

## Preliminary communication

Synthesis and characterization of low valent complexes of molybdenum containing the tridentate ligand  $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  (TRI)

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## Abstract

Reduction of  $[\text{MoCl}_3(\text{TRI})]$  with sodium amalgam in the presence of potential ligands results in the formation of a series of new complexes containing  $\eta^3$ -TRI. These include  $[\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{R})(\text{TRI})]$  (where R = H, Me, MeO),  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{H})(\text{TRI})]$ ,  $[\text{Mo}(\text{TRI})(\text{P}(\text{OR})_3)_3]$  (where R = Me, Et), and *fac*- $[\text{Mo}(\text{N}_2)(\text{TRI})(\text{PMe}_2)_2]$ . Protonation of the arene complexes results in the formation of both mono- and diprotonated complexes.

**Keywords:** Molybdenum; Phosphine; Phosphite; Dinitrogen;  $\eta^6$ -Benzene complex;  $\eta^6$ -Arene complex

The reduction of  $[\text{MoCl}_3(\text{TRI})]$  (I) under various conditions [1] has led to the synthesis of a variety of low-valent molybdenum complexes including *trans*- $[\text{Mo}(\text{N}_2)_2(\text{TRI})(\text{PPh}_3)]$  [2], *fac*- $[\text{Mo}(\text{N}_2)(\text{TRI})(\text{PMe}_2\text{-Ph})_2]$  [3], and  $[\text{Mo}(\eta^6\text{-4-RC}_6\text{H}_4)\text{-P}(\text{C}_6\text{H}_4\text{R-4})_2(\text{TRI})]$  where R = H [1] or  $\text{CH}_3\text{O}$  [4]. In order to investigate the scope of this reaction, particularly in the synthesis of arene complexes, the reduction of  $[\text{MoCl}_3(\text{TRI})]$  with sodium amalgam was carried out in the presence of a series of potential ligands. The results of some of this work are summarized in Scheme 1.

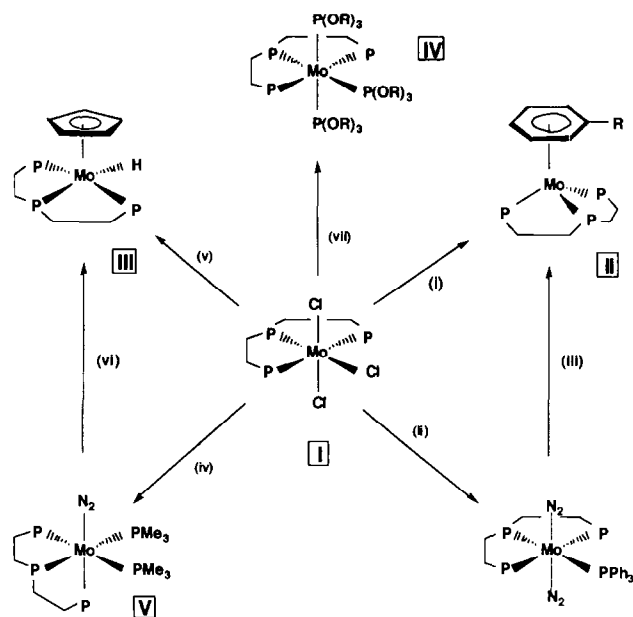
The reduction of  $[\text{MoCl}_3(\text{TRI})]$  with approx. 0.5% sodium amalgam with either benzene, toluene, or anisole as the solvent under an argon atmosphere for 24 h resulted in the formation of the corresponding complex  $[\text{Mo}(\eta^6\text{-arene})(\text{TRI})]$  in 20–50% yield. The new complexes were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectroscopy and elemental analysis. For example, yellow  $[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{TRI})]$  (II) displayed a doublet at 87.21 and a triplet at 104.2 ppm (relative to  $\text{PPh}_3$  at  $-5.8$  ppm) with  $J(\text{P-P}) = 16.6$  Hz in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The benzene ligand appeared as a multiplet due to coupling to the phosphorus atoms in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra centered at 4.07 [q,  $J(\text{H-P}) = 2$  Hz] and 74.82 ppm, respectively. The com-

plexes  $[\text{Mo}(\eta^6\text{-arene})(\text{TRI})]$  displayed two oxidation waves and no reduction wave in the cyclic voltammogram (0.23 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  electrolyte in THF: potentials are quoted versus the ferrocenium-ferrocene couple at 0.0 V). For II the first oxidation is reversible and occurs at  $-0.90$  V whereas the second oxidation occurs at  $-0.27$  V and is pseudoreversible.  $[\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{TRI})]$  underwent a one-electron reversible oxidation at  $-0.83$  V [1].

Protonation of II in THF with excess trifluoroacetic acid produced the monoprotonated species  $[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{H})(\text{TRI})][\text{CF}_3\text{COO}]$ , which was isolated as a pink-tan solid in 95% yield. The hydride resonance appeared as a doublet of triplets at  $-5.94$  ppm [ $J(\text{P-H}) = 4.0, 49.0$  Hz] in the  $^1\text{H}$  NMR spectrum. In the IR (KBr) spectrum an absorption due to  $\nu(\text{C}=\text{O})$  of  $\text{CF}_3\text{COO}^-$  appeared at  $1689\text{ cm}^{-1}$  but there was no absorption observed for  $\nu(\text{MoH})$ . Monoprotonation of the metal also occurred when  $[\text{Mo}(\eta^6\text{-RC}_6\text{H}_4)\text{-P}(\text{C}_6\text{H}_4\text{R})_2(\text{TRI})]$  (R = 4-MeO) was reacted with excess trifluoroacetic acid in THF at  $-77^\circ\text{C}$ . In contrast, Morris and coworkers [5] reported the cleavage of the  $\text{P-C}(\eta^6\text{-arene})$  bond in the  $\eta^6\text{-C}_6\text{H}_5\text{PR}_2$  ligand when complexes such as  $[\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2)(\text{PPh}_3)]$  were treated with strong acids.

Protonation of II with  $\text{HBF}_4$  ether produced the diprotonated complex  $[\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{H})_2(\text{TRI})][\text{BF}_4]_2$  which reverted to the monohydride upon attempted isolation. The hydride ligands appeared as a single

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Scheme 1. All reactions were carried out using a small excess of ca. 0.5% Na–Hg except reactions iii and vi. (i) Aromatic solvent  $C_6H_5R$  ( $R = H, Me, MeO$ ), 23 °C, 24 h. (ii)  $PPh_3$  (1 equivalent),  $N_2$  (60 psi), THF 23 °C, 24 h. (iii) THF, ( $R = PPh_2$  50–60 °C, 24 h. (iv)  $PMe_3$  (2 equivalents),  $N_2$  (1 atm.), THF, (v)  $C_5H_6$  (excess), THF, 23 °C, 6 h. (vi)  $C_5H_6$  (excess), heptane, 75 °C, 5 h. (vii)  $P(OR)_3$  ( $R = Me, Et$ ), THF, 23 °C, 3 h.

doublet of triplets at  $-4.43$  ppm [ $J(P-H) = 23.8, 42.7$  Hz] in the  $^1H$  NMR spectrum. Two equivalent hydrides are seeing the two different types of phosphorus atoms. As the temperature was lowered the doublet of triplets gradually coalesced to a single broad resonance with a peak width at half-height of 150 Hz at  $-50$  °C and  $\approx 550$  Hz at  $-70$  °C, respectively. Previously, Green and coworkers [6] reported the isolation and characterization of mono- and dihydrides formed by the reactions of acid with  $[Mo(\eta^6\text{-arene})(PR_3)_3]$  where arene =  $C_6H_6, C_6H_5Me, C_6H_3Me_3$  and  $R = Me, Et$ . At room temperature, the  $^1H$  NMR spectrum of the dihydrides showed equivalent hydride ligands coupled to three equivalent phosphine atoms whereas at  $-70$  °C the two hydride ligands were nonequivalent. The major difference in the two systems lies with the type of phosphine ligands: a tridentate ligand compared with three monodentate phosphines.

The reduction of **I** together with excess cyclopentadiene in THF produced yellow  $[Mo(\eta^5\text{-}C_5H_5)(H)(TRI)]$  (**III**) in 68% yield [8]. Complex **III** exhibited a doublet of triplets at  $-7.38$  ppm [ $J(H-P) = 9.6, 54.6$  Hz] in the  $^1H$  NMR spectrum due to the hydride. Green and coworkers [7] prepared  $[Mo(\eta^5\text{-}C_5H_5)(H)(PMe_3)_3]$  by the reaction of  $[Mo(PMe_3)_6]$  with cyclopentadiene in petroleum at 80 °C. Complex **III** reacted slowly with  $CDCl_3$  (3 equiv.) in  $CD_2Cl_2$  to yield  $[Mo(\eta^5\text{-}C_5H_5)(Cl)(TRI)]$ .

The reduction of a mixture of **I** and excess  $P(OMe)_3$  in THF (18 h) under dinitrogen (or argon) produced  $[Mo(TRI)(P(OMe)_3)_3]$  (**IVa**) [9] as a yellow solid in 62% yield. In solution, in the dark or under irradiation, **IVa** isomerized to **IVb** [10], with some decomposition noted. A similar reduction conducted in the presence of  $P(OEt)_3$  produced  $[Mo(TRI)(P(OEt)_3)_3]$ , which isomerized more slowly than the corresponding  $P(OMe)_3$  complex, with some decomposition. We believe that one isomer is mer and the other is fac. The  $^{31}P\{^1H\}$  NMR spectrum of both complexes exhibited four sets of resonances assigned to six different phosphorus atoms of the six-phosphorus atom assembly (AA'GNN'X or AA'GMNX) with phosphine phosphorus atoms  $P_a$  and phosphite phosphorus atoms  $P_c$  displaying second order patterns, respectively. The phosphorus atoms of the axial phosphites ( $P_c$ ) of the mer isomer (see Scheme 1) are not equivalent due to the phenyl group on the central phosphorus of TRI being held closer to one of the axial phosphites than the other [11,12]. However, despite this difference, which is not expected to be present in the seemingly more symmetrical fac isomer, it is not possible at this time to differentiate between the two isomers.

Attempts to prepare  $[Mo(TRI)(PMe_3)_3]$  were unsuccessful. The reduction of a mixture of **I** and  $PMe_3$  under argon produced a complex which rapidly formed the mono(dinitrogen) complex *fac*- $[Mo(N_2)(TRI)(PMe_3)_2]$  (**V**) [12] when the mixture was worked up under dinitrogen. Complex **V** was formed directly in 64% yield when the reduction reaction was carried out under dinitrogen; no evidence was found for a bis(dinitrogen) complex. Similar mono(dinitrogen) complexes have been prepared previously by this method [3]. The phosphite complexes displayed no evidence of reaction with dinitrogen either during preparation or by ligand displacement.

Mono- and bis(dinitrogen) complexes of molybdenum were also useful starting materials for the preparation of some of the complexes already listed. For example, the reaction of **V** with cyclopentadiene resulted in the loss of dinitrogen and  $PMe_3$  and the formation of **III**. Heating a sample of *trans*- $[Mo(N_2)_2(TRI)(PPh_3)]$  in THF produced  $[Mo(\eta^6\text{-}C_6H_5PPh_2)(TRI)]$ .

Investigations of the reduction reactions of **I** with other substrates is under way in order to (i) synthesize dinitrogen complexes of  $\{Mo(TRI)\}$  with different coligands and (ii) incorporate unsaturated ligands within the coordination sphere of  $\{Mo(TRI)\}$ .

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## References and notes

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- [8]  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  110.3 (d, 2P,  $J(\text{P}_a\text{P}_b) = 16.6$  Hz,  $\text{P}_a$ ), 134.3 (t, 1P,  $\text{P}_b$ ). Anal. Found (Calc.) for  $\text{C}_{39}\text{H}_{39}\text{P}_3\text{Mo}$ : C, 67.26 (66.97); H, 5.81 (6.02).
- [9] Phosphorus atom assignments [ $\text{P}_b(\text{CH}_2\text{CH}_2\text{P}_{a,a'}\text{Ph}_2)_2$ :  $\text{P}_{c,c',d}(\text{OMe})_3$ ]. **IVa**;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  66.5 (m, 2P,  $\text{P}_{a,a'}$ ), 92.81 (dt, 1P,  $J(\text{P}_b\text{P}_d) = 155.8$  Hz,  $J(\text{P}_b\text{P}_{c,c'}) = 28.5$  Hz,  $\text{P}_b$ ), 168.9 (m, 2P,  $\text{P}_{c,c'}$ ), 178.1 (dp, 1P,  $J(\text{PP}) \approx 38$  Hz,  $\text{P}_d$ ).
- [10] Phosphorus atom assignments [ $\text{P}_b(\text{CH}_2\text{CH}_2\text{P}_{a,a'}\text{Ph}_2)_2$ :  $\text{P}_{c,c',d}(\text{OMe})_3$ ]. **IVb**;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  72.0 (apparent dd, 2P,  $J(\text{PP}) = 38$  Hz,  $J(\text{PP}) = 75.8$  Hz,  $\text{P}_{a,a'}$ ), 100.1 (dt, 1P,  $J(\text{P}_b\text{P}_d) = 148.9$  Hz,  $J(\text{P}_b\text{P}_{c,c'}) = 25.3$  Hz,  $\text{P}_b$ ), 146.0 (m, 2P,  $\text{P}_{c,c'}$ ), 179.9 (dp, 1P,  $J(\text{PP}) \approx 38$  Hz,  $\text{P}_d$ ).
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