Chemistry of Pentakis(trimethyl phosphite)iron(0), [Fe{P(OMe)$_3$}$_5$]

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Summary A new zerovalent iron complex, [Fe{P(OMe)$_3$}$_5$], has been prepared; this volatile molecule has a relatively basic iron atom that is readily protonated and alkylated.

WE have prepared the first zerovalent iron complex with all phosphite ligands by the reduction of $[FeCl_2\{P(OMe)_3\}_3]$ with sodium amalgam in the presence of excess of trimethyl phosphite. Yellow crystals of $[Fe\{P(OMe)_3\}_5]$ were obtained by recrystallization from pentane and vacuum sublimation at 80 °C (sublimation results in some loss due to thermal decomposition). Elemental analyses and its mass and n.m.r. spectra defined its composition and structure. The ^{31}P n m r. spectrum at -80 °C showed an A_2B_3 pattern ($J_{PP'}$ 145 Hz), establishing that the solution-state structure has trigonal bipyramidal geometry. Explicably, the molecule is stereochemically nonrigid.[1]

A relatively high electron density on the iron atom in $[Fe\{P(OMe)_3\}_5]$ tends to dominate its chemistry. Molecular oxygen reacts rapidly with solutions, with oxidation (noncatalytic) of phosphite to phosphate. Protonation at the metal centre is fast with CF_3CO_2H. Some measure of the basicity of the iron atom was realized in the reaction (1) with $NH_4{}^+PF_6{}^-$, which gave a cationic hydride, isolated and

$$[Fe\{P(OMe)_3\}_5] + NH_4{}^+PF_6{}^- \rightarrow [HFe\{P(OMe)_3\}_5]^+PF_6{}^- + NH_3 \quad (1)$$

analysed as the crystalline hexafluorophosphate salt, which has ^1H and $^{31}P\{^1H\}$ spectra that are, respectively, the X and AB_4 parts of the expected AB_4X spectrum. The robust character of this hydride is rather sharply differentiated from the analogous d^8 $[HNi\{P(OEt)_3\}_4]^+$ species.[2] Hydride and phosphite ligands are not highly labile in the iron cation as shown by n.m.r. studies of mixtures of $[HFe\{P(OMe)_3\}_5]^+$ and $P(OMe)_3$ and of $[HFe\{P(OMe)_3\}_5]^+$ and $[Fe\{P(OMe)_3\}_5]$. Consistently, the cationic hydride does not add ethylene nor is it a catalyst for isomerization of hex-1-ene. CF_3CO_2H decomposes the hydride to give hydrogen and ostensibly $[Fe\{P(OMe)_3\}_5]^{2+}$ which appears to have an A_2B_3 spectrum and to be more rigid than the neutral precursor; the octahedral $[Fe\{P(OMe)_3\}_6]^{2+}$ ion, independently synthesized as the $B_{12}H_{12}{}^{2-}$ salt from excess of phosphite, iron(II) iodide, and $Li_2B_{12}H_{12}$, was shown not to be a product of the acid-decomposition of the cationic hydride.

Iodide ion is displaced from MeI by $[Fe\{P(OMe)_3\}_5]$ to give the $[MeFe[P(OMe)_3\}_5]^+$ cation which was isolated as the $PF_6{}^-$ salt. The composition and structure for this six-co-ordinate complex were defined by elemental analyses and n.m.r. studies (AB_4 ^{31}P spectrum). With EtI the putative ethyl cation is too reactive for isolation; ethylene is evolved and the cationic hydride is formed. Reaction of allylic halides with $[Fe\{P(OMe)_3\}_5]$ provides a ready synthesis of a new class of π-allyl complexes of the form $[(\pi\text{-allyl})Fe\{P(OMe)_3\}_4]^+$. The C_3H_5 derivative has allyl C–H resonances characteristic of π-allyl metal structures. Benzyl iodide does not yield a π-benzyl derivative. Coupling occurs and the major products are bibenzyl and $[Fe\{P(OMe)_3\}_3I_2]$.

Unlike the d^{10} analogue[3] $[Ni\{P(OMe)_3\}_4]$, the iron complex does not readily undergo substitution reactions. There is no fast exchange (n.m.r. time scale) between $[Fe\{P(OMe)_3\}_5]$ and $P(OMe)_3$ up to 75°, and carbon monoxide does not detectably react in a day (benzene medium). However, substitution reactions are greatly accelerated by employment of polar solvents. For example with a diethyl ether medium, $[Fe\{P(OMe)_3\}_4CO]$† and $[Fe\{P(OMe)_3\}_3(CO)_2]$ are formed in a day at 25°, and with methanol, substitution to give the dicarbonyl is fast at 25°. Since there is no n.m.r. evidence of $[Fe\{P(OMe)_3\}_5]$ interaction with such polar solvents, the qualitative mechanistic features of this solvent effect are not evident. We[4] find such an effect with other co-ordination complexes, *e.g.* $[HCo\{P(OMe)_3\}_4]$, hence the phenomenon appears to have general synthetic potential. Reaction of $[Fe\{P(OMe)_3\}_5]$ with PF_3 is much faster than with CO and does not require polar reaction media; the product is $[Fe\{P(OMe)_3\}_3(PF_3)_2]$, a stereochemically nonrigid C_{2v}-trigonal bipyramidal species which yields a complex ^{31}P spectrum only at low temperatures and is stereochemically analogous to $[Fe(PMe_3)_3(PF_3)_2]$.[5]

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† Not isolated; spectrally defined.

[1] Precise activation parameters for the intramolecular rearrangement have been determined and will be reported separately by P. Meakin and J. P. Jesson.

[2] C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94**, 2994.

[3] M. Meier, F. Basolo, and R. Pearson, *Inorg. Chem.*, 1969, **8**, 795.

[4] E. L. Muetterties and F. J. Hirsekorn, unpublished data.

[5] E. L. Muetterties and J. W. Rathke, unpublished data.