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Preliminary communication

Phosphonate and related derivatives of iron

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Previous studies have shown that the treatment of $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = Cl, Br or I) with tertiary phosphines PR_3 (R = alkyl or aryl) effects either replacement of a carbonyl group or displacement of the halogen by the ligand to afford derivatives of the type $\pi\text{-}C_5H_5Fe(CO)(PR_3)X$ or $[\pi\text{-}C_5H_5Fe(CO)_2(PR_3)]X$ respectively[1,2]. The tendency for halogen displacement relative to carbonyl replacement increases with the basicity of the ligand and along the series $I<Br<Cl$. Products formed as a result of both modes of reaction are known *e.g.* $\{\pi\text{-}C_5H_5Fe(CO)[P(C_6H_5]_3\}_2PF_6$ but the syntheses required the presence of a strong Lewis acid *e.g.* $AlCl_3$ (ref.2). We have now found that a new type of product may be isolated from the reaction of tertiary phosphites with $\pi\text{-}C_5H_5Fe(CO)_2Cl$.

The reaction of $\pi\text{-}C_5H_5Fe(CO)_2I$ with the ligands $P(OR)_3$ (R = CH_3, C_2H_5 and n-C_4H_9) in benzene at room temperature or under reflux was observed to afford neutral $\pi\text{-}C_5H_5Fe(CO)[P(OR)_3]I$ in high yield. In contrast $\pi\text{-}C_5H_5Fe(CO)[P(OR)_3]Cl$ was found to be a minor product (yield ca. 20%) in the corresponding room temperature reactions involving $\pi\text{-}C_5H_5Fe(CO)_2Cl$ and the tertiary phosphites $P(OR)_3$ (R = CH_3, C_2H_5, n-C_4H_9 and C_3H_5). These reactions afforded two neutral halogen-free derivatives as the major products, their relative yield depending on the ligand to parent carbonyl ratio. The two compounds were separated by means of column chromatography and characterised by elemental analysis and IR and NMR spectroscopy as $\pi\text{-}C_5H_5Fe(CO)_2P(O)(OR)_2$ and $\pi\text{-}C_5H_5Fe(CO)[P(OR)_3]P(O)(OR)_2$ respectively. Confirmatory evidence for the formulation $\pi\text{-}C_5H_5Fe(CO)_2P(O)(OR)_2$ was obtained from a study of the reaction of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with $NaOP(OC_2H_5)_2$ in THF. The product isolated *viz.* $\pi\text{-}C_5H_5Fe(CO)_2P(O)(OC_2H_5)_2$ was identical to the unsubstituted phosphonate obtained from the reaction of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with $P(OC_2H_5)_3$. The IR spectra of $\pi\text{-}C_5H_5Fe(CO)_2P(O)(OR)_2$ contain a peak at ca. 1180 cm^{-1} which is assigned to $\nu(P\text{–}O)$; this peak is shifted to ca. 1160 cm^{-1} for the monosubstituted phosphonates $\pi\text{-}C_5H_5Fe(CO)[P(OR)_3]P(O)(OR)_2$.

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It was further observed that products analogous to the above phosphonates are formed in the corresponding reactions involving tertiary phosphonites and phosphinites. Thus $\pi\text{-}C_5H_5Fe(CO)_2P(O)(C_6H_5)(OC_3H_5)$ and $\pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)(OC_3H_5)_2]\text{-}P(O)(C_6H_5)(OC_3H_5)$ and $\pi\text{-}C_5H_5Fe(CO)_2P(O)(C_6H_5)_2$ and $\pi\text{-}C_5H_5Fe(CO)[P(C_6H_5)_2]\text{-}(OC_3H_5)P(O)(C_6H_5)_2$ were isolated from the reactions of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ with $P(C_6H_5)(OC_3H_5)_2$ and $P(C_6H_5)_2(OC_3H_5)$, in benzene under reflux, respectively.

Addition of the ligands $L = P(OR)_3$ ($R = CH_3$ and C_3H_5), $P(C_6H_5)(OC_3H_5)_2$ and $P(C_6H_5)_2(OC_3H_5)$ to a solution of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ and excess sodium tetraphenylborate in benzene containing a little methanol resulted in the precipitation of $[\pi\text{-}C_5H_5Fe(CO)_2L]B(C_6H_5)_4$ in high yield. This suggests that ionic derivatives of the type $\{\pi\text{-}C_5H_5Fe(CO)_2[P(OR)_3]\}Cl$ are intermediates in the formation of $\pi\text{-}C_5H_5Fe(CO)_2P(O)(OR)_2$ in the reactions discussed above and the mechanism outlined in the scheme is thus proposed.

SCHEME

$$\begin{array}{l}
\pi\text{-}C_5H_5Fe(CO)_2Cl \quad + \quad P(OR)_3 \\
\qquad\qquad\quad \downarrow \\
\{\pi\text{-}C_5H_5Fe(CO)_2[P(OR)_3]\}\ Cl \\
\qquad\qquad\quad \downarrow \\
\pi\text{-}C_5H_5Fe(CO)_2P(O)(OR)_2 \quad + \quad RCl
\end{array}$$

This mechanism is similar to that proposed for the formation of $\pi\text{-}C_5H_5Mo(CO)_2[P(OR)_3]P(OR)_2$ from $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and $P(OR)_3$ (ref.3) and is analogous to the mechanism for the Michaelis–Arbuzov rearrangement involving tertiary phosphites and alkyl halides[4]. Consistent with the proposed mechanism is the observation that the nucleophilic attack of $[\pi\text{-}C_5H_5Mo(CO)_3]^-$ on $\pi\text{-}C_5H_5Fe(CO)_2[P(OCH_3)_3]^+$ afforded $\pi\text{-}C_5H_5Fe(CO)_2P(O)(OCH_3)_2$ and $\pi\text{-}C_5H_5Mo(CO)_3CH_3$. No reaction was observed between $\pi\text{-}C_5H_5Fe(CO)_2P(O)(OCH_3)_2$ and $P(OCH_3)_3$ in refluxing benzene which indicates that $\{\pi\text{-}C_5H_5Fe(CO)[P(OR)_3]_2\}$ Cl is an intermediate in the formation of $\pi\text{-}C_5H_5Fe(CO)[P(OR)_3]P(O)(OR)_2$.

The results presented above together with those of the previously reported study of the reactions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with tertiary alkyl phosphites[3] suggest that the formation of phosphonate derivatives through intermediates of the type $\{M[P(OR)_3]_x(\text{Ligand})_y\}$ Anion (M = metal, R = alkyl will have general application.

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