

Preliminary communication

CYCLOHEPTATRIENYLMOLYBDENUM CHEMISTRY: TERTIARY PHOSPHINE, ALKYL, HYDRIDO, HALOGENO AND RELATED DERIVATIVES

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Summary

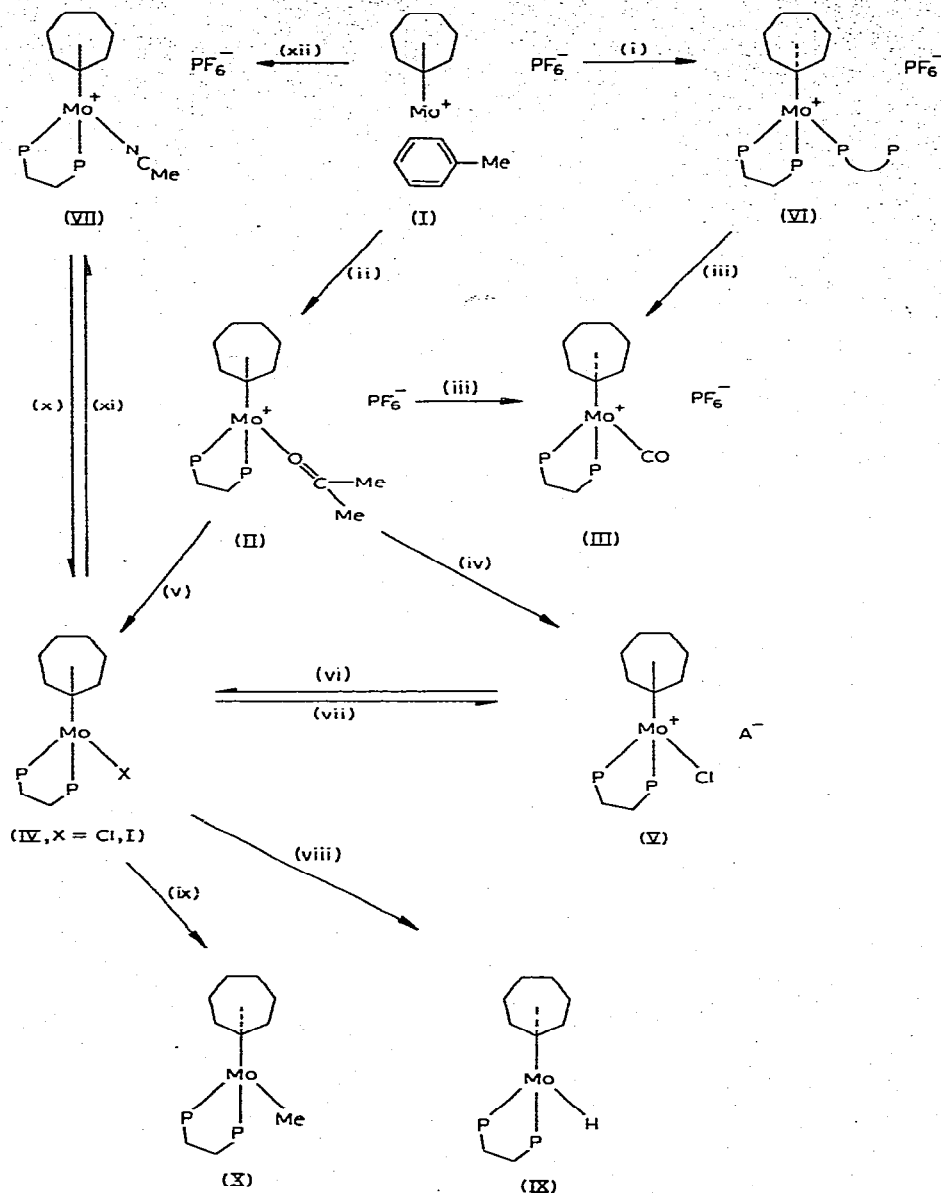
The preparation of the compounds $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Y}]$ ($\text{Y} = \text{Cl, I, Me, H}$), $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Cl}\}^+\text{A}^-$ ($\text{A}^- = \text{PF}_6^-$ or I^-), $\{\text{Mo}(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{L}\}^+\text{PF}_6^-$ ($\text{L} = \text{CO, MeCN}$ or dppe) is described.

Recently we described a versatile synthetic route to η^7 -cycloheptatrienylmolybdenum derivatives via the compound $\{(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{Me})\}^+\text{PF}_6^-$ (I) [1, 2]. Here we describe further studies on cycloheptatrienylmolybdenum derivatives. In particular, we were interested in the extent to which the system $(\eta^7\text{-C}_7\text{H}_7)\text{MoL}_2$ was analogous to the well explored [3] system $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2$ ($\text{L}_2 = (\text{CO})_2$ or bis-1,2-(diphenylphosphino)ethane (dppe)).

The compound I reacts readily with warm acetone giving a red solution and addition of dppe gives brown crystals (II). These in acetone readily react with CO, Cl^- or I^- giving $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{CO}\}^+\text{PF}_6^-$ (III) or $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{X}]$ (IV) ($\text{X} = \text{Cl}$ or I) respectively. The compounds III and IV ($\text{X} = \text{I}$) have been described previously [4]. Surprisingly, II also reacts with dichloromethane giving yellow, air stable crystals of $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Cl}]^+\text{A}^-$, where $\text{A}^- = \text{PF}_6^-$ (V). This is paramagnetic ($\mu_{\text{eff}} = 1.62 \times 10^{-2}$ BM) and the ESR spectrum shows hyperfine structure which may be assigned in part to coupling with two ^{31}P nuclei [$\langle g \rangle$ 1.994; a_{iso} 6.2 gauss, $a_{\text{iso}}(\text{P})$ 22.2 gauss]. The cation V is readily reduced by sodium amalgam to IV ($\text{X} = \text{Cl}$). Cyclic voltametric studies in butyronitrile show reversible oxidation—reduction between V and IV at -0.47 V (relative to Ag/AgCl). Oxidation of IV ($\text{X} = \text{Cl}$) with iodine gives V ($\text{A} = \text{I}^-$).

Treatment of I in ethanol with excess of dppe yields red crystals of stoichiometry corresponding to $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})_2\}^+\text{PF}_6^-$ (VI). However, the ^1H NMR spectrum in deuterioacetone shows a triplet for the C_7H_7 hydrogens (τ 4.95 ppm, $J(\text{P},\text{H})$ 1.6 Hz) corresponding to coupling with only two equivalent

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SCHEME 1

$\text{P} \text{---} \text{P}$ represents $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.

- (i) Excess dppe in EtOH, 80°C for 1 h.
- (ii) Stoichiometric dppe in acetone, reflux for 18 h.
- (iii) CO in acetone, r.t for 1 h.
- (iv) CH_2Cl_2 at r.t. for 10 min ($\text{A} = \text{PF}_6^-$).
- (v) LiX in acetone, 5 min.
- (vi) Na/Hg in tetrahydrofuran, 1 h.
- (vii) I_2 in CH_2Cl_2 ($\text{A} = \text{I}^-$).
- (viii) $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2$ in toluene at 70°C for 30 min.
- (ix) LiMe in ether/tetrahydrofuran, 30 min.
- (x) LiI in CH_2Cl_2 , 1 h at 40°C.
- (xi) MeCN, 1 min at r.t.
- (xii) Stoichiometric dppe in MeCN, reflux for 18 h.

^{31}P nuclei. Also, VI reacts readily with carbon monoxide to give III. It therefore appears that a dppe ligand in VI is unusually labile.

The acetonitrile analogue of III, namely $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{MeCN})\}^+ \text{PF}_6^-$ (VII) may be prepared by treatment of $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{MeCN})_3\}^+ \text{PF}_6^-$ with dppe, or, directly from addition of dppe to solutions of I in acetonitrile.

The red crystalline VII ($\nu(\text{CN})$ 2270 cm^{-1}) reacts rapidly and reversibly with carbon monoxide giving pink crystals of stoichiometry $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{CO})(\text{dppe})(\text{MeCN})\}^+ \text{PF}_6^-$ (VIII).

Treatment of IV ($\text{X} = \text{Cl}$ or I) with $\text{Na}^+ \{\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2\}^-$ gives red crystalline $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{H}]$ (IX) [^1H NMR in C_6D_6 : τ 4.9 ppm, doublet of triplets ($J(\text{P},\text{H})$ 2.0 Hz, $J(\text{C}_7\text{H}_7,\text{Mo-H})$ 1.2 Hz) $\eta^7\text{-C}_7\text{H}_7$; τ 13.9 ppm, triplet ($J(\text{P},\text{H})$ 56 Hz) Mo-H . $\nu(\text{Mo-H})$ 1670 cm^{-1}].

The orange-red $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})\text{Me}]$ (X) is prepared in good yield from IV ($\text{X} = \text{I}$) and methyllithium. [^1H NMR in C_6D_6 : τ 5.1 ppm, triplet, ($J(\text{P},\text{H})$ 1.8 Hz) $\eta^7\text{-C}_7\text{H}_7$; τ 10.4 ppm, triplet ($J(\text{P},\text{H})$ 8.4 Hz) Me].

The above reactions are shown in Scheme 1, the complexes III–X have been fully characterised by microanalysis, IR spectrum and, where appropriate, mass, NMR or ESR spectra. The lability of II precludes full characterisation but analysis and the reactions suggest it to be $\{\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{dppe})(\text{Me}_2\text{CO})\}^+ \text{PF}_6^-$.

Comparison of the above reactions with those of appropriate $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2$ analogues shows similarities, such as the occurrence of alkyl and hydrido species IX and X. However, there are marked differences such as the ability of IV ($\text{X} = \text{Cl}$) to undergo one-electron oxidation to V. We have no evidence that the equilibrium $\eta^5\text{-C}_7\text{H}_7 \rightleftharpoons \eta^7\text{-C}_7\text{H}_7$ occurs in the above systems.

We conclude that this equilibrium does not occur readily under these circumstances.

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