

# Mono-olefin Chelate Complexes of Iron(0) and Ruthenium(0) with an Olefinic Tertiary Phosphine

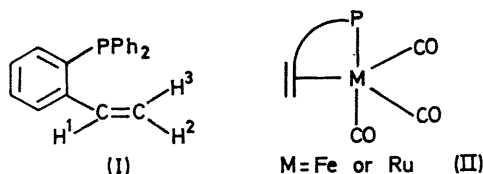
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**Summary** Reaction of 2-vinylphenyl(diphenyl)phosphine,  $o\text{-CH}_2\text{:CH-C}_6\text{H}_4\text{-PPh}_2$  (sp), with  $\text{M}_3(\text{CO})_{12}$  (M = Fe or Ru) gives monomeric complexes  $\text{M}(\text{CO})_3(\text{sp})$  and  $\text{M}(\text{CO})_2(\text{sp})_2$ ; the former are chelate mono-olefin complexes containing bidentate (sp), while  $\text{Fe}(\text{CO})_2(\text{sp})_2$  is shown by our X-ray structural analysis to contain a bidentate (sp) ligand, and a monodentate P-bonded (sp) moiety, in a configuration approximating to a trigonal bipyramid.

MONO-OLEFIN substituted derivatives of  $\text{Fe}(\text{CO})_5$ , e.g.  $\text{C}_2\text{H}_4\text{Fe}(\text{CO})_4$ , are thermally unstable and air-sensitive,<sup>1,2</sup> except when the double bond carries strongly electron-withdrawing substituents.<sup>3,4</sup> The analogous ruthenium derivatives are unknown. The ligand 2-vinylphenyl(diphenyl)phosphine,  $o\text{-CH}_2\text{:CH-C}_6\text{H}_4\text{-PPh}_2$  (sp) (I), which can form either monodentate (P-bonded) or bidentate derivatives, stabilises mono-olefin co-ordination for  $\text{Cr}^0$ ,  $\text{Mo}^0$ ,  $\text{W}^0$ ,  $\text{Mn}^1$ , and  $\text{Re}^1$ ,<sup>5,6</sup> and we have now extended this series to include  $\text{Fe}^0$  and  $\text{Ru}^0$ .

respectively. Both are air-stable and soluble in organic solvents. The ruthenium analogues,  $\text{Ru}(\text{CO})_3(\text{sp})$  (3) and  $\text{Ru}(\text{CO})_2(\text{sp})_2$  (4), are obtained similarly from  $\text{Ru}_3(\text{CO})_{12}$ , the respective yields depending on the  $\text{Ru}_3(\text{CO})_{12}:(\text{sp})$  ratio. Complexes (1) and (3) show three terminal  $\nu(\text{CO})$  i.r.



bands (Table 1), and they also show strong parent-ion peaks in their mass spectra. Co-ordination of the double bond is indicated by the marked upfield shifts of the olefinic protons relative to those of the free ligand, and also by strong <sup>31</sup>P coupling to all three olefinic protons [cf.  $\text{Cr}(\text{CO})_4$

TABLE 1

Properties of  $\text{Fe}^0$  and  $\text{Ru}^0$  complexes of (sp)

Complex	Colour	M.p.	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) <sup>a</sup>
$\text{Fe}(\text{CO})_3(\text{sp})$ (1)	Yellow-brown glassy solid	45—47°	2039, 1972, 1945
$\text{Fe}(\text{CO})_2(\text{sp})_2$ (2)	Yellow crystals	decomp. > 175°	1960, 1893
$\text{Ru}(\text{CO})_3(\text{sp})$ (3)	Orange crystals	63—64°	2060, 1990, 1968 <sup>b</sup>
$\text{Ru}(\text{CO})_2(\text{sp})_2$ (4)	Yellow crystals	170° (decomp. > 175°)	1978, 1917

<sup>a</sup> All bands quoted are very strong; measured in cyclohexane except where stated.

<sup>b</sup> Measured in n-octane.

TABLE 2

<sup>1</sup>H n.m.r. spectra of (sp) and its complexes<sup>a, b</sup>

Compound (sp) <sup>c</sup>	$\delta(\text{H}^1)$ ca. 6.8 (c)	$\delta(\text{H}^2)$ 5.14 (d)	$\delta(\text{H}^3)$ 5.60 (t)	Coupling constants (Hz)
$\text{Cr}(\text{CO})_4(\text{sp})$	5.06 (7 lines)	3.25 (dd)	2.86 (dd)	$ J_{13} 17.5$ $ J_{12} 11.0$ $ J_{23} 1.3$ $ J_{\text{P-H}^1} 1.1$
$\text{Fe}(\text{CO})_3(\text{sp})$	4.0 (8 lines)	2.73 (7 lines)	1.94 (1:2:1 td)	$ J_{13} 13.0$ $ J_{12} 9.0$ $ J_{23} 0$ $ J_{\text{P-H}^1}  =  J_{\text{P-H}^2} 5.0^d$ $ J_{\text{P-H}^3} ca. 2$
$\text{Ru}(\text{CO})_3(\text{sp})$	3.96 (6 lines)	2.45 (7 lines)	1.62(1:2:1 td)	$ J_{13} 9.8$ $ J_{12} 8.5$ $ J_{23} 2.3$ $ J_{\text{P-H}^1} 4.55$ $ J_{\text{P-H}^2} 5.55$ $ J_{\text{P-H}^3} 9.35$
$\text{Fe}(\text{CO})_2(\text{sp})_2$ free co-ordinated	e	5.10 (d)	5.50 (d)	$ J_{13} 9.0$ $ J_{12} 8.5$ $ J_{23} 3.0$ $ J_{\text{P-H}^1} 3.5$ $ J_{\text{P-H}^2} 5.0$ $ J_{\text{P-H}^3} 8.0$
$\text{Ru}(\text{CO})_2(\text{sp})_2$ free co-ordinated	e	5.10 (d)	5.50 (d)	$ J_{13} 17.0$ $ J_{12} 10.0$ $ J_{23} ca. 0$
	2.84 (m)	1.9 (m)	1.9 (m)	f $ J_{13} 17.0$ $ J_{12} 11.0$ $ J_{23} ca. 0$

<sup>a</sup> Measured in  $\text{C}_6\text{D}_6$ , except where indicated;  $\delta$  in p.p.m. downfield of  $\text{Me}_4\text{Si}$  as internal reference; protons are numbered as in (I).

<sup>b</sup> Abbreviations: m, multiplet; d, doublet; dd, doublet of doublets; td, triplet of doublets.

<sup>c</sup> Measured in  $\text{CDCl}_3$ ; chemical shifts are considered more accurate than those in ref. 5; see also A. G. Moritz, J. D. Saxby, and S. Sternhell, *Austral. J. Chem.*, 1968, **21**, 2565.

<sup>d</sup> Assigned incorrectly to  $J_{23}$  in ref. 5; <sup>31</sup>P decoupled spectra confirm present assignment.

<sup>e</sup> Beneath aromatic protons.

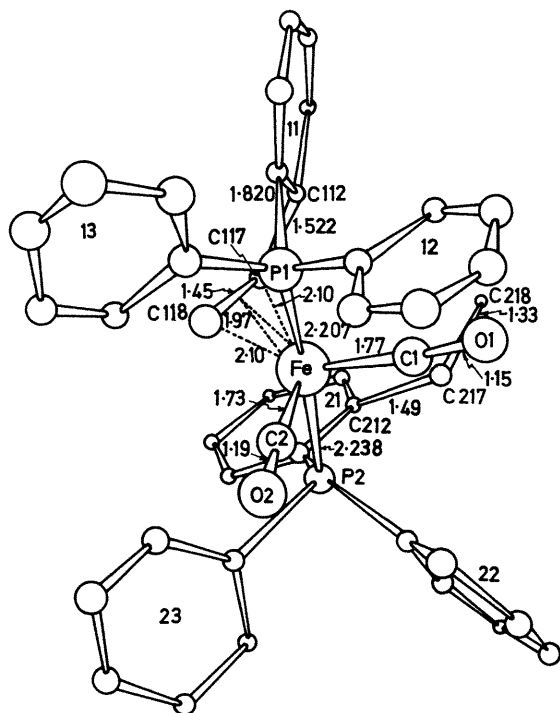
<sup>f</sup> Spectrum too complex to obtain coupling constants.

Reaction of (sp) and freshly prepared  $\text{Fe}_3(\text{CO})_{12}$  (1:1 mol ratio) in n-octane under reflux gives two products,  $\text{Fe}(\text{CO})_3(\text{sp})$  (1) and  $\text{Fe}(\text{CO})_2(\text{sp})_2$  (2) in yields of ca. 20 and 60%,

(sp)]<sup>5</sup> (Table 2). Consequently (1) and (3) are formulated as chelated mono-olefin derivatives with the trigonal bipyramidal structure (II). A surprising feature of their

n.m.r. spectra is the similarity of the magnitudes of the *cis*- and *trans*-coupling constants ( $J_{12}$  and  $J_{13}$ ) of the co-ordinated vinyl group (Table 2).

Complex (2) was originally formulated as  $\text{Fe}(\text{CO})_3(\text{sp})_2$ ,<sup>7</sup> with two mutually *cis*-monodentate, P-bonded (sp) ligands. However, (2) and (4) show only two strong  $\nu(\text{CO})$  bands, and the <sup>1</sup>H n.m.r. spectra show signals assignable to co-ordinated



FIGURE

and unco-ordinated vinyl groups in a 1:1 ratio (Table 2). The proton resonances of the co-ordinated vinyl group appear as two complex multiplets in a 2:1 ratio, indicating strong coupling with mutually *trans* phosphorus atoms. These data suggest that (2) and (4) are derived from (1) and

(3) respectively by substitution of one of the axial carbonyl groups by P-bonded monodentate (sp). X-ray powder diffraction data indicate that  $\text{Fe}(\text{CO})_2(\text{sp})_2$  and  $\text{Ru}(\text{CO})_2(\text{sp})_2$  are isomorphous and probably iso-structural.

The structure of  $\text{Fe}(\text{CO})_2(\text{sp})_2$  has been determined by three-dimensional single-crystal X-ray analysis of 2780 independent reflections [ $F_0^2/\sigma(F_0^2) \geq 3.0$ ] measured on a Picker FACS-1 diffractometer (crystal monochromated  $\text{Cu-K}\alpha$  radiation). The crystals are monoclinic, space group  $P2_1/c$ ,  $a = 13.62$ ,  $b = 18.47$ ,  $c = 24.45$  Å,  $\beta = 145.00^\circ$ ,  $Z = 4$ . With phenyl rings treated as rigid bodies and all atoms isotropic, refinement has converged with  $R = 0.088$ . Mean e.s.d.s of the more important bond lengths in the Figure are: Fe-P, 0.003; Fe-C, 0.01; C-O, 0.025; P-C, 0.005; C-C, 0.02 Å. No allowance has yet been made for absorption and extinction effects.

The configuration about the central iron atom approximates to a trigonal bipyramid. Two carbonyl groups and the vinyl substituent of one (sp) ligand occupy the three equatorial positions, while the phosphorus of the  $\pi$ -olefin bonded (sp) ligand and a second P-bonded monodentate (sp) group occupy the two axial positions. The shortening of Fe-P(1) [2.207(3) Å] compared with Fe-P(2) [2.234(3) Å] reflects the marked chelating ability of (sp).

The co-ordinated olefin is symmetrically bonded to the iron atom and subtends an angle of  $6^\circ$  with the equatorial plane. The bond distances Fe-C(117) and Fe-C(118) are equal [2.10(1) Å] and comparable with Fe-C(olefin) distances in  $\text{Fe}(\text{CO})_4(\text{CH}_2:\text{CHCN})$  [2.10(1)],<sup>8</sup>  $\text{Fe}(\text{CO})_4(\text{CH}:\text{CO}_2\text{H})_2$  [2.04(3)],<sup>9</sup> and  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  [2.12(3) Å],<sup>10</sup> each of which has the olefin in an equatorial site of a trigonal bipyramid. The C-C distance in the co-ordinated olefin [1.45(2) Å] is comparable with those reported for the acrylonitrile<sup>8</sup> and ethylene complexes<sup>10</sup> [1.40(2) and 1.46(6) Å, respectively], and is significantly longer than the C=C distance in the unco-ordinated vinyl group [1.33(2); cf. 1.335 Å expected<sup>11</sup>]. The average Fe-C (carbonyl) distance [1.75(1) Å] is significantly shorter than the equatorial Fe-C (carbonyl) distances found in  $\text{Fe}(\text{CO})_5$  [1.833(4)]<sup>12</sup> and in  $\text{Fe}(\text{CO})_4(\text{C}_2\text{H}_4)$  [1.84(4) Å]<sup>10</sup> by electron diffraction, presumably owing to the strong  $\sigma$ -donor and weak  $\pi$ -acceptor phosphorus ligands in place of CO in the axial positions.

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