Fission of Tertiary Phosphites through Reaction with Hexacarbonylbis-π-cyclopentadienyldimolybdenum

By R. J. HAINES*

(*Research and Process Development, South African Iron and Steel Industrial Corporation Limited, P.O. Box 450, Pretoria, Republic of South Africa*)

and I. L. MARAIS and C. R. NOLTE

(*Department of Inorganic and Analytical Chemistry, University of Pretoria, Pretoria*)

Summary The reactions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with tertiary phosphites $P(OR)_3$ (R = Me, Et, Pr^i, Bu^n, and C_3H_5) afford as well as $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}$-$[\pi\text{-}C_5H_5Mo(CO)_3]$ and $[\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3]_2$, the neutral products $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ and $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3R$ which are formed as a result of the fission of the tertiary phosphite ligand; $PPh(O\text{–}C_3H_5)_2$ and $PPh_2(O\text{–}C_3H_5)$ yield similar products.

IN a previous study it was shown that the reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with various tertiary phosphine ligands L (*e.g.* L = PEt_3 and PPh_3) affords three types of products *viz.* neutral monosubstituted $(\pi\text{-}C_5H_5)_2Mo_2(CO)_5L$, neutral bis-substituted $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$, and ionic bis-substituted $[\pi\text{-}C_5H_5Mo(CO)_2L_2][\pi\text{-}C_5H_5Mo(CO)_3]$.[1] It is now found that a fourth type of product can be isolated from the reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with phosphorous acid esters.

Treatment of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with $P(OR)_3$ (R = Me, Et, Pr^i, and Bu^n) in benzene at room temperature effects disproportionation of the parent compound to afford $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}[\pi\text{-}C_5H_5Mo(CO)_3]$ (I) in high yield. The cations were characterised as the tetraphenylborates, while the presence of $[\pi\text{-}C_5H_5Mo(CO)_3]^-$ was established by means of i.r. The relative intensities of the two terminal carbonyl stretching peaks in the i.r. spectra of $\{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}BPh_4$ (II) are consistent with "*trans*" disposition of the carbonyl groups.[2] Irradiation of benzene solutions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and an excess of $P(OR)_3$ (R = Me, Et, Pr^i, and Bu^n) with u.v. light leads to the formation of the bis-substituted compounds $[\pi\text{-}C_5H_5\text{-}Mo(CO)_2P(OR)_3]_2$ (III). The i.r. spectra of these compounds contain two terminal carbonyl stretching peaks which is consistent with a structure belonging to the molecular point group C_{2h}.

In contrast to the reactions discussed above, the reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with $P(OR)_3$ (R = Me, Et, Pr^i, Bu^n, and C_3H_5) in benzene under reflux does not afford simple substituted derivatives of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$. Instead, $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$ (IV) and $\pi\text{-}C_5H_5Mo\text{-}(CO)_2P(OR)_3R$ (V) are formed as a result of fission of the tertiary phosphite ligand. The compounds, which are formed in equimolar quantities as determined by i.r., were characterised by elemental analyses and i.r. and n.m.r. spectroscopy. One product (V; R = Me) has been previously synthesised by treating $Na[\pi\text{-}C_5H_5Mo(CO)_2P\text{-}(OMe)_3]$ with MeI.[3] For a particular ligand the i.r. spectra of (III), (IV), and (V) measured in CS_2 are identical in the 1200—1000 cm^{-1} region apart from an extra peak at *ca.* 1165 cm^{-1} in the spectra of (IV). This is assigned to ν(P–O), *cf.* ν(P–O) = 1103 cm^{-1} for $Pt_2(Et_2PO)_2(SEt)_2(PEt_3)_2$[4] and 1170—1190 cm^{-1} for $XHgP(O)(OR)_2$ (X = Cl and Br; R = Et, Pr^i, and Bu^n),[5] and is consistent with the formulation $\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2$. Based on the i.r. and n.m.r. evidence, (V) exist as a mixture of the *cis*- and *trans*-isomers in solution while (IV) occur as the *trans*-isomer. Milder conditions are required to effect the fission of $PPh(OC_3H_5)_2$ and $PPh_2(OC_3H_5)$. Thus, $[\pi\text{-}C_5H_5\text{-}Mo(CO)_3]_2$ reacts with these two ligands in benzene at room temperature to afford $\pi\text{-}C_5H_5Mo(CO)_3C_3H_5$ plus $\pi\text{-}C_5H_5Mo\text{-}(CO)_2PPh(OC_3H_5)_2P(O)Ph(OC_3H_5)$ or $\pi\text{-}C_5H_5Mo(CO)_2PPh_2\text{-}(OC_3H_5)P(O)Ph_2$ respectively.

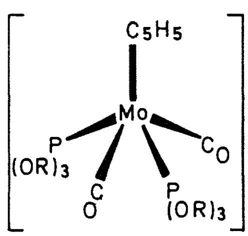
An observation pertinent to the elucidation of the mechanism of formation of (IV) is that (I) decomposes to $\pi\text{-}C_5H_5Mo(CO)_3R$ (VI) and (IV) in benzene under reflux.

$$[\pi\text{-}C_5H_5Mo(CO)_3]_2 + P(OR)_3 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3Mo(CO)_2P(OR)_3\text{-}\pi\text{-}C_5H_5$$

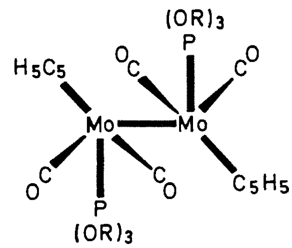
$$\downarrow P(OR)_3$$

$$\pi\text{-}C_5H_5Mo(CO)_2P(OR)_3P(O)(OR)_2 + \pi\text{-}C_5H_5Mo(CO)_3R \leftarrow \{\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]_2\}^+[\pi\text{-}C_5H_5Mo(CO)_3]^- \quad \text{(I)}$$

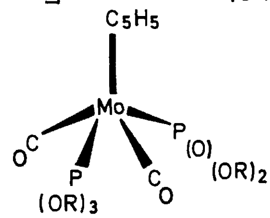
SCHEME



(II)



(III)



(IV)

Further, if this reaction is carried out in the presence of $P(OR)_3$, (V) is formed instead of (VI). (III) is unreactive towards $P(OR)_3$ under the same experimental conditions. The mechanism suggested for the formation of (IV) is shown in the Scheme.

The mechanism is analogous to that for the Michaelis–Arbuzov rearrangement involving tertiary phosphites and alkyl halides with (I) corresponding to the phosphonium intermediate $[(R^1O)_3PR^2]X$.

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