Reactivity of $HFe(CO)_4^-$ towards Phospha-alkenes: a Simple Route to New *P*-Functionalized Diphosphiranes

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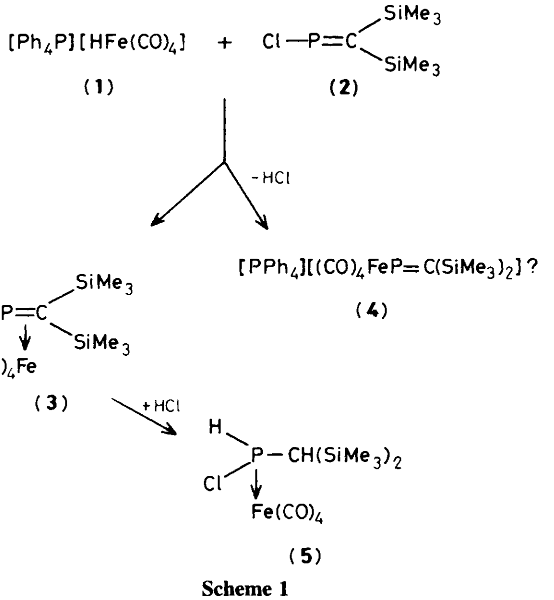
The unexpected synthesis of new free or complexed *P*-functionalized diphosphiranes is reported.

In recent papers, we reported the versatile behaviour of the anionic hydrido carbonyl metallate $[PPh_4][HFe(CO)_4]$ (**1**) towards dichlorophosphines[1,2] or an alkyl alkynyl chlorophosphine.[3] Various reactions, including hydride transfer, HCl elimination, and phosphorus–nitrogen bond cleavage were observed, leading to the preparation of highly functional diphosphines or new anionic phosphido-complexes. On this basis, (**1**) appears to be of considerable interest as a tool for the synthesis of unknown mono- or poly-metallic complexes of phosphorus derivatives.

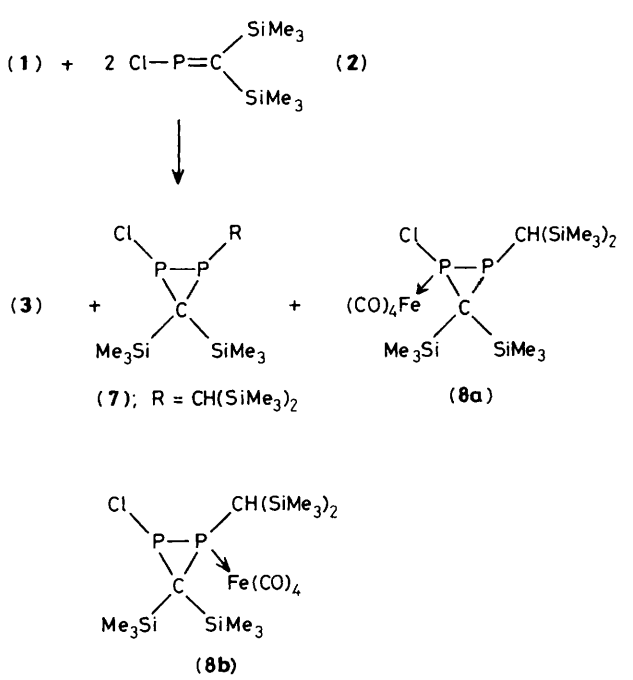
Two competitive reactions occur when an equimolar amount of hydride (**1**) in dichloromethane is added to a dichloromethane solution of the phospha-alkene (**2**) (Scheme 1): (i) elimination of tetraphenylphosphonium chloride and formation of the η^2-phospha-alkene complex (**3**) [$\delta(^{31}P)$ 129 p.p.m., $^1J_{PH}$ 364 Hz, $\delta(^{13}C)$ 28 (d, $^1J_{CP}$ 14.8 Hz, =C)]; and (ii) hydrogen chloride evolution with the formation of a minor product which might be the anionic phospha-alkene complex† $[PPh_4][(CO)_4FeP{=}C(SiMe_3)_2]$ (**4**) [$\delta(^{31}P)$ 516 p.p.m.]. Nevertheless, attempts to isolate this species have failed so far.

The secondary halogenophosphine complex (**5**)‡ arising from the 1,2 addition of hydrogen chloride to the phosphorus–carbon double bond of (**3**) is also formed as a by-product. Complex (**5**) can be obtained directly when $(Me_3Si)_2CHPCl_2$ (**6**) is treated with 1 mol equiv. of hydride (**1**) in dichloromethane solution. A dramatic change occurs when a solution of the hydride (**1**) in dichloromethane is slowly added to pure phospha-alkene (**2**) (2 equiv.), at room temperature. Three main products were characterized (Scheme 2): complex (**3**), the free functionalized diphosphirane (**7**), and its corresponding complex (**8a**) [or (**8b**)]. Compound (**7**)§ was purified by t.l.c. on silica plates (heptane as eluant) and its structure was determined by n.m.r. spectroscopy.¶

It is of interest that the mass spectrum of (**7**) shows the molecular ion peak (*m/z* 414) but the parent peak corresponds to the diphosphirene (**9**) resulting from the intramolecular



Scheme 1



Scheme 2

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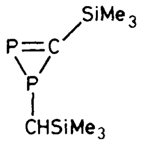
† The ^{31}P n.m.r. spectrum of (**4**) seems to compare well with the $\delta(^{31}P)$ value (642 p.p.m.) given for the corresponding neutral phospha-alkene complex such as (**13**) (Cp = cyclopentadienyl).[4]

‡ Spectroscopic data for (**5**): ^{31}P n.m.r. (CH_2Cl_2) δ 121.3 (d, $^1J_{PH}$ 390 Hz); ^1H n.m.r. ($CDCl_3$) δ 0.08 and 0.28 (s, Me_3Si), 1.1 (s, CH), 7.53 (d, $^1J_{PH}$ 388 Hz, H); i.r. (CH_2Cl_2), 2067, 1983, 1945 cm^{-1}.

§ Carrié *et al.* have recently reported the synthesis of the diphosphirane (**14**).[5]

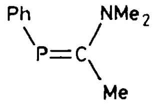
¶ Spectroscopic data for (**7**): $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2) δ −18.17 (P–Cl) and −125.5 [P–$CH(SiMe_3)_2$] (d, J_{PP} 238 Hz); ^1H n.m.r. (CD_2Cl_2) δ 0.14 (d, $^4J_{PH}$ 2.6, <0.5 Hz, $CSiMe_3$), 0.23 (d, $^4J_{PH}$ 1.12 Hz, $CHSiMe_3$), 0.28 (dd, $^4J_{PH}$ 0.7 and 0.64 Hz, $CSiMe_3$), 0.37 (d, $^4J_{PH}$ 1.95 Hz, $CHSiMe_3$); ^{13}C n.m.r. (CD_2Cl_2) δ 1.20, 1.64, 3.37, and 3.53 ($SiMe_3$), 7.68 (d, $^1J_{CH}$ 84.3 Hz, *C*H), 22.65 (dd, $^1J_{PC}$ 73 and 80 Hz, $CSiMe_3$).



(9)

$(Me_3Si)_2CH{-}P$

(10)



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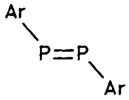

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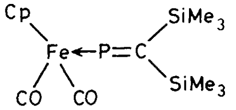
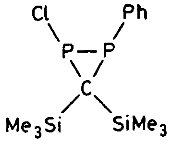


(13)

Ar = 2, 4, 6-$Bu^t_3C_6H_2$



(14)

elimination of chlorotrimethylsilane. Another important peak can be attributed to the phosphinidene (**10**). The exact formulation of compound (**8a**) [or (**8b**)] was mainly established by mass spectrometry [*m/z* 582 with successive loss of 4 CO groups, loss of Fe, followed by the same fragmentations as observed for (**7**)] and ^{31}P n.m.r. spectroscopy. Comparison of the ^{31}P chemical shifts of (**8a**) [or (**8b**)] [$\delta(^{31}P)$ 44.4 and -108.9 p.p.m., $^1J_{pp}$ 264 Hz] and (**7**) strongly indicates that one of the two phosphorus atoms is bonded both to a chlorine atom and to the $Fe(CO)_4$ moiety, allowing us to exclude the structure (**8b**) in favour of (**8a**).

Noteworthy is the fact that the hydride (**1**) does not react with the phospha-alkene (**11**) or the diphosphene (**12**).

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