta^6\text{-}C_6H_6)(dppm)(PPh_2OH)(H)^+$ (**2a**)	143.9	15.0		31
$Mo(\eta^6\text{-}C_6H_6)(dppe)(PPh_2OH)(H)^+$ (**2b**)	142.4	78.0		28
$Mo(\eta^6\text{-}C_6H_6)(dppe)(PPh_2F)(H)^+$ (**3b**)	212.7^e	76.3^f		31
$Mo(\eta^6\text{-}C_6H_6)(dppp)(PPh_2OH)(H)^+$ (**2c**)	134.6	35.3		30
$Mo(\eta^6\text{-}C_6H_6)(dppm)(PMePhOH)(H)^+$ (**2d**)	138.1	15.0		30
$Mo(\eta^6\text{-}C_6H_6)(dppe)(PMePhOH)(H)^+$ (**2e**)	135.8	79.3		30
$Mo(\eta^6\text{-}C_6H_6)(dppe)(PMePhF)(H)^+$ (**3e**)	216.4^g	77.5^h		33
$Mo(\eta^6\text{-}C_6H_6)(dppp)(PMePhOH)(H)^+$ (**2f**)	132.4	35.3		35
$Mo(\eta^6\text{-}C_6H_6)(dptpe)(PMePhOH)(H)^+$ (**2g**)	136.4	78.1, 77.6^i		27, 34
$Mo(\eta^6\text{-}C_6H_6)(dptpe)(PPh_2OH)(H)^+$ (**2h**)	142.0	76.0		28

[a] J_{BC} = 5 Hz (ABX spin system). [b] J_{BC} < 2 Hz (ABX spin system). [c] J_{BC} = 39 Hz (ABC spin system). [d] J_{BC} = 3 Hz (ABX spin system). [e] $^1J_{PF}$ = 927 Hz. [f] $^3J_{PF}$ = 12 Hz. [g] $^1J_{PF}$ = 903 Hz. [h] $^3J_{PF}$ = 11 Hz. [i] J_{BC} = 39 Hz (ABX spin system).

Preparation of $MoCl_4(dppm)$. $MoCl_4(CH_3CN)_2$ (3 g, 9.4 mmol) was added to a solution of $PPh_2CH_2PPh_2$ (3.6 g, 9.4 mmol) in 40 mL of dry benzene and heated to reflux for 2 h in an atmosphere of nitrogen. After the solution was cooled, the product was filtered and washed with 20 mL of benzene: 4 g of the yellow product was recovered (68.8%). The paramagnetic product was used as obtained.

Synthesis of $Mo(\eta^6\text{-}PhPPh_2)(dppm)(PPh_3)$ (1a). PPh_3 (3.4 g, 12.9 mmol) was dissolved in 100 mL of double-distilled THF under argon. $MoCl_4(dppm)$ (4 g, 6.45 mmol) was added and the suspension stirred vigorously for 5 min. Sodium/mercury amalgam (1%, 90 g, 39 mmol) was added and the reaction mixture degassed thoroughly. The reaction mixture is seen to undergo a series of color changes during the first 15 min of the reaction: brown to red to dirty green and finally to brown. After 2 h of vigorous stirring the dark brown THF solution was separated from the residual Na/Hg by means of a cannula and filtered over Celite. The volume was then reduced to approximately 5 mL. Dropwise addition of methanol yields a dark reddish brown highly air-sensitive product. This was dissolved in benzene and chromatographed over alumina under nitrogen to give a bright orange solution. The desired product has the lowest retention time of the products eluted from the column. The product crystallizes as red-orange crystals from benzene/methanol (650 mg, 10%). Anal. Calcd for $C_{61}H_{52}MoP_4$: C, 72.90; H, 5.22. Found: C, 72.55; H, 5.22. ^{1}H NMR (C_6D_6): δ 8.0–6.8 (m, 45 H, C_6H_5), 5.2 (m, 2 H, CH_2), 4.2 (m, 3 H, $\eta^6\text{-}C_6H_5$), 3.4 (m, 2 H, $\eta^6\text{-}C_6H_5$).

Synthesis of $Mo(\eta^6\text{-}PhPMePh)(dptpe)(PMePh_2)$ (1g). $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (200 mg, 0.220 mmol) and $(p\text{-}CH_3C_6H_4)_2PCH_2CH_2P(p\text{-}CH_3C_6H_4)_2$ (dptpe) (100 mg, 0.220 mmol) were dissolved in 10 mL of dry benzene under nitrogen. This orange-red solution was refluxed for 0.5 h. There was no visible color change after this time. The product was very difficult to remove in the presence of the free phosphine, and as a result, the benzene was removed under vacuum and the orange-red oil was placed in a drying pistol (using refluxing acetone as the heat source) for 8 h. The oil was then stirred in dry methanol for 6 h. The bright orange solid obtained upon filtration was recrystallized from toluene/methanol (50 mg, 24%). Anal. Calcd for $C_{55}H_{58}MoP_4{\cdot}0.25C_2H_6OSi$: C, 69.8; H, 6.2. Found: C, 69.8; H, 6.1 (0.25 mol of silicone grease present as indicated also by NMR). ^{1}H NMR (C_6D_6): δ 8.0–6.8 (m, 31 H, C_6H_5 and C_6H_4), 4.9, 4.6, 4.2, 3.7, 3.2 (m, 5 H, $\eta^6\text{-}C_6H_5$), 2.5 (m, 4 H, CH_2), 2.2 (s, 3 H, CH_3 (*p*-tolyl)), 2.1 (s, 3 H, CH_3 (*p*-tolyl)), 2.0 (s, 6 H, CH_3 (*p*-tolyl)), 1.5 (d, 3 H, CH_3, J_{P_AH} = 5 Hz), 1.4 (d, 3 H, CH_3, J_{P_DH} = 4 Hz).

Reactions of 1a–g with Aqueous HBF_4. Aqueous HBF_4 (48%, 1.0 mL) was added dropwise to a solution of the complex (500 mg) in 15 mL of water-saturated benzene at room temperature. After 5 min a brown oil formed, and after 10 min the supernatant became colorless. The benzene supernatant was syringed off and the water removed by forming the azeotrope with benzene. The residue was pumped dry and then redissolved in acetone or THF to record the ^{31}P (Table I) or ^{19}F NMR spectrum (yields of **2a–g**, 40–60% based on ^{31}P integration; the yields of **2d,f** were less than 10%). THF solutions of complexes **2b** and **2e** could be further purified by chromatography over alumina; orange solids or oils (~30% yield) still contaminated with some protonated phosphines were obtained. ^{1}H NMR of these purified samples in acetone-d_6: **2b**, δ 7.5 (m, 30 H), 4.92 (s, 6 H, $\eta^6\text{-}C_6H_6$), 2.5 (br, 4 H, CH_2), −4.96 (dt, 1 H, Mo–*H*, $^2J_{HP}(PPh_2OH)$ = 54.0 Hz, $^2J_{HP}$(dppe) = 31.0 Hz); **2e**, δ 7.5 (m, 30 H), 5.05 (s, 6 H, $\eta^6\text{-}C_6H_6$), 1.40, (d, 3 H, PPhOH*Me*, $^2J_{PH}$ = 7.0 Hz), −5.62 (m, 1 H, Mo–H, see Figure 1). Analysis of reaction mixtures in acetone by ^{31}P NMR (refer to Table I as well): **1a** reaction mixture in acetone gives 66% **2a** on the basis of total observable ^{31}P; also present are $HPPh_3^+$ (δ 27.6), $HPPh_2CH_2CH_2PPh_2^+$ (δ 30.5, −28.9, J_{PP} = 52 Hz) and PPh_3 (δ 2.4), [^{1}H NMR(CD_3COCD_3) of **2a**: δ 5.15 (s, C_6H_6), −4.41 (dt, Mo*H*, J_{PP} = 56, 32 Hz)]; **1b** reaction mixture, 50% **2b**, also **3b**, $[Mo(O)(F)(dppe)_2]^+$, $[PPh_3CMe_2CH_2COMe]^+$, $HPPh_3^+$, PPh_3; **1d** reaction mixture, 15% **2d**, also $HPMePh_2^+$ (δ 26.4), $HPPh_2CH_2CH_2PPh_2^+$; **1e** reaction mixture, 60% **2e**, also **3e**, $HPMePh_2^+$; **1f** reaction mixture, 55% **2f**, also $HPMePh_2^+$, and unidentified species; **1g** reaction

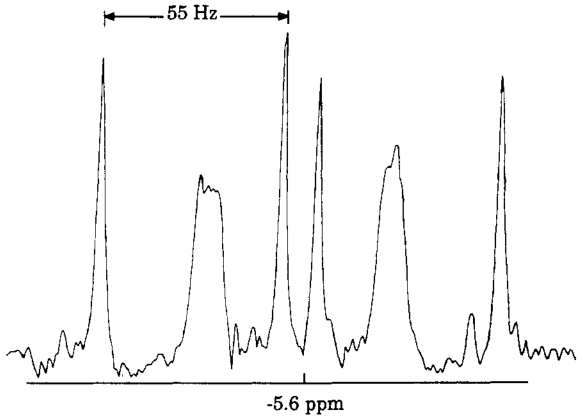


Figure 1. The ^{1}H NMR spectrum in the hydride region of $[MoH(\eta^6\text{-}C_6H_6)(dppe)(PMePhOH)]BF_4$ (**2e**) at 80 MHz in CD_3COCD_3.

Table II. Experimental Details of the Crystal Structure Determinations[a] for [Mo(η^6-C_6H_6)(dppe)(PPh_2F)H]BF_4 (3b), [$PPh_3CH_2C(CH_3)_2COCH_3$]BF_4 (4), and [Mo(O)(F)(dppe)$_2$]BF_4

	$C_{44}H_{41}BF_5MoP_3$	$C_{23}H_{26}BF_4PO \cdot 0.25(C_2H_5)_2O$	$C_{52}H_{48}BF_5MoOP_4$[b]
fw	864.5	454.8	1014.6
cryst color	dark red	colorless	pink
cryst dimens, (mm)	0.075 × 0.1 × 0.275	0.2 mm dia. needle	
system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	Cc
a, Å	18.603 (5)	10.122 (2)	9.921 (1)
b, Å	15.774 (2)	13.186 (3)	22.618 (4)
c, Å	28.011 (8)	18.889 (3)	21.313 (3)
α, deg	90	83.75 (1)	90
β, deg	100.41 (2)	82.65 (1)	92.69 (2)
γ, deg	90	76.99 (2)	90
V, Å^3	8084	2428	4777
Z/ρ_{calcd}, g cm^{-3}/$F(000)$	8/1.42/3536	4/1.24/912	2/1.41
reflns in cell detmn no.; θ range, deg	25; $4.9 < \theta < 11.4$	19; $7.6 < \theta < 16.4$	25; $9 < \theta < 17$
max. scan time,[c] s	65	50	
scan width, deg	$0.65 + 0.35 \tan \theta$	$0.65 + 0.35 \tan \theta$	
max 2θ, deg	48	45	
quadrants	$h,k{\pm}l(0, k, l)$	$h,{\pm}k,{\pm}l$	
no. of refltns measd	13527	6437	
no. of unique reflctns	9589	5204	
std reflctns [no./interval in s]	3/8500	2/7000	
struct soln	Patterson (Mo)	direct methods	
	blocked least-squares Fourier + ΔF Fourier[d,e]		
hydrogen atoms	difference Fourier	difference Fourier	
least-squares weights	$\{\sigma^2(F) + 0.00079F^2\}^{-1}$	$\{\sigma^2(F) + 0.00123F^2\}^{-1}$	
no. of reflctns with $I > 3\sigma(I)$	3266	2416	
R factors: R (wR)	0.081 (0.076)	0.085 (0.087)	
convergence, largest Δ/σ	0.23	0.09	
high peak in final diff map, e Å^{-3}	0.69 (near disordered B(2)F_4^-)	0.47 (near disordered Et_2O)	

[a] Enraf-Nonius CAD-4 diffractometer; graphite crystal monochromator; Mo Kα radiation (λ = 0.71069 Å); T = 298 K; ω–2θ scans. [b] [MoO(OH)(dppe)$_2$]BF_4[11] is monoclinic, Cc, with a = 9.973 (3) Å, b = 22.589 (8) Å, c = 21.256 (6) Å, β = 92.85 (2)°, and V = 4783 (4) Å^3. [c] Prescan at 10 deg min^{-1}. Prescan intensity accepted if $I/\sigma(I) > 25$; otherwise scan speeds chosen to give this ratio within maximum scan time specified; ca. 10% loss in intensities of standards for **3b** corrected for after data reduction. [d] Programs: SDP package on PDP-11/23 and SHELX on Gould 9705 computers. [e] Mo, P, F (except B(2)F_4^-) with anisotropic thermal parameters. Refinement of the population parameters of the F atoms in the $PFPh_2$ ligands [to check whether the ligand might be P(OH)Ph_2] resulted in values of 0.91 (3) and 1.06 (3).

mixture, 15% **2g**, also $HPMePh_2^+$, [Mo(O)(F)(dptpe)$_2$]$^+$ (δ 39.4, J_{PF} = 40.8 Hz), and unidentified species.

Reactions of Complexes 1b or 1e with $HBF_4 \cdot Et_2O$. The complex (100 mg) was dissolved in 5 mL of dry benzene under argon to give a brown solution for **1b** or an orange one for **1e**. $HBF_4 \cdot Et_2O$ (Aldrich) was added dropwise at room temperature with stirring to this solution. A brown oily precipitate formed immediately. Addition was continued until the supernatant was colorless. The supernatant was decanted and the residue pumped to dryness. **1e** gave a dark red oil that contained equal amounts of **2e** and **3e** that could not be separated. The residual solid from **1b** was dissolved in THF and chromatographed over alumina giving a red-orange solution. A red orange solid that is contaminated with small amounts of **2b** and $HPPh_3^+$ may be isolated by addition of Et_2O and cooling to −40 °C. **3b**: ^{1}H NMR (CD_3COCD_3) δ 7.5 (m, 30 H), 5.19 (s, 6 H, η^6-C_6H_6), 2.5 (br, 4 H, CH_2), −5.14 (dtd, 1 H, Mo–H, $^2J_{HP}$(PPh_2F) = 58.1 Hz, $^2J_{HP}$(dppe) = 31.0 Hz, $^3J_{HF}$ = 2.4 Hz); ^{19}F NMR (CD_3COCD_3) δ −120.0 (dt, 1 F, $^1J_{FP}$ = 926.0 Hz, $^2J_{PF}$ = 12.0 Hz), −148.8 (s, $^{10}BF_4^-$), −148.9 (s, $^{11}BF_4^-$), −149.9 (b, BF_3OH^-); ^{31}P NMR (CH_3COCH_3) δ 75.2 (dd, 2 P, dppe, $^2J_{PP}$ = 31.8 Hz, $^3J_{PF}$ = 12.0 Hz), 212.8 (dt, 1 P, PPh_2F, $^1J_{PF}$ = 926.0 Hz, $^2J_{PP}$ = 31.8 Hz). **3e**: ^{1}H NMR (CD_3COCD_3) δ 7.5 (m, 30 H), 5.30 (s, 6 H, η^6-C_6H_6), 1.56 (dd, 3 H, PPhFMe, $^2J_{PH}$ = 6.3 Hz, $^3J_{FH}$ = 11.4 Hz), −5.50 (m, 1 H, Mo–H, see Figure 1); ^{31}P NMR (CH_3COCH_3) δ 77.5 (dd, 2 P, dppe, $^2J_{PP}$ = 33.2 Hz, $^3J_{PF}$ = 11.1 Hz), 216.4 (dt, 1 P, PPh_2F, $^1J_{PF}$ = 903.0 Hz, $^2J_{PP}$ = 33.2 Hz).

Reaction of 1b with CF_3SO_3H. The same procedure as the above $HBF_4 \cdot Et_2O$ reaction was used. The ^{31}P NMR spectrum gave peaks for $HPPh_3^+$, **2b** (60%) and [MoH(η^6-C_6H_6)(dppe)($PPh_2OSO_2CF_3$)]BF_4 {40%, ^{31}P NMR (THF) δ 165.2 (dq, $^2J_{PP}$ = 27 Hz, $^4J_{PF}$ = 5 Hz, PPh_2O–), 78.2 (d, $^2J_{PP}$ = 27 Hz, dppe)}.

Reaction of 1b with HF(g). **1b** (100 mg, 0.098 mmol) was dissolved in 5 mL of benzene. The solution was stirred vigorously, and HF was introduced into the atmosphere above the solution. A brown oil formed instantaneously. The flow of HF was stopped, and the flask purged vigorously with argon and allowed to cool. The supernatant was syringed off and neutralized. The brown oil was then dissolved in acetone. The ^{31}P spectrum reveals the presence of both **2b** and **3b**.

Crossover Reaction Involving 1d and Mo(η^6-$PhPPh_2$)(dppe)($PMePh_2$). Mo(η^6-PhPPhMe)(dppm)($PMePh_2$) (60 mg, 0.072 mmol) and Mo(η^6-$PhPPh_2$)(dppe)($PMePh_2$)[5a] (60 mg, 0.063 mmol) were dissolved in 5 mL of benzene. Aqueous HBF_4 was added dropwise with vigorous stirring until precipitation was complete after approximately 0.5 h. The colorless supernatant liquid was separated from the brown oil with a syringe and the oil pumped to dryness. The brown residue was then redissolved in acetone. No products were isolated. The ^{31}P NMR spectrum indicated the presence of **2a**, **2b**, **2d**, and **2e** in the ratio 1:5:5:1.

Crossover Reaction Involving 1b and 1f. The complexes (60 mg of each) were dissolved in water-saturated benzene and reacted as above. The ^{31}P NMR spectrum indicated the presence of **2b**, **2c**, **2e**, and **2f** in the ratio 1:1:1:7.

Crossover Reaction Involving 1b and 1g. Each of the complexes (60 mg) was also reacted as above. The ^{31}P NMR spectrum indicated that **2b**, **2e**, **2g**, and **2h** were present in the ratio 1:1:1:1.

The Lack of Reaction of 2b with 2g. The ^{31}P spectrum indicated that this mixture (80 mg of each) in 5 mL of acetone was unchanged after stirring for 24 h.

X-ray Structure Determination of 3b and 4. Crystals of complex **3b** were obtained by slow diffusion of diethyl ether into an acetone solution of **3b** (not chromatographed) in a long glass tube under nitrogen. White needles of [$PPh_3CMe_2CH_2COMe$]BF_4 (**4**) and dark red crystals of **3b** were obtained together with an amorphous dark material. The crystal of **3b** was wedged into a 0.2–0.3 mm Lindemann capillary and sealed under nitrogen. Intensity data for **3b** and **4** were collected utilizing the options specified in Table II. For each reflection background counts were

Table III. Selected Bond Distances and Bond Angles for $[Mo(\eta^6\text{-}C_6H_6)(dppe)(PPh_2F)H]BF_4$ (3b)[a]

Bond Lengths (Å)

Mo(1)–P(1)	2.430 (6) [2.435 (7)]	P(1)–C(111)	1.85 (2) [1.84 (2)]
Mo(1)–P(2)	2.492 (6) [2.483 (7)]	P(1)–C(121)	1.87 (2) [1.83 (2)]
Mo(1)–P(3)	2.377 (7) [2.389 (6)]	P(2)–C(2)	1.81 (2) [1.83 (2)]
Mo(1)–C(11)	2.35 (2) [2.25 (2)]	P(2)–C(211)	1.80 (2) [1.90 (2)]
Mo(1)–C(12)	2.36 (2) [2.34 (2)]	P(2)–C(221)	1.87 (2) [1.84 (2)]
Mo(1)–C(13)	2.35 (2) [2.41 (2)]	P(3)–F(1)	1.641 (15) [1.645 (13)]
Mo(1)–C(14)	2.30 (2) [2.32 (2)]	P(3)–C(311)	1.84 (2) [1.83 (2)]
Mo(1)–C(15)	2.26 (2) [2.31 (2)]	P(3)–C(321)	1.87 (2) [1.81 (2)]
Mo(1)–C(16)	2.34 (2) [2.39 (2)]	C···C (η^6-Ph)	1.38 (3)–1.45 (3) [1.36 (3)–1.42 (3)]
Mo(1)–Ct[b]	1.86 [1.88]		
Mo(1)–H(11)	1.75 (13) [1.51 (13)]	C(1)–C(2)	1.51 (3) [1.52 (3)]
P(1)–C(1)	1.87 (2) [1.84 (2)]		

Bond Angles (deg)

P(1)–Mo(1)–P(2)	78.3 (2) [77.7 (2)]	Mo(1)–P(2)–C(2)	106.5 (6) [105.6 (7)]
P(1)–Mo(1)–P(3)	104.1 (2) [105.5 (2)]	Mo(1)–P(2)–C(211)	118.1 (7) [124.8 (7)]
P(1)–Mo(1)–Ct[b]	125.8 [125.1]	Mo(1)–P(2)–C(221)	123.9 (7) [117.0 (7)]
P(1)–Mo(1)–H(11)	67 (4) [72 (5)]	C(2)–P(2)–C(211)	101.4 (10) [102.1 (9)]
P(2)–Mo(1)–P(3)	91.0 (2) [90.8 (2)]	C(2)–P(2)–C(221)	100.4 (10) [104.7 (9)]
P(2)–Mo(1)–Ct[b]	118.6 [117.2]	C(211)–P(2)–C(221)	103.0 (10) [100.2 (9)]
P(2)–Mo(1)–H(11)	134 (4) [132 (5)]	Mo(1)–P(3)–F(1)	118.1 (5) [119.0 (6)]
P(3)–Mo(1)–Ct[b]	124.8 [125.2]	Mo(1)–P(3)–C(311)	121.0 (7) [117.0 (8)]
P(3)–Mo(1)–H(11)	70 (4) [64 (5)]	Mo(1)–P(3)–C(321)	115.5 (7) [119.3 (8)]
H(11)–Mo(1)–Ct[b]	107 [110]	F(1)–P(3)–C(311)	98.9 (8) [98.0 (8)]
Mo(1)–P(1)–C(1)	112.1 (7) [112.0 (7)]	F(1)–P(3)–C(321)	97.8 (8) [97.0 (9)]
Mo(1)–P(1)–C(111)	113.7 (7) [112.0 (7)]	C(311)–P(3)–C(321)	101.7 (9) [102.6 (10)]
Mo(1)–P(1)–C(121)	121.2 (7) [126.3 (8)]	P(1)–C(1)–C(2)	110.0 (13) [109.9 (13)]
C(1)–P(1)–C(111)	103.2 (9) [104.8 (10)]	P(2)–C(2)–C(1)	110.3 (14)
C(1)–P(1)–C(121)	103.5 (9) [100.1 (10)]	P(3)–C(3)–C(4)	112.2 (15)
C(111)–P(1)–C(121)	101.0 (9) [99.2 (10)]		

[a] Values for the corresponding distances and angles in the second molecule are given in square brackets. [b] Ct = centroid of η^6-phenyl rings.

recorded by extending the scan by 25% on either side of each peak and for one-fourth of the scan time. Lorentz and polarization corrections were applied to all data collected. No absorption corrections were considered necessary [$\mu R \simeq 0.05$ for **3b** and even smaller for 4]. Both structures were solved as indicated in Table II, missing atoms being located in F or ΔF Fourier maps. For both compounds the location and refinement of the second BF_4^- anion in each asymmetric unit was hampered by disorder. Several models were tried, and for **3b** the best results were obtained with an approximately trigonal-bipyramidal arrangement of the F atoms due to two BF_4^- tetrahedra sharing a common face. However, it was not possible to resolve separate boron positions and refinement of a single atom at the center of the trigonal bipyramid did not converge as there was significant oscillation in the parameters. Accordingly the position of B(2) from the ΔF Fourier was fixed, and only its temperature factor was refined in the final cycles of least squares. Apart from some residual features around this anion, the remaining peaks in a further ΔF Fourier were associated with H atoms. Two of the stronger peaks were due to the hydride ligands bonded to Mo, and these were then included in the least squares with fixed temperature factors. Other H atoms (representing 9% of the electron density) were not included. Refinement in several large blocks (Mo, P, and F anisotropic) and minimizing $\sum \omega \Delta F^2$ then converged to the final agreement indices in Table II. Neutral-atom scattering factors were taken from ref 35 or were stored in the program (SDP package). Selected bond lengths and bond angles in **3b** are given in Table III. Final positional parameters and their estimated standard deviations and complete tables of bond lengths and bond angles and structure factors for **3b** and 4 have been deposited as supplementary material.

$[PPh_3CMe_2CH_2COMe]BF_4 \cdot 0.25(C_2H_5)_2O$. Apart from the X-ray determination, compound **4** was also characterized by NMR: ^1H NMR (CD_3COCD_3) δ 8.0–7.4 (m, 15 H, C_6H_5), 3.25 (d, 2 H, CH_2, $^3J_{PH}$ = 8 Hz), 1.99 (s, 3 H, $COCH_3$), 1.78 (d, 6 H, $C(CH_3)_2$, $^3J_{PH}$ = 19 Hz); ^{31}P NMR (CH_3COCH_3) δ 32.3.

***trans*-$[Mo(O)(F)(dppe)_2]BF_4$.**[10] The structure of pink crystals of this compound were verified by a preliminary X-ray study by J. Irwin and D. H. Farrar as being isomorphous with the violet crystals of *trans*-$[Mo(O)(OH)(dppe)_2]BF_4$.[11] The O and F positions were established as being disordered, and no further refinements are contemplated. Crystallographic data are given in Table II. Solutions of this complex turn blue upon exposure to oxygen. IR: ν(Mo=O) 942 cm^{-1}. ^1H NMR: δ 7.5 (m, 20 H, C_6H_5), 2.98 (m, 4 H, CH_2). ^{19}F NMR: δ −118.6 (qn, 1 F, $^2J_{PF}$ = 40.3 Hz). ^{31}P NMR: δ 40.6 (d, 4 P, $^2J_{PF}$ = 40.3 Hz).

Results

Starting Complexes 1a–f. The complexes $Mo(\eta^6\text{-}PhPPh_2)\{PPh_2(CH_2)_nPPh_2\}(PPh_3)$ [n = 1 (dppm, **1a**, red solid), n = 2 (dppe, **1b**, brown),[5a] or n = 3 (dppp, **1c**, brown)] are prepared by reduction of the corresponding tetrachloride $MoCl_4\{PPh_2(CH_2)_nPPh_2\}$ with Na/Hg amalgam in the presence of excess PPh_3 in THF solution under Ar. The complexes are very oxygen sensitive. The yield of **1a** is poor because it must be separated by chromatography from two other complexes which are suspected to contain η^1-dppm ligands. The synthesis of η^6-arylphosphine complexes is under steric control.[5a] The results here are consistent with our observation that the formation of the η^6-arylphosphine complex by a σ to π rearrangement is favored when the sum of the Tolman cone angles[12] of the diphosphine (θ = 245° for dppm, 250° for dppe, and 255° for dppp) and two monodentate phosphines (θ = 145° for each PPh_3) falls in the correct range ($\theta \approx$ 500–545°).[5a] This might explain why the preparation of the sterically crowded complex **1c** is so difficult to reproduce.

Complexes **1b** and **1c** have a labile σ-bonded PPh_3 ligand which is readily substituted by smaller ligands such as N_2, H_2, $PMePh_2$, or PF_3 at 20 °C (ref 5a and 9 and this work). Complex **1a** with the smaller diphosphine ligand, dppm, does not substitute readily nor form an N_2 complex at 20 °C. This may be why complex **1a** but not **1b** or **1c** can survive chromatography over alumina. This is also consistent with our prior observation that σ-bonded ligands will be labilized when the cone angle sum of the four phosphorus donors in the complex exceeds 540°.[5a]

The complexes $Mo(\eta^6\text{-}PhPMePh)\{PPh_2(CH_2)_nPPh_2\}(PMePh_2)$ [n = 1 (dppm, **1d**, red solid), n = 2 (dppe, **1e**,

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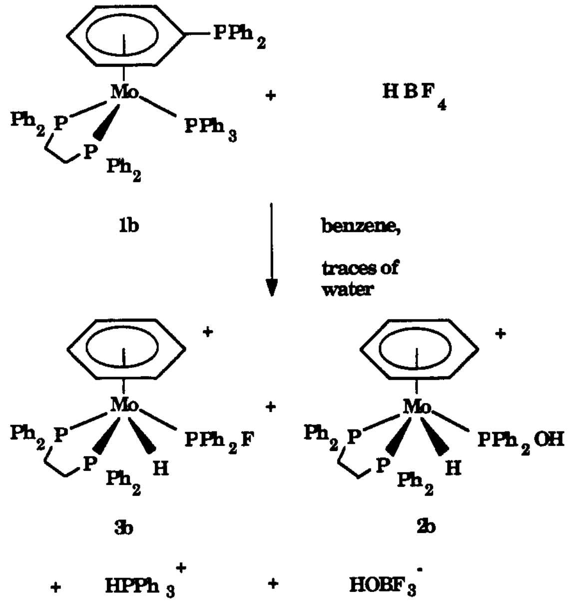
[10] Ellis, R.; Henderson, R. A.; Hills, A.; Hughes, D. L. *J. Organomet. Chem.* **1987**, *333*, C6.

[11] Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1978**, *17*, 668.

[12] Tolman, C. A. *Chem. Rev.* **1977**, *254*, 243–255.

Scheme I. Reaction of 1b with $HBF_4 \bullet Et_2O$



orange),[5d] or $n = 3$ (dppp, **1f**, red)] are prepared by substitution of η^1-$PMePh_2$ ligands of the crowded complex Mo(η^6-PhPMePh)($PMePh_2$)$_3$ (sum of $\theta = 544°$)[5f] by the corresponding diphosphine in benzene at 20 °C in 10 h. Complex **1g**, Mo(η^6-PhPMePh)(dptpe)($PMePh_2$) [dptpe = P(p-tolyl)$_2CH_2CH_2$P(p-tolyl)$_2$], was also prepared from the above starting material by heating in benzene at 80 °C for 0.5 h. Complexes **1d** and **1e** have also been prepared from $MoCl_4${$PPh_2(CH_2)_nPPh_2$} in a similar fashion to complexes **1a–c**. The complexes are oxygen sensitive but do not react with N_2 or substitute readily at 20 °C as expected from their cone angle sums (**1d**, 512°; **1e**, 522°; **1f**, 527°). The phosphorus atoms of the diphosphine ligands in these four complexes are diastereotopic because of the chiral center in the η^6-PhPMePh ligand. Thus they give ABX (**1d,e,g**) or ABC (**1f**) spin systems in the ^{31}P NMR spectra (Table I).

Products of the Protonation Reactions. Dropwise addition of $HBF_4 \cdot Et_2O$ to Mo(η^6-$PhPPh_2$)(dppe)(PPh_3) (**1b**) in dry benzene leads to the rapid formation of a brown oil. NMR spectra of the oil dissolved in acetone indicates that a complicated reaction involving the cleavage of a P–C bond and formation of a P–F bond is occurring. The latter is signalled in the ^{31}P NMR spectrum by a low-field multiplet with a large, characteristic $^1J_{PF}$ of 927 Hz coupling similar in magnitude to the PF_3 derivative of **1b**, Mo(η^6-$PhPPh_2$)(dppe)(PF_3), with $^1J_{PF} = 1238$ Hz, δ(^{31}P of PF_3) = 154.8 ppm.[9] One hydride multiplet with $^3J_{HF}$ coupling (due to **3b**) and another one with a similar chemical shift and multiplet pattern apart from $^3J_{HF}$ (due to **2b**) are apparent in the ^1H NMR spectrum. Crystals of **3b** obtained from acetone were characterized by X-ray crystallography (see below and Figure 2). Over time the acetone solvent condensed with protonated phosphine and gave water and [$PPh_3CMe_2CH_2C(O)Me$]BF_4 which was isolated as white crystals and identified by X-ray diffraction (eq 1). ^{19}F NMR indicated the presence of hydrolyzed BF_4^-, another product of the reaction of Scheme I. The pink complex *trans*-[Mo(O)(F)(dppe)$_2$]BF_4[10] was isolated in low, variable yield from the reaction mixture by chromatography; this arises from a paramagnetic impurity which occasionally contaminates complex **1b**. Complexes **2b** and **3b** could not be separated by chromatography. The same products are obtained if Mo(η^6-$PhPPh_2$)(dppe)(N_2) or Mo(η^6-$PhPPh_2$)(dppe)(H)$_2$ are used in place of **1b**.

$$HPPh_3^+ + 2CH_3COCH_3 \rightarrow \underset{4}{[PPh_3CMe_2CH_2C(O)Me]BF_4} + H_2O \quad (1)$$

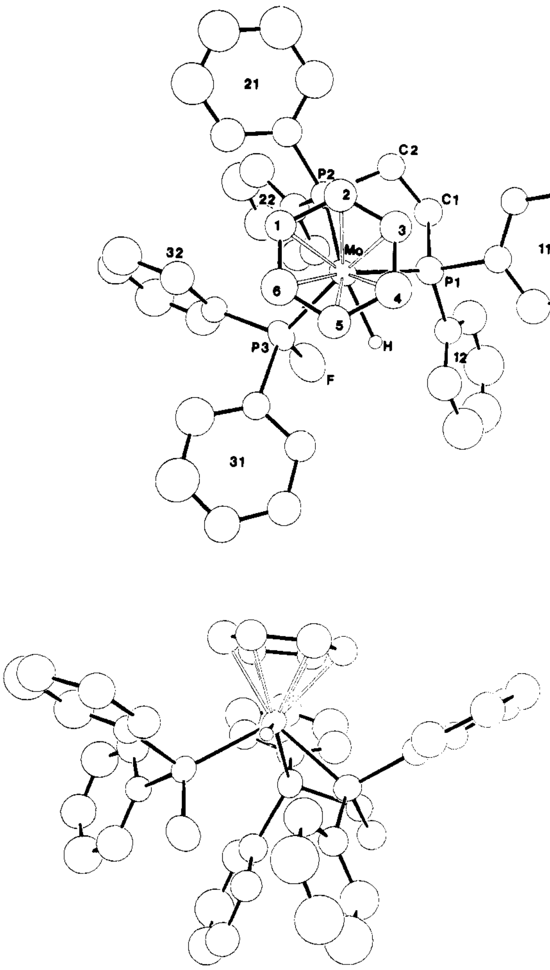


Figure 2. Two views (ORTEP) of cation 1 of [MoH(η^6-C_6H_6)(dppe)(PPh_2F)]BF_4 (**3b**). Thermal ellipsoids are drawn at the 50% probability level, the hydride ligand with a fixed thermal parameter.

The evidence for the structure of **2b** and its congeners **2a–h** is indirect since the hydroxyl group has not been observed by NMR. Similarly the proton on the OH of the ligand P(OEt)$_2$(OH) in an iron complex could also not be located.[13] Complexes **2** are greatly favored over the fluorophosphine products **3** when aqueous HBF_4 is used (Scheme II); however, for **1b** one observes 60% of **2b** and 40% of **3b**. ^{31}P NMR indicates that major species in the acetone solutions from reactions with **1a-c** are complexes **2a-c** (see Table I, 40–60% yield based on ^{31}P integration) along with [$HPPh_3$]BF_4 and PPh_3. Reactions with **1d-g** in acetone give complexes **2d-g** (see Table I, 50–60% yield based on ^{31}P integration) along with [$HPMePh_2$]BF_4. The latter converts to [$PMePh_2CMe_2CH_2C(O)Me$]BF_4. Small amounts of **3b** and **3e** are also present in the reaction mixtures of **1b** and **1e**.

If acetone-d_6 solutions of the reaction mixtures are prepared, then the aldol condensation reaction (eq 1) produces HDO that exchanges deuterium with both the hydride and hydrogen on the PRPhOH ligands. This gives a new resonance due to the PRPhOD ligand; for example,

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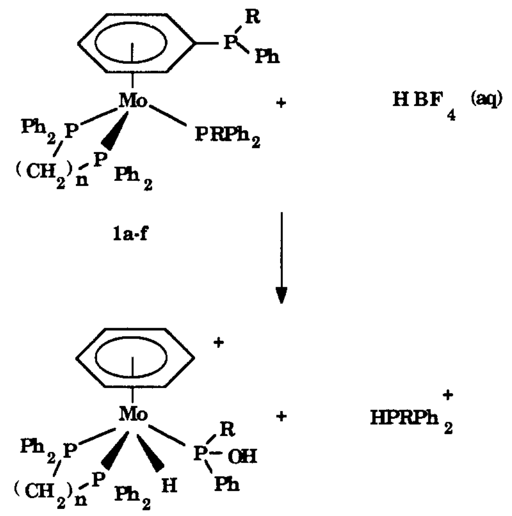
(13) Shaw, S. Y.; DuBois, D. A.; Watson, W. H.; Neilson, R. H. *Inorg. Chem.* **1988**, *27*, 976–977.

Scheme II. Reaction of Complexes 1 with HBF_4(aq)



	R	n
2a	Ph	1
2b	Ph	2
2c	Ph	3
2d	Me	1
2e	Me	2
2f	Me	3

for **1b**, $\delta(^{31}P(PPh_2OD))$ = 142.2 (t of 1:1:1 t, $^2J_{PP}$ = 28 Hz, $^2J_{PD} \approx$ 6 Hz). Also a new resonance for the η^6-C_6H_6 group appears in the ^1H NMR spectrum at 4.93 ppm for **1b** as the hydride resonance disappears.

THF solutions of the oils produced in Scheme II contained mainly complexes **2a–f**. The ^{31}P chemical shifts for the PPh_2OH and PMePhOH ligands were shifted upfield by approximately 3 ppm relative to the peaks in acetone solutions (Table I); for example, $\delta(PPh_2OH)$ = 139.0 for **2b** in THF. Differences in hydrogen-bonding interactions of the hydroxyl group probably account for this shift. The THF solutions sometimes underwent acid-catalyzed polymerization to a gel; BF_3 is the likely catalyst in this case.

The reactions (Schemes I and II) occur only with less coordinating acids such as HF, HBF_4, and CF_3SO_3H. A major product from the reaction of **1b** with CF_3SO_3H under anhydrous conditions is $[MoH(\eta^6\text{-}C_6H_6)(dppe)(PPh_2OSO_2CF_3)]BF_4$. When CH_3CO_2H, CF_3CO_2H, and HCl are used, mixtures of paramagnetic products are produced.

Crystal Structures. The two cations in the asymmetric unit of **3b** differ significantly from each other only in the orientations of the phosphorus substituents. A best molecular fit based on the Mo and P atoms agree to within 0.34 Å of each other with the maximum deviations occurring between the rings on atoms P(1)/P(4) and P(3)/P(6) (Supplementary material).

In both cations the geometry at the Mo atoms is a 4:3 piano stool with the η^6-phenyl ring occupying the three vertices of the "seat" while the remaining vertices are occupied by the three P atoms and the hydride ligand (Figure 2). Notably, the $PFPh_2$ and H ligands are cis to one another. Due to the small size of the hydride (cone angle 75°)[12] the atoms P(1) and P(3) bend toward this ligand resulting in a P(1)MoP(3) angle of 104.1 (2)°.

The present Mo–H distances are rather inaccurate but appear to be comparable to values observed elsewhere.[14] The trans influence of the hydride ligand on the atom P(2) [HMoP(2) = 134 (4)°] lengthens (by 0.06 Å) the Mo–P(2) bond relative to the Mo–P(1) bond to the other end of the dppe ligand. A similar effect has been commented upon for $MoH_2(PMe_3)_5$ (**5**).[15] Both Mo–P[dppe] distances are longer than the Mo–P(3) distance to the $PFPh_2$ ligand [2.377 (7) Å] despite the fact that the cone angle for $PFPh_2$ (θ = 131°) is larger than that for $^1/_2$(dppe) (θ = 125°). This distance is also substantially shorter than the Mo–P distances in the seven-coordinate complexes $Mo(\eta^6\text{-}C_6H_6)Me_2(PMe_2Ph)_2$[16] [Mo–P = 2.463 (3) and 2.477 (3) Å; θ_{PMe_2Ph} = 122°], $Mo(\eta^6\text{-}C_6H_5CH_3)Me_2(PMe_2Ph)_2$[16] [Mo–P = 2.467 (1), 2.476 (1) Å; θ_{PMe_2Ph} = 122°], and **5** [Mo–P = 2.403 (3), 2.478 (3) Å; θ_{PMe_3} = 118°]. The shortness of the Mo–P(3) distance is consistent with the enhancement of the π-acceptor properties of the ligand PR_3 when one or more of the R groups are replaced by F.[17] To our knowledge only one other structure containing the $PFPh_2$ ligand, *trans*-$Mo(CO)_4(PPh_2NH_2)(PPh_2F)$ (**6**), has been reported,[18] and the Mo–P bond length to the PPh_2F ligand [2.414 (1) Å] is 0.06 Å shorter than that to the PPh_2NH_2 ligand [2.471 (1) Å] but is still longer than the present distance.

In the independent $PFPh_2$ ligands of **3b** the P–F bond lengths [1.641 (15) and 1.645 (13) Å] can be compared to the P–F bond length in **6** [1.614 (2) Å] and the shorter P–F distances in *trans*-$NiBr_2(PFBu^t{}_2)_2$ [1.579 (7) Å][19] and in a (methylamino)diflurophosphine iron complex [1.567 (3) and 1.564 (3) Å].[20] The present MoPF angles [118.1 (5) and 119.0 (6)°] are significantly larger than the angle involving the $PFPh_2$ ligand in **6** [113.1 (1)°]. The long P–F bond also results in large differences in the angles at P(3) [and P(6)] as the phenyl rings bend away from Mo [average MoPPh = 118.2°; range of 115.5 (7)–121.0 (7)°] and toward the F atoms [average PhPF = 97.9°].

The arene ring is planar to within experimental error, and the centroid lies directly above the Mo atom. This is the first example of an (η^6-arene)ML_4 complex with a planar phenyl ring. The average Mo–C distance is 2.33 Å, close to the average found in other (η^6-arene)ML_4 complexes. There is no apparent alternation in the C–C distances.

The asymmetric unit in **4** contains two independent cations and anions as well as small amounts of disordered Et_2O about centers of symmetry. As with **3b**, one BF_4^- anion in **4** is disordered and was treated in a similar manner. In the two cations the P–C bond lengths to the CMe_2CH_2COMe moieties are 1.852 (10) and 1.863 (10) Å while the average P–Ph bond length is 1.796 [6] Å {range 1.792 (12)–1.807 (12) Å}. Similarly the average RPPh and PhPPh bond angles are 110.8 [14]° {range 108.9 (5)–112.1 (5)°} and 108.1 [10] {range 107.0 (5)–109.9 (5)°}. Very similar dimensions are observed for other alkylamine-substituted triphenylphosphonium compounds that have been observed to have antischistosomal activity.[21,22]

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(14) (a) Antsyshkina, A. S.; Dikareva, L. M.; Porai-Koshits, M. A.; Ostrikova, V. N.; Stripkin, Y. V.; Volkov, O. G.; Pasynskii, A. A.; Kalinnikov, V. T. *Koord. Khim.* **1985**, *11*, 82. (b) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(15) Hursthouse, M. B.; Lyons, D.; Thornton-Pett, M.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1983**, 476–477.

(16) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans* **1979**, 1519–1523.

(17) (a) Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033–7037. (b) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064–4065. (c) Orpen, G. A.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310–1311.

(18) Bradley, F. C.; Wong, E. H.; Gabe, E. J.; Lee, F. L. *Inorg. Chim. Acta* **1986**, *120*, L21.

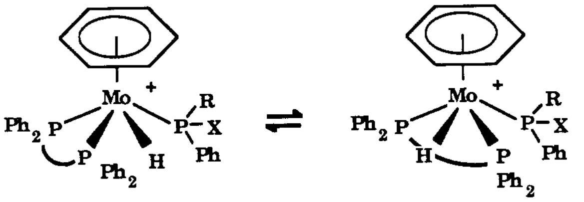
(19) Sheldrick, W. S.; Stelzer, O. *J. Chem. Soc., Dalton Trans.* **1973**, 926.

(20) Newton, M. G.; King, R. B.; Chang, M.; Gimeno, J. *J. Am. Chem. Soc.* **1979**, *101*, 2627.

(21) Czerwinski, E. W. *Acta Crystallogr., Sect. C* **1986**, *C42*, 236.

(22) Dubourg, A.; deCastro Dantas, T. N.; Klaébé, A.; Declercq, J. P. *Acta Crystallogr., Sect. C* **1986**, *C42*, 112.

Scheme III. Interconversion of Cis and Trans Isomers of Fluxional Complexes 2 (X = OH) and 3 (X = F)



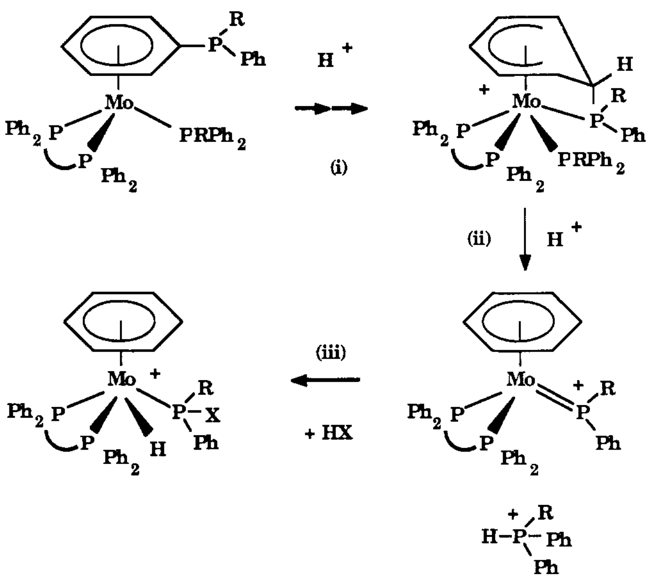
NMR Properties of Complexes 2 and 3. The ^1H NMR spectra of complexes 2 and 3 show a singlet due to the η^6-benzene ring. The chemical shift of these resonances are shifted to low field relative to those of the arene rings on the ligands.

The coupling patterns of the hydride resonances are too simple to be explained by the rigid structures shown in Schemes I and II and Figure 2. These formally seven-coordinate complexes are fluxional, and so the diphosphine phosphorus atoms become equivalent and their couplings become averaged. Thus the hydride pattern of complexes **2b** or **3b** is a doublet of triplets although the latter is further split by $^3J_{HF}$. The dppe phosphorus atoms are diastereotopic in complexes **2e** and **3e** because of the chiral PMePhX group but this cannot explain the pattern shown in Figure 1. Instead this is likely to be the dynamically averaged spectrum of a mixture of cis and trans isomers interconverting as in Scheme III. Some support for this comes from the low-temperature spectrum (-60 °C) of **3e** which partially decoalesces into a more complex pattern, although overlap with the resonances of **2e**, which are temperature-invariant, prevents complete interpretation. The ^{31}P and ^{19}F NMR spectra are also consistent with fluxional, square-based piano-stool structures.

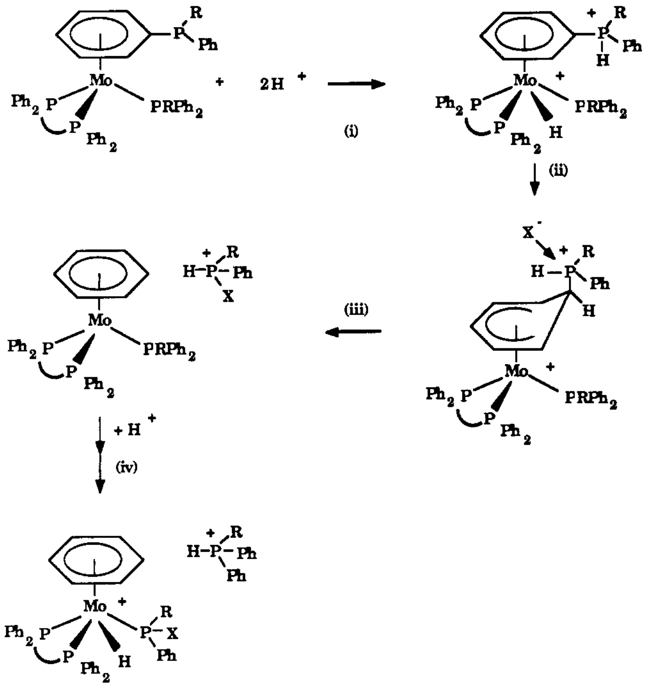
Fluxionality has been suspected in other square-based piano-stool complexes. The complex $[Mo(\eta^6\text{-}C_6H_5Et)(dmpe)(PMe_3)H]^+$[3] gives a similar hydride spectrum to **2b**. Interconverting isomers similar to those of Scheme III have been proposed for the complex $Mo(H)_2(\eta^6\text{-}PhPMePh)(PMePh_2)_2$.[5b] Both neutral and cationic carbonyl phosphine complexes of molybdenum-containing η^5-cyclopentadienyl or η^6-arene ligands have been examined by Faller[23] and by Flood.[24] On the assumption that the arene or cyclopentadienyl ligands effectively occupy one coordination site they both proposed trigonal-bipyramidal intermediates in the fluxionality. The spectrum reported for $[\{MoH(\eta^6\text{-}C_6H_3Me_3)(dmpe)\}_2N_2](BF_4)_2$ is difficult to explain.[4]

Mechanistic Considerations. We can rule out arene exchange as the source of the η^6-benzene ring in complexes **2b** and **3b** because the same products are obtained by the reactions of **1b** with $HBF_4{\cdot}Et_2O$ in C_6D_6, toluene, or THF although for THF solvent polymerization often occurs. In addition we have observed deuterium incorporation into the η^6-benzene ligand by ^2H NMR when **1** is treated with DF.[25] Complexes **1d–f** give only PMePh fragments, and so it is the P–C bond of the η^6-bonded ligand which is being cleaved. **2b** is not formed by direct hydrolysis of **3b** because the addition of water to a solution of **3b** causes hydrolysis of the P–F bond only over a period of weeks.

Scheme IV. An Intramolecular Mechanism for the P–C Cleavage Reaction Which Has Been Ruled Out by the Crossover Experiments



Scheme V. The Favored Mechanism Involving Exo Release of the PRPh$^+$ Fragment as HPXRPh$^+$



Two types of mechanisms could be proposed. The first involves the intramolecular migration of the PRPh$^+$ fragment as in Scheme IV. This reaction could proceed by (i) protonation at the metal, H migration to the ring, a suprafacial H shift to the substituted carbon (or direct exo protonation of the ring), and coordination of the phosphorus and (ii) elimination of the σ-bonded $PRPh_2$ ligand and formation of a Mo=PRPh$^+$ reactive intermediate (iii) which undergoes nucleophilic attack by HF or H_2O. Stable complexes containing the groups $W{=}PiPr_2$,[26] $Mo{=}PPh(N(SiMe_3)_2)$,[27] and $Mo{=}P(OCMe_2CMe_2O)$[28] have recently been reported, and they are susceptible to

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(23) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852–5860.

(24) Flood, T. C.; Rosenberg, E.; Sarhangi, A. *J. Am. Chem. Soc.* **1977**, *99*, 4334–4340.

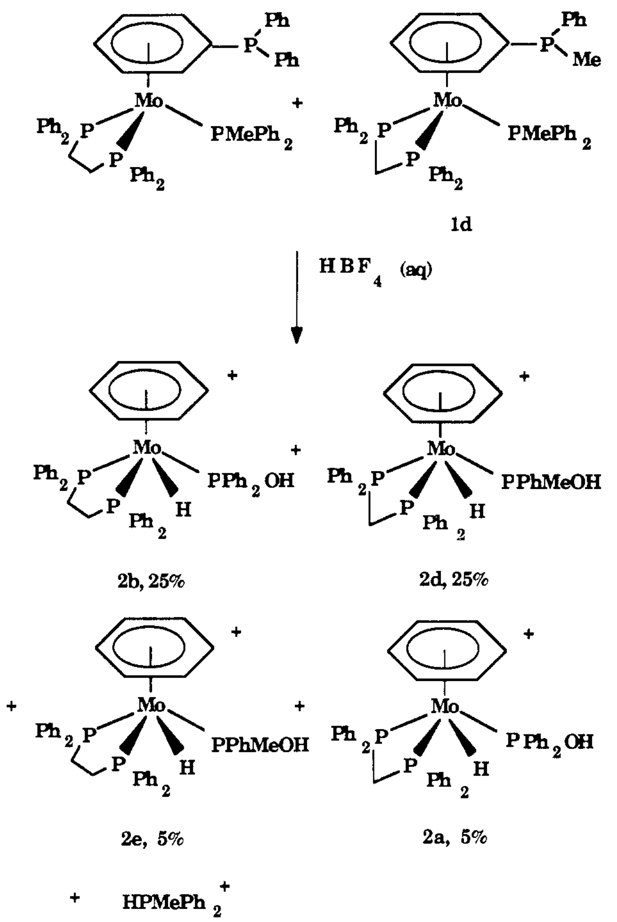
(25) DF(aq) was generated by bubbling HF through D_2O for 5 min. ^2H NMR shows a broad peak at δ 4.92 corresponding to the η^6-benzene.

(26) Jorg, K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 92–93.

(27) McNamara, W. F.; Dussler, E. N.; Paine, R. T.; Ortiz, J. V. *Organometallics* **1986**, *5*, 380–383.

(28) Gross, E.; Jorg, K.; Fiederling, K.; Gottlein, A.; Malisch, W.; Boesse, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 738–739.

Scheme VI. Reaction between HBF_4(aq) and a Mixture of 1d and $Mo(\eta^6\text{-}PhPPh_2)(dppe)(PMePh_2)$ Which Is Made from 1b and $PMePh_2$



attack by H_2O. A second type involves the exo release of the $PRPh^+$ fragment as $HPXRPh^+$ (Scheme V). This mechanism could go by (i) protonation of the metal and dangling phosphorus, (ii) migration of hydride to the substituted carbon and nucleophilic attack by HF or H_2O on the $PHRPh^+$ group, (iii) exo release of $HPXRPh^+$ and protonation of the metal, and (iv) substitution of the σ-bonded $PRPh_2$ ligand by the smaller, more π-accepting ligand PRXPh. The last step would also be favored by the higher Brønsted basicity of the $PRPh_2$ ligand.

These two possibilities can be distinguished by a crossover experiment (Scheme VI) as long as the product ions 2 or 3 are substitution inert. The latter was demonstrated by mixing solutions of complexes **2b** and **2g** and showing that no exchange of PPh_2OH and PMePhOH ligands occurs. This is reasonable since uncoordinated dialkyl phosphinites and diphenylfluorophosphines are highly susceptible to disproportionation in solution.[29] Complexes 2 and 3 are stable in solution under nitrogen in the absence of water for weeks with no evidence of decomposition or disproportionation of these ligands. The metal–ligand bond strengths could be high for these ligands assuming that the short Mo–P bond length observed for the $PFPh_2$ ligand of **3b** (Table III) is an indication.

The mechanism involving the exo release of the "dangling" phosphorus (Scheme V) is supported by crossover experiments. In one reaction (Scheme VI) a mixture of **1d** and $Mo(\eta^6\text{-}PhPPh_2)(dppe)(PMePh_2)$ was reacted with aqueous HBF_4. The formation of the crossover products **2e** and **2a**, which do not arise from ligand exchange between the other products **2b** and **2d** is evidence for this mechanism. The nonstatistical distribution of products could indicate that the immediate products of P–C bond cleavage ($\{Mo(\eta^6\text{-}C_6H_6)(dppe)(PMePh_2), HPMePhOH^+\}$, for example) have a good chance of reacting with each other while they remain trapped in a solvent cage. In another reaction a mixture of **1b** and **1f** was reacted with aqueous HBF_4. Again crossover products **2c** and **2e** were formed as well as **2b** and **2f**.

Some of the steps proposed in Scheme V have precedents. In step (i) protonation is most likely to occur both at the metal and dangling phosphorus atom these being the two most basic sites in the complex. Green and coworkers[2] showed that complexes of this type may be protonated twice at the metal to give a dihydride. The dangling phosphorus atom has been shown to act as a Lewis base in reactions with 9-BBN[5b] and with metal carbonyls.[5g,30] Migration of the hydride from the metal to the η^6-arene ring, step ii, has been proposed as the mechanism of H/D exchange when complexes $Cr(\eta^6\text{-arene})(CO)_2(L)$ are treated with CF_3COOD. Spin saturation transfer measurements on complex **2b** have given no evidence for migration of the metal-bound hydride to the ring, but this process may shut down after the coordination of the dialkyl phosphinite.

We are aware of only one other case of phosphorus fluorination by HBF_4, a reaction reported by Desobry and Kundig:[31]

$$Cr(\eta^6\text{-}C_{10}H_8)(P(OMe)_3)_3 \xrightarrow[CH_2Cl_2]{HBF_4,\ -30\ ^\circ C} Cr(\eta^6\text{-}C_{10}H_8)(P(OMe)F_2)_3$$

This reaction was related to a report by Bigorgne,[32] who observed that coordinated $P(OMe)_3$ reacted stepwise with BF_3 to give the corresponding mono- and difluorophosphites. More recently, Nakazawa et al.[33] described the conversion of $P(OMe)_3$ on molybdenum to $P(OMe)_2F$ by use of $BF_3{\cdot}Et_2O$. However, reaction of **1b** with 1 equiv of $BF_3{\cdot}Et_2O$ resulted only in extensive decomposition.

Casey and co-workers[34] have observed P–C bond cleavage in η^5-cyclopentadienyl-bridged dimers to give a phosphido bridge after prolonged photolysis under H_2. Coupled with our present observation, it seems likely that such groups may be too fragile to be used to stabilize homogeneous transition-metal catalysts.

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Supplementary Material Available: Tables of positional and anisotropic thermal parameters, complete bond lengths and bond angles, and results of molecular fits for **3b** and tables of positional and thermal parameters and bond lengths and bond angles for 4 (21 pages); listings of structure factors for **3b** and 4 (16 pages). Ordering information is given on any current masthead page.

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(29) Brown, C.; Murray, M.; Schmutzler, R. *J. Chem. Soc. C* **1970**, 878–881.

(30) Elschenbroich, C.; Stohler, F. *J. Organomet. Chem.* **1974**, *67*, C51–C54.

(31) Desobry, V.; Kundig, E. P. *Helv. Chim. Acta* **1981**, *64*, 1288–1297.

(32) Demersman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1972**, *35*, 125–129.

(33) Nakazawa, H.; Morimasa, K.; Kushi, Y.; Yoneda, H. *Organometallics* **1988**, *7*, 458–463.

(34) Casey, C. P.; Bullock, R. M. *Organometallics* **1984**, *3*, 1100–1104.

(35) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.