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Preliminary communication

The addition of triphenylphosphine and pyridine to cyclohexadienyl- and cycloheptadienyl-iron tricarbonyl cations

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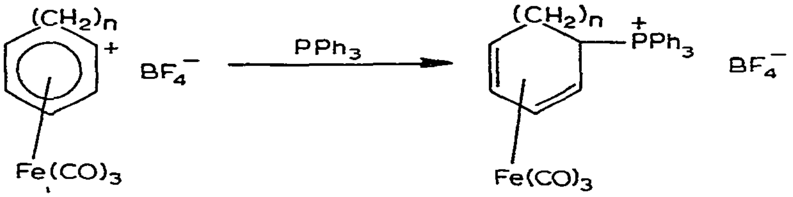
SUMMARY

Addition of triphenylphosphine to cyclohexadienyl- or cycloheptadienyl-iron tricarbonyls leads to the formation of phosphonium ions in which attack of the Ph_3P has occurred at the dienyl fragment.

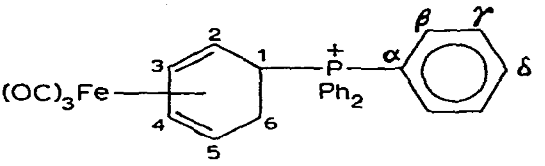
Cationic dienyl complexes of iron tricarbonyl are known to undergo attack by a range of nucleophilic reagents, the site of attack depending on the nucleophilic employed. In all previous studies attack by bases such as tertiary phosphines has been found to occur at the metal atom, leading to the replacement of one carbonyl group, although the addition of tertiary alkylamines to the dienyl fragment has been noted[1]. We now report the addition of triphenylphosphine to the organic group in the cationic cyclohexadienyl and cycloheptadienyl complexes of iron tricarbonyl, (I) and (II), respectively.



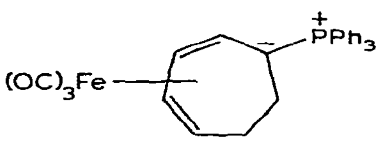
(I), $n = 1$
(II), $n = 2$

(III) $n = 1$
(IV) $n = 2$

The addition of excess triphenylphosphine to a suspension of either (I) and (II) in dichloromethane rapidly leads to a clear solution. Addition of ether to these solutions brings about the separation of off-white crystalline materials. Identification of these compounds follows from their analytical data which indicates the formulae



(III)



(V)

$[Ph_3P(C_6H_7)Fe(CO)_3]BF_4$ (III) and $[Ph_3P(C_7H_9)Fe(CO)_3]BF_4 \cdot CH_2Cl_2$ (IV) and their ^1H NMR spectra. The proposed structure of complex (III) is given, the structure of (IV) is similar. In agreement, the proton decoupled ^{13}C NMR spectra of (III) showed the following features: (in acetone-d_6) δ −210.4 (s, carbonyls), −137.5 (s, C_δ), −134.6 (d, J(P–C)8 Hz, C_β or C_γ), −130.8 (d, J(P–C)10 Hz, C_β or C_γ), −119.1 (d, J(P–C)80 Hz, C_α), −86.4 (s, C_3 and C_4), −60.5 (d, J(P–C)7 Hz, C_5), −53.1 (d, J(P–C)10 Hz, C_2), −32.1 (d, J(P–C)37 Hz, C_1) and −27.8 (d, J(P–C)5 Hz, C_6). These assignments were obtained by selective double irradiation at the proton resonances. The complexes are stable in air and are readily soluble in polar organic solvents.

TABLE 1

M–CO ABSORPTIONS

Complex	*ν(CO) (cm^{-1})*
(I) in CH_2Cl_2	2086s, 2016s
(I) in C_5H_5N	2083s, 2008s
(III) in CH_2Cl_2	2065s, 1994s
(IV) in CH_2Cl_2	2060s, 1986s

There is evidence for a similar reaction of pyridine with complex (I). This follows from an examination of the IR spectrum of (I) in the presence of pyridine, a shift of ν(CO) being observed (see Table 1) and also from the ^1H NMR spectrum of (I) in pyridine-d_5, which is fully consistent with amine addition. No evidence for adduct formation between (I) and Ph_3As has been obtained.

Phosphonium ions of the type (III) and (IV) are potential precursors of organometallic ylids, *e.g.* (V). Such ylids would offer a useful route for the preparation of methylene-substituted rings via a Wittig reaction. However, attempts to produce (V) from (IV) either with triethylamine or [1,8-bis(dimethylamino)naphthalene] were unsuccessful, and no reaction was observed. This presumably reflects the large steric hindrance arising from the bulky Ph_3P grouping, which will add to the ligand with an *exo*-configuration to the metal. Reaction of (III) with n-butyllithium in ether gave a highly unstable red solution, and addition of benzaldehyde to this solution under reflux produced no identifiable products after 5 hours.

Although the direct reaction of Ph_3P does not lead to substitution on the metal in these examples, we have been able to effect such substitution by initial displacement of carbon monoxide by iodide followed by treatment with triphenylphosphine in the presence of silver ion, thus utilising the weaker nucleophilicity of the iodide for the dienyl fragment and its greater nucleophilicity for the metal.

$$\begin{tikzcd}
(\text{Dienyl})\text{Fe}(\text{CO})_3{}^+ \arrow[r, "\text{I}^-"] & (\text{Dienyl})\text{Fe}(\text{CO})_2\text{I} \arrow[d, "\text{Ag}^+/\text{Ph}_3\text{P}"] \\
& [\text{DienylFe}(\text{CO})_2\text{Ph}_3\text{P}]^+
\end{tikzcd}$$

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REFERENCES

1 P. McArdle and H. Sherlock, *J. Organometal. Chem.*, 52 (1973) C29.