Nucleophilic Addition of Tertiary Phosphines to Co-ordinated Benzene in the Bis(benzene)iron(II) Cation

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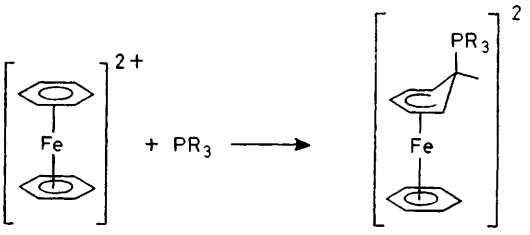
Summary Tertiary phosphines rapidly add to one of the benzene rings in the bis(benzene)iron(II) cation to yield air-stable phosphonium salts.

The addition of phosphines to co-ordinated cyclic π-hydrocarbons has recently received considerable attention.[1-7] It was first shown[4] in 1976 that even benzene can be sufficiently activated *via* metal co-ordination to allow tertiary phosphine addition [equation (1)]. Even with the strongly nucleophilic tri-n-butylphosphine, however, the authors were unable to isolate the phosphonium adduct owing to the ready reversibility and small equilibrium constant of equation (1).

$$[(C_6H_6)Mn(CO)_3]^+ + PBu^n{}_3 \rightarrow [(C_6H_6{\cdot}PBu_3)Mn(CO)_3]^+ \quad (1)$$

We report here that the addition of an excess of the phosphines PR_3 ($R = Bu^n$, Ph, or *p*-tolyl) to the hexafluorophosphate salt of bis(benzene)iron(II)[8] (**1**) in acetonitrile followed by addition of diethyl ether yields air-stable, orange crystals of the phosphonium salt (**2**) [equation (2)]. Analytical and conductivity data (in nitromethane) are in good agreement with the proposed products. We believe that the phosphonium adducts (**2**) are the first examples of addition of the phosphines PPh_3 and P(*p*-tolyl)$_3$ to a non-substituted benzene ring.



(1) (2) (2)

^{1}H N.m.r. data strongly support the assertion that phosphine addition occurs on one benzene ring only, even in the presence of a large excess of the phosphine. The n.m.r. spectrum of (**1**) in CD_3CN consists of a single resonance at τ 3·00. The $PBu^n{}_3$ adduct (**2**; $R = Bu^n$) has resonances at τ 2·87 (t, H^4), 3·62 (s), 4·87 (t, $H^{3,5}$), 5·78 (q, H^1 *endo*), and 6·45 (t, $H^{2,6}$) with relative area 1 : 6 : 2 : 1 : 2. The τ 3·62 band is due to the benzene ring in (**2**). The cyclohexadienyl ring assignments were made by spin-decoupling experiments and by comparison with previous work.[4] Addition of an excess of $PBu^n{}_3$ does not alter the n.m.r. spectrum of the co-ordinated rings, implying that addition to both benzene rings does not occur.

Analytical and i.r. data as well as n.m.r. spectra in CD_3NO_2 show that the $PBu^n{}_3$ adduct (**2**) crystallizes with

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one molecule of unco-ordinate MeCN. The other adducts [R = PPh_2 or $P(p\text{-tolyl})_3$] do not crystallize with MeCN.

The reaction is too rapid to follow by the stopped-flow method; however, variable temperature n.m.r. spectra of the PPh_3 and $P(p\text{-tolyl})_3$ adducts in CD_3CN show that these phosphines exchange rapidly at room temperature and equilibrate all twelve protons on the benzene rings. At −40 °C the exchange is slow on the n.m.r. time-scale and the spectra become similar to that of the PBu^n_3 adduct discussed above. A detailed kinetic study of these exchange reactions is in progress.

This work is the first report of phosphine addition to an arene ring that leads to an isolable product. The benzene rings in (**1**) seem to be as electrophilic towards phosphines as the very electrophilic cycloheptatriene[3] in $[(C_7H_8)Mn(CO)_3]^+$, and therefore it is surprising that phosphine addition to both rings does not occur. However, Helling *et al.*[9] have shown that bis adducts do indeed form with such powerful bases as Ph^- and Bu^-.

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