Substantial differences in the two spectra are evident. In THF solutions, bands are seen at ~529, 405, and 285 nm, while in the solid-state bands are seen at ~771, 540 (sh), 361 (sh), and 295 nm. The spectrum of Fe(DBSQ)(DBCAT)(bpy) was also studied in THF solution in the temperature range 300–230 K and in the solid state over the range 300–30 K. However, no new bands or unusual spectral shifts were seen. If Fe(DebSQ)(DBCAT)(bpy) is a mixed-valence complex in the solid state, apparently it does not exhibit absorption in the near-IR associated with an IT band. The appreciable change in the spectrum upon dissolution of the complex in THF could again reflect the type of change in electronic structure seen above for the phenQ complex.

### Summary and Cmomments

There Fe(phenSQ)(phenCAT)(nitrogen base) complexes were prepared and characterized to be monomeric high-spin Fe(III) complexes containing both semiquinone and catecholate ligands in the solid state. The mixed-valence character was substantiated, in part, by the observance for solids and for solutions in low dielectric constant solvents of an intervalence transfer band at 1100 nm. In solvents of high dielectric constant, the electronic absorption spectrum undergoes a dramatic change. It is possible that an *intra*molecular electron transfer has occurred to give a $\mathrm{Fe^{II}(phenSQ)_2}$(nitrogen base) complex.

The five Fe(DBSQ)(DBCAT)(nitrogen base) complexes prepared in this study were found to be oligomeric high-spin Fe(III) complexes in the solid state; they also each have one semiquinone and one catecholate ligand and are, consequently, mixed valence. Upon dissolution in all organic solvents tested, a dramatic change in the electronic spectrum is seen from that observed for the solids. In both series of complexes, a relatively strong *intra*molecular antiferromagnetic exchange interaction between the unpaired electrons of the metal ion exists.

The above phenQ and DBQ Fe(III) complexes are not yet the best models of the ($\mathrm{Q_I^-{\cdot}FeQ_{II}^-{\cdot}}$) site in bacterial photosynthetic electron transport chains. It is necessary to get better control on the oxidation state of the iron ion. The iron in the site is indicated to be high-spin Fe(II). It should be possible, however, to prepare such a high-spin Fe(II) complex with two semiquinone moieties attached to the ligand framework. Various nitrogeneous macrocyclic ligands and phosphorus ligands could be used to keep the iron in the high-spin divalent state. It is also required for the model that the semiquinone be derived from a *p*-quinone.

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**Registry No.** $\mathrm{Fe(DBSQ)_3}$, 64020-89-9; $\mathrm{Fe(phenSQ)_3}$, 39797-84-7; Fe(phenSQ)(phenCAT)(bpy), 83573-04-0; Fe(phenSQ)(phenCAT)(phen), 83573-05-1; Fe(phenSQ)(phenCAT)(dmbpy), 83573-06-2; Fe(DBSQ)(DBCAT)(bpy), 83573-07-3; Fe(DBSQ)(DBCAT)(phen), 83573-08-4; Fe(DBSQ)(DBCAT)(en), 83573-09-5; Fe(DBSQ)(DBCAT)(py), 83573-10-8; Fe(DBSQ)(DBCAT)(dmbpy), 83573-11-9; iron pentacarbonyl, 13463-40-6.

**Supplementary Material Available:** Listing of the variable-temperature magnetic susceptibility data (11 pages). Ordering information is given on any current masthead page.

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# Competitive Rates of Reactions of Molybdenum Atoms with Arenes

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**Abstract:** The relative rates of reactions of Mo atoms with arene mixtures at approximately −170 °C are spaced over the small overall range of 3.7 for the following arenes: toluene, *tert*-butylbenzene, *o*-xylene, $\alpha,\alpha,\alpha$-trifluorotoluene, *N,N*-dimethylaniline, fluorobenzene, methyl benzoate, and anisole.

While it is generally assumed that reactions of metal atoms with substrates must have low activation energies if they are to compete successfully with the low-activation-energy process of diffusion and aggregation of bulk metal, there has been no kinetic evidence reported that would test this hypothesis. Low discrimination between a pair of different substrates (competition reactions) would strongly support this hypothesis. We have examined this question with a study of the competition reactions of substituted arenes for molybdenum atoms to give bis($\eta^6$-arene)molybdenum,[1-7]

$$\mathrm{C_6H_5F + C_6H_5R \xrightarrow[-196\ ^\circ C]{Mo} (\eta^6\text{-}C_6H_5F)_2Mo + (\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5R)Mo + (\eta^6\text{-}C_6H_5R)_2Mo} \quad (1)$$

where R is $\mathrm{CH_3}$, 1,2-dimethyl, $\mathrm{C(CH_3)_3}$, $\mathrm{CF_3}$, $\mathrm{N(CH_3)_2}$, $\mathrm{CO_2CH_3}$, or $\mathrm{OCH_3}$, and have found that the reactions proceed with low discrimination.

The competition reactions between two substituted arenes for molybdenum atoms were conducted by the condensation of a mixture of the two arenes, with a metal to ligand ratio of 20–50:1, at temperatures near −196 °C. The resulting matrix was then warmed to room temperature, and the unreacted substrates were removed by pumping. The mixtures of sandwich compounds were removed from the reactor as ethereal solutions, filtered, and freed of solvent before the crude reaction mixture was analyzed by $^1$H and $^{19}$F NMR in $\mathrm{C_6D_6}$ at room temperature; from the product distributions, the relative rates of the competition reactions were then determined.

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Table I. NMR and Physical Data for Bis(arene)molybdenum Sandwich Compounds

| compound | physical data | NMR data[a,g] |
|---|---|---|
| $(\eta^6\text{-}C_6H_5F)_2Mo^{b,d}$ | green, mp 120 °C dec | $^1H$ δ 4.0 (m, 1 H, para, $C_6H_5$); 4.32 (t, 2 H, meta, $C_6H_5$); 5.15 (d, 2 H, ortho, $C_6H_5$)<br>$^{19}F$ 150.4 ppm, s |
| $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo^c$ | green, mp 175–178 °C | $^1H$ δ 1.83 (s, 6 H, $C_6H_4(CH_3)_2$); 4.52 (s, 4 H, $C_6H_4$) |
| $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo^d$ | | $^1H$ δ 1.88 (s, 6 H, $C_6H_4(CH_3)_2$); 4.39, 4.65 (m, mixed); 5.05 (t, $C_6H_5F$)<br>$^{19}F$ 156.9 ppm, s |
| $(\eta^6\text{-}C_6H_5C(CH_3)_3)_2Mo^c$ | green, mp 109–110.5 °C | $^1H$ δ 1.20 (s, 9 H, $-C(CH_3)_3$); 4.55 (m, 3 H, meta, para $C_6H_5$); 4.68 (m, 2 H, ortho, $C_6H_5$) |
| $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5C(CH_3)_3)Mo^d$ | | $^1H$ δ 1.20 (s, 9 H, $-C(CH_3)$; 4.52, 4.65 (m, mixed); 5.07 (d, 2 H, ortho, $C_6H_5F$)<br>$^{19}F$ 152.7 ppm, s |
| $(\eta^6\text{-}C_6H_5CH_3)_2Mo^{b,d,e}$ | green | $^1H$ δ 1.85 (s, 3 H, $-CH_3$; 4.58 (s, 5 H, $C_6H_5$) |
| $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CH_3)Mo^d$ | | $^1H$ δ 1.85 (s, 3 H, $-CH_3$); 4.55 (m, mixed); 5.08 (d, 2 H, ortho, $C_6H_5F$)<br>$^{19}F$ 154.7 ppm, s |
| $(\eta^6\text{-}C_6H_5CF_3)_2Mo^c$ | emerald green, mp 92–92.5 °C | $^1H$ δ 4.44 (m, 3 H, meta, para, $C_6H_5$); 4.85 (m, 2 H, ortho, $C_6H_5$)<br>$^{19}F$ 59.9 ppm, s |
| $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CF_3)Mo^d$ | | $^{19}F$ ppm 59.7 (s, 3 F, $-CF_3$); 147.9 (s, 1 F, $-F$) |
| $(\eta^6\text{-}C_6H_5N(CH_3)_2)_2Mo^{b,d}$ | red-brown, mp 90.5–91.0 °C | $^1H$ δ 2.25 (s, 6 H, $-N(CH_3)_2$); 4.60 (s, 5 H, $C_6H_5$) |
| $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5N(CH_3)_2)Mo^d$ | | $^1H$ δ 2.18 (s, 6 H, $-N(CH_3)_2$); 4.51 (m, mixed); 5.22 (d, 2 H, ortho, $C_6H_5F$)<br>$^{19}F$ 152.1 ppm, s |
| $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo^{b,c,f}$ | red-orange, mp 135–136 °C | $^1H$ δ 3.53 (s, 3 H, $-CO_2CH_3$); 4.50 (t, 1 H, $^3J_{3,2}$ = 4.8 Hz, para, $C_6H_5$); 4.62 (dd, 2 H, $^3J_{2,3}$ = 4.8 Hz, $^3J_{2,1}$ = 5.8 Hz, meta, $C_6H_5$); 5.55 (d, $^3J_{1,2}$ = 5.8 Hz, 2 H, ortho, $C_6H_5$) |
| $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CO_2CH_3)Mo^d$ | | $^1H$ δ 3.51 (s, 3 H, $-CO_2CH_3$; 4.60 (m, mixed); 5.19 (d, 2 H, ortho, $C_6H_5F$); 5.61 (d, 2 H, ortho, $C_6H_5CO_2CH_3$)<br>$^{19}F$ 149.4 ppm, s |
| $(\eta^6\text{-}C_6H_5OCH_3)_2Mo^{b,d}$ | green, mp 57–59 °C | $^1H$ δ 3.18 (s, 3 H, $-OCH_3$); 4.38 (br m, 3 H, meta, para, $C_6H_5$); 4.91 (d, 2 H, ortho, $C_6H_5$) |
| $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5OCH_3)Mo^d$ | | $^1H$ δ 3.15 (s, 3 H, $-OCH_3$); 4.38 (br m, mixed); 4.91 (d, mixed); 5.12 (d, 2 H, ortho, $C_6H_5F$)<br>$^{19}F$ 151.9 ppm, s |
| $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo^{c,f,h}$ | | $^1H$ δ 1.81 (s, 6 H, $C_6H_4(CH_3)_2$); 3.49 (s, 3 H, $CO_2CH_3$); 4.44 (t, $^3J_{3,2}$ = 5.1 Hz, 1 H, para, $C_6H_5CO_2CH_3$); 4.55 (dd, meta, $^3J_{2,1}$ = 3.6 Hz, $^4J_{2,4}$ = 1.8 Hz. 2 H, $C_6H_4$ $C_6H_4(CH_3)_2$); 4.62 (dd, 2 H, $^3J_{2,1}$ = 5.1 Hz, $^3J_{2,3}$ = 5.1 Hz, meta, $C_6H_5CO_2CH_3$); 4.75 (dd, ortho, $^3J_{1,3}$ = 1.8 Hz, 2 H, $C_6H_4(CH_3)_2$); 5.36 (d, 2 H, $^3J_{1,2}$ = 5.1 Hz, ortho, $C_6H_5CO_2CH_3$) |

[a] $^1H$ given as chemical shift (multiplicity, number of protons assignment) if known and $^{19}F$ as shift in ppm, multiplicity. Mixed refers to either aromatic ring of the mixed sandwich complex. Assignments are made after the fashion of Graves and Lagowski.[8] [b] From ref 5. [c] Isolated compound. [d] Recognized as a component in a mixture. [e] From ref 4. [f] Bruker 200 MHz, this work. [g] $^{19}F$ NMR spectra were recorded at 93 MHz and $^1H$ NMR spectra, except where noted, at 60 MHz in $C_6D_6$. $^{19}F$ spectra, in ppm, are upfield and were referenced to external OFCl$_3$. $^1H$ NMR spectra, in δ, were referenced to internal $C_6D_6$ (δ 7.15). [h] The aromatic protons at the $C_6H_4(CH_3)_2$ ligand were assigned by the NOE enhancement between the $CH_3$ group and the ortho protons of $C_6H_4(CH_3)_2$.

Since the sandwich compounds are air sensitive, the method of analysis had to be one in which the crude reaction mixtures were examined directly to minimize any loss of material. Even though the metal atom reactions proceed cleanly, some of the ligands used, e.g., methyl benzoate and *N,N*-dimethylaniline, are rather involatile; therefore the method had to be one in which the results were unambiguous in the event of ligand contamination. Arene complexes of transition metals exhibit characteristic[8-10] upfield shifts in both $^1H$ and $^{19}F$ NMR. The combination of these NMR techniques proved to be suitable for the analysis of the product mixtures. The NMR data of the sandwich compounds are summarized in Table I.

The competition pairs were chosen with an eye to convenience in analyzing the three-component mixtures. Usually fluorobenzene was used as one of the reactants. The two homoproducts were always known, and the mixed product was identified by difference. For example, the $^{19}F$ resonances were always resolved for $(\eta^6\text{-}C_6H_5F)_2Mo$ and $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5Z)Mo$. Care was used in selecting Z's so that singlets in the $^1H$ spectra could be used to distinguish $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5Z)$ and $(\eta^6\text{-}C_6H_5Z)_2$.

The $^{19}F$ spectra consisted of two well-resolved singlets in the 147–158 ppm (reference to external $CFCl_3$): one at 150.4 ppm for $(\eta^6\text{-}C_6H_5F)_2Mo$ and the other for the mixed complex $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5Z)Mo$.

The $^1H$ NMR spectra of the mixtures were more complex. The region between δ 5.00 and 5.20 consisted of two doublets that were assigned to the hydrogens ortho to the fluorine atom: δ 5.15 to the ortho hydrogens of $(\eta^6\text{-}C_6H_5F)_2Mo$ and the other doublet to the hydrogens ortho to the fluorine in $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5Z)Mo$. The singlets for the various Z's occur at higher fields. Confidence in these assignments came from the assignment of all absorptions, and in one instance, the isolation of a pure mixed complex.

The mixed complex, $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)$-Mo, was separated by column chromatography on silica gel. The mixed complex was a golden, air-sensitive compound (yield of 18% based on molybdenum vaporized).

The area ratios for a number of competition reactions were used to determine the molar ratios of products reported in Table II.

It is sensible to calculate the relative rates involved in the competition reactions from the product distributions in Table II if the products are obtained with kinetic rather than thermodynamic control. It was necessary to show that there was no arene exchange either with unreacted ligand or with the $C_6D_6$ used in

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Table II. Relative Molar Amounts[a] of Sandwich Compounds from Competitions of 1:1 Mole Ratios of Arene–Fluorobenzene Mixtures

| arene | $MB_2$, $(\eta^6\text{-}C_6H_5F)_2Mo$ | MAB, $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-arene})Mo$ | $MA_2$, $(\eta^6\text{-arene})_2Mo$ | arene[b] flux | $k_a/k_b$ |
|---|---|---|---|---|---|
| 1,2-$C_6H_4(CH_3)_2$ | 1 (11) | 3.5 (38) | 4.6 (51) | 0.5 | 2.15 |
|  | 1 (14) | 3.3 (46) | 2.9 (40) | 0.8 | 1.70 |
|  | 1 (14) | 3.1 (43) | 3.1 (43) | 1.1 | 1.75 |
| $C_6H_5C(CH_3)_3$ | 1 (11) | 3.4 (37) | 4.7 (52) | 0.6 | 2.17 |
|  | 1 (9) | 3.8 (35) | 6.3 (57) | 0.6 | 2.51 |
| $C_6H_5CH_3$ | 1 (8) | 4.8 (38) | 6.7 (54) | 0.7 | 2.60 |
|  | 1 (8) | 5.4 (43) | 6.0 (48) | 0.5 | 2.45 |
| $C_6H_5CF_3$ | 1 (13) | 3.8 (49) | 2.9 (38) | 0.6 | 1.71 |
| $C_6H_5N(CH_3)_2$ | 1 (19) | 3.1 (58) | 1.2 (23) | 0.4 | 1.10 |
| $C_6H_5CO_2CH_3$ | 1 (27) | 2.1 (56) | 0.6 (18) | 0.4 | 0.81 |
| $C_6H_5OCH_3$ | 1 (35) | 1.4 (49) | 0.4 (15) | 0.5 | 0.65 |
| 1,2-$C_6H_4(CH_3)_2$ | 1 (26) | 0.6 (15) | 2.3 (59) | 0.08 |  |
|  | 1 (31) | 0.4 (12) | 1.8 (57) | 0.10 |  |
| 1,2-$C_6H_4(CH_3)_2$[c] | 1 (49) | 0.8 (39) | 0.2 (12) | 0.5 | 0.5 |
|  | 1 (50) | 0.7 (37) | 0.3 (14) | 0.6 | 0.53 |

| arene | $MB_2$, $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$ | MAB mixed | $MA_2$, $(\eta^6\text{-1,2-}C_6H_4(CH_3)_2)_2Mo$ | arene flux | $k_a/k_b$ |
|---|---|---|---|---|---|
| 1,2-$C_6H_4(CH_3)_2$ | 1 (17) | 3.5 (60) | 1.4 (23) | 0.4 | 1.16 |
| $C_6H_5CO_2CH_3$ | 1 (16) | 3.8 (61) | 1.4 (23) | 0.40 | 1.20 |

[a] Numbers in parentheses are the normalized molar percentages. [b] Arene flux is the rate at which the solution of arenes was added to the reactor in mL/min. [c] 3:1 mole ratio fluorobenzene/*o*-xylene reaction.

the NMR samples. Arene exchange might occur during the reaction due to the white light produced from the evaporation of molybdenum wire at 2400 °C or thermally during warmup of the matrix or while the solution was standing at room temperature either during the time it takes to remove the unreacted ligand or by contact with the $C_6D_6$ during the analysis. Photolysis of $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$ in toluene and in a toluene/$C_6D_6$ solution for 63 h in a UV cell and 21 h in a NMR tube, respectively, with a medium-pressure water-cooled mercury lamp showed no evidence of arene exchange. That no arene exchange occurs during warmup of the matrix was shown by the experiment where toluene was added at −196 °C to a freshly prepared matrix of Mo in methyl benzoate. After warmup, the product was exclusively $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$, uncontaminated by $(\eta^6\text{-}C_6H_5CH_3)_2Mo$ or $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}C_6H_5CH_3)Mo$. This result also indicates that the reactions to form the sandwich compounds occur prior to the melting of the matrix. Heating a toluene solution of $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$ at 110 °C for 8 h results in 20% conversion to $(\eta^6\text{-}C_6H_5CH_3)(\eta^6\text{-}C_6H_5CO_2CH_3)Mo$, without formation of any $(\eta^6\text{-}C_6H_5CH_3)_2Mo$. These are forcing conditions compared to the exposure of the product mixture at room temperature employed in the analysis. Johnson and Muetterties[11] observed no arene exchange products when $(\eta^6\text{-}C_6H_5CH_3)_2Mo$ was heated in benzene at 150 °C.

**Analysis of the Competition Data.** A stepwise formation of the sandwich compounds is reasonable, with arenes A and B competing for M initially and subsequently for MA and MB, the metal–arene intermediate.

$$A + M \xrightarrow{k_1} MA \tag{2}$$

$$B + M \xrightarrow{k_2} MB \tag{3}$$

$$A + MA \xrightarrow{k_3} MA_2 \tag{4}$$

$$B + MA \xrightarrow{k_4} MAB \tag{5}$$

$$A + MB \xrightarrow{k_5} MAB \tag{6}$$

$$B + MB \xrightarrow{k_6} MB_2 \tag{7}$$

The data can be analyzed with the assumption that the relative rates for M reacting with the arenes A and B to make half-sandwiches are the same as the relative rates for the arenes reacting with MA or MB: $k_1/k_2 = k_3/k_4 = k_5/k_6$ These rate ratios can be relabeled $k_a/k_b$. Using a steady-state approximation,[12] we can derive the following expression:

$$\frac{MA_2}{MB_2} = \frac{k_1k_3(k_5[A] + k_6[B])}{k_2k_4(k_3[A] + k_4[B])}\frac{[A]^2}{[B]^2} \tag{8}$$

This simplifies to:

$$\frac{k_a}{k_b} = \frac{[B]}{[A]}\left(\frac{MA_2}{MB_2}\right)^{1/2} \tag{9}$$

The values of $k_a/k_b$ are listed in Table II. Since only the yields of $MA_2$ and $MB_2$ are used in this calculation, some measure of the validity of the simplifying assumption is obtained by examining how well these $k_a/k_b$ enable one to calculate the yields of the mixed-sandwich MAB. The calculated MAB values are listed in Table III, and the modest success of this calculation indicates that the assumptions were reasonable. The species M and MA show the same selectivity in adding an arene ligand.

The relative reactivities of the arenes, shown in Table IV, were obtained from the $k_a/k_b$ values by assigning 1.0 to $C_6H_5F$. The range of the reactivities for this set of ligands is only 3.7. Since these competitions are occurring at temperatures of approximately −150 to −180 °C, the expectation that Mo atoms would show little selectivity is borne out. If these differences in the rates were ascribed entirely to differences in activation energies, this factor of 3.7 corresponds to a $\Delta E_{act}$ of ~200 cal/mol.

**Effect of Low Flux of Substrate.** An interesting physical phenomenon was revealed with a low flux of substrate to the reaction zone. The flux of substrates was normally 0.50 mL/min. When this was reduced to ≤0.10 mL/min, the product composition for the fluorobenzene/*o*-xylene (1:1 mole ratio) competition reaction changed from 51:38:11 to 58:13:29 for $(\eta^6\text{-1,2-}C_6H_4(CH_3)_2)_2Mo$:$(\eta^6\text{-}C_6H_5F)(\eta^6\text{-1,2-}C_6H_4(CH_3)_2)Mo$:$(\eta^6\text{-}C_6H_5F)_2Mo$. The change in the product composition is particularly noteworthy, especially the amount of the mixed complex that becomes smaller than either of the homo sandwiches. The formation of small amounts of MAB and larger amounts of $MA_2$ and $MB_2$ strongly indicates the segregation of the arenes into separate domains, one rich in A, the other in B, rather than the homogeneous glass required for a valid competition reaction. We propose that, at low flux, the arene reactants segregate as a eutectic mixture. The

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Table III. Calculated Product Molar Percentages[a, b]

| arene | $(\eta^6\text{-}C_6H_5F)_2Mo$ | $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-arene})Mo$ | $(\eta^6\text{-arene})_2Mo$ |
|---|---|---|---|
| $1,2\text{-}C_6H_4(CH_3)_2$ | 10 (11) | 44 (38) | 47 (51) |
| | 14 (14) | 47 (46) | 39 (40) |
| | 13 (14) | 46 (43) | 40 (43) |
| $C_6H_5C(CH_3)_3$ | 10 (11) | 43 (37) | 47 (52) |
| | 8 (9) | 41 (35) | 51 (57) |
| $C_6H_5CH_3$ | 8 (8) | 40 (38) | 52 (54) |
| | 8 (8) | 41 (43) | 50 (48) |
| $C_6H_5CF_3$ | 23 (13) | 46 (49) | 39 (38) |
| $C_6H_5N(CH_3)_2$ | 23 (19) | 50 (58) | 27 (23) |
| $C_6H_5CO_2CH_3$ | 30 (27) | 49 (56) | 20 (18) |
| $C_6H_5OCH_3$ | 37 (35) | 48 (49) | 16 (15) |
| $1,2\text{-}C_6H_4(CH_3)_2$ [c] | 44 (49) | 44 (39) | 11 (12) |
| | 43 (50) | 45 (37) | 12 (14) |

| arene | $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$ | $(\eta^6\text{-}C_6H_5CO_2CH_3)\text{-}(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$ | $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$ |
|---|---|---|---|
| $1,2\text{-}C_6H_4(CH_3)_2$ | 18 (17) | 43 (60) | 32 (23) |
| $C_6H_5CO_2CH_3$ | 21 (16) | 50 (61) | 29 (23) |

[a] Product distributions were calculated as described in text. [b] Experimentally obtained molar percentages (from Table II) are in parentheses. [c] 3:1 fluorobenzene/*o*-xylene reaction.

Table IV. Relative Rates of Reactions of Mo Atoms with Arenes

| arene | | arene | |
|---|---|---|---|
| $C_6H_5CH_3$ | 2.6 | $C_6H_5N(CH_3)_2$ | 1.1 |
| $C_6H_5C(CH_3)_3$ | 2.2 | $C_6H_5F$ | (1.0) |
| $1,2\text{-}C_6H_4(CH_3)_2$ | 2.2 | $C_6H_5CO_2CH_3$ | 0.8 |
| $C_6H_5CF_3$ | 1.7 | $C_6H_5OCH_3$ | 0.7 |

molybdenum atoms deposited with high arene flux react before the fluid crystallizes, while at low arene flux, the molybdenum atoms land on a matrix that is partially segregated. A substantial amount of the heat flux to the cold walls derives from the heats of condensation of the arenes. This is balanced by the loss of heat through the matrix and glass walls to the liquid-nitrogen bath. Thus, high arene flux will result in a higher condensation-surface temperature (also the matrix is thicker in the high flux experiments).

An important corollary is that the molybdenum atoms must react with the arenes in the high-flux system before the medium becomes rigid, since otherwise there would be no difference between the high- and low-flux cases.

## Experimental Section

The metal-atom reactor has been described.[13] Diethyl ether was dried over Na ribbon; hexane and benzene were refluxed over Na–K alloy by using benzophenone ketyl as an indicator. The 50-mil molybdenum wire was obtained from the H. C. Cross Co.[14] The molybdenum complexes are air sensitive and were handled with standard Schlenck techniques. NMR spectra were recorded in $C_6D_6$ dried over Na and vacuum distilled prior to use; all samples were sealed in vacuo. The solutions are stable indefinitely, $^1H$ NMR spectra were recorded on Varian A60, EM 360, or Brüker 200 spectrometers with $C_6D_6$ as a reference. $^{19}F$ NMR spectra were recorded on a JEOL PS-100 spectrometer operating at 93 MHz with fluorobenzene as an external reference. The upfield shifts were then extrapolated relative to $CFCl_3$ and are so reported.

Yields are based on the amount of molybdenum vaporized and are uncorrected. Melting points were obtained in capillary tubes sealed under nitrogen and are uncorrected. mass spectra were recorded on an AEI MS-902 or on a Kratos MS9/50 spectrometer. The parent-ion and fragmentation patterns exhibited the characteristic Mo isotopes pattern and are reported for the $^{98}Mo$ isotope except where noted. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer as KBr disks.

**CAUTION**: Molybdenum vaporizing at 2400 °C produces an intense white light, and the wire should not be observed directly. The black residues left after extraction with diethyl ether can be pyrophoric, and the reactor vessel should therefore be removed under a nitrogen flush.

The competition reactions were run in the same general way. The degassed solution of the desired mole ratio of arenes was introduced into the reactor by means of an addition tube equipped with a Fischer–Porter Teflon needle valve. After the metal-deposition phase, the matrix was warmed to room temperature and the unreacted arenes were removed by pumping. The material remaining was extracted several times with diethyl ether until the extract was clear. The extracts were filtered, the ether was removed on a Schlenk line, and samples were made up for analysis.

**Competition Reaction of 1,2-Dimethylbenzene and Fluorobenzene for Molybdenum.** A 22-mL sample of a 1:1 mole ratio solution of fluorobenzene/*o*-xylene was cocondensed with 592.6 mg (6.04 mmol) of molybdenum over a period of 45 min (flux of 0.5 mL/min). The $^1H$ NMR integral ratio was 2.63:1 for $(\eta^6\text{-}1,2\text{-}C_6H_4(C\mathit{H}_3)_2)_2Mo$:$(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(C\mathit{H}_3)_2)Mo$. The $^{19}F$ NMR integral ratio was 1:1.68 for $(\eta^6\text{-}C_6H_5F)_2Mo$:$(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)(\eta^6\text{-}C_6H_5F)Mo$. The product distribution was 11% $(\eta^6\text{-}C_6H_5F)_2Mo$, 38% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 51% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$.

**Competition Reaction of *tert*-Butylbenzene and Fluorobenzene for Molybdenum.** A 15.5-mL sample of a 1:1 mole ratio solution of *tert*-butylbenzene/fluorobenzene was cocondensed with 493.2 mg (5.03 mmol) of molybdenum over a period of 27 min (flux of 0.6 mL/min). The $^1H$ NMR integral ratio of aromatic to methyl protons was 1:1.17. The $^{19}F$ NMR integral ratio was 1.73:1 for $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5C(CH_3)_3)Mo$:$(\eta^6\text{-}C_6H_5F)_2Mo$. The product distribution was 11% $(\eta^6\text{-}C_6H_5F)_2Mo$, 37% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5C(CH_3)_3)Mo$, and 52% $(\eta^6\text{-}C_6H_5C(CH_3)_3)_2Mo$. A second experiment where 30 mL of a 1:1 solution was cocondensed with 499.8 mg (5.1 mmol) of Mo over 53 min (flux of 0.6 mL/min) had an $^1H$ NMR integration of 1:1.21 and an $^{19}F$ NMR integration of 2.03:1 with a product distribution of 9% $(\eta^6\text{-}C_6H_5F)_2Mo$, 35% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5C(CH_3)_3)Mo$, and 57% $(\eta^6\text{-}C_6H_5C(CH_3)_3)_2Mo$.

**Competition Reaction of Toluene and Fluorobenzene for Molybdenum.** A 25.5-mL sample of a 1:1 mole ratio solution of toluene/fluorobenzene was condensed with 510.9 mg (5.21 mmol) of molybdenum over a period of 39 min (flux of 0.7 mL/min). The $^1H$ NMR integral ratio of aromatic to methyl protons was 2.48:1. The $^{19}F$ NMR integral ratio was 1:2.49 for $(\eta^6\text{-}C_6H_5F)_2Mo$:$(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CH_3)Mo$. The product distribution was 8% $(\eta^6\text{-}C_6H_5F)_2Mo$, 38% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CH_3)Mo$, and 54% $(\eta^6\text{-}C_6H_5CH_3)_2Mo$. A second experiment where 35.5 mL of the 1:1 solution was cocondensed with 477.6 mg (4.87 mmol) of Mo for 65 min (flux of 0.5 mL/min) had an $^1H$ NMR integration of 2.57:1 and an $^{19}F$ integration of 1:2.59. The product distribution was 8% $(\eta^6\text{-}C_6H_5F)_2Mo$, 43% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CH_3)Mo$, and 48% $(\eta^6\text{-}C_6H_5CH_3)_2Mo$.

**Competition Reaction of Benzotrifluoride and Fluorobenzene for Molybdenum.** A 19.5-mL sample of a 1:1 mole ratio solution of benzotrifluoride/fluorobenzene was cocondensed with 497.3 mg (5.07 mmol) of molybdenum over a period of 34 min (flux of 0.6 mL/min). The $^{19}F$ integral ratio was 1:1.67:0.35:0.19 for $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5C\mathit{F}_3)\text{-}Mo$:$(\eta^6\text{-}C_6H_5C\mathit{F}_3)_2Mo$:$(\eta^6\text{-}C_6H_5\mathit{F})(\eta^6\text{-}C_6H_5CF_3)Mo$:$(\eta^6\text{-}C_6H_5\mathit{F})_2Mo$. The product distribution was 13% $(\eta^6\text{-}c_6H_5F)_2Mo$, 49% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CF_3)Mo$, and 38% $(\eta^6\text{-}C_6H_5CF_3)_2Mo$.

**Competition Reaction of *N*,*N*-Dimethylaniline and Fluorobenzene for Molybdenum.** A 14.0-mL sample of a 1:1 mole ratio solution of *N*,*N*-dimethylaniline/fluorobenzene was cocondensed with 511.3 mg (5.21 mmol) of molybdenum over a period of 34 min (flux of 0.4 mL/min). The $^1H$ NMR integral ratio was 1:1.28 for $(\eta^6\text{-}C_6H_5N\text{-}$

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(13) Dobson, J. E.; Remick, R. T.; Wilburn, B. E.; Skell, P. S. *Inorg. Synth.* **1979**, *19*, 80–86.

(14) H. Cross Co., 363 Park Avenue, Weekhawken, NJ, 07087.

$(CH_3)_2)_2Mo:(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5N(CH_3)_2)Mo$. The $^{19}F$ NMR integral ratio was 1:1.53 for $(\eta^6\text{-}C_6H_5F)_2Mo:(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5N(CH_3)_2)Mo$. The product distribution was 19% $(\eta^6\text{-}C_6H_5F)_2Mo$, 58% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5N(CH_3)_2)Mo$, and 23% $(\eta^6\text{-}C_6H_5N(CH_3)_2)_2Mo$.

**Competition Reaction of Methyl Benzoate and Fluorobenzene for Molybdenum.** A 13-mL sample of a 1:1 mole ratio solution of methyl benzoate/fluorobenzene was cocondensed with 594.8 mg (6.07 mmol) of molybdenum over the course of 34 min (flux of 0.4 mL/min). The $^1H$ NMR integral ratio was 1:1.59 for $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo:(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CO_2CH_3)Mo$. The $^{19}F$ NMR integral ratio was 1:0.98 for $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CO_2CH_3)Mo:(\eta^6\text{-}C_6H_5F)_2Mo$. The product distribution was 27% $(\eta^6\text{-}C_6H_5F)_2Mo$, 56% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5CO_2CH_3)Mo$, and 18% $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$.

**Competition Reaction of Anisole and Fluorobenzene for Molybdenum.** A 17.8-mL sample of a 1:1 mole ratio solution of anisole/fluorobenzene was cocondensed with 473.9 mg (4.83 mmol) of molybdenum over the course of 35 min (flux of 0.5 mL/min). The $^1H$ NMR integral ratio was 1:1.61 for $(\eta^6\text{-}C_6H_5OCH_3)_2Mo:(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5OCH_3)Mo$. The $^{19}F$ NMR integral ratio was 1.41:1 for $(\eta^6\text{-}C_6H_5F)_2Mo:(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5OCH_3)Mo$. The product distribution was 35% $(\eta^6\text{-}C_6H_5F)_2Mo$, 49% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}C_6H_5OCH_3)Mo$, and 15% $(\eta^6\text{-}C_6H_5OCH_3)_2Mo$.

**Competition Reaction of Fluorobenzene and *o*-Xylene (3:1) for Molybdenum.** A 22.5-mL sample of a 3:1 mole ratio solution of fluorobenzene/*o*-xylene was cocondensed with 518.5 mg of molybdenum over a period of 39 min (flux of 0.6 mL/min). The $^1H$ NMR integration was 1.33:1 for $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo:(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$. The $^{19}F$ NMR integration was 2.69:1 for $(\eta^6\text{-}C_6H_5F)_2Mo:(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$. The product distribution was 50% $(\eta^6\text{-}C_6H_5F)_2Mo$, 37% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 14% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$. A second experiment where 30 mL of a 3:1 solution was cocondensed with 593.7 mg (6.05 mmol) of Mo had an $^1H$ NMR ratio of 1.57:1 and an $^{19}F$ NMR integration ratio of 2.60:1. The product distribution was 49% $(\eta^6\text{-}C_6H_5F)_2Mo$, 39% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 12% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$.

**Competition Reaction of Fluorobenzene and *o*-Xylene for Molybdenum at a Low Flux.** A 2.7-mL sample of a 1:1 mole ratio solution of fluorobenzene/*o*-xylene was cocondensed with 509.5 mg (5.20 mmol) of molybdenum over a period of 24 min (flux of 0.1 mL/min). The $^1H$ NMR integral ratio was 9.57:1 for $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo:(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)(\eta^6\text{-}C_6H_5F)Mo$. The $^{19}F$ NMR ratio was 1:0.18 for $(\eta^6\text{-}C_6H_5F)_2Mo:(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$. The product distribution was 31% $(\eta^6\text{-}C_6H_5F)_2Mo$, 12% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 57% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$. A second experiment where 1.8 mL of a 1:1 solution was cocondensed with 603.1 mg (6.15 mmol) of Mo over a period of 16 min (flux of 0.08 mL/min) had a $^1H$ NMR ratio of 8.09:1 and $^{19}F$ NMR integral ratio of 1:0.28. The product distribution was 26% $(\eta^6\text{-}C_6H_5F)_2Mo$, 15% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 59% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$.

**Competition Reaction between Fluorobenzene and *o*-Xylene for Molybdenum at a High Flux.** A 30-mL sample of a 1:1 mole ratio solution of fluorobenzene/*o*-xylene was cocondensed with 158.2 mg (1.61 mmol) of molybdenum over a period of 38 min (flux of 0.8 mL/min). The $^1H$ NMR integral ratio was 1:1.67 for $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo:(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$. The $^{19}F$ NMR integral was 1.63:1 for $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo:(\eta^6\text{-}C_6H_5F)_2Mo$. The product distribution was 14% $(\eta^6\text{-}C_6H_5F)_2Mo$, 46% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 40% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$. A second experiment where 30 mL of a solution was cocondensed with 98 mg (0.1 mmol) of Mo over the course of 28 min (flux of 1.1 mL/min) had an $^1H$ NMR integral ratio of 1.0:2.04 and an $^{19}F$ NMR integral ratio of 1.51:1. The product distribution was 14% $(\eta^6\text{-}C_6H_5F)_2Mo$, 43% $(\eta^6\text{-}C_6H_5F)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 43% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$.

**Competition Reaction between Methyl Benzoate and *o*-Xylene for Molybdenum.** A 17.8-mL sample of a 1:1 mole ratio solution of methyl benzoate/*o*-xylene was cocondensed with 624.6 mg (6.37 mmol) of molybdenum over a period of 49 min (flux of 0.36 mL/min). The $^1H$ NMR integral ratio for $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo:(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$ was 1.91:1 and for $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo:(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$ was 1.37:1. The product distribution was 16% $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$, 61% $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 23% $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$. A second experiment where 18 mL of a 1:1 solution was cocondensed with 607.7 mg (6.20 mmol) of Mo over the course of 43 min (flux of 0.4 mL/min) had integral ratios of 1.78:1 and 1.32:1, respectively. The product distribution was 17% $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$, 60% $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$, and 23% $(\eta^6\text{-}C_6H_4(CH_3)_2)_2Mo$.

The crude reaction mixture from the second reaction was chromatographed on a coarse silica gel column. Two fractions were eluted with benzene, and one fraction was eluted with tetrahydrofuran (THF). The first fraction consisted of 123.5 mg (6.4%) of a green compound, which was identified as $(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)_2Mo$ by its $^1H$ NMR and mass spectra. The second fraction consisted of 371.3 mg (17.6%) of a golden compound, which was identified as $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)Mo$: high-resolution mass spectrum, found 340.0334, calcd 340.0360 ($C_{16}H_{18}O_2{}^{98}Mo$), found 338.0337, calcd 338.0352 ($C_{16}H_{18}O_2{}^{96}Mo$); IR (KBr disk) cm$^{-1}$ 3050 (w), 1730 (s), 1700 (s), 1605 (w), 1455 (s), 1440 (s), 1382 (w), 1315 (w), 1280 (s), 1190 (w), 1178 (w), 765 (m), 745 (m), 710 (s), 500 (w), 435 (w), 385 (w), 355 (w). The third fraction, eluted with THF, consisted of 80.1 mg (3.5%) of a red compound, which was identified as the known[5] $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$.

**Control Reaction of Methyl Benzoate with Molybdenum.** A three-necked 100-mL round-bottomed flask equipped with a stir bar and two addition tubes was attached to the reactor. One addition tube contained methyl benzoate and the other tube contained toluene. An 11-mL sample (87.9 mmol) of methyl benzoate was cocondensed with 554.3 mg (5.66 mmol) of molybdenum over a period of 79 min. As soon as the Mo wire broke, 15 mL of toluene was added to the forzene matrix. As the red matrix warmed to room temperature, it became brown. After removal of the unreacted substrates, the material was extracted with diethyl ether and the red solution filtered. Analysis by $^1H$ NMR and low-resolution mass spectroscopy showed that it was the known[5] $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$.

**Bis($\eta^6$-*tert*-butylbenzene)molybdenum(0).** A 22-mL sample (142 mmol) of *tert*-butylbenzene was cocondensed with 547.6 mg (5.7 mmol) of molybdenum over a period of 41 min. The light green matrix was warmed to room temperature, and the unreacted substrate was pumped off. The material was extracted with ether and filtered. Sublimation of the crude material at 50–51 °C gave 598.2 mg (28.7%) of an air-sensitive green solid: mp 109–110.5 °C; mass spectrum, *m/e* 366 (M$^+$), 294, 253; high-resolution mass spectrum; found 364.1223, calcd 364.1236 ($C_{20}H_{28}{}^{96}Mo$), found 360.1299, calcd 360.1253 ($C_{20}H_{28}{}^{92}Mo$); IR (KBr disk) cm$^{-1}$ 3060 (m), 2906 (m), 1472 (m), 1458 (m), 1435 (m), 1389 (m), 1380 (m), 1375 (m), 1355 (m)8 1128 (m), 1050 (m), 995 (m), 989 (m), 869 (m), 851 (m), 780 (ms), 762 (m), 699 (m), 512 (m), 489 (m), 435 (m), 410 (m), 370 (s).

**Bis($\eta^6$-*o*-xylene)molybdenum (0).** A 10-mL sample (82.9 mmol) of *o*-xylene was cocondensed with 394.3 mg (4.02 mmol) of molybdenum over a period of 46 min. The light green matrix was warmed to room temperature and the excess substrate removed by pumping. The material was extracted with ether and filtered. Sublimation of the crude material at 60 °C yielded 375.9 mg (30%) of an air-sensitive green solid: mp 175–178 °C (with marked dec); mass spectrum, *m/e* 310 (M$^+$); high-resolution mass spectrum, found 310.0621, calcd 310.0620 ($C_{16}H_{20}{}^{98}Mo$); IR (KBr disk) cm$^{-1}$ 3020 (m), 2900 (m), 1450 (m), 1382 (s), 1370 (m), 970 (m), 740 (m), 715 (m), 415 (s), 375 (s), 349 (s).

**Bis($\eta^6$-benzotrifluoride)molybdenum(0).** A 16-mL sample (130 mmol) of freshly distilled benzotrifluoride was cocondensed with 551.7 mg (5.63 mmol) of molybdenum over a period of 40 min. After the green matrix warmed to room temperature and the excess substrate was pumped off, the residue was extracted with ether and the solution filtered. The crude material can be purified by sublimation at 40–42 °C or by crystallization. Crystallization from hexane gave 748.1 mg (34%) of air-sensitive emerald green needles: mp 92–92.5 °C with darkening at 88.5 °C; mass spectrum, *m/e* 390 (M$^+$), 371 (–F), 263, 244 ($-C_6H_5CF_3$); high-resolution mass spectrum, found 389.9736, calcd 389.9742 ($C_{14}H_{10}F_6{}^{98}Mo$), found 388.9741, calcd 388.9744 ($C_{14}H_{10}F_6{}^{97}Mo$); IR (KBr disk) cm$^{-1}$ 3060 (w), 1475 (m), 1400 (m), 1325 (s), 1315 (s), 1265 (m), 1160 (s), 1120 (s), 1070 (s), 1045 (s), 980 (s), 855 (w), 865 (w), 810 (m, sh), 795 (s), 770 (m), 760 (m), 673 (s), 635 (s), 475 (s), 455 (s), 440 (s), 355 (s).

**Arene Exchange of Bis($\eta^6$-methyl benzoate)molybdenum(0) with Toluene.** A 30-mL sample of dry, degassed toluene was added to a Schlenck tube containing 113.7 mg (0.307 mmol) of $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$ and a stirring bar. A condenser and bubbler were attached, and the assembly was purged with $N_2$ for 10 min. The mixture was refluxed for 8 h. Analysis of the mixture by $^1H$ NMR (Brüker 200) and low-resolution mass spectroscopy showed that it consisted of 20% $(\eta^6\text{-}C_6H_5CO_2CH_3)(\eta^6\text{-}C_6H_5CH_3)Mo$, with the rest of the mixture $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$. The mixed complex had its M$^+$ ion at 326 *m/e*, and in the $^1H$ NMR (Brüker 200) spectrum, $\delta$ 3.47, s for the $-CO_2CH_3$, and at $\delta$ 1.72, s for the $-CH_3$, with the aromatic protons buried under the aromatic protons at $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$.

**Photolysis of Bis($\eta^6$-methyl benzoate)molybdenum(0).** A 70.5-mg sample (0.19 mmol) of $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$ dissolved in 5 mL of degassed toluene was syringed into an evacuable UV cell. The solution was then degassed and photolyzed for 63 h with a medium-pressure, water-cooled mercury lamp. Analysis of the material, after removal of the toluene, by low-resolution mass spectroscopy showed only the starting material to be present. In a second experiment a solution containing 29.7 mg (0.08 mmol) of $(\eta^6\text{-}C_6H_5CO_2CH_3)_2Mo$, 17 $\mu$L (0.08 mmol) of $C_6H_5CH_3$, and 0.75 mL of $C_6D_6$ was photolyzed for 21 h in an NMR tube

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with a medium-pressure Hanovia lamp. No evidence of exchange was observed in the $^1H$ NMR spectrum (Brüker 200).

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**Registry No.** ($\eta^6$-1,2-$C_6H_4(CH_3)_2)_2Mo$, 82963-82-4; ($\eta^6$-$C_6H_5F$)($\eta^6$-1,2-$C_6H_4(CH_3)_2$)Mo, 82963-83-5; ($\eta^6$-$C_6H_5F)_2Mo$, 52346-33-5; ($\eta^6$-$C_6H_5F$)($\eta^6$-$C_6H_5C(CH_3)_3$)Mo, 82963-84-6; ($\eta^6$-$C_6H_5C(CH_3)_3)_2Mo$, 82963-85-7; ($\eta^6$-$C_6H_5F$)($\eta^6$-$C_6H_5CH_3$)Mo, 82963-86-8; ($\eta^6$-$C_6H_5CH_3)_2Mo$, 12131-22-5; ($\eta^6$-$C_6H_5F$)($\eta^6$-$C_6H_5CF_3$)Mo, 82963-87-9; ($\eta^6$-$C_6H_5CF_3)_2Mo$, 82963-88-0; ($\eta^6$-$C_6H_5F$)($\eta^6$-$C_6H_5N(CH_3)_2$)Mo, 82963-89-1; ($\eta^6$-$C_6H_5N(CH_3)_2)_2Mo$, 52346-32-4; ($\eta^6$-$C_6H_5F$)($\eta^6$-$C_6H_5CO_2CH_3$)Mo, 82963-90-4; ($\eta^6$-$C_6H_5CO_2CH_3)_2Mo$, 52346-35-7; ($\eta^6$-$C_6H_5F$)($\eta^6$-$C_6H_5OMe$)Mo, 82978-82-3; ($\eta^6$-$C_6H_5OMe)_2Mo$, 52346-31-3; 1,2-dimethylbenzene, 95-47-6; fluorobenzene, 462-06-6; molybdenum, 7439-98-7; *tert*-butylbenzene, 98-06-6; toluene, 108-88-3; benzotrifluoride, 98-08-8; *N*,*N*-dimethylaniline, 121-69-7; methyl benzoate, 93-58-3; anisole, 100-66-3.

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# Dihydrido Olefin and Solvento Complexes of Iridium and the Mechanisms of Olefin Hydrogenation and Alkane Dehydrogenation

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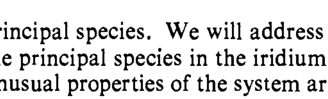
**Abstract:** Tests for homogeneity are applied to the catalysts $[Ir(cod)L_2]A/CH_2Cl_2/H_2$ (cod = 1,5-cyclooctadiene; A = $BF_4$; L = $PPh_3$, $PMePh_2$) and their possible generality is discussed. $[Ir(cod)L_2]A$ (L = $PPh_3$) reacts with $H_2$ and S (S = solvent) to give the isolable complexes $[IrH_2S_2L_2]A$ (**1**) in which the displacement order of the M–S groups is $H_2O \approx$ THF < *t*-BuOH < *i*-PrOH < $Me_2CO$ < EtOH < MeOH < MeCN. The utility of this order in understanding our alkane activation system based on **1** and the effects of S on catalytic hydrogenation are discussed. **1** (S = $H_2O$) reacts at −80 °C with olefins to give $[IrH_2(ol)_2L_2]A$ (ol = $C_2H_4$, $C_3H_8$) and $[IrH_2(ol)(H_2O)L_2]A$ (ol = PhCH=$CH_2$, $C_5H_8$, *t*-BuCH=$CH_2$). Their role in hydrogenation is discussed in the light of stepwise catalytic $^1H$ NMR studies at −80 to +25 °C, in which they appear to be intermediates in catalysis. A catalytic cycle is proposed. Selectivity in competitive experiments is discussed. The rhodium analogues do not exhibit similar properties.

## Introduction

In this paper we discuss rigorous tests of the homogeneity of hydrogenation catalysts, in particular $[Ir(cod)L_2]A$ (cod = 1,5-cyclooctadiene; L = $PR_3$; A = $BF_4$), as well as the synthesis and properties of two classes of related complexes $[IrH_2S_2L_2]A$ and $[IrH_2(ol)_2L_2]A$ (S = solvent; ol = olefin). The dihydrido olefin complexes are intermediates in the catalytic reaction and can be detected when the reaction is run in an NMR experiment in a stepwise fashion. A mechanism is proposed. Finally, the relevance of these results to our alkane dehydrogenation system is also discussed.

$[Ir(cod)L_2]A$ (cod = 1,5-cyclooctadiene; L = $PMePh_2$; A = $BF_4$) and related compounds are alkene hydrogenation complexes of an unusual type.[3,4] The reaction is highly solvent sensitive: in $CH_2Cl_2$ the system is very active and reduces even tetrasubstituted olefins very rapidly, but in EtOH it is almost inactive. In contrast, the Rh analogue shows a much less significant solvent dependence.[3] The rates (in catalytic cycles $h^{-1}$) for the reduction of 1-hexene by the following systems expressed as (metal, solvent) are as follows: (Ir, $CH_2Cl_2$), 5000 > (Rh, $CH_2Cl_2$), 4000 > (Rh, EtOH), 600 > (Ir, EtOH), 5. For hindered olefins, e.g., 1-methylcyclohexene, the rate advantage for the iridium system becomes even more marked: (Ir, $CH_2Cl_2$), 1900 $\gg$ (Rh, $CH_2Cl_2$), (Rh, EtOH), (Ir, EtOH), $\simeq 1$. These results cannot be understood by restricting oneself to considering the nature of the catalyst precursor charged into the reactor at the outset, but rather in terms of the properties of all the species present under catalytic conditions. In the cases we shall discuss, one species (the principal species) seems to predominate (>95%) in the reaction mixture. This may often be the case, since (as long as there are no dead-end side equilibria on the catalytic cycle) the occurrence of a markedly slow step in the catalytic cycle will tend to lead to a buildup of the preceding species. In the catalytic cycle shown, for example,



A will be the principal species. We will address the question of the nature of the principal species in the iridium catalyst in this paper. Other unusual properties of the system are the selectivity and insensitivity both to oxidizing functionality in the solvent or substrate and to the presence of air, and we shall also discuss the origin of some of these effects.

We have also developed a closely related alkane dehydrogenation system[4] involving $[IrH_2S_2L_2]BF_4$ (S = $H_2O$ or $Me_2CO$, L = $PPh_3$), which may share some intermediates with the hydrogenation system mentioned above.

It was suggested to us by several colleagues[5] that all these properties are very unusual for a homogeneous system, so unusual,

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