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Preliminary communication

η^6-ARENE AND CARBONYL DERIVATIVES OF THE $[PhP(CH_2CH_2PPh_2)]Mo^0$ MOIETY

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Summary

The synthesis of the η^6-arene complex $[(triphos)Mo(\eta^6\text{-}4\text{-}CH_3OC_6H_4)P(C_6H_4OCH_3\text{-}4)_2]$ (I, where triphos = $PhP(CH_2CH_2PPh_2)_2$) is reported as well as reactions of *trans*-$Mo(N_2)_2(triphos)[P(C_6H_4OCH_3\text{-}4)_3]$ with carbon monoxide to give *trans*- and *cis*-dicarbonyl- and *fac*-tricarbonyl-phosphine complexes of molybdenum(0).

The reduction of $MoCl_3$(triphos) with sodium amalgam in THF solution (eq. 1) under an argon atmosphere in the presence of added tertiary phosphine ($R = C_6H_4OCH_3\text{-}4$) produced the orange η^6-arene complex (I) in good yield.

$$MoCl_3(triphos) + PR_3 \xrightarrow[THF]{Na/Hg;Ar} \underset{(I)}{[(triphos)Mo(\eta^6\text{-}4\text{-}CH_3OC_6H_4)P(C_6H_4OCH_3\text{-}4)_2]} \quad (1)$$

An analogous compound, $(PhMe_2P)_3Mo(\eta^6\text{-}C_6H_5PMe_2)$, prepared under similar conditions has been reported [1] and its crystal structure determined [2].

In a typical reaction an excess of a 0.8% sodium amalgam was added to a flask containing 1.4045 g (1.906 mmol) of $MoCl_3$(triphos), 1.1440 g (3.246 mmol) of $P(C_6H_4OCH_3\text{-}4)_3$ and 150 ml of tetrahydrofuran (THF). The mixture was stirred under an argon atmosphere for 3 h. The resulting orange-brown solution was filtered through Celite using a fine frit. The filtration was repeated. While argon was bubbled through the filtrate, methanol was added

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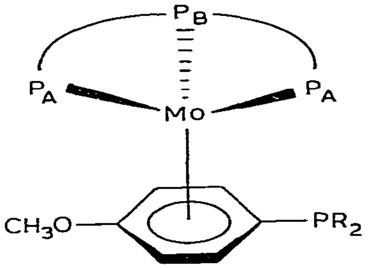

($\overset{\frown\frown}{PPP}$ = triphos)

until an orange precipitate began to form (approximately an equal volume of methanol). Bubbling was discontinued and the suspension allowed to stand for 1.5 h. A further small volume of methanol was added to see whether or not more solid would precipitate from the brownish colored supernatant. After a further 0.5 h, the orange, microcrystalline product was filtered off, washed with methanol and then pentane, and dried in vacuo. The yield was 0.9900 g, 54%. When necessary, recrystallization may be accomplished from a THF/methanol solution. A representation of the structure is shown. No specific rotamer is implied. The proton-decoupled 40.5 MHz ^{31}P NMR spectrum of I in C_6D_6 solution clearly shows the non-coordinated phosphorus atom at 1.3 ppm (relative to 85% H_3PO_4) with coupling to the unique phosphorus atom P_B of triphos, $J(P—P_B)$ 3.4 Hz. The chemical shifts for P_A and P_B are 99.3 and 76.9 ppm, respectively with $J(P_A—P_B)$ 9.4 and $J(P—P_A)$ 0 Hz. Complex I is oxygen sensitive in solution but is reasonably stable as a solid in air*.

Complex I was first isolated by us as a co-product during the reduction of $MoCl_3$(triphos) with sodium amalgam in THF solution under a dinitrogen atmosphere in the presence of added tertiary phosphine (eq. 2; R = Ph, $C_6H_4CH_3$-4 and $C_6H_4OCH_3$-4) to produce the bis(dinitrogen) complex II [3,4]. Only when R = $C_6H_4OCH_3$-4 has the η^6-arene complex been isolated pure.

$$MoCl_3(\text{triphos}) + PR_3 \xrightarrow[\text{THF}]{\text{Na/Hg;}N_2} \textit{trans}\text{-}Mo(N_2)_2(\text{triphos})(PR_3) \qquad (2)$$

(II)

Carbon monoxide was bubbled through a solution of II (R = Ph) in THF solution cooled to −90°C while the solution was irradiated for 1.5 h with three 100 W light bulbs. The extent of reaction was determined by withdrawing aliquots of the solution, placing them on a salt plate, allowing solvent to evaporate and recording the infrared spectrum between 2200 and 1600 cm^{-1}. The absorption band due to ν(NN) of II at 1955 cm^{-1} rapidly began to diminish while a band at 1812 cm^{-1} assigned to ν(CO) of *trans*-$Mo(CO)_2$(triphos)(PPh_3) appeared. However, before all N_2 had been displaced, ν(CO) due to *cis*-$Mo(CO)_2$(triphos)(PPh_3) (III) began to appear at 1852 and 1790 cm^{-1}, and the intensity of ν(CO) due to the *trans*-isomer began to diminish. Assignment of structures was based upon ν(CO) of known *cis*- and

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*A sample of I contained in a screw-capped vial sitting on the bench top showed no appreciable signs of decomposition after one year.

trans-Mo(CO)$_2$(dppe)$_2$ where dppe = $Ph_2PCH_2CH_2PPh_2$ [5,6]. Pure III was obtained at the conclusion of the reaction provided the temperature was kept below 0°C. As the temperature increased, loss of PPh_3 occurred and the known *fac*-Mo(CO)$_3$(triphos) (IV) was formed [7].

Pure III was obtained by removing solvent at 0°C and recrystallizing the light-yellow solid from THF/heptane solution. The ^{31}P NMR spectrum of III determined in a C_6D_6/CH_2Cl_2 solution showed that triphos was meridional. ^{31}P NMR spectral data: PPh_3, doublet of triplets, 54.7 ppm, $J(P—P_B)$ 91.6, $J(P—P_A)$ 25.8 Hz; P_A, doublet, 47.3 ppm, $J(P_A—P_B)$ 0 Hz; P_B, doublet, 94.4 ppm [8]. IR spectral data: ν(CO)(KBr) 1855, 1790 cm^{-1}.

Complex IV was most easily obtained by heating at reflux a benzene solution of III under carbon monoxide. Identical results were obtained beginning with II. ^{31}P NMR spectral data: P_A, doublet, 55.8 ppm, J(PP) 2.9 Hz; P_B, triplet, 82.8 ppm. This agrees well with previously reported data [9]. IR spectral data: ν(CO)(KBr) 1934, 1855, 1830 cm^{-1}; (CH_2Cl_2) 1937, 1848 cm^{-1} [7]. In the diamagnetic complexes of molybdenum that we have studied containing triphos it has been observed that when triphos adopts a meridional configuration $J(P_A—P_B)$ 0 Hz whereas when triphos is facial $J(P_A—P_B) > 0$ Hz.

Further work is in progress to explore the scope of the (triphos)-molybdenum(0) moiety as a coordinating environment.

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