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Inorganica Chimica Acta 281 (1998) 153–159

Inorganica Chimica Acta

Synthesis and characterization of arene, mono- and dihydrido-arene, monohydrido-cyclopentadienyl, and phosphite complexes of molybdenum containing the tridentate ligand $PhP(CH_2CH_2PPh_2)_2$

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Received 20 March 1997; accepted 20 February 1998

Abstract

The reduction of $[MoCl_3(TRI)]$, where $TRI = PhP(CH_2CH_2PPh_2)_2$, with sodium amalgam in benzene, toluene or anisole resulted in the formation of the corresponding $[Mo(\eta^6\text{-arene})(TRI)]$ complex. Each complex displayed a reversible one-electron oxidation in the cyclic voltammogram at ~ -1.0 V versus the ferrocenium/ferrocene couple at 0.0 V, corresponding to the oxidation of Mo(0) to Mo(1+). A second pseudo-reversible oxidation occurred at ~0.7 V more positive. Monoprotonation of the arene complexes with CF_3COOH in THF resulted in the isolation of $[Mo(H)(\eta^6\text{-arene})(TRI)][CF_3COO]$ (δ(MoH) ~ -6 ppm). In neat CF_3COOH or HBF_4, evidence of diprotonation of the arene complexes was observed in the ^1H NMR spectra. Upon work-up, only the monoprotonated product was isolated. $[Mo(TRI)(P(OMe)_3)]$ was formed by the reduction of $[MoCl_3(TRI)]$ in the presence of a small excess of $P(OMe)_3$. Attempts to prepare $[Mo(TRI)(PMe_3)_3]$ by a similar method resulted in a product that readily absorbed N_2 to form *fac*-$[Mo(N_2)(TRI)(PMe_3)_2]$. Yellow $[Mo(H)(\eta^5\text{-}C_5H_5)(TRI)]$ was formed by (i) the reduction of $[MoCl_3(TRI)]$ with sodium amalgam in the presence of cyclopentadiene, or (ii) heating *fac*-$[Mo(N_2)(TRI)(PMe_3)_2]$ with cyclopentadiene in heptane, or (iii) heating *trans*-$[Mo(N_2)_2(TRI)(PPh_3)]$ with cyclopentadiene in THF.

Keywords: Molybdenum complexes; Arene complexes; Phosphite complexes; Hydride complexes

1. Introduction

Polydentate ligands such as cyclopentadienyl, arenes, chelating organophosphines and pyrazoylborates have been used extensively to stabilize unusual transition metal complexes and to control the number of coordination sites available for metal-based chemistry [1]. The reduction of $[MoCl_3(tri)]$, where tri = tridentate organophosphine, under various conditions in the presence of potential ligands represents a useful method of preparing low-valent molybdenum complexes that retain the tridentate ligand [2,3]. Thus, the reduction of $[MoCl_3(TRI)]$, where $TRI = PhP(CH_2CH_2PPh_2)_2$, in THF with sodium amalgam produced (i) *trans*-$[Mo(N_2)_2(TRI)(PPh_3)]$ with excess N_2 and 1 equiv. of PR_3 ($PR_3 = PPh_3$ and PPh_2Me) [4], (ii) *fac*-$[Mo(N_2)(TRI)(PMe_2Ph)_2]$ with 4 equiv. of N_2 and 2 equiv. of PMe_2Ph [5], (iii) $[Mo(N_2)(TRI)(L_2)]$, where $L_2 = Me_2PCH_2PMe_2$, $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, and $1,2\text{-}C_6H_4(AsMe_2)_2$, with excess N_2 and 1 equiv. of L_2 [5], and (iv) $[Mo(\eta^6\text{-}ArPAr_2)(PAr_3)_3]$, where $Ar = 4\text{-}MeOC_6H_5$, with 1 equiv. of PAr_3 under argon [6]. Dahlenburg and Pietsch [3] carried out similar reduction reactions starting with $[MoCl_3(TRIP)]$, where $TRIP = RP(CH_2CH_2CH_2PPh_2)_2$ (R = Me, Ph), which led to the isolation and characterization of complexes such as *trans*-$[Mo(N_2)_2(TRIP)(PMe_{3-n}Ph_n)]$ (TRIP, R = Ph; n = 0, 1, 2), *cis*- and *trans*-$[Mo(N_2)_2(TRIP)(PMe_3)]$ (TRIP, R = Me), $[MoH_2(TRIP)(PMe_3)_2]$, and $[Mo(\eta^6\text{-}Ar)(TRIP)]$, where $Ar = C_6H_6$, C_6H_5Me and $1,3,5\text{-}C_6H_3Me_3$. Morris and coworkers recognized the value of the reduction method to prepare a series of η^6-arene–molybdenum complexes especially of the type $[Mo(\eta^6\text{-}ArPR_2)(PR_3)_3]$ [7]. The first complex of this type, $[Mo(\eta^6\text{-}C_6H_5PMe_2)(PMe_2Ph)_3]$, was prepared by Chatt and Wedd by reducing a mixture of $[MoCl_3(THF)_3]$ and PMe_2Ph with magnesium under argon [8,9]. Previously, Green and Silverthorn [10] prepared complexes of the type $[Mo(\eta^6\text{-arene})(PR_3)_3]$ by the reaction of $[Mo(\eta^6\text{-arene})_2]$ with a phosphine or phosphite. They studied the mono- and dipro-

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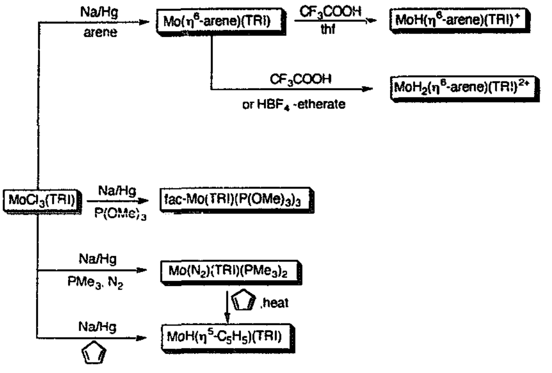
0020-1693/98/$ - see front matter
PII S0020-1693(98)00162-5



Scheme 1.

tonation of the complexes, the results of which can be related to the basicity of the PR_3 ligands. We became interested in the observation of Morris and coworkers that one of the phosphines in $[Mo(\eta^6\text{-}C_6H_5PMePh)(PMePh_2)_3]$ was labile and could be replaced by CO, t-BuNC, CH_3CN, PMe_3, PMe_2Ph, and N_2 [7]. Such mixed-ligand complexes have been prepared from $[Mo(\eta^6\text{-arene})_2]$, e.g. $[Mo(\eta^6\text{-}C_6H_5\text{-}Me)((C_2F_5)_2PCH_2CH_2P(C_2F_5)_2)(N_2)]$ [11].

In this paper we describe the results of the reduction of $[MoCl_3(TRI)]$ in the presence of different substrates. Included are the synthesis and characterization of (i) a series of η^6-arene complexes of molybdenum containing TRI and (ii) $[MoH(\eta^5\text{-}C_5H_5)(TRI)]$. This method was also used to prepare the mixed phosphine–phosphite complex $[Mo(TRI)(P(OMe)_3)_3]$. The results of protonation of the arene complexes are discussed. Some of this work, which is summarized in Scheme 1, has appeared previously [12].

2. Experimental

All reactions were performed under an atmosphere of high purity dinitrogen or argon. All solvents were dried rigorously by heating at reflux over an appropriate drying agent, followed by distillation under N_2. Solvents were saturated with N_2 or Ar immediately prior to use. Chemicals were purchased from commercial sources and used without further purification. $[Mo(\eta^6\text{-MeO-4-}C_6H_4)P(C_6H_4OMe\text{-}4)_2(TRI)]$ and $[MoCl_3(TRI)]$, which is a mixture of *fac* and *mer* isomers in solution [13], were prepared by published methods [4,6]. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Proton, ^{31}P and ^{13}C NMR spectra were recorded on either a Varian VXR-200 spectrometer (^1H 200 MHz, ^{31}P 81 MHz), a GE Ω-300 (^1H 300 MHz, ^{31}P 122 MHz, ^{13}C 76 MHz) or a GE Ω-500 (^1H 500 MHz, ^{31}P 202 MHz, ^{13}C 126 MHz). All ^{31}P and ^{13}C NMR spectra were proton decoupled. All chemical shifts are referenced to Me_4Si (^1H and ^{13}C) and PPh_3 (^{31}P) −5.8 ppm (versus 85% H_3PO_4 = 0.0 ppm). Phosphorus atom assignments are as follows: $PhP_b(CH_2CH_2P_aPh_2)_2$, br broad, qu quintet. FT-IR spectra were recorded using an Analect RFX-65 FT-IR spectrometer. Cyclic voltammetry was performed in a two-compartment three-electrode cell. The working electrode was a platinum wire, which was probed by a Luggin capillary connected to a silver pseudo-reference electrode; a tungsten auxiliary electrode was employed. The electrolyte was 0.2 M $[Bu_4N][PF_6]$ in dry distilled THF. Potentials quoted are referenced to the ferrocenium/ferrocene couple = 0.0 V (0.535 V versus SCE in this electrolyte) [14].

2.1. Preparation of $[Mo(\eta^6\text{-}C_6H_6)(TRI)]$

Benzene (10 ml) and $[MoCl_3(TRI)]$ (0.50 g, 0.68 mmol) were added to sodium amalgam (Na/Hg, 0.6 g/124 g) and the mixture stirred (18 h) under argon. The brown solution was decanted through Celite and reduced to ~2 ml. Methanol (15 ml) was added and N_2 bubbled through the solution to complete precipitation of the yellow product. The solid was washed with methanol (2×25 ml) and dried in vacuo. The yield of product was 0.2 g (0.3 mmol, 40%). ^{31}P NMR (C_6D_6): δ 87.21 (d, 2P, $^2J(P_a\text{–}P_b)$ = 16.6 Hz, P_a), 104.2 (t, 1P, P_b). ^1H NMR (C_6D_6): δ 8.0–6.6 (m, 25H, Ph), 4.07 (q, 6H, $^3J(H\text{–}P)$ = 2 Hz, C_6H_6), 2.1 (m, 4H, PCH_2), 1.7 (m, 4H, PCH_2). ^{13}C NMR (toluene): δ 74.8 (s, C_6H_6). *Anal.* Calc. for $C_{40}H_{39}MoP_3$: C, 67.8; H, 5.55; P, 13.1. Found: C, 65.4; H, 5.49; P, 14.5%.

2.2. Preparation of $[Mo(\eta^6\text{-}C_6H_5OMe)(TRI)]$

This complex was prepared similarly in 52% yield. ^{31}P NMR (CD_2Cl_2): δ 87.5 (d, 2P, $^2J(P_a\text{–}P_b)$ = 13.9 Hz, P_a), 102.6 (t, 1P, P_b). ^1H NMR (CD_2Cl_2): δ 8.0–7.0 (m, 25H, Ph), 3.93 (br s, 2H, C_6H_5), 3.85 (br s, 1H, C_6H_5), 3.73 (br s, 2H, C_6H_5), 2.84 (s, 3H, OCH_3), 2.5 (m, 2H, PCH_2), 2.3 (m, 2H, PCH_2), 1.7 (m, 2H, PCH_2), 1.1 (m, 2H, PCH_2). ^{13}C NMR (C_6D_6): δ 114.3, 76.50, 69.31, 63.84 (all s, η^6-C_6H_5), 55.30 (s, OCH_3), 32.9 (m, CH_2), 31.0 (m, CH_2). *Anal.* Calc. for $C_{41}H_{41}MoOP_3$: C, 66.7; H, 5.60; P, 12.6. Found: C, 66.2; H, 5.55; P, 12.8%.

2.3. Preparation of $[Mo(\eta^6\text{-}C_6H_5CH_3)(TRI)]$

This complex was prepared similarly in 30% yield. ^{31}P NMR (THF): δ 87.81 (d, 2P, $^2J(P_a\text{–}P_b)$ = 15.4 Hz, P_a), 104.81 (t, 1P, P_b). ^1H NMR (C_6D_6): δ 7.9–6.8 (m, 25H, Ph), 4.3 (m, 1H, C_6H_5), 4.0 (m, 4H, C_6H_5), 2.2 (m, 4H, PCH_2), 1.8 (m, 2H, PCH_2), 1.70 (s, 3H, CH_3), 0.8 (m, 2H, PCH_2). ^{13}C NMR (THF): δ 109.2, 75.8, 75.7, 71.0 (all s, η^6-C_6H_5), 20.4 (s, CH_3). *Anal.* Calc. for $C_{41}H_{41}MoP_3$: C, 68.1; H, 5.72; P, 12.9. Found: C, 67.4; H, 5.52; P, 13.6%.

2.4. Preparation of $[Mo(\eta^6\text{-}C_{10}H_8)(TRI)]$

Naphthalene (0.48 g, 3.74 mmol), $[MoCl_3(TRI)]$ (0.5 g, 0.68 mmol) and THF (30 ml) were added to sodium amalgam (Na/Hg, 0.48 g/117 g). The reaction was stirred (1 h) under argon and then under dinitrogen (15 h). The product was isolated in 40% yield by the method reported above. ^{31}P NMR (toluene): δ 81.02 (d, 2P, $^{2}J(\mathrm{P_a{-}P_b}) = 13.8$ Hz, $\mathrm{P_a}$), 112.08 (t, 1P, $\mathrm{P_b}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 8.0–6.5 (m, 29H, PPh and η^6-$\mathrm{C_6H_4C_4}H_4$), 4.2 (m, 2H, η^6-$\mathrm{C_6}H_4\mathrm{C_4H_4}$), 3.9 (m, 2H, η^6-$\mathrm{C_6}H_4\mathrm{C_4H_4}$), 2.2–1.6 (m, 8H, $\mathrm{PCH_2}$). *Anal.* Calc. for $\mathrm{C_{44}H_{41}MoP_3}$: C, 69.7; H, 5.45. Found: C, 64.7; H, 5.22%.

2.5. Preparation of [Mo(TRI)(P(OMe)$_3$)$_3$]

A mixture of THF (20 ml), [$\mathrm{MoCl_3}$(TRI)] (0.516 g, 0.700 mmol) and $\mathrm{P(OMe)_3}$ (0.284 ml, 2.29 mmol) was added to sodium amalgam (Na/Hg, 0.156 g/20 g). The reaction was stirred (18 h) under dinitrogen before the yellow–brown solution was decanted through Celite. The volume of solution was reduced to ~8 ml and pentane (30 ml) was added to precipitate a yellow solid. The yield was 0.323 g (0.322 mmol, 46%). Frequently there is a small amount of the other isomer present. The product can be recrystallized from THF:MeOH (1:2 by volume). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 66.5 (m, 2P, $\mathrm{P_a}$), 92.8 (dt, 1P, $^{2}J(\mathrm{P_b{-}P_d}) = 155.8$ Hz, $^{2}J(\mathrm{P_b{-}P_c}) = 28.5$ Hz, $\mathrm{P_b}$), 168.9 (m, 2P, $\mathrm{P_c}$), 178.1 (dq, 1P, $^{2}J(\mathrm{P{-}P}) \approx 38$ Hz, $\mathrm{P_d}$).

2.6. Stability of Mo(TRI)(P(OMe)$_3$)$_3$] in solution

A few milligrams of [Mo(TRI)(P(OMe)$_3$)$_3$] in $\mathrm{C_6D_6}$ were added to an NMR tube and the ^{31}P NMR spectrum monitored. After 5 days, less than 5% change was observed with no free $\mathrm{P(OMe)_3}$ detected. The experiment was repeated with a small quantity of $\mathrm{P(OMe)_3}$ added (< 1 equiv.). After 18 days, complete conversion to a second complex had occurred. ^{31}P NMR ($\mathrm{C_6D_6}$): δ 72.0 (apparent dd, 2P, $^{2}J(\mathrm{P{-}P}) = 38$ Hz, $^{2}J(\mathrm{P{-}P}) = 76$ Hz, $\mathrm{P_a}$), 100.1 (dt, 1P, $^{2}J(\mathrm{P_b{-}P_d}) = 148.9$ Hz, $^{2}J(\mathrm{P_b{-}P_c}) = 25.3$ Hz, $\mathrm{P_b}$), 146.0 (m, 2P, $\mathrm{P_c}$), 179.9 (dp, 1P, $^{2}J(\mathrm{P{-}P}) \approx 38$ Hz, $\mathrm{P_d}$).

2.7. Preparation of [Mo(N$_2$)(TRI)(PMe$_3$)$_2$]

A mixture of THF (30 ml), [$\mathrm{MoCl_3}$(TRI)] (0.5 g, 0.7 mmol) and $\mathrm{PMe_3}$ (0.14 ml, 1.3 mmol) was added to sodium amalgam (Na/Hg, 0.4 g/115 g). The reaction was stirred (24 h) under dinitrogen. The orange solution was decanted through Celite and the solvent was removed in vacuo. After drying (24 h) in vacuo, the orange–brown solid was placed in the dry box. The solid turned orange–red over 24 h (under $\mathrm{N_2}$). The yield was 0.4 g (0.4 mmol, 60%). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 90.2 (dm, 1P, $\mathrm{PPh_2}$), 72.6 (dm, 1P, PPh), 64.2 (m, 1P, $\mathrm{PPh_2}$), −11.4 (m, 2P, $\mathrm{PMe_3}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.8–6.6 (m, 25H, Ph), 1.71 (d, 9H, $^{2}J(\mathrm{H{-}P}) = 4.4$ Hz, PMe), 0.78 (d, 9H, $^{2}J(\mathrm{H{-}P}) = 5.1$ Hz, PMe), series of broad singlets 3.5–1.0 due to $\mathrm{PCH_2}$. IR (KBr): ν(NN) 1963 cm^{-1} (vs).

2.8. Preparation of [MoH(η^5-C$_5$H$_5$)(TRI)]

An excess of freshly distilled cyclopentadiene (0.66 ml) and THF (25 ml) were added to a mixture of [$\mathrm{MoCl_3}$(TRI)] (0.4 g, 0.5 mmol) and sodium amalgam (Na/Hg, 0.3 g/70 g) cooled to 0°C. The reaction mixture was stirred (2 h at 0°C, and 4 h at room temperature) under $\mathrm{N_2}$. The yellow solution was decanted and filtered through Celite. The solution volume was reduced to ~5 ml and pentane (75 ml) was added to precipitate a yellow solid. The yield of product was 0.26 g (0.4 mmol, 70%). ^{31}P NMR ($\mathrm{CD_2Cl_2}$): δ 110.4 (d, 2P, $^{2}J(\mathrm{P_a{-}P_b}) = 30.2$ Hz, $\mathrm{P_a}$), 134.4 (t, 1P, $\mathrm{P_b}$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.8–7.0 (m, 25H, Ph), 3.93 (s, 5H, $\mathrm{C_5H_5}$), 2.8–2.4 (m, 2H, $\mathrm{CH_2}$), 2.4–2.0 (m, 2H, $\mathrm{CH_2}$), 2.0–1.4 (m, 4H, $\mathrm{CH_2}$), −7.38 (td, 1H, $^{2}J(\mathrm{H{-}P_a}) = 54.6$ Hz, $^{2}J(\mathrm{H{-}P_b}) = 9.6$ Hz, MoH). IR (KBr): ν(MoH) 1828 cm^{-1}. *Anal.* Calc. for $\mathrm{C_{39}H_{39}MoP_3}$: C, 67.26; H, 5.64. Found: C, 67.26; H, 5.81%. This complex was also prepared by heating a mixture of *trans*-[Mo($\mathrm{N_2}$)$_2$(TRI)($\mathrm{PPh_3}$)] and cyclopentadiene (4 equiv.) in heptane (25 ml) under argon for 5 h.

2.9. Preparation of [MoH(η^6-C$_6$H$_6$)(TRI)][CF$_3$COO]

[Mo(η^6-$\mathrm{C_6H_6}$)(TRI)] (0.19 g, 0.27 mmol) was dissolved in THF (20 ml) and $\mathrm{CF_3COOH}$ (0.44 ml, 5.6 mmol) was added. The mixture changed from brown–yellow to red–brown. The reaction was stirred for 15 min. The volume of the solution was reduced to 2 ml. Water (20 ml) was added and a black residue was obtained. The residue was recrystallized from THF/$\mathrm{H_2O}$ (5 ml/20 ml), THF/pentane (7 ml/40 ml), and then acetone/$\mathrm{H_2O}$ (5 ml/50 ml) to afford a pink-tan powder. The tan powder was dried in vacuo to yield 0.21 g (0.26 mmol, 95%). ^{31}P NMR (acetone-d_6): δ 90.22 (d, 2P, $^{2}J(\mathrm{P_a{-}P_b}) = 32.2$ Hz, $\mathrm{P_a}$), 110.3 (t, 1P, $\mathrm{P_b}$). ^{1}H NMR (acetone-d_6): δ 7.4 (m, 25H, Ph), 4.82 (s, 6H, η^6-$\mathrm{C_6H_6}$), 3.8–1.8 (m, 8H, $\mathrm{CH_2}$), −5.94 (td, 1H, $^{2}J(\mathrm{H{-}P_b}) = 3.6$ Hz, $^{2}J(\mathrm{HP_a}) = 49.0$ Hz, MoH). ^{13}C NMR (acetone-d_6): δ 94.67 (s, η^6-$\mathrm{C_6H_6}$). IR (KBr): ν(C=O) 1689 cm^{-1} (s).

2.10. Preparation of [MoH(η^6-C$_6$H$_5$Me)(TRI)][CF$_3$COO]

To [Mo(η^6-$\mathrm{C_6H_5Me}$)(TRI)] (0.2 g, 0.3 mmol) was added $\mathrm{CF_3COOH}$ (2 ml) in toluene (20 ml). Following the immediate reaction, $\mathrm{H_2O}$ (25 ml) was added. Volatiles were removed in vacuo to give a brown residue. The residue was washed with pentane (20 ml) and dried in vacuo. The product was recrystallized from acetone/$\mathrm{H_2O}$ (5 ml/30 ml) to give a red-tan powder which was dried in vacuo. The yield was 0.2 g (0.3 mmol, 90%). ^{31}P NMR (THF): δ 90.72 (d, 2P, $^{2}J(\mathrm{P_a{-}P_b}) = 32.1$ Hz, $\mathrm{P_a}$), 109.97 (t, 1P, $\mathrm{P_b}$). ^{1}H NMR (acetone-d_6): δ 7.9–7.2 (m, 25H, Ph), 4.93 (t, 2H, $^{2}J(\mathrm{P{-}H}) = 5.8$ Hz), 4.71 (d, 2H, $^{2}J(\mathrm{P{-}H}) = 5.5$ Hz), 4.17 (t, 1H, $^{2}J(\mathrm{P{-}H}) = 5.8$ Hz) (η^6-$\mathrm{C_6H_5}$), 3.1 (m, 2H, $\mathrm{PCH_2}$), 2.8 (m, 2H, $\mathrm{PCH_2}$), 2.3 (m, 2H, $\mathrm{PCH_2}$), 1.81 (s, 3H, $\mathrm{CH_3}$), −5.95 (t, 1H, $^{2}J(\mathrm{P_a{-}H}) = 51.5$ Hz, MoH). ^{13}C NMR (THF; η^6-$\mathrm{C_6H_5}$): δ 86.12 (s), 90.67 (s), 92.72 (s), 103.17 (s).

2.11. Preparation of [MoH(η^6-C$_6$H$_5$OMe)(TRI)][BF$_4$]

To [Mo(η^6-$\mathrm{C_6H_5OCH_3}$)(TRI)] (0.15 g, 0.20 mmol) in anisole (10 ml) was added $\mathrm{HBF_4 \cdot Et_2O}$ (1.0 ml, 8.2 mmol).

The mixture was stirred for 15 min. Water (50 ml) was added to precipitate a tan residue. The residue was washed with Et_2O (60 ml) to give 0.10 g of a yellow powder (0.12 mmol, 60%). ^{31}P NMR (acetone-d_6): δ 90.42 (d, 2P, $^2J(P_a{-}P_b) = 31.7$ Hz, P_a), 109.10 (t, 1P, P_b). ^1H NMR (acetone-d_6): δ 8.0–7.0 (m, 25H, Ph), 4.84 (t, 2H, $^2J(P{-}H) = 5.6$ Hz), 4.52 (d, 2H, $^2J(P{-}H) = 5.5$ Hz), 4.34 (t, 1H, $^2J(P{-}H) = 5.6$ Hz) (η^6-C_6H_5), 3.15 (s, 3H, OCH_3), 3.1 (m, 2H, PCH_2), 2.7 (m, 2H, PCH_2), 2.3 (m, 2H, PCH_2), 1.8 (m, 2H, PCH_2), −6.18 (td, 1H, $^2J(H{-}P_a) = 52.7$ Hz, $^2J(H{-}P_b) = 6.72$ Hz, MoH). (Minor component (see text): −5.93 (td, $^2J(H{-}P_a) = 49$ Hz, $^2J(H{-}P_b) = 4.0$ Hz, MoH).) ^{13}C NMR (acetone-d_6): δ 101.8, 88.5, 76.3, 67.8 (all s, η^6-C_6H_5), 56.1 (OCH_3). *Anal.* Calc. for $C_{41}H_{42}P_3BF_4OMo$: C, 59.6; H, 5.12; P, 11.2. Found: C, 56.7; H, 5.15; P, 13.0%.

2.12. Preparation of [MoH(η^6-MeO–4-C_6H_4P(C_6H_4OMe-4)$_2$)(TRI)][CF_3COO]

To 0.1 g (0.10 mmol) of [Mo(η^6-RPR_2)(TRI)] (R = C_6H_4OMe-4) in THF (5 ml) was added CF_3CO_2H (0.03 ml, 0.4 mmol) at −78°C. After 1 h, volatiles were removed, while the solution was warmed to room temperature, leaving an oily residue. The residue was washed with pentane (30 ml) and water (30 ml) to give a yellow powder. The powder was collected and dried in vacuo to give 0.05 g (0.05 mmol, 50%) of product. ^{31}P NMR (acetone-d_6): δ 83.62 (d, 2P, $^2J(P_a{-}P_b) = 28.7$ Hz, P_a), 101.73 (t, 1P, P_b), 13.12 (s, 1P, P_x). ^1H NMR (acetone-d_6): δ 8.0–6.6 (m, Ph, C_6H_4OMe), 4.7 (br s, 2H, η^6-C_6H_4OMe), 4.5 (br s, 2H, η^6-C_6H_4OMe), 3.7 (s, 6H, OCH_3), 3.25 (s, 3H, OCH_3), 3.5–1.8 (series of multiplets, PCH_2), −6.6 (tt, 1H, $^2J(H{-}P_a) = 55.4$ Hz, $^2J(H{-}P_b) \approx {}^2J(H{-}P_x) \approx 10$ Hz, MoH).

2.13. Reaction of [Mo(η^6-C_6H_6)(TRI)] with CF_3COOH

A few milligrams of [Mo(η^6-C_6H_6)(TRI)] were added to an NMR tube containing CF_3COOH. Within 15 min, the ^{31}P and ^1H NMR spectra indicated a single new species believed to be $[Mo(H)_2(\eta^6\text{-}C_6H_6)(TRI)]^{2+}$. The same species was formed in $HBF_4 \cdot$ etherate. ^{31}P NMR: δ 66.11 (d, 2P, $^2J(P_a{-}P_b) = 4.02$ Hz, P_a), 88.55 (t, 1P, P_b). ^1H NMR: δ 7.8–7.0 (m, Ph), 5.29 (s, 6H, η^6-C_6H_6), 3.0 (m, PCH_2), 2.2 (m, PCH_2), −4.43 (td, 2H, $^2J(H{-}P_a) = 42.7$, $^2J(H{-}P_b) = 22.8$ Hz, MoH_2). After several hours, resonances due to new phosphorus-containing species began to appear in the ^{31}P NMR spectrum.

2.14. Reaction of [Mo(η^6-C_6H_5OMe)(TRI)] with CF_3COOH

This reaction was carried out as described above with the same result. ^{31}P NMR: δ 68.05 (br s, 2P, P_a), 87.35 (br s, 1P, P_b). ^1H NMR: δ 7.9–6.7 (m, Ph), 5.5 (t, 1H, $J(H{-}H) = 7.2$ Hz, C_6H_5OMe), 4.98 (d, 2H, C_6H_5OMe), 4.6 (br s, 2H, C_6H_5OMe), 3.8 (s, 3H, OCH_3), 3.1 (m, PCH_2), 2.8 (m, PCH_2), 2.2 (m, PCH_2), −4.38 (td, 2H, $^2J(H{-}P_a) = 42.4$ Hz, $^2J(H{-}P_b) = 25.0$ Hz, MoH_2).

2.15. Reaction of [Mo(η^6-C_6H_5Me)(TRI)] with CF_3COOH

This reaction was carried out as described above with the same result. ^{31}P NMR: δ 68.44 (br s, 2P, P_a), 88.68 (br s, 1P, P_b). ^1H NMR: δ 7.9–6.8 (m, Ph), 5.2 (br s), 5.0 (m), 4.9 (s), 4.76 (br s), (5H, η^6-C_6H_5), 3.92 (m, 2H), 2.88 (m, 4H), 2.16 (m, 2H), (4CH_2, TRI), 2.24 (s, 3H, CH_3), −4.37 (td, 2H, $^2J(H{-}P_a) = 42.73$ Hz, $^2J(H{-}P_b) = 21.98$ Hz, MoH_2).

2.16. Reaction of [MoH(η^5-C_5H_5)(TRI)] with $CDCl_3$

To 0.15 g (0.22 mmol) of [MoH(η^5-C_5H_5)(TRI)] in ~0.5 ml of CD_2Cl_2 in an NMR tube was added 0.052 ml (0.64 mmol) of $CDCl_3$. The reaction was monitored by ^{31}P NMR spectroscopy. After 114 h, the ratio of reactant to product was 8:92. Pentane was added to precipate a red solid. ^{31}P NMR (CH_2Cl_2): δ 131.7 (t, 1P, $^2J(P_a{-}P_b) = 27$ Hz, P_b), 85.2 (d, 2P, P_a). FAB mass spectrum, $m/z = 732.1$ (M^+, calc. for [MoCl(η^5-C_5H_5)(TRI)], $C_{39}H_{38}{}^{35}ClP_3{}^{98}Mo = 732.1$). The product [MoCl($\eta^5$-$C_5H_5$)(TRI)] has been characterized completely by Cole et al. [13].

3. Results and discussion

3.1. Preparation and characterization of [Mo(η^6-arene)(TRI)]

The synthesis of the arene complexes was straightforward using the aromatic ligand as solvent, except in the case of naphthalene and PAr_3 [2,5,15] where THF was used as solvent. Generally, the elemental analyses of arene complexes and their derivatives were low in carbon. Purification of all complexes was continued until the ^{31}P NMR spectrum indicated the presence of a single diamagnetic phosphine-containing complex. The ^{31}P NMR spectra of all four complexes displayed a doublet and triplet with $J_{PP} \sim 15$ Hz. The presence of the η^6-arene group was clearly evident in the ^1H and ^{13}C NMR spectra which were as expected compared with published data, for example, (i) ^1H NMR, $[(C_6H_{6-n})(Me)_n]Mo(CO)_3$ [16], $[(C_6H_{6-n})(OMe)_n]Mo(CO)_3$ ($n = 0$–3) [17] and $[1,4\text{-}(C_6H_4XY)Mo(CO)_3]$ [18], and (ii) ^{13}C NMR, $[(C_6H_{6-n})(Me)_n]\text{–}Mo(CO)_3$ ($n = 3, 4$ and 6) [19] and 63 $[(arene)Cr(CO)_3]$ complexes [20]. The ring protons were shifted ~3 ppm upfield and in the case of the C_6H_6 complex the single resonance appeared as an apparent quartet owing to coupling to the three phosphorus atoms of TRI. Likewise the resonances due to the η^6-arene carbon atoms were shifted upfield by ~52 ppm; C-1 of the anisole complex was shifted 46 ppm.

The oxidation potential is related directly to the HOMO energy and hence is a measure of the relative electron richness

Table 1
Electrochemical data for [Mo(η^6-arene)(TRI)] complexes [a]

Complex	$E_{1/2}$	i_{pa}/i_{pc}	ΔE_p (mV)	E_p [b]
[Mo(η^6-C_6H_6)(TRI)]	−0.90	1.0	100	−0.27
[Mo(η^6-$C_6H_5CH_3$)(TRI)]	−0.93	1.0	84	−0.29
[Mo(η^6-$C_{10}H_8$)(TRI)]	−0.92	1.1	100	−0.20
[Mo(η^6-$C_6H_5OCH_3$)(TRI)]	−1.00	1.1	100	−0.25

[a] Potentials are quoted vs. the ferrocenium/ferrocene couple 0.0 V (0.535 V vs. SCE) and were measured by cyclic voltammetry in 0.2 M [NBu_4][PF_6]–THF at a Pt electrode using a scan rate of 50 mV s^{-1}.
[b] E_p is the peak potential of irreversible oxidation.

of the arene complexes. The results obtained from a cyclic voltammogram study of the arene complexes are listed in Table 1. Each complex displayed a reversible one-electron oxidation ~ −1 V versus the ferrocenium/ferrocene couple at 0.0 V, corresponding to the oxidation of Mo(0) to Mo(1+). The trend in $E_{1/2}$ values was as expected with the benzene complex being the most difficult to oxidize. The anisole complex was oxidized more easily than the other complexes, reflecting the importance of the π-donation of the OCH_3 substitutent. The $E_{1/2}$ value for [Mo(η^6-$C_6H_5PPh_2$)(TRI)], recorded at a vitreous carbon electrode under similar conditions, was −0.83 V [2]. A similar series of arene–molybdenum complexes prepared by Cotton et al. [7c] with η^6-$C_6H_5PR_2$ (PR_2 = PMePh or PMe_2) and monodentate phosphine ligands gave analogous results. Each complex in the TRI series displayed a second pseudo-reversible oxidation (E_p) at ~0.7 V more positive. No reduction wave was observed in THF for any of the complexes studied.

3.2. Protonation of [Mo(η^6-arene)(TRI)] complexes

Protonation of the arene complexes with (i) CF_3COOH or $HBF_4 \cdot Et_2O$ in solution resulted in the formation of a monohydride complex (arene = C_6H_6, $C_6H_5CH_3$, $C_6H_5OCH_3$ and 4-$CH_3OC_6H_4P(C_6H_5$–4-$OCH_3)_2$) and (ii) neat CF_3COOH or $HBF_4 \cdot OEt_2$ resulted in a dihydride complex (arene = C_6H_6, $C_6H_5CH_3$, $C_6H_5OCH_3$). These results were similar to those reported earlier by Green et al. [10c] and Morris et al. [7d] although with different acids. Protonation of [Mo(η^6-C_6H_6)(TRI)] with excess CF_3COOH in THF produced the monohydride [MoH(η^6-C_6H_6)(TRI)][CF_3COO] which was isolated as a pink-tan solid in 95% yield. In the IR (KBr) spectrum an absorption due to ν(C=O) of CF_3COO^- appeared at 1689 cm^{-1} but there was no absorption observed for ν(MoH). The hydride resonance appeared as a triplet of doublets at −5.94 ppm ($J(P_{trans}$–H) = 3.6, $J(P_{cis}$–H) = 49.0 Hz) in the ^{1}H NMR spectrum. In the monohydride derived from the $C_6H_5CH_3$ complex the hydride resonance appeared as a triplet at −5.95 ppm ($J(P_{cis}$–H) = 51.5 Hz and $J(P_{trans}$–H) ≈ 0 Hz). Monoprotonation of the $C_6H_5OCH_3$ complex with $HBF_4 \cdot OEt_2$ in anisole solution resulted in the formation of a monohydride. However, close inspection of the hydride region of the ^{1}H NMR spectrum revealed two sets of triplets of doublets in the ratio of 10:1. The hydride chemical shift (δ = −5.9 ppm) of the minor product is essentially identical with those for the hydrides derived from the C_6H_6 and $C_6H_5CH_3$ complexes whereas the hydride chemical shift and coupling constants due to the major product are slightly different: δ = −6.18 (J(P–H) = 52.7 and 6.7 Hz). Without further information, it is assumed that these two hydrides are isomers. Monoprotonation of molybdenum also occurred when [Mo(η^6-RC_6H_4)$P(C_6H_4R)_2$(TRI)] (R = 4-MeO) reacted with 4 equiv. of CF_3COOH in THF. The reaction was run at −78°C for 1 h before solvent and unreacted CF_3COOH were removed in vacuo. This procedure avoided the type of reaction reported by Morris et al. [7d] in which cleavage of the P–C(η^6-arene) bond occurred in the η^6-$C_6H_5PR_2$ ligand when complexes such as [Mo(η^6-$C_6H_5PPh_2$)($Ph_2PCH_2CH_2PPh_2$)(PPh_3)] were treated with strong acids like $HBF_4 \cdot OEt_2$ and CF_3SO_3H. On the basis of the crystal structures of similar [MoH(η^6-arene)(PR_3)$_3$]$^+$ complexes [7d,21–23], which have been shown to have a pseudo-square-based pyramidal geometry, we propose that the hydride ligand occupies a pseudo-equatorial position between the two terminal phosphorus atoms of the TRI ligand. Kowalski and Ashby have shown that monoprotonation of [Mo(η^6-arene)(TRIPOD)], where TRIPOD = $CH_3C(CH_2PPh_2)_3$, to yield the metal hydride involves initial exo protonation of the arene ligand to give an arenium ion complex followed by protonation of the metal by the endo hydrogen. Such a mechanism may be operating with the similar TRI ligand complexes.

Diprotonation of molybdenum was observed to occur when the arene complex was dissolved in CF_3COOH or $HBF_4 \cdot OEt_2$. Attempts to isolate the dihydrides were unsuccessful and resulted in recovery of the corresponding monohydride. Whereas monoprotonation of the neutral arene complexes resulted in a small downfield shift of the two phosphorus chemical shifts (~3 for P_a and ~6 ppm for P_b), diprotonation resulted in a large upfield shift (~21 for P_a and ~16 ppm for P_b). The hydride ligands appeared as a triplet of doublets at ~ −4.4 ppm with $J(P_{trans}$–H) significantly larger than for the monohydrides. In solution at room temperature the two hydride ligands were equivalent. As the temperature was lowered, the triplet of doublets coalesced gradually to a single broad resonance with a peak width at half-height of ~550 Hz at −77°C. The ^{1}H NMR spectra of analogous dihydrides prepared by Green et al. [22] with three PMe_3 ligands in place of TRI showed equivalent hydride ligands. At low temperature, however, the two hydrides became inequivalent. The positions of the two hydride ligands were not found in the crystal structure of [W(η^6-$C_6H_5CH_3$)(PMe_3)$_3$$H_2$][$PF_6$]$_2$. However, space-filling models and the P–W–P angles suggested that the two hydrides fit *trans* to the arene-ring centroid and *trans* to one of the PMe_3 ligands [22]. A similar structure is possible for [MoH_2(η^6-arene)(TRI)]$^{2+}$.

3.3. Preparation and characterization of [Mo(TRI)L$_3$]

The reduction of a mixture of [MoCl$_3$(TRI)], which is composed of *fac* and *mer* isomers in solution [13], and excess P(OMe)$_3$ in THF (18 h) under dinitrogen (or argon) produced [Mo(TRI)(P(OMe)$_3$)$_3$] (**Ia**) as a yellow solid in 62% yield. Complex **Ia** was stable in benzene solution upon irradiation (366 nm, 24 h) and when heated at 100°C (sealed tube, 6 h), but converted slowly completely to a second complex **Ib** over ~18 days at room temperature in the presence of ~1 equiv. of P(OMe)$_3$ (Fig. 1). The ^{31}P NMR spectra of both complexes exhibited four sets of resonances assigned to the six-phosphorus atom assembly. The spectra do not change when recorded at different magnetic fields, 81, 121 and 202 MHz. We were unable to simulate all sections of the ^{31}P NMR spectra. This may be because each complex may exist in more than one conformation owing to anticipated steric crowding around molybdenum [24]. Phosphite ligands are known to adopt different conformations [25].

Each possible isomer (*fac* or *mer*, Fig. 2) has C_s symmetry, although distortion from idealized geometry has been found in the solid state of complexes such as *fac*-[Mo(CO)$_3$(TRI)] [26], *fac*-[MoBr(TRI)(Me$_2$PCH$_2$PMe$_2$)] [27] and *fac*-[Mo(CO)(TRI)(Ph$_2$PCH$_2$PPh$_2$)] [28]. The ^{31}P NMR spectrum of *fac*-[Mo(TRI)(P(OMe)$_3$)$_3$] (Fig. 2) is expected to exhibit four sets of resonances whereas *mer*-[Mo(TRI)(P(OMe)$_3$)$_3$] (Fig. 2) is expected to exhibit five because of the positional differences of the two mutually *trans* phosphite ligands due to the fixed orientation of the unique phenyl group [29,30]. Thus the ^{31}P NMR data support the assignment of **Ia** as the *fac* isomer. According to the ^{31}P NMR spectrum, **Ib** has the same symmetry as **Ia** although there are significant changes in chemical shifts, particularly the 20 ppm upfield shift of the pair of phosphite ligands. With the data available it is not possible to identify **Ib** at this time.

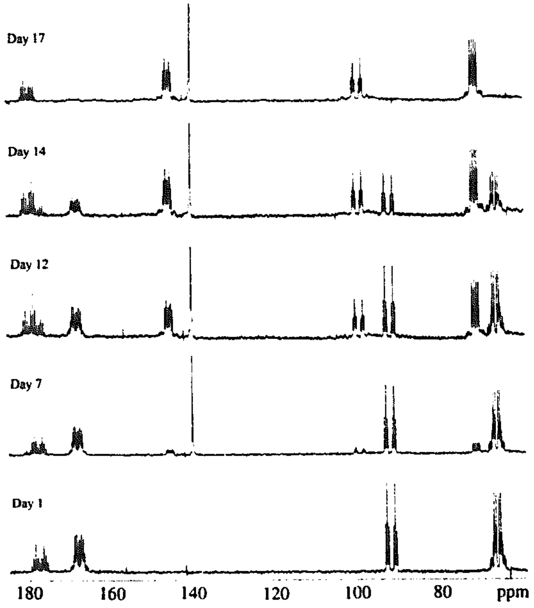


Fig. 1. Change in ^{31}P NMR spectrum of [Mo(TRI)(P(OMe)$_3$)$_3$] in C$_6$D$_6$ with time at room temperature. Approximately 1 mol of P(OMe)$_3$ (δ = 142.51) was added after the spectrum of day 1 was recorded.

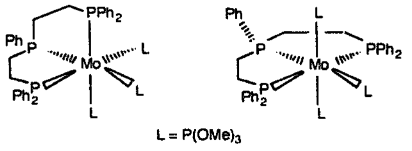


Fig. 2. *Fac* and *mer* isomers of [Mo(TRI)(P(OMe)$_3$)$_3$].

Reduction of [MoCl$_3$(TRI)] conducted in the presence of P(OEt)$_3$ produced [Mo(TRI)(P(OEt)$_3$)$_3$] which changes similarly although more slowly than the corresponding P(OMe)$_3$ complex, and with some decomposition.

Attempts to prepare [Mo(TRI)(PMe$_3$)$_3$] were unsuccessful. The reduction of a mixture of [MoCl$_3$(TRI)] and PMe$_3$ under argon produced a complex which rapidly formed the mono(dinitrogen) complex *fac*-[Mo(N$_2$)(TRI)(PMe$_3$)$_2$] (**II**) when the mixture was worked up under dinitrogen. The ^{31}P NMR spectrum of the reaction mixture under argon suggested that a complex containing one TRI and two PMe$_3$ per molybdenum was the major species present in solution. The ^{31}P NMR spectrum of **II** displayed three separate resonances for TRI: a multiplet at 64.2 ppm and two doublets of multiplets at 72.6 and 90.2 ppm respectively. The two PMe$_3$ ligands were part of an ABMQX spin system and appeared as a broad multiplet. These data best fit a structure in which TRI is *fac* with one terminal phosphorus *trans* to N$_2$ and the other *trans* to a PMe$_3$ ligand.

Complex **II** was formed directly in 64% yield when the reduction reaction was carried out under dinitrogen. Similar mono(dinitrogen) complexes have been prepared previously by this method [4]. No evidence was found for a bis(dinitrogen) complex. This contrasted with the interesting results reported by Dahlenburg and Pietsch [3] in which the reduction of *mer*-[MoCl$_3$[RP(CH$_2$CH$_2$CH$_2$PR$_2$)$_2$]] (R = Me or Ph), under dinitrogen and in the presence of a monodentate phosphine, formed not only mono- and bis(dinitrogen) complexes but also *cis* and *trans*, and *mer* and *fac* isomers.

3.4. Preparation and characterization of [MoH(η^5-C$_5$H$_5$)(TRI)]

The reduction of [MoCl$_3$(TRI)] together with excess cyclopentadiene in THF produced yellow [MoH(η^5-C$_5$H$_5$)(TRI)] (**III**) in 68% yield. Complex **III** can also be prepared by heating a mixture of (i) cyclopentadiene and *fac*-[Mo(N$_2$)(TRI)(PMe$_3$)$_2$] in heptane at 75°C under argon for 5 h or (ii) *trans*-[Mo(N$_2$)$_2$(TRI)(PPh$_3$)] and cyclopentadiene in THF under argon. In the ^{1}H NMR spectrum of **III** the hydride appeared as a triplet of doublets at −7.38 ppm. Green and coworkers [31] prepared [MoH(η^5-C$_5$H$_5$)-

$(PMe_3)_3]$ by the reaction of $[Mo(PMe_3)_6]$ with cyclopentadiene in petroleum at 80°C. The slow reaction of **III** with $CDCl_3$ (3 equiv.) in CD_2Cl_2 was monitored by observing the ^{31}P NMR spectrum. As resonances due to **III** decreased in intensity, corresponding resonances assigned to $[MoCl(\eta^5\text{-}C_5H_5)(TRI)]$ appeared, a complex that has been characterized recently by Poli et al., including a crystal structure [13].

Acknowledgements

We thank the National Institutes of Health (Grant GM-38613), the National Science Foundation EPSCoR Grant, and the University of Nebraska-Lincoln Research Council for support of this research. H.H.H. thanks the Hariri Foundation of Beirut for fellowship support. We thank Jeanenne Dean for help with the NMR work.

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