Intramolecular Coupling Reaction of Phosphino–thioenolato Iron(II) Complexes with Alkynes. Crystal Structure of $[\overline{\text{Fe}\{\eta^3\text{-Ph}_2\text{P–CH=C(Bu}^t)\text{S–C}}\text{=CHPh}\}(\text{CO})(\text{PMe}_3)_2]\text{BF}_4$

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$[\text{FeCl}\{\eta^2\text{-Ph}_2\text{PCH=C(R)S}\}(\text{PMe}_3)(\text{CO})(\text{L})]$ complexes, prepared by ligand substitution, react with phenylacetylene in the presence of AgBF_4 or NaPF_6 and lead to carbon–sulphur bond formation between the β-phosphino–thioenolate ligand and the phenylvinylidene–iron intermediate, as shown by *X*-ray diffraction analysis.

Chelating β-phosphinoketonate ligands play an important role in promoting selective organometallic reactions such as nickel-catalysed alkene oligomerisation,[1] carbon–carbon bond forming reactions with carbon dioxide[2] or isocyanate,[3] and the building of polydentate phosphines.[4] Complexes of their sulphur analogues of type $\{\eta^2\text{-Ph}_2\text{PCH=C(R)S}\}\text{M}$ have been obtained only recently[5] and display specific properties, especially as proton traps for the formation of polyfunctional tripodal ligands.[6] We now report a new reaction leading to the coupling of the β-phosphinothioketonate ligand with a terminal alkyne which allows access to novel iron complexes containing functionalised polydentate phosphines.

Organometallic complexes with labile metal–halogen bonds are potential precursors of electrophilic vinylidene– and carbene–metal complexes on reaction with terminal alkynes.[7] Nucleophilic properties could be expected for the β-phosphinothioketonate ligand co-ordinated to an iron(II) centre,[6] and we have examined the reaction of derivatives of complex (**1**), containing both the β-phosphinothioketonate ligand and an iron–chlorine bond with phenylacetylene.

The readily available but unstable complex (**1**) was converted (by treatment with a three-fold excess of PMe_3) into the more stable trimethylphosphine derivatives (**2**) and (**3**) (Scheme 1). Surprisingly, the reaction is strongly solvent dependent: at room temperature after 48 h, in hexane–ether (1:1) the monosubstituted product (**2**) is obtained in 95% yield and in dichloromethane the disubstituted complex (**3**) is selectively formed and isolated in 75% yield; the transformation (**2**) → (**3**) in the presence of an excess of PMe_3 does not occur in dichloromethane at 25 °C, but only takes place in heptane at reflux for 6 h (91%). Spectroscopic data show that complex (**2**) retains the structure of (**1**) with *cis*-carbonyls and *trans*-phosphorus nuclei and that complex (**3**) contains equivalent PMe_3 groups, both *cis* to the (Ph_2P) ^{31}P nucleus.†

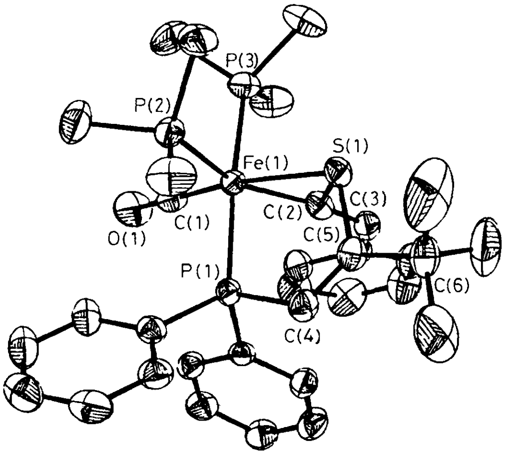

Figure 1. Molecular structure of $[\overline{\text{Fe}\{\eta^3\text{-Ph}_2\text{P–CH=C(Bu}^t)\text{S–C}}\text{=CHPh}\}(\text{CO})(\text{PMe}_3)_2]\text{BF}_4$ (**9a**) (ORTEP view). Selected bond distances (Å) and angles (°): Fe–S 2.259(1), Fe–C(1) 1.725(3), Fe–C(2) 1.900(4), Fe–P(1) 2.228(1), Fe–P(2) 2.279(1), Fe–P(3) 2.258(1), S(1)–C(2) 1.799(3), S(1)–C(5) 1.816(5), C(2)–C(3) 1.332(5), C(4)–C(5) 1.316(6); C(1)–Fe–S(1) 162.7(1), C(2)–Fe–S(1) 50.4(1), Fe–C(2)–C(3) 162.1(3), S(1)–C(2)–C(3) 122.6(3), P(1)–Fe–C(2) 85.4(1).

The chloride ligand of (**3**) is very labile as the cationic acetonitrile derivative (**4**) is obtained in 85% yield as a bright yellow crystalline precipitate by reacting (**3**) with NaBPh_4 in methanol in the presence of acetonitrile. Complex (**4**) is stable in solution only in the presence of an excess of acetonitrile. The acetonitrile ligand of (**4**) is easily displaced at room temperature by carbon monoxide or the phosphorus ligands PMe_3 and P(OMe)_3 to afford the cationic derivatives (**5**), (**6**), and (**7**) in good yields (70—90%) (Scheme 1). The structures of the compounds have been established on the basis of their ^1H and ^{31}P n.m.r. spectra.†

The acetonitrile derivative of (**4**) is not labile enough to be displaced by phenylacetylene. However, complex (**2**) reacts with phenylacetylene at room temperature either in dichloromethane with a slight excess of AgBF_4 (6 h) or in the more polar methanol–dichloromethane (2:1) medium but in the presence of an excess of NaPF_6 (24 h). Yellow, crystallized complexes (**8a**) (60%) and (**8b**) (85%) were isolated, respectively (Scheme 2) [(**8b**): ^1H n.m.r. (CDCl_3, 300 MHz) δ 7.93 (dd, =C*H*Ph,$^4J_{\text{PH}}$ 4.3 and 5.1 Hz), 6.62 (d, PCH=,$^2J_{\text{PH}}$ 6.2 Hz)].† Under similar conditions, complex (**3**) leads to

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† All compounds reported have microanalytical and spectroscopic data in accord with their assigned structures. *Selected spectroscopic data* for (**2**): i.r. (Nujol) ν(CO) 2013, 1961, ν(C=C) 1520 cm^{-1}, ^1H n.m.r. (CDCl_3, 80 MHz) δ 5.90 (d, PCH=,$^2J_{\text{PH}}$ 9 Hz), 1.67 (dd, PMe_3,$^2J_{\text{PH}}$ 10 Hz, $^4J_{\text{PH}}$ 1Hz); $^{31}\text{P-}\{1\text{H}\}$ n.m.r. (CDCl_3, 32.38 MHz) δ 72.5 (PPh_2), 13.7 p.p.m. (PMe_3), $^2J_{\text{PP}}$ 119 Hz.

For (**3**): i.r. (Nujol) ν(CO) 1917, ν(C=C) 1510 cm^{-1}; ^1H n.m.r. (CDCl_3, 80 MHz) δ 6.05 (d, PCH=, $^2J_{\text{PH}}$ 5 Hz) 1.04 (t, PMe_3, $|^2J_{\text{PH}} + {}^4J_{\text{P'H}}| = 8$ Hz); $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. (CDCl_3, 121.496 MHz) δ 79.1 (t, PPh_2), 6.7 p.p.m. (d, PMe_3), $^2J_{\text{PP}}$ 55 Hz.

For (**4**): i.r. (Nujol) ν(CO) 1915, ν(C=C) 1515 cm^{-1}, $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. (CDCl_3, 32.38 MHz) δ 68.6 (t, PPh_2), 4.9 p.p.m. (d, PMe_3), $^2J_{\text{PP}}$ 59 Hz.

For (**5**): i.r. (Nujol) ν(CO) 2030, 1970, ν(C=C) 1525 cm^{-1}; $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. (CDCl_3, 121.496 MHz) δ 63.72 (dd, PPh_2, $^2J_{\text{PP}}$ 78 and 58 Hz) 10.91 and 1.63 p.p.m. (dd, PMe_3, $^2J_{\text{PP}}$ 61 Hz).

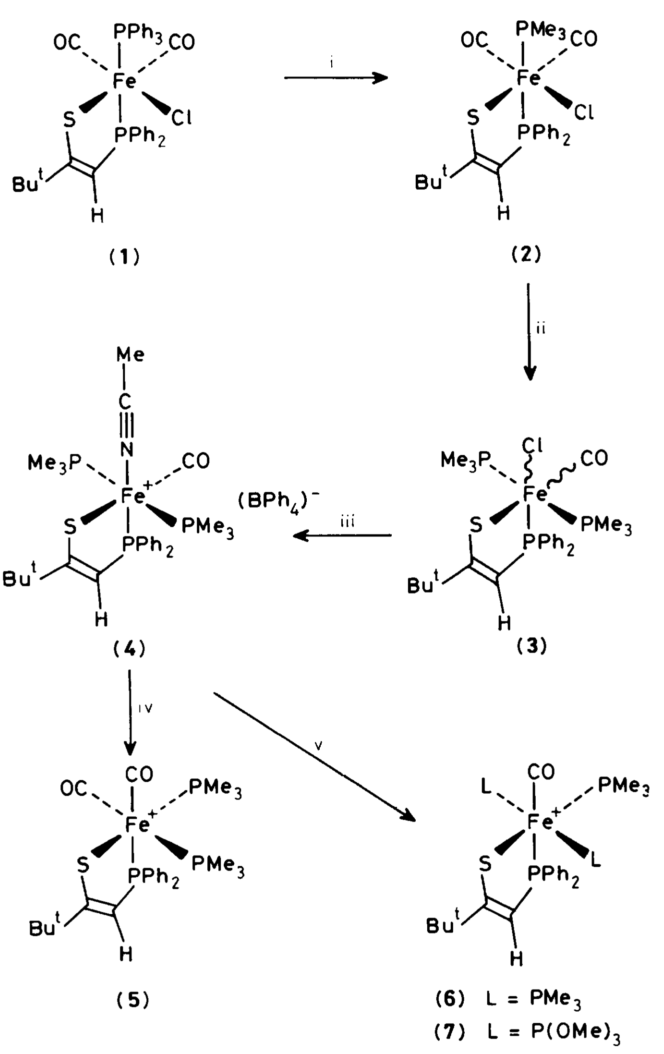
For (**6**): i.r. (Nujol) ν(CO) 1925, ν(C=C) 1505 cm^{-1}; $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. (CDCl_3 121.496 MHz) δ 70.02 (dt, PPh_2) 13.36 (dt, PMe_3), 2.73 p.p.m. (dd, 2PMe_3), $^2J_{\text{PP}}$ 83, 57, 53 Hz.

For (**7**): i.r. (Nujol) ν(CO) 1958, ν(C=C) 1525 cm^{-1}; $^{31}\text{P-}\{^1\text{H}\}$ (CDCl_3, 121.496 MHz) δ 139.17 [dd, 2P(OMe)_3], 72.08 (dt, PPh_2), 20.57 p.p.m. (dt, PMe_3), $^2J_{\text{PP}}$ 94, 86, 68 Hz.

For (**8b**): i.r. (Nujol) ν(CO) 2042, 1985 cm^{-1}; $^{31}\text{P-}\{^1\text{H}\}$ n.m.r. (CDCl_3, 121.496 MHz) δ 80.22 (PPh_2), 19.71 p.p.m. (PMe_3), $^2J_{\text{PP}}$ 101 Hz.

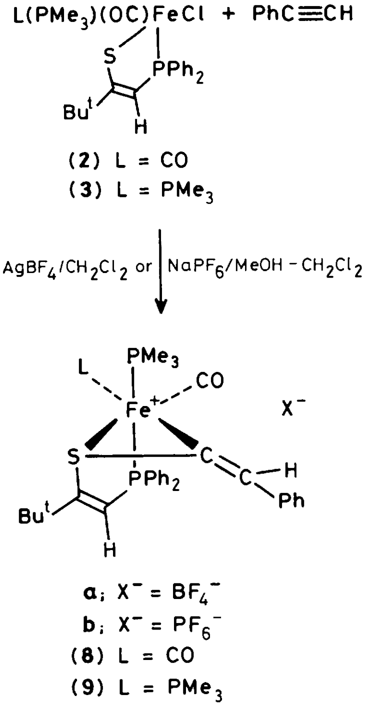
For (**9a**): i.r. (Nujol) ν(CO) 1910, ν(BF_4) 1055 cm^{-1}.

For (**9b**): i.r. (Nujol) ν(CO) 1910, ν(PF_6) 840 cm^{-1}; ^{31}P n.m.r. (CD_3CN, 32.38 MHz) δ 78.2 (dd, PPh_2, $^2J_{\text{PP}}$ 109 and 38 Hz), 20.3 and 1.48 p.p.m. (dd, PMe_3, $^2J_{\text{PP}}$ 42 Hz).



Scheme 1. *Reagents and conditions:*, i, PMe$_3$, hexane, room temp.; ii, PMe$_3$, heptane; iii, NaBPh$_4$, MeCN; iv, CO, 1 atm.; v, L = PMe$_3$ or 2L, L = P(OMe)$_3$.

complexes (**9a**) (60%) and (**9b**) (65%) (Scheme 2) [(**9b**): ^{13}C-{^{1}H} n.m.r. (CD$_3$CN, 75.469 MHz) δ 185.95 [d(dd) Fe–C(S)=,$^2J_{PC}$30, 27, 19 Hz], 178.88 [dd,=C(Bu^t)S,$^2J_{PC}$ 17,$^3J_{PC}$ 6 Hz), 143.46 (s, =CHPh)].† As spectroscopic data of similar complexes (**8**—**9**)† only indicated some modification of the η^2-Ph$_2$PCH=C(Bu^t)S ligand and the incorporation of phenylacetylene, a single crystal *X*-ray structural analysis was carried out on complex (**9a**).‡ The ORTEP plot of the structure in Figure 1 shows that the formation of (**9**) results from the coupling of the sulphur atom of the β-phosphinothioketonate ligand with the vinylidene carbon atom arising from phenylacetylene. It is noteworthy that the PhCH=C(S)Fe skeleton is almost planar and orthogonal to the P(1)–C(4)=C(5)S ligand plane. The large Fe–C(2)–C(3) angle [162.1(3)°] indicates that the PhCH=C group, rather than a vinyl group, keeps the memory of a vinylidene ligand, even if the Fe–C(2) bond distance [1.900(4) Å] is slightly longer than that of a Fe–C(carbene) bond.[6]



Scheme 2

The sulphur–carbon bond coupling leading to complexes (**8**) and (**9**) corresponds to the nucleophilic addition of the sulphur atom to the electrophilic carbon of the vinylidene–iron intermediate. This reaction can be compared, but strongly contrasts with, the electrophilic addition of sulphur to the electron-rich Os^0(=C=CHPh)(PPr$^i_3$)(η^6-C$_6$H$_6$) complex leading to an Os^{II}(η^2-S–C=CHPh) moiety.[8] It contrasts also, probably because of the distance of the reactive sites, with our previous studies[6] showing that the C(4) olefinic carbon atom of the {Ph$_2$P–C(4)=C(R)S} Fe moiety is the most basic site. We are currently studying the potential of the new bidentate ligand.

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References

1 W. Keim, A. Behr, B. Kruber, B. Hoffmann, F. H. Kowaldt, V. Kürschner, B. Limbäcker, and F. P. Sistig, *Organometallics*, 1986, **5**, 2356, and references therein.

2 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**, 5115.

3 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt, and D. Nobel, *J. Chem. Soc., Chem. Commun.*, 1987, 488.

4 P. Braunstein, D. Matt, D. Nobel, and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1987, 1530.

5 P. Robert, H. Le Bozec, P. H. Dixneuf, F. Hartstock, N. J. Taylor, and A. J. Carty, *Organometallics*, 1982, **1**, 1148.

6 A. Samb, B. Demerseman, P. H. Dixneuf, and C. Mealli, *Organometallics*, 1988, **7**, 26.

7 M. I. Bruce and A. J. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 59.

8 R. Weinand and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1985, 1145.

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‡ *Crystal data*: C$_{33}$H$_{44}$P$_3$SBF$_4$OFe, monoclinic, $P2_1/c$, a = 17.001(5), b = 11.142(2), c = 20.425(4) Å, β = 113.49(2)°, U = 3549.3(1.5) Å^3, Z = 4, D_c = 1.355 g cm^{-3}. Data collected on a Enraf-Nonius CAD-4 diffractometer with Mo-K_α radiation [6283 measured (2θ ≤ 50°), 4432 used ($I \geq 3\sigma(I)$ reflections]. The structure was solved by Patterson methods and refined to R = 0.043, (R_w = 0.047). Anisotropic temperature factors for all the non-hydrogen atoms were used in the least-squares refinement with the exception of phenyl carbon atoms treated as D_{6h} rigid bodies. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.