Reactions of (Pentamethylcyclopentadienyl)di(carbonyl)(tri-2,4,6-*tert*-butylphenyl)iminophosphaneiron with Electrophiles: Formation of Metallophosphenium Complexes

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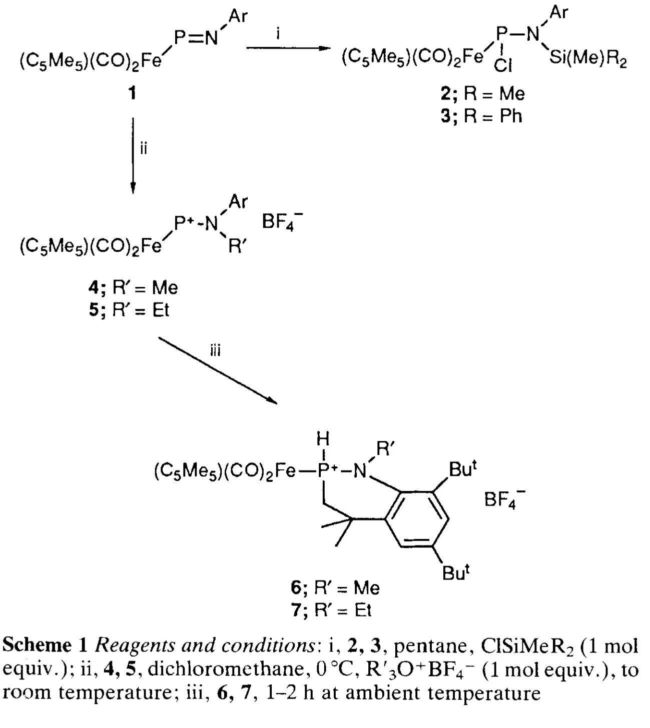
Reactions of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P\text{=}N(2,4,6\text{-}Bu^t_3C_6H_2)]$ **1** with chlorosilanes afford the metallo-halo-aminophosphanes $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P(Cl)N(SiMeR_2)(2,4,6\text{-}Bu^t_3C_6H_2)]$ **2** and **3**; the metalloaminophosphenium complexes $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}PN(R')(2,4,6\text{-}Bu^t_3C_6H_2)]^+BF_4^-$ **4** and **5** were obtained by treatment of **1** with oxonium salts, and rearranged to form the cationic azaphosphorinane complexes **6** and **7**.

Metalloiminophosphane complexes, *i.e.* η^1-coordinated phosphorus–nitrogen pπ systems acting as one-electron donors to metal fragments, have recently become available.[1] Here, we report on reactions of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P\text{=}NAr]$ **1** (Ar = $2,4,6\text{-}Bu^t_3C_6H_2$) with chlorosilanes and Meerwein-type oxonium salts, the outcome of which could not *a priori* be predicted. Having two reactive centres, the double-bond system and the metal fragment, the above molecules might react involving either the metal–phosphorus bond or the coordinated ligand. The intrinsic stability of **1**, however, implied a reactivity predominantly based on the PN-π-system.

Reactions with chlorosilanes proceed with attack of the electrophile on nitrogen, and the resulting metallophosphanes **2** and **3** were identified spectroscopically.† These reactions are complete within one to two weeks at ambient temperatures, and no cleavage of the iron–phosphorus bond is observed. The addition of the electrophilic moiety to the nitrogen atom is remarkable in that a charge-controlled process is invoked rather than an orbital-controlled process. With regard to the latter, attack of the electrophile at the phosphorus centre would be favoured.

Treatment of **1** with tertiary oxonium compounds of the type $R_3O^+BF_4^-$ (R = Me or Et) constitutes another example of electrophilic attack at the nitrogen atom of the iminophosphane moiety in **1**. However, the resulting alkylation products **4** and **5**, which can be identified spectroscopically, are rather unstable, as might be expected from the extreme Lewis acidity of such species.

Owing to the low coordination number and the formal positive charge at phosphorus the ^{31}P resonances are found at



Scheme 1 *Reagents and conditions*: i, **2**, **3**, pentane, $ClSiMeR_2$ (1 mol equiv.); ii, **4**, **5**, dichloromethane, 0 °C, $R'_3O^+BF_4^-$ (1 mol equiv.), to room temperature; iii, **6**, **7**, 1–2 h at ambient temperature

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† **2**, ^{31}P NMR: δ 343.1; ^{1}H NMR: δ 7.4 (2H, br s, $Bu^t_3C_6H_2$), 1.5 (18H, d, *o*-CMe_3), 1.4 (9H, s, *p*-CMe_3), 1.1 (15H, br s, C_5Me_5) and 0.7 (9H, s, $SiMe_3$). **3**, ^{31}P NMR: δ 345.3; ^{1}H NMR: δ 7.4 (2H, s, Bu^t_3 $(_6H_2)$, 7.3 (10H, m, $SiPh_2$), 1.5 (18H, s, *o*-CMe_3), 1.3 [9H, s, *p*-(Me_3)], 1.2 (15H, br s, C_5Me_5) and 0.6 (3H, S, SiMe).

extremely low field, *viz.* δ 965.1 and 963.2 (H_3PO_4 external, C_6D_6), respectively. The deshielding of the phosphorus nuclei is greatly enhanced by the metal substituent, and bearing in mind that **4** and **5** can alternatively be viewed as cationic, terminal phosphinidene complexes the observed chemical shifts are perhaps less surprising. Nevertheless, they provide strong evidence for the formation of the species depicted above. Furthermore, these shift values are in excellent agreement with δ value of 954 reported by Gladysz *et al.*[2] for a metallophosphenium intermediate formed at −90 °C during the reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P(Cl)NPr^i{}_2]$ with $CPh_3{}^+PF_6{}^-$. Derivatives **4** and **5** appear to be kinetically more stable (detection at ambient temperatures!), which may be attributed to the steric bulk of the 2,4,6-tri-*tert*-butylphenyl group.

However, as might be expected from their kinship with singlet-carbenes and silylenes they also undergo further reactions, namely insertions into σ-bonds.[3] Here, C–H bond activation at a *tert*-butyl group in the *ortho*-position with concomitant cyclization, which is well known for compounds containing the $2,4,6\text{-}Bu^t{}_3C_6H_2$ substituent,[4] furnished the cationic azaphosphorinane complexes **6** and **7**. This was inferred from their spectroscopic data‡ showing clearly that one *tert*-butyl group had reacted. Moreover, the ^{31}P resonances shifted to higher field (δ 168.1 and 166.3, respectively), and this, together with the large proton couplings ($^1J_{HP}$ 473 and 475 Hz, respectively) were clearly indicative of four-coordinated phosphorus nuclei. The stretching frequencies for the terminal carbonyl ligands were shifted by *ca.* 40 cm^{-1} to higher wavenumbers with respect to **1**, as expected for cationic species.

Interestingly, mass-spectrometric investigations of **7** did not show the molecular ion but a signal of high intensity (42%) attributable to the molecular ion of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP(F)\text{–}N(Et)Ar]$ **8** reduced by two carbonyl units. The generation of **8**, which is analogous to the above-mentioned metallo-halo-aminophosphanes **2** and **3**, is accounted for by the dissociation of the $BF_4{}^-$ anion proven by the detection of BF_3. The presence of **8** in solution is readily excluded by the absence of a characteristic $^1J_{FP}$ coupling in the ^{31}P NMR spectrum. The further fragmentation proceeds *via* two apparently equivalent routes, the elimination of either fluoroethane or ethane with subsequent extrusion of isobutene in both cases.

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‡ **6**, $^{31}P\{^1H\}$ NMR: δ 168.1; ^{31}P NMR: δ 168.1 (d, *J* 473 Hz); ν_{max}/cm^{-1}: 2035m and 1191s; $^{13}C\{^1H\}$ NMR: δ 211.3 (d, *J* 10.2 Hz, FeCO), 209.9 (s, FeCO), 150.3 (s, PNC), 149.3 (d, *J* 2.5 Hz, PNCCC*C*), 135.9 (s, PNC), 135.3 (s, PNC), 124.3 (br s, PNCC*C*), 119.6 (s, PNCC*C*), 100.8 (s, C_5Me$_5$), 63.8 (d, *J* 17.1 Hz, PCH_2), 54.1 (d, *J* 4.0 Hz, PCH_2CMe_2), 37.1 (br s, NCH_2), 35.1, 34.9, 33.4 (s, *o*-*C*Me$_3$, *p*-*C*Me$_3$, NCH$_2$*Me*), 33.2 (br s, PCH$_2$C*Me*$_2$), 33.0 (br s, PCH$_2$*C*Me$_2$), 31.6, 31.3 (s, *o*-C*Me*$_3$, *p*-C*Me*$_3$), and 9.5 (d, *J* 10 Hz, C$_5$*Me*$_5$).

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