better understanding of the currently used agents and, in addition, should lead to a more rational design of new diagnostic organ imaging agents.

Acknowledgment. We thank Mr. Harvey Trop and Professor Alan Davison of the Massachusetts Institute of Technology for determining the magnetic susceptibilities of the complexes and for many helpful discussions and suggestions.

Registry No. $[Ph_4As][TcO(SCH_2CH_2S)_2]$, 69216-12-2; $[Ph_4As][TcO(SCH_2CH(CH_3)S)_2]$, 70209-06-2; $[Ph_4As][TcO(SCH_2CH_2CH_2S)_2]$, 70178-66-4; $NH_4{}^{99}TcO_4$, 34035-97-7.

Supplementary Material Available: Tables listing the infrared and Raman spectral data and the magnetic susceptibility data (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Chemistry of the (η^6-Arene)tris(pyridine)molybdenum(I) Cation

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The new, highly reactive, parmagnetic compounds $[(\eta^6\text{-arene})Mo(py)_3]PF_6$ (arene = benzene or toluene) have been prepared by the reaction of pyridine (py) with $[(\eta^6\text{-arene})_2Mo]PF_6$. The pyridine ligands are readily replaced by 1-methylimidazole (1-Me-Im) yielding $[(\eta^6\text{-}C_6H_6)Mo(1\text{-Me-Im})_3]PF_6$. The pyridine complexes also react with carbon monoxide yielding *trans*-$[Mo(CO)_2(py)_4]PF_6$ which readily and reversibly loses one molecule of carbon monoxide under nitrogen affording the compound $[Mo(CO)(py)_4]_n{}^{n+}(PF_6{}^-)_n$ ($n \geq 2$). Magnetic susceptibility and electrochemical data are also reported.

Introduction

We have previously reported the synthesis of a series of "electron-rich" 18-electron molybdenum complexes of the type $(\eta^6\text{-arene})MoL_3$ (arene = benzene or toluene; L = a tertiary phosphine or phosphite ligand) as part of a systematic search for highly reactive molybdenum systems.[1,2] However, the chemistry of these compounds was found to be limited by their kinetic inertness toward ligand substitution reactions. Recently, an investigation into the synthesis of related 17-electron molybdenum(I) complexes has been undertaken in order to obtain more reactive systems. This paper reports the preparation and characterization of the new paramagnetic cations $[(\eta^6\text{-arene})Mo(py)_3]^+$ (arene = benzene or toluene), $[(\eta^6\text{-}C_6H_6)Mo(1\text{-Me-Im})_3]^+$, and the carbon monoxide reaction products *trans*-$[Mo(CO)_2(py)_4]^+$ and $[Mo(CO)(py)_4]_n{}^{n+}$. Part of this work has been briefly communicated.[3]

Experimental Section

Physical Measurements. The infrared spectra were obtained on a Perkin-Elmer Model 237 grating spectrophotometer. The magnetic susceptibilities were obtained at room temperature by using the Gouy method. The conductivity measurements were carried out by using previously described methods.[4] The carbon monoxide liberation measurements were made on a high-vacuum line and the carbon monoxide gas was identified by infrared spectroscopy. The electrochemical experiments were carried out at room temperature at a platinum electrode by using a PAR Model 170 electrochemistry system. A saturated colomel reference electrode was used.

Materials. Literature methods were used to prepare $(\eta^6\text{-}C_6H_6)_2Mo$,[5] $(\eta^6\text{-}CH_3C_6H_5)_2Mo$,[6] and $[(\eta^6\text{-}C_6H_6)_2Mo]I$.[7] Reagent grade pyridine was distilled from CaH_2 before use. The 1-methylimidazole was obtained from Aldrich Chemical Co. and used without further purification. Common solvents were reagent grade and used without further purification. Ammonium hexafluorophosphate was purchased from Alfa. Tetra-*n*-butylammonium hexafluorophosphate[8] and $[Ni(py)_6](PF_6)_2$[9] were prepared by published methods. All reactions and purifications were carried out under a prepurified nitrogen or argon atmosphere.

Preparations. Bis(η^6-benzene)molybdenum(I) Hexafluorophosphate, $[(\eta^6\text{-}C_6H_6)_2Mo]PF_6$. The crude iodide salt obtained by treating a benzene solution of 5.1 g of $(\eta^6\text{-}C_6H_6)_2Mo$ with 2.6 g of iodine was isolated and taken up in 300 mL of warm methanol. The solution was filtered over Filter Aid and 5 g of NH_4PF_6 dissolved in 25 mL of degassed methanol quickly added. A yellow crystalline solid precipitated almost immediately. After the mixture stood at −15 °C for 2 h, the solid was collected, washed with 25 mL of cold methanol (2×), and dried in vacuo; yield 6.1 g (76%).

Bis(η^6-toluene)molybdenum(I) Hexafluorophosphate, $[(\eta^6\text{-}MeC_6H_5)_2Mo]PF_6$. A rapidly stirred solution of 12.3 g of $(MeC_6H_5)_2Mo$ in 250 mL of benzene was treated dropwise with a solution of 5.5 g of iodine in 74 mL of benzene. The crude iodide salt was collected and taken up in 250 mL of warm methanol. The dark orange solution was filtered over Filter Aid and 11.5 g of NH_4PF_6 in 25 mL of degassed methanol quickly added. The warm solution was reduced under vacuum to a volume of ca. 100 mL. After the mixture stood for 12 h at −15 °C, the yellow crystals were collected, washed with 35 mL of cold methanol, and dried in vacuo; yield 14.8 g (79%).

(η^6-Benzene)tris(pyridine)molybdenum(I) Hexafluorophosphate, $[(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3]PF_6$. A solution of 1.8 g of $[(C_6H_6)_2Mo]PF_6$ in 5 mL of pyridine was warmed to 55 °C for 1.5 h. A total of 50 mL of 95% ethanol was then added slowly at room temperature and the solution cooled to −15 °C for 5 h. The dark maroon crystalline solid was collected, washed with 15 mL of cold 95% ethanol, and dried

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Table I. Elemental Analyses and Solution Conductivity Data

	elemental analyses, %													
	calcd						found							
compd	C	H	N	P	F	Mo	C	H	N	P	F	Mo	Λ_0,[a] Ω^{-1}	M[b]
$[(C_6H_6)_2Mo]PF_6$	36.3	3.4					36.3	3.1						
$[(MeC_6H_5)_2Mo]PF_6$	39.6	3.8				22.6	37.8	4.1				22.9		
$[(C_6H_6)Mo(C_5H_5N)_3]PF_6$	45.3	3.8	7.2		20.5		44.7	3.8	7.6		19.9			
$[(MeC_6H_5)Mo(C_5H_5N)_3]PF_6$	46.3	4.1	7.4		20.0	16.8	46.3	3.9	7.5		20.0	17.1	74	900
$[(C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$	38.2	4.3	14.9		20.2		38.2	3.9	14.9		20.4			
$[Mo(CO)_2(C_5H_5N)_4]PF_6$	43.0	3.3	9.1	5.0	18.5	15.6	42.7	3.4	9.2	5.4	18.1	16.2	79	1120
$[Mo(CO)(C_5H_5N)_4]_n{}^{n+}(PF_6{}^-)_n$	43.1	3.5	9.6	5.3	19.5	16.4	42.9	3.6	9.9	5.4	19.8	16.6		
$[(n\text{-}Bu)_4N]PF_6$[c]													72	866
$[Ni(C_5H_5N)_6](PF_6)_2$[d]													70	1540

[a] Equivalent conductivity at 20 °C in pyridine. [b] Slope of $(\Lambda_0 - \Lambda_e)$ vs. $C_e{}^{1/2}$ plot. [c] Standard 1:1 electrolyte for conductivity measurements. [d] Standard 2:1 electrolyte.

in vacuo; yield 2.13 g (85%). An analytically pure sample was obtained by recrystallization from pyridine–benzene and finally pyridine–95% ethanol.

(η^6-Toluene)tris(pyridine)molybdenum(I) Hexafluorophosphate, $[(\eta^6\text{-}MeC_6H_5)Mo(C_5H_5N)_3]PF_6$. A solution of 2.5 g of $[(MeC_6H_5)_2Mo]PF_6$ in 5 mL of pyridine was warmed to 55 °C for 1.5 h. A total of 75 mL of 95% ethanol was slowly added causing small violet crystals to precipitate. After the mixture stood at −15 °C for 12 h, the solid was collected, washed with 10 mL of cold 95% ethanol, and dried in vacuo; yield 2.6 g (75%). A second recrystallization from pyridine–95% ethanol gave analytically pure material.

(η^6-Benzene)tris(1-methylimidazole)molybdenum(I) Hexafluorophosphate, $[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$. A solution of 2.2 g of $[(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3]PF_6$ in 10 mL of 1-methylimidazole was warmed to 45 °C for 0.5 h. Diethyl ether (110 mL) was added to the solution at room temperature and the mixture cooled to −15 °C. When all of the brown oil had settled out, the pale yellow supernatant was filtered off and the flask evacuated on a high-vacuum line at room temperature for 12 h. The resultant crystalline mass was well washed with 15 ml of cold (0°C) 95% ethanol. The yellow solid was collected and dried in vacuo; yield 1.5 g (68%).

***trans*-Tetrakis(pyridine)dicarbonylmolybdenum(I) Hexafluorophosphate, *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$.** A solution of 1 g of $[(\eta^6\text{-}MeC_6H_5)Mo(C_5H_5N)_3]PF_6$ in 5 mL of pyridine was stirred under a carbon monoxide atmosphere (30 lb/in.^{2} excess pressure over atmospheric) for 3 h at room temperature. The solution was placed on a 6 in. × 0.5 in. alumina column made up in pyridine, which was cooled to a temperature of ca. −30 °C by means of a jacket containing ethanol to which dry ice was periodically added. The compound was eluted as a rather broad band with cold pyridine. A total of ca. 50 mL of a bright red solution was collected in a flask cooled to −78 °C. The solution was then warmed to −15 °C and 200 mL of benzene quickly added. After the mixture stood at 0 °C for 12 h, the red solid was collected, washed with 25 mL of diethyl ether, and dried in vacuo. The product was recrystallized in the following manner: a 50:50 mixture of pyridine–diethyl ether (40 mL) was added to the solid with stirring at −15 °C. The ether was then slowly removed in vacuo until only a small quantity (ca. 5 mg) of solid remained undissolved. The solution was quickly filtered and 100 mL of diethyl ether was added dropwise at −15 °C. The dark red crystalline solid was collected, washed with 25 mL of diethyl ether, and dried in vacuo; yield 0.8 g (74%).

Tetrakis(pyridine)carbonylmolybdenum(I) Hexafluorophosphate, $[Mo(CO)(C_5H_5N)_4]_n{}^{n+}(PF_6{}^-)_n$. A solution of 0.2 g of *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ in 10 mL of pyridine was warmed to 65 °C for 3 h. Benzene (15 mL) was then slowly added to the warm solution with stirring. The red solid was collected, washed with 5 mL of pyridine, and dried in vacuo; yield 0.12 g (63%).

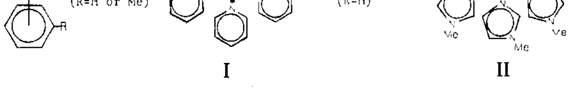
Reaction of $[Mo(CO)(C_5H_5N)_4]_n{}^{n+}(PF_6{}^-)_n$ with Carbon Monoxide. A suspension of 0.1 g of $[Mo(CO)(C_5H_5N)_4]_n{}^{n+}(PF_6{}^-)_n$ in 5 mL of pyridine was stirred at 50 °C under 1 atm of carbon monoxide for 2 h. The solution was then cooled to 0 °C and 100 mL of benzene slowly added. The crude *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ obtained was purified as described above; yield 0.05 g (50%). An IR spectrum showed the final product to be pure *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$.

Carbon Monoxide Liberation from *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ and $[Mo(CO)(C_5H_5N)_4]_n{}^{n+}(PF_6{}^-)_n$ + Iodine. A cold (0 °C) solution of 0.099 g (0.161 mmol) of *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ in 15 mL of pyridine was placed in one arm of a two-arm vessel. The other arm was filled with a solution of 2 g (1.6 mmol) of I_2 in 15 mL of pyridine. The solutions were then frozen in a dry ice–acetone bath and the vessel evacuated on a high-vacuum line. After complete degassing of the solutions, the temperature of which was not allowed to exceed −15 °C, the solution containing the *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ was warmed to ca. 50 °C and then periodically frozen in order to transfer any gas liberated to a calibrated vessel. After gas liberation had ceased, a total of 0.150 mmol of gas was collected, which is 93% of theory for liberation of 1 mol of CO/mol of *trans*-$[Mo(CO)_2[C_5H_5N)_4]PF_6$. The resultant deep red suspension of $[Mo(CO)(C_5H_5N)_4]_n{}^{n+}(PF_6{}^-)_n$ was then reacted with the pyridine–I_2 solution. A further 0.154 mmol (96%) of gas was liberated. The liberated gas was identified as CO by IR spectroscopy.

Results and Discussion

Arene Complexes. The reaction between $[(\eta^6\text{-arene})_2Mo]PF_6$ (arene = benzene or toluene) and pyridine at 50 °C affords the new 17-electron compounds $[(\eta^6\text{-arene})Mo(C_5H_5N)_3]PF_6$ (I) as air-sensitive, dark maroon, crystalline solids in high yield. The compounds are paramagnetic with $\mu_{eff} = 1.8\ \mu_B$ corresponding to one unpaired electron. Conductivity measurements in pyridine solution (Table I) are consistent with a 1:1 electrolyte formulation. A medium-intensity band at 790 cm^{-1} (KBr) in the IR region is assigned as the aromatic C–H out-of-plane bending mode (ν_{11}) and is within the normal range observed for metal–arene complexes.[10]

A solution of compound I (arene = benzene) in 1-methylimidazole quickly changes color from red to yellow at 25 °C. Addition of diethyl ether to the solution affords very air-sensitive yellow crystals of the compound $[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$ (II) in good yield. Compound II is paramagnetic with $\mu_{eff} = 1.9\ \mu_B$. A C–H out-of-plane bending frequency is observed at 775 cm^{-1} (KBr) in the IR region. The above reactions are summarized in eq 1.



I II

(1)

The facile reaction observed for compound I with 1-methylimidazole shows that it is very reactive toward ligand substitution reactions. This is in marked contrast to the Mo(0) analogues (η^6-arene)MoL$_3$ (L = CO or a tertiary phosphine) where replacement of a single L ligand, if it occurs at all, requires forcing conditions.[11] Solvents other than pyridine or a closely related nitrogen base cause rapid decomposition of compound I to intractable solids.

Carbonyl Complexes. A pyridine solution of compound I reacts readily with 1 or 2 atm of carbon monoxide giving a bright red solution from which dark red crystals of the

Table II. Cyclic Voltammetry Data

compd	$E_{1/2}$,[a] V	ΔE_p, mV	i_{Red}/i_{Ox}	scan rate, mV/s
$[(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3]PF_6$	−0.96[b]	95	1.4	200
		87	1.8	100
		85	2.4	50
$[(\eta^6\text{-}MeC_6H_5)Mo(C_5H_5N)_3]PF_6$	−1.09[b]	122	1.5	100
$[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$	ca. −1.7[c]	ca. 100	ca. 5.0	100
$[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$	ca. −2.0[d]	ca. 125	ca. 4.0	100
trans-$[Mo(CO)_2(C_5H_5N)_4]PF_6$	−1.03[b]	103	1.1	200
		93	1.1	100
		82	1.2	50

[a] Potentials vs. SCE. [b] Pyridine solution. [c] 1-Methylimidazole solution. [d] 90% pyridine–10% 1-methylimidazole solution.

compound $[Mo(CO)_2(C_5H_5N)_4]PF_6$ (III) can be obtained in good yield. The compound is paramagnetic with $\mu_{eff} = 1.8$ μ_B. The solid is only slowly decomposed by air. Conductivity measurements in pyridine solution (Table I) are consistent with a 1:1 electrolyte formulation. A single CO band in the IR region at 1800 cm^{-1} in pyridine solution [1790 cm^{-1} (KBr)] indicates a trans configuration of the carbonyl groups. The CO frequency observed for compound III is close to that observed for trans-$Mo(CO)_2(DPE)_2$[12] (DPE = 1,2-bis(diphenylphosphino)ethane), where $\nu_{CO} = 1820$ cm^{-1}, showing that the Mo(I) complex is very electron rich. It was thus surprising to find that compound III readily loses one molecule of carbon monoxide under a dinitrogen or argon atmosphere to give a very air-sensitive red solid of composition $[Mo(CO)(C_5H_5N)_4]_n^{n+}(PF_6^-)_n$ (IV). Compound III is regenerated on warming a suspension of compound IV in pyridine under 1 atm of carbon monoxide. The conversion of compound III to compound IV may proceed through an intermediate compound such as $[Mo(CO)(C_5H_5N)_5]PF_6$; see below. Compound IV is paramagnetic with $\mu_{eff} = 1.7$ μ_B per Mo atom. A very low carbonyl stretching frequency is observed at 1550 cm^{-1} (Nujol mull) in the IR region suggesting the presence of bridging carbonyl groups. The low solubility and highly reactive nature observed for compound IV have precluded obtaining conductivity data so that the value of n in the above formulation is unknown. Gas evolution measurements on a vacuum line confirm the loss of one CO molecule per molecule of compound III in pyridine solution. Reaction of the resultant pyridine solution of compound IV with an excess of iodine on the vacuum line results in quantitative evolution of the remaining coordinated carbon monoxide. The above reactions are summarized in eq 2.

$$[(\eta^6\text{-arene})Mo(C_5H_5N)_3]PF_6 \xrightarrow[py]{CO} \underset{III}{trans\text{-}[Mo(CO)_2(C_5H_5N)_4]PF_6} + \text{arene}$$

$$-CO\downarrow\uparrow+CO$$

$$\text{other products} + CO \xleftarrow[py]{\text{excess } I_2} \underset{IV}{(1/n)[Mo(CO)(C_5H_5N)_4]_n^{n+}(PF_6^-)_n} \quad (2)$$

Tatsumi et al.[13] have recently shown the conversion of trans-$Mo(CO)(N_2)(DPE)_2$ to $[Mo(CO)(DPE)_2]_n$ and $Mo(CO)L(DPE)_2$ (L = a donor compound such as pyridine). The IR carbonyl stretching frequency in $[Mo(CO)(DPE)_2]_n$ is observed at 1807 cm^{-1} (KBr) and in $Mo(CO)L(DPE)_2$ in the range 1690–1813 cm^{-1} depending on L. The value of n in $[Mo(CO)(DPE)_2]_n$ was not determined. However, the relatively high CO frequency of 1807 cm^{-1} indicates the presence of a terminal CO ligand in contrast to compound IV where a bridging CO ligand is strongly suggested by the low CO stretching frequency of 1550 cm^{-1}.

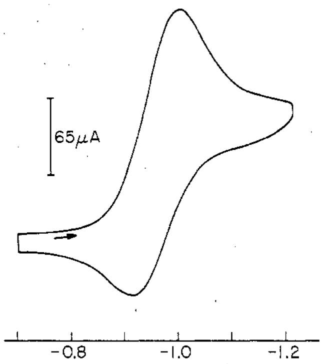


Figure 1. Cyclic voltammogram for the reduction of $[(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3]PF_6$ in 0.05 M $[(n\text{-}Bu)_4N]PF_6$–pyridine at Pt vs. SCE (25 °C). The scan rate is 100 mV/s.

The addition of diethyl ether to the supernatant pyridine solution resulting from the room-temperature conversion of trans-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ to $[Mo(CO)(C_5H_5N)_4]_n^{n+}(PF_6^-)_n$ yielded some fine pink needles along with some unreacted trans-$[Mo(CO)_2(C_5H_5N)_4]PF_6$. A new strong CO band is observed at 1750 cm^{-1} (KBr) in the IR region. Attempts to obtain a pure sample of this new compound have so far been unsuccessful. However, on the basis of the observations of Tatsumi et al.[13] it appears likely that the compound is $[Mo(CO)(C_5H_5N)_5]PF_6$.

Stable 17-electron cations such as $[Cr(CNR)_6]^+$,[14] $[Mn(CNR)_6]^{2+}$[15] (CNR = an alkyl or aryl isocyanide ligand), trans-$[M(CO)_2(DPE)_2]^+$ (M = Cr,[16] Mo,[17] W[17]), trans-$[Mn(CO)_2(DPE)_2]^{2+}$,[18] and $[(\eta^5\text{-}C_5H_5)Mn(CO)(DPE)]^+$[19] have previously been reported. Electrochemical investigations have shown that the compound $(\eta^5\text{-}C_5H_5)Mn(CNR)_3$ undergoes a facile one-electron oxidation to $[(\eta^5\text{-}C_5H_5)Mn(CNR)_3]^+$.[20] However, attempts to isolate a stable 17-electron cation were unsuccessful, and this was attributed to ligand dissociation. Electrochemical investigations on the cations cis,trans-$[M(CO)_2(L_2)_2]^+$ (M = Cr, Mo, W) (L_2 = 1,2-bis(diphenylphosphino)ethane[12] or bis(diphenylphosphino)methane[21]) showed that the cis complexes undergo a rapid rearrangement to the trans complexes. Furthermore, studies on the unstable, photochemically produced 17-electron carbonyls $(\eta^5\text{-}C_5H_5)Mo(CO)_3$,[22] $Mn(CO)_5$,[23,24] and $Re(CO)_5$[25] have shown that they are very labile toward ligand-substitution reactions. The facile ligand-substitution reactions observed for the complexes reported in the present work are further evidence that 17-electron metal complexes are likely to be quite reactive.

Electrochemistry. Figure 1 shows the cyclic voltammogram for the reduction of $[(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3]PF_6$ in pyridine solution. A partially reversible one-electron redox couple is obtained at −0.96 V vs. SCE. The data in Table II show that at slower scan rates the ratio of i_{Red}/i_{Ox} is considerably greater than 1.0 indicating fairly rapid decomposition of the $(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3$ formed. Similar results were observed for $[(\eta^6\text{-}MeC_6H_5)Mo(C_5H_5N)_3]PF_6$. Coulometry at a controlled potential of −1.4 V vs. SCE on the toluene derivative in

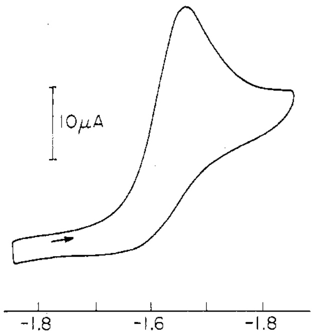


Figure 2. Cyclic voltammogram for the reduction of $[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$ in 0.05 M $[(n\text{-}Bu)_4N]PF_6$–1-methylimidazole at Pt vs. SCE (25 °C). The scan rate is 100 mV/s.

pyridine solution with $[(n\text{-}Bu)_4N]PF_6$ as supporting electrolyte gave $n = 1.05$, which is very close to the expected value of 1.0 for a one-electron reduction. Anodic scans on the benzene and toluene derivatives showed only irreversible oxidation waves beginning near 0 V vs. SCE which were not further investigated.

Figure 2 shows the cyclic voltammogram for the reduction of $[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$ in 1-methylimidazole solution. The couple observed at ca. −1.7 V vs. SCE is considerably less reversible than that observed for $[(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3]PF_6$. Similar results (Table II) were observed for $[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$ in 90% pyridine–10% 1-methylimidazole solution with $[(n\text{-}Bu)_4N]PF_6$ as supporting electrolyte. The shift toward a more negative potential on going from the pyridine compound to the 1-methylimidazole compound is consistent with the observations on Re(II) pyridine and imidazole complexes and is attributable to the poorer π-acceptor properties of the imidazole ring.[26]

The above electrode processes are described by eq 3.

$$[(\text{arene})MoL_3]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} (\text{arene})MoL_3 \rightarrow \text{other products} \quad (3)$$

Figure 3 shows the cyclic voltammogram for the reduction of *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ in pyridine solution under 1 atm of carbon monoxide. A highly reversible one-electron redox couple is observed at −1.03 V vs. SCE. Coulometry at a controlled potential of −1.3 V vs. SCE in pyridine solution with $[(n\text{-}Bu_4)N]PF_6$ as supporting electrolyte gave $n = 1.06$ which is close to the expected value of 1.0 for a one-electron reduction. The electrode processes are described by eq 4.

$$trans\text{-}[Mo(CO)_2(C_5H_5N)_4]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} trans\text{-}Mo(CO)_2(C_5H_5N)_4 \quad (4)$$

Anodic scans showed only irreversible oxidation waves beginning near 0.4 V vs. SCE which were not further investigated.

A reversible one-electron reduction has also been observed for the cation *trans*-$[Mo(CO)_2(DPE)_2]^+$.[12] Values of $E_{1/2}$ near 0 V were observed in several solvents vs. Ag/AgCl electrode. Unfortunately, direct comparison of the $E_{1/2}$ values cannot be made due to the different nature of the solvents used in the two studies and the presence of the aqueous–nonaqueous junction potential in the present work.

Conclusion

A series of "electron-rich" Mo(I) complexes have been synthesized by employing good donor ligands such as pyridine or 1-methylimidazole. The Mo(I) complexes are very reactive toward ligand replacement reactions which is consistent with previous observations on 17-electron complexes.[22-25] The high reactivity observed for the complexes reported here makes them attractive as precursors to new types of Mo complexes and possibly as catalytic species. The facile reaction of one of the compounds, $[(\eta^6\text{-}MeC_6H_5)Mo(C_5H_5N)_3]PF_6$, with methanethiol has recently been reported,[3] and further investigations are in progress.

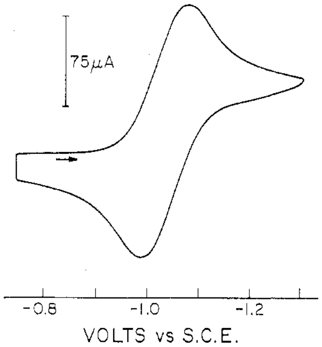


Figure 3. Cyclic voltammogram for the reduction of *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$ in 0.1 M $[(n\text{-}Bu)_4N]PF_6$–pyridine at Pt vs. SCE (25 °C). The scan rate is 100 mV/s.

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Registry No. $[(\eta^6\text{-}C_6H_6)_2Mo]PF_6$, 59464-76-5; $[(\eta^6\text{-}MeC_6H_5)_2Mo]PF_6$, 69547-10-0; $[(\eta^6\text{-}C_6H_6)Mo(C_5H_5N)_3]PF_6$, 69547-02-0; $[(\eta^6\text{-}MeC_6H_5)Mo(C_5H_5N)_3]PF_6$, 69547-08-6; $[(\eta^6\text{-}C_6H_6)Mo(C_3H_3N_2Me)_3]PF_6$, 70197-27-2; *trans*-$[Mo(CO)_2(C_5H_5N)_4]PF_6$, 70197-29-4; $[Mo(CO)(C_5H_5N)_4]_n{}^{n+}(PF_6^-)_n$, 70197-31-8; $(\eta^6\text{-}C_6H_6)_2Mo$, 12129-68-9; $(\eta^6\text{-}MeC_6H_5)_2Mo$, 12131-22-5.

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