(Fluoroalkyl)phosphine Chemistry of Molybdenum. Synthesis, Structure, and Properties of Molybdenum(0) Arene Complexes $(\eta^6\text{-}C_6H_5R)Mo[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2](L)$

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The synthesis of $(\eta^6\text{-}C_6H_5Me)Mo[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2](N_2)$ (**1**) from the reaction of $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) with $(\eta^6\text{-}C_6H_5Me)_2Mo$ under dinitrogen is reported. Similar treatment of $(\eta^6\text{-}C_6H_6)_2Mo$ with dfepe yielded the dinitrogen-bridged dimer $\{(\eta^6\text{-}C_6H_6)Mo(dfepe)\}_2(\mu\text{-}N_2)$ (**2**), which exists in equilibrium with the corresponding monomer **2a**. The electron-withdrawing power of the (fluoroalkyl)phosphine dfepe is reflected in the remarkably high $\nu(N_2)$ frequencies observed for **1** (2133 cm^{-1}) and **2a** (2144 cm^{-1}). The dinitrogen ligand in **1** is readily displaced by other two-electron donors H_2, CO, MeCN, and pyridine to quantitatively form the corresponding stable adducts **3–6**; ligand-exchange experiments establish the following ligand-binding affinity order: CO > MeCN ≈ H_2 > py ≈ N_2 > THF. A trans structure for dihydride **3** is proposed. Cyclic voltammetric studies of **1** and **4–6** confirm the electron-poor nature of the $(\eta^6\text{-}C_6H_5Me)Mo(dfepe)$ moiety, with $E_{1/2}(ox)$ for carbonyl complex **4** (+1.06 V vs SCE) shifted almost 0.9 V higher in potential than values reported for isostructural donor phosphine systems. Complexes **1** and **6** have been structurally characterized at −100 °C. Crystal data for **1**: monoclinic, $P2_1/n$, with a = 10.032 (2) Å, b = 8.4075 (15) Å, c = 29.785 (5) Å, β = 91.38 (1)°, V = 2511.4 (7) Å^3, Z = 4, R_F = 3.21%, and R_{wF} = 5.16%. Crystal data for **6**: triclinic, $P\bar{1}$, with a = 9.921 (1) Å, b = 10.386 (2) Å, c = 29.612 (5) Å, α = 84.215 (13)°, β = 81.80 (1)°, γ = 67.38 (1)°, V = 2784.2 (8) Å^3, Z = 4, R_F = 2.58%, and R_{wF} = 3.77%. The Mo–P bond lengths for **1** (2.319 (1), 2.327 (1) Å) and **6** (2.321 (1), 2.347 (1) Å) are among the shortest known.

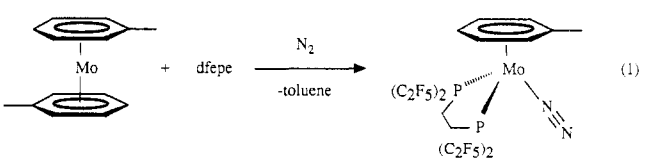
Introduction

$(\eta^6\text{-arene})_2Mo$ complexes serve as useful precursors to a wide variety of low-valent molybdenum systems.[1] In phosphine substitution chemistry, the lability of one or both of the arene ligands is strongly dependent on the phosphine steric and electronic properties. For example, treatment of $(\eta^6\text{-}C_6H_5R)_2Mo$ (R = H, Me) with excess PF_3,[2] $F_2PC_6H_{10}PF_2$,[3] or $R_2PCH_2CH_2PR_2$ (R = Me, Ph)[4] at elevated temperatures results in displacement of both arene groups to give $(PR_3)_6Mo$ complexes, whereas only monoarene $(\eta^6\text{-arene})Mo(PR_3)_3$ complexes are obtained from thermolysis with excess PPh_2Me, $PPhMe_2$, $PPh_2(OMe)$, $P(OMe)_3$, or $P(OPh)_3$.[5] No reaction is observed with bulky PPh_3 or the more basic phosphines PMe_3 and PEt_3. Although the reactivity of $(\eta^6\text{-arene})Mo(PR_3)_3$ complexes toward ligand substitution is limited,[6] a number of electron-rich bisphosphine derivatives $(\eta^6\text{-arene})Mo(PR_3)_2(L)$ (L = N_2, H_2, CO) are accessible via reduction of the Mo(II) allyl dimer, $[(\eta^6\text{-arene})Mo(\eta^3\text{-}C_3H_5)Cl]_2$.[7]

We have recently begun to explore the potential of the new π-acceptor (fluoroalkyl)phosphine chelate $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) and related ligands as substitutes for carbon monoxide in electrophilic systems where the poor steric control or noninnocence of spectator CO ligands is problematic.[8] As part of our continuing investigations of low-valent group-VI substitution chemistry, we find that treatment of $(\eta^6\text{-}C_6H_5R)_2Mo$ (R = H, Me) with excess dfepe under an N_2 atmosphere results in selective displacement of a single arene ligand under mild conditions to directly afford the electron-poor dinitrogen complexes $(\eta^6\text{-}C_6H_5Me)Mo(dfepe)(N_2)$ (**1**) and $\{(\eta^6\text{-}C_6H_6)Mo(dfepe)\}_2(\mu\text{-}N_2)$ (**2**). Although compounds **1** and **2** are isostructural to donor phosphine complexes $(\eta^6\text{-}C_6H_5Me)Mo(PR_3)_2(N_2)$ (PR_3 = PPh_3, PPh_2Me) and $\{(\eta^6\text{-}C_6H_3Me_3)Mo(dmpe)\}_2(\mu\text{-}N_2)$ reported in the early 1970's by Green and Silverthorn,[7a,c] spectroscopic, structural, and chemical evidence presented here suggests that these complexes and related derivatives are reasonable electronic analogues to the essentially unknown class of carbonyl complexes, $(\eta^6\text{-arene})Mo(CO)_2(L)$.[9]

Results and Discussion

Synthesis of $(\eta^6$-arene)Mo(dfepe)(L) Complexes. Treatment of a suspension of $(\eta^6\text{-}C_6H_5Me)_2Mo$ in ether or THF with 1.8 equiv of dfepe at −78 °C under N_2 (1 atm) gave a deep red solution, which became light yellow upon warming to 20 °C. Removal of the volatiles under vacuum followed by extraction of the residue under N_2 by petroleum ether and cooling to 0 °C afforded orange crystalline $(\eta^6\text{-}C_6H_5Me)Mo(dfepe)(N_2)$ (**1**) in 40% yield (eq 1). The



(1)

formulation of **1** is in accord with ^1H, ^{13}C, ^{19}F, and ^{31}P NMR data and IR data (see Experimental Section) and has been confirmed by X-ray crystallography (vide infra). The strong π-acceptor ability of dfepe is clearly reflected in the very high $\nu(N_2)$ value observed, 2133 cm^{-1} (heptane solution), which is 133 cm^{-1} higher than that of the donor phosphine complex $(\eta^6\text{-}C_6H_5Me)Mo(PPh_3)_2(N_2)$[7a] and comparable to $\nu(N_2)$ values reported for the carbonyl-substituted compounds *trans*-$(Ph_2PCH_2CH_2PPh_2)_2Mo(CO)(N_2)$ (2128 cm^{-1}),[10] $(\eta^6\text{-}C_7H_8)Mo(CO)_2(N_2)$ (2173

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cm^{-1}),[11] and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(N_2)CH_3$ (2191 cm^{-1}).[12] Although the stability of $(\eta^6\text{-arene})Mo(PR_3)_2(N_2)$ complexes has been previously ascribed to strong π-donor properties of the electron-rich metal center, the stability of electron-poor **1** relative to these donor phosphine systems is certainly comparable. Solutions of **1** are stable indefinitely in hydrocarbon, aromatic, or ethereal solvents under a N_2 atmosphere, and only ca. 50% decomposition was observed in boiling toluene after 30 min. In the solid state, however, slow decomposition under vacuum or N_2 atmosphere occurs at ambient temperature.

In contrast to the monomeric structure of **1**, the reaction between $(\eta^6\text{-}C_6H_6)_2Mo$ and excess dfepe at 20 °C yielded the sparingly soluble dimeric complex, $\{(\eta^6\text{-}C_6H_6)Mo(dfepe)\}_2(\mu\text{-}N_2)$ (**2**; eq 2) as a moderately air-stable crys-

$$(\eta^6\text{-}C_6H_6)_2Mo + \text{dfepe} \xrightarrow[-C_6H_6]{Et_2O,\ N_2} [(\eta^6\text{-}C_6H_6)Mo(dfepe)]_2(\mu\text{-}N_2) \quad (2)$$

talline orange solid. The absence of a $\nu(N_2)$ band in the infrared spectrum together with the presence of an intense band at 2020 cm^{-1} in the solid-state Raman spectrum of **2** is consistent with a centrosymmetric structure analogous to that of $\{(\eta^6\text{-}C_6H_3Me_3)Mo(dmpe)\}_2(\mu\text{-}N_2)$.[7c] In solution, however, infrared and NMR evidence indicate that the major species present under a nitrogen atmosphere is not **2** but the corresponding monomer, $(\eta^6\text{-}C_6H_6)Mo(dfepe)(N_2)$ (**2a**). Solution infrared spectra under nitrogen exhibit a $\nu(N_2)$ band at 2144 cm^{-1} (heptane) attributed to **2a**, which reversibly decreases in intensity upon purging with argon. The equilibrium composition is readily quantified by ^1H NMR: For a saturated C_6D_6 solution under nitrogen, two C_6H_6 singlets are observed at δ 4.29 and 4.45 in a 20:1 ratio. Under argon the relative intensities shift to 1:3, confirming the assignment of these peaks to **2a** and **2**, respectively.

Ligand Substitution Studies. The substitution chemistry of **1** with other two-electron ligands has been examined to further define the steric and electronic environment of the $(\eta^6\text{-toluene})Mo(dfepe)$ moiety. Treatment of **1** with H_2, CO, MeCN, or excess pyridine at room temperature results in quantitative displacement of N_2 and formation of stable products **3–6**, respectively (eq 3).

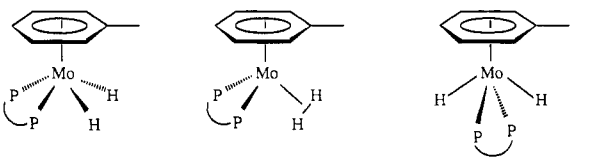
$$(\eta^6\text{-}C_6H_5Me)Mo(dfepe)N_2 + L \xrightarrow{-N_2} (\eta^6\text{-}C_6H_5Me)Mo(dfepe)(L) \quad (3)$$

L = 2H (**3**)
= CO (**4**)
= MeCN (**5**)
= py (**6**)

Excess pyridine is required in the synthesis of **6** due to competitive ligand exchange with ambient N_2 (for $[\mathbf{6}]_0 \approx$ 0.15 M, a 3:1 equilibrium mixture of **6** and **1** in benzene under 590 Torr of N_2 is established after several hours, as judged by ^1H NMR). No exchange between **1** and THF was observed by ^1H NMR.

^1H NMR data for the η^6-toluene groups in this series of compounds appear to reflect subtle changes in the molybdenum coordination environment. In the ^1H NMR spectrum of complex **6** the toluene methyl group appears as a singlet at δ 0.41, shifted sharply upfield from the normal 1.38–1.59 ppm range observed for the methyl groups of complexes **1** and **3–5**. This upfield shift is attributed to a significant through-space interaction of the methyl group in **6** with the π-system of the pyridine ligand, in accord with the observed eclipsed orientation of the ring methyl and the pyridine ring plane in the solid state (see Figure 3). With the exception of hydride complex **3**, all η^6-toluene complexes display a characteristic three-multiplet pattern for the ortho, meta, and para ring protons. For **3**, the resonance for the para ring proton is shifted approximately 1.3 ppm downfield and overlaps with the meta ring proton signal. In light of the following discussion we believe this shift is symptomatic of a change in coordination geometry.

The nature of the hydride coordination in **3** is of interest, since there are three possible ground-state structures to consider, *cis*-MoH_2 (**3a**), $Mo(\eta^2\text{-}H_2)$ (**3b**), or *trans*-MoH_2 (**3c**). Although **3** exhibits a simple triplet hydride reso-



3a **3b** **3c**

nance at δ −8.45 ($^2J_{HP}$ = 63 Hz) which, together with ^{19}F NMR data, is clearly consistent with trans-dihydride structure **3c**, previous workers have invoked a fluxional cis-dihydride structure as a preferred alternative.[7a,13] We favor a trans-dihydride structure **3c** for the following reasons:

(1) No spectral changes for the hydride resonance are observed down to −80 °C. While a low-energy fluxional process cannot be ruled out, there appears to be no overriding reason to invoke one since several stable *trans*-$(\eta^n\text{-}C_nR_n)M(R_2P\frown PR_2)LL'$ systems are now known.[14]

(2) The large $^2J_{PH}$ value observed for **3**,[15] together with T_1 ^1H NMR data (790 ms, 226 K, 270 MHz) and the absence of any resolvable $^1J_{HD}$ coupling for the H–D isotopomer of **3** clearly rule out structure **3b**.[16,17] Since $\nu(N_2)$ for the corresponding N_2 complex **1** falls in the range 2060–2150 cm^{-1}, where a preference for $\eta^2\text{-}H_2$ over cis-dihydride coordination is proposed to occur,[18] an alternative trans coordination mode **3c** would seem to be most in accord with these observations. However, the fact that both formation of **3** from **1** and reversible displacement of H_2 from **3** by acetonitrile occur under mild conditions (see below) necessarily implies that isomerization to cis intermediates **3a** or **3b** is a low-energy process.

A qualitative study of ligand-binding preferences for the $(\eta^6\text{-}C_6H_5Me)Mo(dfepe)$ fragment is revealing. On the basis

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(17) Values of $^1J(H,D) \geq 22$ Hz are typically observed for $\eta^2\text{-}H_2$ metal phosphine complexes. (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (c) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780.
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Table I. Summary of Crystallographic Data for (η^6-C_6H_5Me)Mo(dfepe)(N_2) and (η^6-C_6H_5Me)Mo(dfepe)(py)

	$C_{17}H_{12}F_{20}N_2P_2Mo$	$C_{22}H_{17}F_{20}NP_2Mo$
cryst size, mm	0.29 × 0.36 × 0.72	0.25 × 0.56 × 0.58
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
temp, °C	−100	−100
A Å	10.032 (2)	9.921 (1)
b, Å	8.408 (2)	10.386 (2)
c, Å	29.785 (5)	29.612 (5)
α, deg		84.22 (1)
β, deg	91.38 (1)	81.80 (1)
γ, deg		67.38 (1)
V, Å^3	2511.4 (7)	2784.2 (8)
Z	4	4
ρ_{calc} g/cm^3	2.069	1.988
wavelength, Å	0.71073	0.71073
mol wt	782.14	833.23
μ, cm^{-1}	7.92	7.20
T_{max}/T_{min}	0.384/0.336	
2θ range, deg	4.0–51.0	4.0–42.0
scan type	Ω	Ω
scan range	1.7	2.0
no. of reflns measd	5148	6132
no. of unique reflns	4564	5684
no. of $F > 6.0\sigma(F)$	3864	4854
R_F, %	3.21	2.64
R_{wF}, %	5.16	3.90
goodness of fit	0.87	0.93

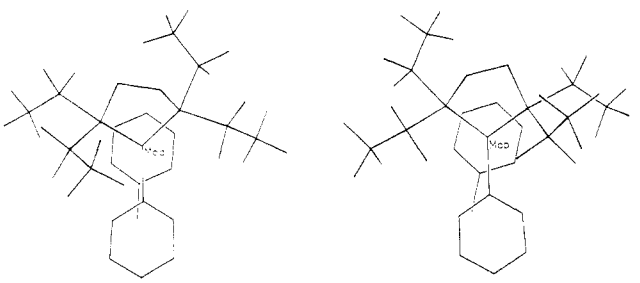

Figure 1. Conformation comparison of crystallographically independant (η^6-C_6H_5Me)Mo(dfepe)Mo(py) molecules A and B. Molecule A is shown to the right.

of a series of ligand competition studies, the relative ordering for ligand binding affinity is found to be CO > MeCN ≈ H_2 > py ≈ N_2 > THF. A comparison of this ordering with ligand affinity series reported for *fac*-$L_3Mo(CO)_3$ and $W(CO)_3(PCy_3)_2$ systems (CO > py > MeCN > N_2 > H_2)[19] shows that the binding of the more sterically demanding pyridine ligand is anomalously weak, consistent with an increased steric congestion in the coordination sphere of (η^6-toluene)Mo(dfepe) relative to $W(CO)_3(PCy_3)_2$.[20] Crystallographic data for **6** discussed below support this interpretation. In addition, the binding affinity of H_2 is found to be exceptionally high, as evidenced by the facile ligand exchange of **5** with H_2 (300 Torr) at ambient temperature to give a 4:1 equilibrium mixture of **5** and **3** (^{1}H NMR). This competitive exchange is in marked contrast to the essentially irreversible displacement of η^2-H_2 by nitriles reported for $W(CO)_3(PCy_3)_2(L)$ and *trans*-$(dppe)_2Mo(CO)(L)$ systems[17a,20] and lends further indirect support for a low-energy trans ground state **3c**.

Crystallographic Studies. To further assess the steric and electronic environment of (η^6-arene)Mo(dfepe)(L) systems, the solid-state structures of compounds **1** and **6** have been determined by X-ray crystallography at −100 °C. Crystal and data collection parameters are summarized in Table I. Atomic coordinates and relevant geometrical parameters are given in Tables II–IV. **6** crystallizes in the triclinic space group $P\bar{1}$, with two crystallographically independent molecules A and B in the unit

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for (η^6-C_6H_5Me)Mo(dfepe)(N_2)

atom	x	y	z	U^a
Mo	3382 (1)	2009 (1)	911 (1)	24 (1)
P(1)	3749 (1)	2582 (1)	1666 (1)	39 (1)
P(2)	1289 (1)	1465 (1)	1195 (1)	28 (1)
N(1)	2893 (3)	4339 (3)	785 (1)	35 (1)
N(2)	2701 (4)	5580 (4)	687 (1)	56 (1)
C(1)	2223 (4)	2682 (7)	2004 (1)	60 (2)
C(2)	1177 (4)	1568 (6)	1818 (1)	56 (1)
C(3)	4438 (4)	4608 (6)	1848 (1)	58 (1)
C(4)	5766 (5)	5128 (6)	1660 (2)	67 (2)
C(5)	4802 (4)	1061 (5)	2016 (1)	62 (2)
C(6)	5287 (5)	1250 (6)	2505 (2)	85 (2)
C(7)	−181 (3)	2799 (4)	1044 (2)	44 (1)
C(8)	−587 (4)	2999 (5)	548 (2)	63 (2)
C(9)	543 (3)	−625 (4)	1113 (1)	40 (1)
C(10)	−853 (4)	−1143 (5)	1263 (2)	51 (1)
C(11)	3983 (3)	1961 (4)	159 (1)	35 (1)
C(12)	3240 (3)	582 (4)	246 (1)	38 (1)
C(13)	3629 (3)	−451 (4)	599 (1)	38 (1)
C(14)	4787 (3)	−145 (4)	860 (1)	42 (1)
C(15)	5532 (3)	1251 (4)	775 (1)	40 (1)
C(16)	5135 (3)	2277 (4)	431 (1)	37 (1)
C(17)	3584 (5)	311 (5)	−209 (1)	57 (1)
F(1)	4537 (3)	4734 (4)	2306 (1)	83 (1)
F(2)	3527 (3)	5707 (3)	1705 (1)	76 (1)
F(3)	6692 (3)	4056 (4)	1749 (1)	82 (1)
F(4)	6164 (3)	6510 (4)	1843 (1)	100 (1)
F(5)	5686 (3)	5338 (4)	1223 (1)	81 (1)
F(6)	5932 (3)	718 (4)	1787 (1)	74 (1)
F(7)	4019 (3)	−277 (3)	2015 (1)	71 (1)
F(8)	5777 (4)	−129 (5)	2650 (1)	107 (2)
F(9)	4301 (3)	1685 (5)	2765 (1)	94 (1)
F(10)	6255 (3)	2351 (5)	2533 (1)	93 (1)
F(11)	−1316 (2)	2398 (3)	1258 (1)	57 (1)
F(12)	174 (2)	4255 (3)	1199 (1)	65 (1)
F(13)	−1647 (3)	3926 (5)	508 (1)	109 (2)
F(14)	−891 (3)	1612 (4)	370 (1)	84 (1)
F(15)	383 (3)	3637 (4)	314 (1)	78 (1)
F(16)	1413 (2)	−1606 (3)	1334 (1)	59 (1)
F(17)	582 (2)	−1031 (3)	671 (1)	54 (1)
F(18)	−1075 (2)	−670 (3)	1679 (1)	66 (1)
F(19)	−1798 (2)	−584 (3)	995 (1)	58 (1)
F(20)	−949 (3)	−2723 (3)	1257 (1)	79 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

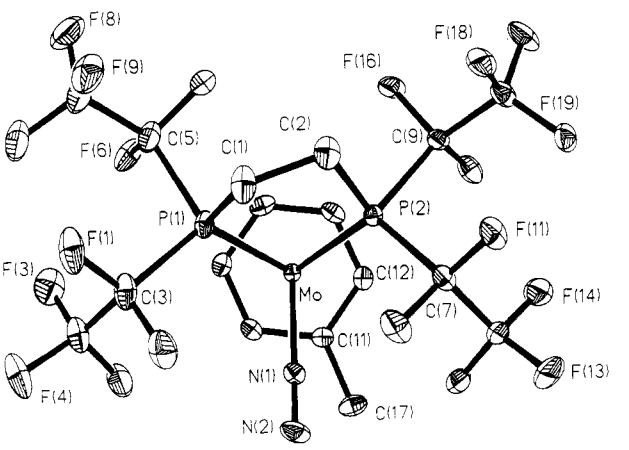

Figure 2. ORTEP view of (η^6-C_6H_5Me)Mo(dfepe)Mo(N_2) (**1**) with atom-labeling scheme.

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Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for (η^6-C_6H_5Me)Mo(dfepe)(py)

atom	x	y	z	U^a
Mo	12700 (1)	3590 (1)	983 (1)	16 (1)
P(1)	11694 (1)	1859 (1)	1087 (1)	21 (1)
P(2)	10795 (1)	4440 (1)	1562 (1)	19 (1)
N(1)	14644 (3)	2287 (3)	1350 (1)	19 (1)
C(1n)	15605 (4)	1084 (3)	1168 (1)	26 (1)
C(2n)	16900 (4)	278 (4)	1331 (1)	33 (1)
C(3n)	17266 (4)	702 (4)	1708 (1)	34 (1)
C(4n)	16339 (4)	1932 (4)	1894 (1)	30 (1)
C(5n)	15048 (4)	2694 (4)	1706 (1)	26 (1)
C(1)	9936 (4)	2278 (4)	1471 (1)	29 (1)
C(2)	9907 (4)	3237 (4)	1838 (1)	26 (1)
C(3)	12642 (4)	-66 (4)	1320 (1)	32 (1)
C(4)	12923 (5)	-302 (4)	1821 (1)	38 (1)
C(5)	10940 (4)	1346 (4)	590 (1)	31 (1)
C(6)	11985 (5)	458 (4)	215 (1)	43 (1)
C(7)	9014 (4)	6042 (4)	1446 (1)	27 (1)
C(8)	7896 (4)	5850 (4)	1178 (1)	36 (1)
C(9)	10996 (4)	5063 (4)	2134 (1)	25 (1)
C(10)	11448 (4)	6322 (4)	2122 (1)	29 (1)
C(11)	14711 (4)	3952 (4)	496 (1)	24 (1)
C(12)	14022 (4)	3353 (4)	256 (1)	26 (1)
C(13)	12459 (4)	3967 (4)	240 (1)	31 (1)
C(14)	11656 (4)	5270 (4)	429 (1)	32 (1)
C(15)	12325 (4)	5834 (4)	700 (1)	31 (1)
C(16)	1383((4)	5158 (3)	746 (1)	29 (1)
C(17)	16345 (4)	3351 (4)	519 (1)	32 (1)
C(1)	13960 (3)	-657 (2)	1068 (1)	41 (1)
F(2)	11855 (3)	-869 (2)	1279 (1)	43 (1)
F(3)	13868 (3)	-1578 (3)	1904 (1)	72 (1)
F(4)	11694 (3)	-145 (3)	2096 (1)	61 (1)
F(5)	13451 (3)	581 (3)	1947 (1)	51 (1)
F(6)	10157 (2)	2592 (2)	379 (1)	38 (1)
F(7)	9943 (3)	739 (2)	735 (1)	41 (1)
F(8)	12503 (3)	-890 (3)	343 (1)	67 (1)
F(9)	11334 (3)	574 (3)	-158 (1)	65 (1)
F(10)	13138 (3)	810 (3)	87 (1)	60 (1)
F(11)	9408 (2)	7061 (2)	1196 (1)	32 (1)
F(12)	8198 (2)	6658 (2)	1831 (1)	34 (1)
F(13)	8525 (2)	5163 (2)	802 (1)	40 (1)
F(14)	6911 (3)	7081 (3)	1055 (1)	59 (1)
F(15)	7162 (3)	5142 (3)	1430 (1)	47 (1)
F(16)	9819 (2)	5290 (2)	2461 (1)	34 (1)
F(17)	12120 (2)	3955 (2)	2309 (1)	31 (1)
F(18)	12655 (3)	6148 (2)	1839 (1)	41 (1)
F(19)	11696 (3)	6539 (3)	2530 (1)	47 (1)
F(20)	10389 (3)	7485 (2)	1981 (1)	44 (1)

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

cell. Apart from a slight rotation about the ring centroid–Mo axis and the folding of one C_2F_5 unit, these molecules are essentially mirror images (Figure 1); the metrical data presented in Tables IV and V and discussed below are for molecule A. As shown in Figures 2 and 3, both **1** and **6** adopt a conventional three-legged piano stool geometry with the η^6-toluene methyl group oriented adjacent to the sterically preferred Mo–(N_2) and Mo–(py) axes. No intermolecular close contacts are observed for either monomeric species. The Mo–C(ring) distances for **1** (2.283 (3)–2.333 (3) Å) and **6** (2.226 (4)–2.419 (4) Å) average to 2.305 and 2.319 Å, respectively, intermediate between the shorter distances observed in electron-rich molecules (η^6-arene)Mo(L_3) (L_3 = arene, L = donor phosphine; 2.277–2.281 Å),[21] and the longer distances associated with electron-poor carbonyl derivatives (η^6-arene)Mo($CO)_3$, 2.347–2.392 Å).[22] Unlike the trends noted for Mo–C(ring) distances, average arene C–C distances are

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Table IV. Selected Bond Distances (Å) and Angles (deg) for (η^6-C_6H_5Me)Mo(dfepe)(N_2) and (η^6-C_6H_5Me)Mo(dfepe)(py)[a]

	(η^6-C_6H_5Me)Mo-(dfepe)(N_2)	(η^6-C_6H_5Me)Mo(dfepe)-(py)
	Bond Distances	
Mo–P(1)	2.319 (1)	2.346 (1)
Mo–P(2)	2.327 (1)	2.321 (1)
Mo–CNT	1.825	1.839
Mo–N(1)	2.052 (3)	2.241 (3)
N(1)–N(2)	1.099 (4)	
Mo–C(11)	2.333 (3)	2.418 (4)
Mo–C(12)	2.317 (3)	2.338 (3)
Mo–C(13)	2.283 (3)	2.226 (4)
Mo–C(14)	2.302 (4)	2.309 (4)
Mo–C(15)	2.295 (3)	2.302 (4)
Mo–C(16)	2.303 (3)	2.318 (4)
C(11)–C(17)	1.505 (5)	1.505 (5)
C(11)–C(12)	1.405 (5)	1.383 (6)
C(12)–C(13)	1.412 (5)	1.438 (5)
C(13)–C(14)	1.405 (5)	1.405 (5)
C(14)–C(15)	1.417 (5)	1.705 (7)
C(15)–C(16)	1.389 (5)	1.411 (5)
C(16)–C(11)	1.420 (5)	1.429 (5)
P(1)–C(1)	1.856 (4)	1.864 (4)
P(1)–C(3)	1.912 (5)	1.953 (3)
P(1)–C(5)	1.945 (4)	1.947 (5)
P(2)–C(2)	1.863 (4)	1.855 (4)
P(2)–C(7)	1.899 (4)	1.950 (3)
P(2)–C(9)	1.922 (3)	1.936 (4)
av C–F (CF_2)	1.364 (5)	1.366 (5)
av C–F (CF_3)	1.324 (6)	1.328 (5)
N(1)–C(1n)		1.353 (4)
C(1n)–C(2n)		1.360 (5)
C(2n)–C(3n)		1.381 (6)
C(3n)–C(4n)		1.369 (5)
C(4n)–C(5n)		1.382 (5)
C(5n)–N(1)		1.338 (5)
	Bond Angles	
P(1)–Mo–P(2)	79.2 (1)	77.4 (1)
P(1)–Mo–CNT	131.2	133.5
P(2)–Mo–CNT	130.8	126.8
N(1)–Mo–CNT	119.7	113.2
N(2)–N(1)–Mo	173.9 (3)	
Mo–P(1)–C(1)	115.0 (1)	116.0 (1)
Mo–P(1)–C(3)	120.5 (1)	126.8 (1)
Mo–P(1)–C(5)	117.1 (1)	121.7 (1)
Mo–P(2)–C(2)	115.4 (1)	117.6 (1)
Mo–P(2)–C(7)	120.0 (1)	121.0 (1)
Mo–P(2)–C(9)	119.1 (1)	124.6 (1)

[a] CNT = centroid of toluene ring.

Table V. Electrochemical Data for (η^6-C_6H_5Me)Mo(dfepe)(L) Complexes and Related Mo^0 Compounds[a]

complex	solvt	E_2^1(ox), V	Δ_p, mV	scan rate, mV/s	i_c/i_a
(η^6-C_6H_5Me)Mo-(dfepe)(N_2), **1**	CH_2Cl_2	0.71	122	5000	0.27
(η^6-C_6H_5Me)Mo-(dfepe)(CO), **4**	CH_2Cl_2	0.90	81	1000	0.96
	THF	1.06	150	1000	0.20
(η^6-C_6H_5Me)Mo-(dfepe)(MeCN), **5**	CH_2Cl_2	0.21	68	100	0.95
	THF	0.36	75	100	0.92
(η^6-C_6H_5Me)Mo-(dfepe)(py), **6**	CH_2Cl_2	0.22	66	100	0.90
	THF	0.37	100	1000	0.78
(η^6-$C_6H_5PPh_2$)Mo-(dppe)(CO)[b]	THF	0.15			
(η^6-$C_6H_5PPh_2$)Mo-(dppe)(N_2)[b]	THF	−0.03			
(η^6-C_6H_5Me)Mo(py)$_3$[c]	py	−1.09			
trans-[((p-$CF_3C_6H_4$)$_2$-PCH_2)$_2$]$_2$Mo(N_2)$_2$[d]	THF	0.30			

[a] Potentials reported vs SCE, T = 293 K (THF) or 273 K (CH_2Cl_2); the supporting electrolyte was 0.2 M [Bu_4N][ClO_4]. [b] See ref 17. [c] See ref 6. [d] See ref 39.

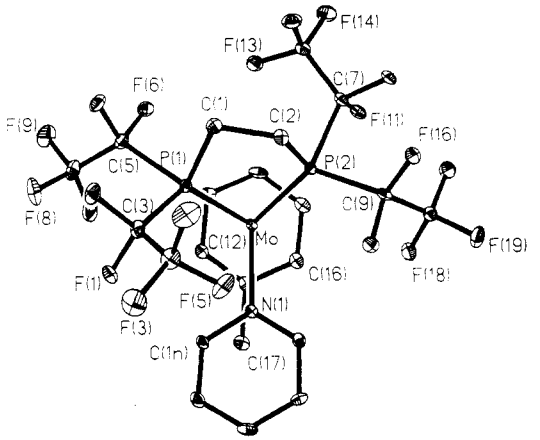

Figure 3. ORTEP view of (η^6-C_6H_5Me)Mo(dfepe)Mo(py) (**6**) with atom-labeling scheme.

relatively insensitive to electronic changes at the metal center; the values for **1** (1.408 (5) Å) and **6** (1.413 (5) Å) are quite typical. No systematic correlation of Mo–C and C–C distances with trans ligand effects or changes in arene hapticity is apparent.

Although the average ring coordination parameters for **1** and **6** are essentially identical, the toluene group in complex **6** is significantly more distorted. Mean deviations from ring planarity are 0.006 Å for **1** and 0.038 Å for **6**. In addition, whereas the toluene methyl group in **1** lies directly in the arene plane (deviation = 0.001 Å toward Mo), a 0.129-Å planar distortion away from the metal center is found for **6**, consistent with increased steric crowding.

To our knowledge only four (fluoroalkyl)phosphine complexes have been crystallographically characterized prior to this report, $(Ph_2PCH_2CH_2P(CF_3)_2)MCl_2$ (M = Pd, Pt),[23] $(Me_2PCF_2CHFPMe_2)Mo(CO)_4$,[24] and $[\{(CF_3)_2PC(CH_3)P(CF_3)_2\}Pt(\mu\text{-}Cl)]_2$.[25] CF_2 bond distances for **1** and **6** average 1.365 (6) Å, somewhat longer than the 1.340 (3) Å value reported for the C–F bonds of the free (fluoroalkyl)phosphine $P(CF_3)_3$.[26] The pronounced sensitivity of C–F distances to substituent electronegativity effects has been noted previously.[27]

The most noticeable difference between the (η^6-C_6H_5Me)Mo(dfepe) units of **1** and **6** apparent from Figures 1–3 is the folding of the C_2F_5 phosphine substituents. Because of the increased lateral steric demand of the pyridine ligand in **6**, the C(9)–C(10) fluoroethyl unit is rotated up toward the arene and away from the plane of the pyridine. To accommodate this shift, the C(7)–C(8) and C(5)–C(6) units pivot and force the remaining C(3)–C(4) group to redirect below the pyridine plane. Despite this conformational change, close contacts between F(5)–N(1) (2.84 Å) and F(11)–C(15) (2.79 Å) persist. The closest nonbonding contacts for **1** are between F(12)–N(1) (3.02 Å) and F(2)–N(1) (3.03 Å). A classical estimate of phosphine steric influence using Tolman's criterion[28] for dfepe in molecules **1** and **6** provides a useful basis for comparison with other phosphines. The individual half-angle values for C_2F_5 groups in **1** ($\theta/2$ = 83°, 67° for P(1); 84°, 65° for P(2)) and **6** ($\theta/2$ = 75°, 74° for P(1); 77°, 79° for P(2)) vary significantly; however, the average values of 75° and 76° are quite close. The mean cone angle value θ calculated for dfepe, 129°, is comparable to that of $Ph_2PCH_2CH_2PPh_2$ (θ = 125°) and is much larger than any other ligand of similar acceptor strength.

The relatively weak binding of pyridine suggested by ligand-exchange studies is not reflected in the Mo–N(1) bond length for **6**, 2.241 (3) Å, a distance that appears to be quite typical for Mo(0)–N(sp2) coordination (literature values 2.21–2.28 Å).[29] Instead, a 9.5° tilt of the pyridine ring plane (mean deviation 0.009 Å) toward the arene group relative to the Mo–N(1) ligation axis is observed. This ligand tilt is due to the close backside approach of the C(3)–C(4) group and probably contributes to the apparent lowered binding energy.

The nature of N_2 ligation in complex **1** is of particular interest. Although metrical data for dinitrogen coordination are relatively insensitive to electronic changes at the metal center, a comparison of Mo(1)–N(1) (2.052 (3) Å) and N(1)–N(2) (1.099 (4) Å) bond lengths with literature data (Mo–N range 1.97–2.07 Å; N–N range 1.09–1.15 Å)[10,30] reveals that Mo–N and N–N are at the long and short ends of the scale, consistent with a minimal degree of back-bonding. It should be noted that the most extreme values for Mo–N_2 coordination are reported for *trans*-$(Ph_2PCH_2CH_2PPh_2)_2Mo(CO)(N_2)$ (Mo–N = 2.07 (1), N–N = 1.09 (2) Å), a molecule where N_2 occupies an electron-poor coordination site trans to carbon monoxide,[10] and *cis*-$(PMe_3)_4Mo(N_2)_2$ (Mo–N = 1.97 (1), N–N = 1.15 (1) Å), in which N_2 is trans to a strongly basic PMe_3 ligand.[30d]

The most significant structural features of both structurally characterized (η^6-C_6H_5Me)Mo(dfepe) complexes are the remarkably short Mo–P bond distances observed (2.327 (1), 2.319 (1) Å for **1**; 2.347 (1), 2.321 (1) Å for **6**). These values are among the shortest Mo(0)–P bond lengths to date, surpassing the value of 2.369 Å reported for Mo–PF_3 in $(CO)_5Mo(PF_3)$.[31,32] For comparison, distances for donor phosphine and phosphite systems are in the range 2.40–2.52 Å, or 0.07–0.19 Å longer than the dfepe complexes. It is interesting to note that the shortest average Mo–P donor phosphine distances are reported for the closely related arene complexes $\{(\eta^6\text{-}C_6H_3Me_3)Mo(dmpe)\}_2(\mu\text{-}N_2)$ (2.402 Å)[21b] and $(\eta^6\text{-}C_6H_5PMePh)Mo(PMePh_2)_2(CN^tBu)$ (2.418 Å).[21c] Although crystallographic data are often cited as evidence for metal–ligand multiple bonding,[33] the separation of intrinsic π-acceptor behavior

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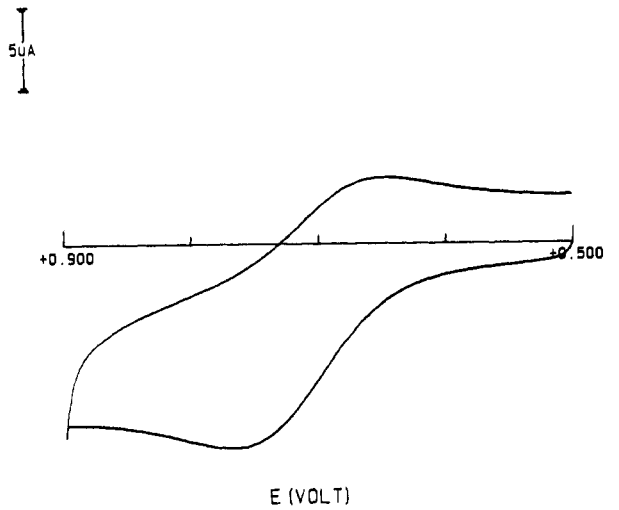

Figure 4. Cyclic voltammogram of 1.0 mM (η^6-C_6H_5Me)Mo(dfepe)Mo(N_2) under N_2 in CH_2Cl_2/0.2M Bu_4NClO_4 at a Pt electrode with ν = 5.0 V/s at 273 K.

from accompanying changes in phosphine lone-pair hybridization must be properly addressed.[34] For (fluoroalkyl)phosphines, an upper limit estimate of hybridization effects can be obtained from crystallographic data for the unsymmetrical diphosphine complexes $[(CF_3)_2PCH_2CH_2PPh_2]MCl_2$ (M = Pd, Pt), which exhibit a 0.06–0.07 Å difference between $(CF_3)_2P$–M and Ph_2P–M bond lengths, respectively.[23] If on conservatively assumes that this bond shortening is due solely to increased "s" character in the phosphorus lone pair,[27b] the average difference between Mo–P bond lengths for 1 and $\{(\eta^6$-$C_6H_3Me_3)Mo(dmpe)\}_2(\mu$-$N_2)$ (0.08 Å) is almost entirely accounted for. In the absence of any further comparative data, conclusions regarding multiple bonding in these systems remain debatable.

Electrochemical Studies. While infrared and Raman data for complexes 1, 2, and 4 provide a useful indirect measure of metal dπ energetics, a more direct and complementary probe of metal electron density[35] is given by cyclic voltammetric studies of (π-arene)Mo(PR_3)$_2$(L) systems. Data for 1 and 4–6 are summarized in Table V. In CH_2Cl_2 solution, complexes 4–6 all exhibited diffusion-controlled reversible oxidation waves at moderate scan rates (≥400 V/s). No reduction waves were observed down to −2.0 V. At slower scan rates, quasi-reversible behavior was observed that is consistent with an EC process involving the irreversible decomposition of the corresponding 17-electron radical cations. From chronoamperometric measurements[36] the decomposition rate constant for carbonyl cation 4^+ is estimated to be 0.10 ± 0.02 s^{-1}. The decomposition kinetics for 5^+ and 6^+ were not examined in detail. Qualitatively, however, the rate constants both appear to be roughly half that found for 4^+. The dinitrogen complex 1 forms the least stable cation, with appreciable cathodic return current observed only at higher scan rates. At a scan rate of 5 V/s, the ratio i_c/i_a was 0.27 with a peak separation Δ_p of 122 mV (Figure 4). More return current was attained at higher scan rates, but at these rates the initial anodic peak was too drawn out and a value for $E_{1/2}$(ox) could not be determined.

The electrochemical reversibility of all the redox couples examined is lowered in THF solution. Acetonitrile adduct 5 affords the most stable cation, with $E_{1/2}$(ox) = +0.36 V, Δ_p = 75 mV, and a current ratio of essentially unity at 100 mV/s. As was the case for CH_2Cl_2 measurements, the oxidation potential of pyridine adduct 6 in THF (+0.37 V) is virtually the same as that of 5, but the cation 6^+ is much less stable. Quasi-reversible electrochemical behavior is observed with an i_c/i_a scan rate dependence consistent with a decomposition rate of approximately 1.5 s^{-1}. In THF the carbonyl cation 4^+ is short-lived. At a sweep rate of 1 V/s some return current is seen with $E_{1/2}$(ox) = +1.06 V, Δ_p = 150 mV, and $i_a/i_c \approx 0.20$. As was the case for 1 in CH_2Cl_2, more return current was observed at higher scan rates at the expense of anodic wave distortion. The dinitrogen complex 1 exhibited an irreversible anodic wave at +0.93 V with no return current at scan rates up to 50 V/s.

A comparison of oxidation potentials for 1 and 4–6 with values reported for other molybdenum(0) systems listed in Table V is revealing. Assuming that ring substituent effects are relatively small,[37] the substitution of dfepe for dppe in isostructural (π-arene)Mo(PR_3)$_2$(CO) complexes results in about a +0.9 V anodic shift in potential. Even more pronounced is the 1.5-V difference in Mo^0/Mo^+ between 6 and the pyridine complex (η^6-C_6H_5Me)Mo(py)$_3$. The 180-mV potential difference between complexes 1 and 4 is quite typical for isostructural $L_nM(CO)$ and $L_nM(N_2)$ complexes, which generally have a $\Delta E_{1/2}$(ox) of less than 200 mV.[18] Although no $E_{1/2}$(ox) for 1 could be obtained in THF for direct comparison with other known molybdenum dinitrogen systems, $\Delta[E_{1/2}(THF) - E_{1/2}(CH_2Cl_2)]$ for 4–6 is effectively constant and allows us to assign a value of +0.86 V for 1 in this solvent. This estimated oxidation potential is more than 0.5 V above the previous highest reported $E_{1/2}$(ox) for a Mo^0–dinitrogen complex.[40]

A number of workers have utilized correlations between infrared data and electrochemical data as a predictive tool in evaluating binding site properties for d^6 octahedral metal systems.[18,35d–f,40,41,42] For octahedral d^6 systems with metal-based nonbonding HOMOs,[39] Leigh and Pickett have proposed a linear relationship between oxidation potential and a set of empirical ligand parameters P_L, where $E_{1/2}(L_nM(CO))$ is taken as a measure of the electron-richness of the metal binding site and β is a measure of its polarizability (eq 4).[42] A least-squares fitting of

$$E_{1/2}(L_nM(L')) = E_{1/2}(L_nM(CO)) + \beta P_{L'} \quad (4)$$

$E_{1/2}$(ox) values for complexes 4–6 to this equation using the appropriate values for P_L gives an estimated β of 1.18.

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This value is above the range reported for *trans*-$(dppe)_2Mo(L)(L')$ complexes ($0.50 < \beta < 1.00$), suggesting that the electron-deficient binding site of (η^6-C_6H_5Me)-Mo(dfepe) is relatively soft. The significance and applicability of parameters derived from eq 4 is certainly open to question; however, the general conclusion is consistent with the anticipated influence of a π-arene donor ligand trans to the binding site.

Conclusions. The displacement of an arene ligand from $(arene)_2Mo$ by dfepe to yield complexes of the type (arene)Mo(dfepe)(L) is unprecedented for conventional donor phosphine or fluorophosphine ligands. We ascribe this difference in reactivity to the unique combination of π-acceptor ability and steric control that (fluoroalkyl)-phosphines such as dfepe possess. Vibrational spectroscopy, structural data, and electrochemical studies help quantify the coordination properties of dfepe in this specific class of compounds and indicate that the (arene)-Mo(dfepe) 16-electron fragment may effectively serve as a sterically demanding electronic analogue to (arene)Mo-$(CO)_2$. Since carbonyl complexes $(arene)Mo(CO)_2(L)$ are essentially unknown, a fruitful comparison with our system is precluded; work is currently in progress to prepare analogues to well-known isoelectronic $CpM(CO)_2(L)$ (M = Mn, Re)[43] and $[CpM(CO)_2(L)]^+$ (M = Fe, Ru)[44] systems and explore this concept in more detail.

Electron-poor group-VI and -VII dinitrogen complexes are comparatively rare and are largely limited to the carbonly derivatives (η^6-arene)$Cr(CO)_2(N_2)$,[45] $CpM(CO)_x(PR_3)_{2-x}(N_2)$ (x = 1 or 2; M = Mn, Re),[46] $(PR_3)_{4-x}(CO)_xReCl(N_2)$ (x = 1 or 2; R = Ph, OMe),[47] *trans*-$(PR_3)_4Mo(CO)(N_2)$,[10,48] and $(PR_3)_2M(CO)_3(N_2)$ (M = Mo, W).[49] Although the N_2 ligand in such systems should be reasonably electrophilic, ancillary carbonyl ligands are generally the preferred site of nucleophilic attack and effectively preempt this potential mode of N_2 activation.[50] Since complex 1 provides a unique example of an electron-poor group-VI dinitrogen compound without carbonyl functionality, its reactivity toward nucleophilic reagents is of particular interest and is currently under investigation.

Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of nitrogen by using Schlenk, high-vacuum line, and/or glovebox techniques.[51] Dry, oxygen-free solvents were vacuum distilled prior to use. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on a Mattson Cygnus 100 or Perkin-Elmer 1600 FTIR instrument as Nujol mulls, unless otherwise noted. Raman spectra for 2 were obtained on a custom-built spectrometer consisting of a J-Y U1000 double monochromator, a Spectra Physics 2016 Kr^+ ion laser, and Ortec photon-counting electronics. NMR spectra were obtained with a JEOL JNM-FX270 or GSX-400 instrument. ^{19}F spectra were referenced to CF_3CO_2Et as an internal standard (75.32 ppm vs $CFCl_3$, with upfield chemical shifts taken to be positive). ^{31}P spectra were referenced to a 85% H_3PO_4 external standard. (η^6-$C_6H_5Me)_2Mo$ and (η^6-$C_6H_6)_2Mo$ were prepared following literature procedures.[7a,52] $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ was prepared as described previously.[8]

(η^6-C_6H_5Me)Mo[$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$]$N_2$ (1). A solution of dfepe (2.04 g, 36 mmol) in 15 mL of diethyl ether was added dropwise to a slurry of (η^6-$C_6H_5Me)_2Mo$ (0.503 g, 18 mmol) in 25 mL of ether at −78 °C under an N_2 atmosphere. After the addition was complete, the reaction mixture was allowed to warm slowly to ambient temperature. At approximately −10 °C, a homogeneous deep red–orange solution was obtained, which upon further warming turned light yellow and gave a white precipitate. After 36 h the volatiles were removed under vacuum and the residue was taken up in 30 mL of hexane and filtered under nitrogen. Cooling to −15 °C gave deep orange crystals of 1 (0.544 g, 39%), which were collected, dried under vacuum for 30 min, and stored under nitrogen at −30 °C. Due to slow decomposition at room temperature, a satisfactory analysis was not obtained. IR (Nujol, KCl, cm^{-1}) 2108 vs (2133 in heptane), 1292 s, 1216 vs, 1193 m, 1104 s, 950 m. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C) δ 4.63 (m, 2 H, *m*-C_6H_5Me), 4.45 (d, 2 H, $^3J_{HH}$ = 5.9 Hz, *o*-C_6H_5Me), 3.61 (m, 1 H, *p*-C_6H_5Me), 1.74 (m, 4 H, PCH_2), 1.43 (s, 3 H, C_6H_5*Me*). ^{13}C NMR (benzene-d_6, 67.8 MHz, 25 °C) δ 120.1 (qm, $^1J_{CF} \approx 290$ Hz, CF_3), 104.2 (s, *ipso*-C_6H_5Me), 86.9 (d, $^1J_{CH}$ = 173 Hz, C_6H_5Me), 85.9 (d, $^1J_{CH}$ = 175 Hz, C_6H_5Me), 79.3 (d, $^1J_{CH}$ = 175 Hz, *p*-C_6H_5Me), 20.8 (tt, $^1J_{CH}$ = 139 Hz, J_{CP} = 20 Hz, PCH_2), 18.8 (q, $^1J_{CH}$ = 129 Hz, C_6H_5*Me*). ^{31}P NMR (benzene-d_6, 109.1 MHz, 22 °C) δ 126.0 (ps q, $^1J_{FP} \approx 80$ Hz). ^{19}F NMR (benzene-d_6, 253.7 MHz, 25 °C) δ 78.42, 78.46 (s, CF_3), 107–113 (m, PCF_2).

{(η^6-C_6H_6)Mo[$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$]}$_2$($\mu$-$N_2$) (2). To a slurry of $(C_6H_6)_2Mo$ (245 mg, 0.97 mmol) in 15 mL of ether was added 1.6 g of dfepe (2.83 mmol) at ambient temperature. After 3 days, the resulting orange precipitate was dissolved by adding more ether (120 mL of total volume), and the solution was filtered and evaporated to dryness. The filtrate residue was slurried in a minimal amount of petroleum ether and the solution was filtered off to remove excess dfepe. Addition of 3 mL of ether and cooling to −50 °C gave 200 mg (28%) of orange crystalline 2 after cold filtration and drying under vacuum. Anal. Calcd for $C_{32}H_{20}F_{40}Mo_2N_2P_4$: C, 25.48; H, 1.34; N, 1.86. Found: C, 25.58; H, 1.32; N, 1.81. IR (KCl, cm^{-1}) 1417 w, 1295 s, 1223, 1206 s, 1147 w, 1122 s, 1104, 1079 m, 1049 m, 968 m, 948, 842 m. Raman (solid, excitation wavelength 532 nm) 2020 vs. ^1H NMR (benzene-d_6, 399.65 MHz, 20 °C) δ 4.29 (s, 5 H, C_6H_6), 1.73 (m, 4 H, PCH_2). ^{31}P NMR (benzene-d_6, 161.70 MHz, 20 °C) δ 126.9 (m). ^{19}F NMR (benzene-d_6, 376.05 MHz, 20 °C) δ 77.63, 77.66 (s, CF_3), 107–112 (m, PCF_2).

Spectroscopic Data for (η^6-C_6H_6)Mo[$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$]($N_2$) (2a). IR (KCl, N_2-saturated heptane solution, cm^{-1}) 2144. ^1H NMR (benzene-d_6, 399.65 MHz, 20 °C) δ 4.45 (s, 5 H, C_6H_6), 1.75 (m, 4 H, PCH_2). ^{19}F NMR (benzene-d_6, 376.05 MHz, 20 °C) δ 81.46, 81.49 (s, CF_3), 107–112 (m, PCF_2).

(η^6-C_6H_5Me)Mo[$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$]$H_2$ (3). A solution of dfepe (1.00 g, 17.7 mmol) in 10 mL of diethyl ether was added dropwise to a solution of (η^6-$C_6H_5Me)_2Mo$ (0.292 g, 10.4 mmol) in 20 mL of toluene at −78 °C. After complete addition, the N_2 atmosphere was pumped off and replaced by 1 atm of hydrogen, and the reaction mixture was allowed to warm to ambient temperature. The volatiles were removed after 48 h, and the yellow residue was extracted with petroleum ether. Concentration of the filtrate to ca. 3 mL and cooling to −78 °C gave after filtration and drying in vacuo (0.386 g (49%) of bright yellow crystalline 3. Although complex 3 is thermally stable, it should be stored at −30 °C to prevent slow solid-state exchange with ambient dinitrogen (approximately 50% exchange after 2 weeks, as judged by ^1H NMR). Anal. Calcd for $C_{17}H_{14}F_{20}MoP_2$: C, 27.00; H, 1.87. Found: C, 27.12; H, 1.77. IR (KCl, cm^{-1}) 1825 w (sh), 1800 w, 1516, 1412 w, 1303 s, 1219 vs, 1203 s, 1131 s, 1112 s, 959 s. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C) δ 4.75 (ps d, 4 H, $^3J_{HH}$ =

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3 Hz, *m,o*-C_6H_5Me), 4.45 (m, 1 H, *p*-C_6H_5Me), 1.59 (d, $^2J_{PH}$ = 11.7 Hz, 4 H, PCH_2), 1.42 (s, 3 H, C_6H_5Me). ^{31}P NMR (benzene-d_6, 109.1 MHz, 22 °C) δ 127.9 (m). ^{19}F NMR (benzene-d_6, 253.7 MHz, 25 °C) δ 77.00 (s, CF_3), 114.11 (ABX, (ν(A)−ν(B)) = 942 Hz, $^2J_{FF}$ = 304 Hz, $^2J_{FP}$ = 53, 33 Hz; CF_2P). The HD-labeled isotopomer of **3** was prepared in situ by the addition of HD via syringe to a C_6D_6 solution of **1**.

(η^6-C_6H_5Me)Mo[$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$]CO (4). An ether solution of **1**, prepared from 0.475 g of (η^6-$C_6H_5Me)_2Mo$ (17 mmol) and 1.64 g of dfepe (28.9 mmol) by using the procedure described above, was stirred under 1 atm of CO for 4 h at room temperature. Removal of volatiles, extraction with petroleum ether, and precipitation at −78 °C afforded 0.460 g (35%) of light yellow **4**. Anal. Calcd for $C_{17}H_{12}F_{20}MoOP_2$: C, 27.64; H, 1.55. Found: C, 26.95; H, 1.30. IR (KCl, cm^{-1}) 1886 vs (1922 in heptane), 1295 s, 1215 vs, 1192 m, 1103 m, 1087 m. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C) δ 4.92 (m, 2 H, *m*-C_6H_5Me), 4.70 (d, 2 H, $^3J_{HH}$ = 6.2 Hz, *o*-C_6H_5Me), 4.35 (t, 1 H, $^3J_{HH}$ = 6.2 Hz, *p*-C_6H_5Me), 1.77 (m, 4 H, PCH_2), 1.59 (s, 3 H, C_6H_5Me). ^{13}C NMR (benzene-d_6, 67.8 MHz, 22 °C) δ 223.7 (s, Mo(CO)), 119.7 (qm, $^1J_{CF} \approx 287$ Hz, CF_3), 107.2 (s, *ipso*-C_6H_5Me), 91.3 (d, $^1J_{CH}$ = 180 Hz, C_6H_5Me), 89.6 (d, $^1J_{CH}$ = 168 Hz, C_6H_5Me), 20.1 (q, $^1J_{CH}$ = 131 Hz, C_6H_5Me). ^{31}P NMR (benzene-d_6, 109.1 MHz, 22 °C) δ 131.1 (m). ^{19}F NMR (benzene-d_6, 253.7 MHz, 25 °C) δ 73.31 (s, CF_3), 72.18 (d, $^3J_{FP}$ = 18 Hz, CF_3), 110–114 (m; PCF_2).

(η^6-C_6H_5Me)Mo[$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$](MeCN) (5). Acetonitrile (2 mL) was added to a solution of **1** (10 mL, Et_2O), prepared from 0.220 g of (η^6-$C_6H_5Me)_2Mo$ (0.79 mmol) and 0.72 g of dfepe (1.27 mmol). After stirring at room temperature for 1 h, the volatiles were removed and the residue was dried under high vacuum for 3 h. Extraction of the residue with petroleum ether, concentration to 4 mL, and cooling to −78 °C gave after filtration 0.217 g (35%) of orange microcrystalline **5**. Anal. Calcd for $C_{19}H_{15}F_{20}MoNP_2$: C, 28.70; H, 1.90; N, 1.76. Found: C, 28.93; H, 1.84; N, 1.75. IR (KCl, cm^{-1}) 2258 s, 1287 vs, 1217 vs, 1191 vs, 1101, 946 s, 844 m, 776 s, 744 s. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C) δ 4.70 (m, 2 H, *m*-C_6H_5Me), 4.48 (d, 2 H, $^3J_{HH}$ = 5.5 Hz, *o*-C_6H_5Me), 3.44 (m, 1 H, *p*-C_6H_5Me), 1.93 (m, 4 H, PCH_2), 1.38 (s, 3 H, C_6H_5Me), 0.75 (s, 3 H, MeCN). ^{31}P NMR (benzene-d_6, 109.1 MHz, 22 °C) δ 122.8 (m). ^{19}F NMR (benzene-d_6, 253.7 MHz, 25 °C) δ 78.33, 78.37 (s, CF_3), 106–113 (m, PCF_2).

(η^6-C_6H_5Me)Mo[$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$]($C_5H_5N$) (6). Pyridine (2 mL) was distilled into a solution of **1** (0.165 g, 0.21 mmol) in 10 mL of petroleum ether at −78 °C. Upon warming to room temperature, the light yellow solution gradually became deep orange. After 2 h the volatiles were removed under vacuum and the residue was extracted with petroleum ether. Filtration, concentrating to ca. 3 mL, and cooling to −78 °C afforded 0.136 g (77%) of red-orange crystalline **6**. Anal. Calcd for $C_{22}H_{17}F_{20}MoNP_2$: C, 31.71; H, 2.06; N, 1.68. Found: C, 31.73; H, 2.02; N, 1.89. IR (KCl, cm^{-1}) 1599 w, 1483 m, 1424 w, 1288 vs, 1203 vs, 1094 vs, 940 s, 873 m. ^1H NMR (benzene-d_6, 269.7 MHz, 22 °C) δ 8.50 (dd, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H, *o*-C_5H_5N), 6.43 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5, 1 H, *p*-C_5H_5N), 6.00 (ps t, $J_{HH} \approx 7$ Hz, 2 H, *m*-C_5H_5N), 4.78 (m, 2 H, *m*-C_6H_5Me), 4.29 (d, 2 H, $^3J_{HH}$ = 5.5 Hz; *o*-C_6H_5Me), 3.06 (m, 1 H, *p*-C_6H_5Me), 1.93 (m, 4 H, PCH_2), 0.41 (s, 3 H, C_6H_5Me). ^{31}P NMR (benzene-d_6, 109.1 MHz, 22 °C) δ 117.7 (m). ^{19}F NMR (benzene-d_6, 253.7 MHz, 25 °C) δ 77.84, 78.12 (s, CF_3), 103–107 (m, PCF_2).

Ligand-Exchange Studies. All ligand-exchange experiments were carried out in sealed NMR tubes and monitored by ^1H NMR. Exchanges of complexes with N_2, CO, and H_2 were carried out under 500–600 Torr of gas pressure; for liquid substrates (MeCN and pyridine), between 1 and 2 equiv was used. For highly labile complexes **1** and **6**, displacement with CO, H_2, or MeCN occurred at 20 °C within 1 h. For the less labile adducts **3** and **5**, exchange with CO was complete after 24 h at 65 °C. No displacement of CO from **4** by MeCN or H_2 occurred after prolonged heating at 120 °C. With the exception of the N_2/py and MeCN/H_2 exchange couples discussed in the text, all displacements were essentially quantitative.

Electrochemical Measurements. Cyclic voltammetry experiments were performed under a nitrogen atmosphere for complexes **1** and **3–5** using either a EG & G Princeton Applied Research 273 Potentiostat/Galvanostat with a Kipp & Zonen BD91 recorder or a BioAnalytical Systems 100A electrochemical analyzer with a Hewlett-Packard 7475A plotter. Voltammetry for pyridine complex **6** was conducted under argon to eliminate exchange with N_2. Measurements were taken at a platinum disk working electrode in CH_2Cl_2 or THF solutions containing 0.2 M *n*-Bu_4NClO_4 as the supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) were operationally referenced to either Ag/$AgClO_4$(0.4 M)$_{solv}$ or Ag/AgCl(3.0 M)$_{aq}$) and corrected to SCE by using a ferrocene/ferrocenium couple as an common internal standard. Under our conditions, the values for Cp_2Fe^+/Cp_2Fe couple in THF and CH_2Cl_2 versus SCE were found to be +0.509 and +0.465 V, respectively.

X-ray Structure Determinations. X-ray data were collected on a Nicolet R3m/V automated diffractometer system with a dedicated MicroVAX II computer system and fitted with an LT-2 low-temperature device. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. The parameters used during collection of diffractometer data for complexes **1** and **6** are summarized in Table I. Suitable crystals for both compounds were sealed in glass capillaries under nitrogen. Since a preliminary structure for **1** at ambient temperature revealed excessive thermal motion and/or disorder for two of the C_2F_5 groups, subsequent structure analyses were carried out at −100 °C. All computations used the SHELXTL PLUS (Version 3.4) program library (Nicolet Corp., Madison, WI).

(η^6-C_6H_5Me)Mo(dfepe)(N_2) (1). A large orange prism of **1** was grown from petroleum ether at 0 °C under nitrogen and was cut down to a suitable size for study. Unit cell dimensions were derived from a least-squares fit of 36 random reflections (23° ≤ 2θ ≤ 30°). The Laue symmetry was determined to be $2/m$. Data were collected by using the ω-scan technique with a variable scan rate of 3.0–30.0°. Analysis of systematic absences for the total date set indicated that the space group was $P2_1/n$. Three standard reflections monitored after every 100 data collected showed no systematic variation; the *R* for averaging 259 redundant data was 0.015. Data were corrected for absorption using an empirical ellipsoidal model based on φ-scans for 12 reflections with 8° ≤ 2θ ≤ 50°.

The structure of **1** was solved by using the SHELXTL PLUS Patterson interpretation program, which revealed almost all the non-hydrogen atoms on the initial *E* map. All remaining non-hydrogen atoms were located in subsequent difference fourier maps and were refined anisotropically. Hydrogen atom positions were added in ideal calculated positions with *d*(C–H) = 0.96 Å and refined with separate common isotropic thermal parameters for the arene hydrogen and ligand backbone hydrogen sets. Methyl hydrogens were refined as a rigid group with a common fixed isotropic thermal parameter. C(5)–F(7) and C(6)–F(8) distances deviated by more than 4σ above average C–F bond distances and were constrained to 1.366 (3) and 1.324 (1), respectively, in the final refinements. No significant deviations of C–F distances for other atom pairs with or without this constraint were noted. In the final refinement all shift/esd ratios were less than 0.023 with no unusually high variable correlations apparent. The final Fourier difference map showed no peak greater than 0.67 e/Å^3.

(η^6-C_6H_5Me)Mo(dfepe)(py) (6). A deep red block of **6** suitable for study was chipped off a large prism grown from a petroleum ether solution at 0 °C containing a few milliliters of excess pyridine. Unit cell dimensions were derived from a least-squares fit of 45 random reflections (23° ≤ 2θ ≤ 30°) and indexed by using a triclinic lattice. The choice of the centrosymmetric space group $P\bar{1}$ requiring two independent molecular units was indicated by the calculated unit cell density and was confirmed by the subsequent solution and successful refinement of the structure. Data were collected by using the ω-scan technique with a variable scan rate of 4.0–30.0°. Three standard reflections monitored after every 100 data collected showed no systematic variation. No correction for absorption was applied.

The structure solution and refinement procedures were the same as above. Pyridine and ligand backbone idealized hydrogen positions were refined with fixed common isotropic thermal parameters. Arene and methyl hydrogen thermal parameters were set to 1.2–1.3 times the isotropic equivalent for the attached carbon. Because of the large number of parameters (828) in the final stages of refinement, independent molecules A and B were alternately block refined to convergence with shift/esd ratios less

than 0.15. The final Fourier difference map showed no peak greater than 0.59 e/Å^3.

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Note Added in Proof. Two structural reports of fluorophosphine Mo(0) complexes with very short Mo(0)–P bond distances comparable to those detailed in this paper have been brought to our attention.[53,54]

Supplementary Material Available: Tables of complete data collection parameters, atomic coordinates for **6**, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters (19 pages); listings of calculated and observed structure factors (38 pages). Ordering information is given on any current masthead page.

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Models for Multicenter Catalysts. 4.[1-3] Reactions of Binuclear Hydrides with Alkynes and the Structure of $[Ir_2(H)_2Cl(CH_3O_2CC{=}C(H)CO_2CH_3)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$-$[BF_4]\cdot 3THF$, a Model Hydrogenation Intermediate Containing Mutually Adjacent Alkenyl and Hydrido Ligands

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The reaction of $[Ir_2(H)_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$ (1) with 2 equiv of dimethyl acetylenedicarboxylate (DMA) in THF or acetone yields $[Ir_2(CH_3O_2CC{=}C(H)CO_2CH_3)_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$. This cationic species is the result of alkyne insertion into both of the Ir–H bonds of compound 1. Further reaction of this species with dihydrogen yields $[Ir_2(H)_2Cl(CH_3O_2CC{=}C(H)CO_2CH_3)_2(CO)_2(DPM)_2][BF_4]$ (DPM = $Ph_2PCH_2PPh_2$), which is a stable complex containing mutually adjacent alkenyl and hydrido ligands. This compound crystallizes in the space group $P2_1/c$ with a = 18.675 (5) Å, b = 15.775 (3) Å, c = 26.371 (4) Å, β = 96.38 (2)°, and Z = 4. The structure has refined to R = 0.054 and R_w = 0.062 on the basis of 5775 unique observations and 590 parameters varied. Although the hydride ligands were not directly located in the X-ray study, their positions can be inferred from the positions of the heavy atoms and from the NMR studies. One is located in a terminal site on one Ir adjacent to an alkenyl group, while the other is bridging the two metals, resulting in an Ir–Ir separation of 3.2895 (7) Å. A mechanism is proposed for one pathway by which alkynes may be hydrogenated by binuclear species such as 1. It is proposed that hydrogenation occurs at each individual metal center in turn but that the coordinative unsaturation required at different stages occurs by movement of the chloride ligand back and forth from one metal to the other. The reactions of 1 with 2-butyne and ethylene yield 2-butenes and ethane, respectively, in the absence of H_2 and suggest an alternate intermolecular mechanism for hydrogenation. The reaction of alkynes with the mixed-metal species, $[RhIr(H)_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$, does not appear to result in insertion but rather displaces H_2 from the complex, yielding alkyne-bridged species.

Introduction

Preliminary studies done within this research group[1-5] have attempted to delineate the sites of attack, accessible bonding modes, and ligand mobilities involved in reactions of dihydrogen and unsaturated substrates with binuclear DPM-bridged complexes (DPM = $Ph_2PCH_2PPh_2$). One of the primary goals of such studies was to gain information relevant to alkyne hydrogenation catalysis in the presence of two or more adjacent metals. It has been shown that alkyne hydrogenation is catalyzed by the binuclear complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BPh_4]$,[6] $[Rh_2(H)_2(CO)_2(DPM)_2]$,[7,8] and $[Rh_2Cl_2(\mu\text{-}CO)(DPM)_2]$,[9] although information about possible intermediates was lacking. Of particular interest were suggestions[1,10,11] that the two ad-

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