Preliminary Investigations on the Chemistry of $(\eta^4-1$ -Phosphabutadiene)tricarbonyliron Complexes. Synthesis and X-Ray Crystal Structure Analysis of a $(\eta^4-2$ -Phosphabutadiene)-tricarbonyliron Complex[†]

Angela Marinetti, Siegfried Bauer, Louis Ricard and François Mathey*

Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

The reaction of the η^2 -complexed and half-masked dialdehyde [Fe(CO)₄{trans-(MeO)₂CHCH=CHCHO}] with the 'phospha-Wittig' reagent [W(CO)₅{PHPhPO(OEt)₂}] yields, after unmasking of the second aldehyde functionality, the 1-phosphabutadiene complex [Fe(CO)₃{ η^4 -O=CHCH=CHCH=PPh[W-(CO)₅]}], **4**. The aldehyde functionality of **4** normally reacts with methyllithium, a phosphorus ylide, LiAlH₄, or a dimercaptan to give the expected products in high yield without destruction of the (η^4 -1-phosphadiene)tricarbonyliron moiety. Thus, Fe(CO)₃ is a convenient protecting group for the otherwise unstable 1-phosphadiene unit. Similarly, the reaction of isobutyraldehyde with the phospha-Wittig reagent [W(CO)₅{*trans*-PhCH=CHPHPO(OEt)₂}] yields a (2- phosphabutadiene)pentacarbonyltungsten complex whose X-ray crystal structure analysis shows a planar, transoid, but not delocalized 2-phosphadiene unit. Reaction of this complex with [Fe₂(CO)₉] gives a complex with a planar, cisoid and fully delocalized 2-phosphadiene unit according to the X-ray data.

Extensive research is currently carried out on the phosphorus analogues of classical unsaturated hydrocarbon π complexes.¹ The phosphorus atom obviously displays an exceptional ability to replace carbon atoms in the skeleton of any of these π complexes. In line with this, we have recently discovered that it is possible to prepare stable η^4 -1-phosphabutadiene complexes.^{2,3} Since free 1-phosphadienes tend to cyclize^{4,5} except when they are kinetically stabilized by bulky substituents, and since steric hindrance destroys the reactivity of the diene unit,[‡] it is, in practice, very difficult to develop a versatile chemistry with these species. Thus, their stabilization by complexation offers a unique opportunity fully to develop their synthetic potential. In this work, we describe the results of our first investigations on the chemistry of these complexes and show how it is possible to transpose their synthesis to get the previously unknown η^4 -2-phosphabutadiene complexes.

Results and Discussion

Since our aim was to develop the chemistry of the phosphadiene unit, we first decided to study some classical electrophilic substitutions such as acylation and formylation at the γ terminal carbon. These reactions are well known in the case of



Scheme 1 (a) LiBu, tetrahydrofuran (thf), -70 °C; (b) [Fe(CO)₄-(EtCH=CHCHO)], 25 °C, 1 h

† Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: eV $\,\approx\,1.60\,\times\,10^{-19}$ J.

 \ddagger For example, neither [4 + 2] cycloadditions nor η^4 complexations have ever been described with sterically hindered 1-phosphadienes.

 $(\eta^4$ -butadiene)tricarbonyliron.⁸ For that purpose, we prepared the 4-ethyl-substituted compound 2 using the already described 'phospha-Wittig' approach³ (Scheme 1). Unfortunately, all our attempts with 2 and MeC(O)Cl + AlCl₃ in dichloromethane or HC(O)NMe₂ + P(O)Cl₃ failed to give the expected 4-acetyl and 4-formyl derivatives. In the first case, decomposition by AlCl₃ occurred and in the second case no reaction was observed. A possible adverse effect of the C₄ substitution was envisaged but could not be corrected because this substitution is essential for the success of the synthesis of complexes such as 2.

Taking into account the central role played by the formyl derivatives in the chemistry of (η^4 -diene)tricarbonyliron compounds,⁹ we decided to introduce a masked aldehyde functionality *via* the phospha-Wittig synthesis. Unmasking of the carbonyl group was then performed using a described procedure¹⁰ (Scheme 2).



The availability of compound 4 allowed us to study the efficiency of $Fe(CO)_3$ as a protecting group for the phosphadiene toward a variety of reagents. This protection appears to be very efficient indeed. The carbonyl group of 4 was allowed to react with methyllithium, a phosphorus ylide, lithium aluminium hydride, and a mercaptan to give the expected products in high yields (Scheme 3). Upon acidic treatment the



Scheme 3 (a) LiMe, thf, -70 to $25 \,^{\circ}C$; (b) water, NH_4^+ ; (c) $Ph_3P=CHCO_2Me$, thf, $70 \,^{\circ}C$, $20 \,^{o}min$; (d) LiAlH₄, AlCl₃, Et₂O; -70 to $-50 \,^{\circ}C$, H^+ (water); (e) HS(CH₂)₃SH, BF₃•Et₂O, CHCl₃, 25 $^{\circ}C$, 1 h

alcohols 5a, 5b, and 7 gave the expected carbocations which yielded the corresponding olefin 9 in the first case and the corresponding ether 10 in the second case (Scheme 4). Com-





Scheme 4 (*i*) HBF₄, Et₂O, 25 °C, 1 h; (*ii*) HBF₄, Et₂O, 25 °C, 2 h

plexes 5 and 10 were obtained as mixtures of isomers due to the planar chirality of the phosphadiene–Fe(CO)₃ unit. In the case of 6 the external C=C double bond has either the Z or E stereochemistry. The ¹H NMR spectra of all these compounds (Table 1) give two clues concerning the stereochemistry of the phosphadiene unit. The α -proton of the phosphadiene shows no coupling with phosphorus. According to our previous work³ this observation unambiguously demonstrates that the phenyl P substituent is in the plane of the phosphadiene unit and the W(CO)₅ complexing group out of this plane on the opposite side to iron (Fig. 1). On the other hand, the ${}^{3}J(H_{\beta}-H_{\gamma})$ coupling of *ca*. 9 Hz in all these compounds is close to that of 9.6 Hz recorded for the only structurally characterized compound of this class ³ and to the corresponding coupling (9.19 Hz) in (η^{4} -butadiene)tricarbonyliron.¹¹ This observation confirms that the initial *trans* stereochemistry of the starting aldehyde used in the phospha-Wittig synthesis (Scheme 2) has been retained in the phosphadiene unit and that the substituents at the γ -carbon occupy the *exo* position (Fig. 1).



Fig. 1 Stereochemistry of the $(\eta^4$ -phosphadiene)tricarbonyliron complexes

We then turned our attention toward the 2-phosphabutadiene system. At the moment only a few hindered 2-phosphadienes are known^{6,12} and they have not been characterized by X-ray analysis. We first synthesised a 'free' 2-phosphadiene unit **12** using the 'phospha-Wittig' approach (Scheme 5). Only one



isomer of the 2-phosphadiene was obtained and was submitted to X-ray analysis. The molecular structure (Fig. 2) shows a planar transoid phosphadiene unit with the two substituents (Ph and Me₂CH) *trans* to the central C-P bond. The W(CO)₅ complexing group lies in the diene mean plane contrary to that which occurs in the η^4 -1-phosphadiene-Fe(CO)₃ complexes: distance of W to the PC(1)C(2)C(3) mean plane = 0.0821 \pm 0.0003 Å. However, in spite of the planarity of the phosphadiene unit, no delocalization apparently takes place and the two P=C and C=C subunits seem to be independent. Indeed, the P-C(1) bond length has a normal value for a single bond (*ca.* 1.80 Å) and the P=C and C=C bonds are very short [1.626(7) and 1.33(1) Å respectively]. Besides, **12** reacts as a normal phospha-



Fig. 2 ORTEP plot of complex **12**. Ellipsoids are scaled to enclose 50% of the electronic density; hydrogen atoms are omitted for clarity. Principal bond distances (Å): W–P 2.472(2), P–C(1) 1.799(8), P–C(3) 1.626(7), C(1)–C(2) 1.33(1), C(2)–C(7) 1.45(1) and C(3)–C(4) 1.52(1). Selected bond angles (°): W–P–C(1) 125.1(3), W–P–C(3) 129.3(3), C(1)–P–C(3) 105.6(4), P–C(1)–C(2) 122.1(6), C(1)–C(2)–C(7) 124.4 (7) and P–C(3)–C(4) 125.8(6)

Table 1 Proton NMR data for 4-substituted 1-phenyl-1-phosphabutadiene complexes $[Fe(CO)_3[\eta^4-RCH=CHCH=PPh[W(CO)_5]]^a$

Complex	Substituent R	$\delta(\mathbf{H}_{a})^{b}$	$\delta(H_{\beta})$ [³ J(H _{\beta} -P)]	δ(H _γ)	$^{3}J(\mathrm{H}_{\alpha}-\mathrm{H}_{\beta})$	³ <i>J</i> (Н _β –Н _γ)
2	Et	4.78	ca. 4.8	2.15	c	c
3	$CH(OMe)_2$	4.82	5.54	2.20	6.33	9.03
	() 1		[21.5]			
4	СНО	4.88	5.87	2.20	6.50	8.79
			[22.84]			
5b	CH(OH)Me ^d	4.80	5.48	2.17	6.32	9.17
			[22.77]			
5a		4.79	5.32	2.22	6.44	9.14
			[23.03]			
	/					
6b	CH=CHCO ₂ Me ^a	4.73	5.05	2.84	6.35	9.25
	trans		[21.85]			
6a	cis	4.87	ca. 4.9	4.36	6.45	9.60
7	CH ₂ OH	4.78	5.24	2.22	6.40	9.30
	0		[22.32]			
8	_°	4.83	5.32	2.48		
	cí È		[22.4]		6.49	8.93
	`s/					
0	CH-CH	171	5.01	2.00	6 3 1	0.00
,	$c_1 - c_1_2$	4.74	5.01	2.39	0.34	9.00
			[22.0]			

^{*a*} J in Hz. Data recorded at 200 MHz in $C_6 D_6$, standard SiMe₄. Some additional ¹H NMR data are given in the Experimental section. ^{*b* 2} J(H_a-P) = 0. ^{*c*} Unresolved coupling constant. ^{*d*} **b**, Major isomer; **a**, minor isomer.

alkene complex with a variety of reagents.* No obvious explanation is available since the energy levels of the π orbitals corresponding to the C=C and P=C subunits are, *a priori*, close so that an efficient mixing is possible.† In spite of this absence of delocalization, **12** easily reacts with [Fe₂(CO)₉] to give the corresponding η^4 complex **13** (Scheme 6). The indicated yield



Scheme 6 (a) $[Fe_2(CO)_9]$, thf, 40 °C, 40 min; (b) toluene, reflux, 1.5 h

corresponds to a chromatographed and recrystallized product. The actual yield of the reaction is much higher. Complex 13 was submitted to X-ray analysis. The molecular structure (Fig. 3) shows a planar cisoid phosphadiene unit as expected. The $W(CO)_5$ complexing group lies in the diene mean plane as in the previous case. In contrast, full delocalization occurs in 13. The two P-C bonds are almost equal at 1.743(4) and 1.753(4) Å. The C(1)-C(2) bond is much longer than previously [1.397(6) Å]. The iron atom is at 1.6284(6) Å from the diene mean plane. Another interesting point concerns the $W(CO)_5$ complexing group: the P-W bond length is strictly equal in 12 and 13 (2.472 Å) exactly as if the lone pair at phosphorus and the phosphadiene system involved in the complexations of tungsten and iron were completely independent. This P-W bond length is much shorter than in the σ , η^4 -1-phosphadiene complex whose structure was described in our previous work³ [2.591(1) Å]. Besides, the ${}^{1}J(P-W)$ coupling constants are respectively equal to 254, 264, and 225 Hz for 12, 13, and the 1-phosphadiene-Fe(CO)₃-W(CO)₅ complex. These data suggest that phos-



Fig. 3 ORTEP plot of complex 13. Ellipsoids are scaled to enclose 50% of the electronic density; hydrogen atoms are omitted for clarity. Principal bond distances (Å): W–P 2.472(1), Fe–P 2.275(1), Fe–C(1) 2.102(4), Fe–C(2) 2.201(4), Fe–C(3) 2.150(4), P–C(1) 1.743(4), P–C(3) 1.753(4), C(1)–C(2) 1.397(6), C(2)–C(7) 1.480(6) and C(3)–C(4) 1.508(6). Selected bond angles (°): P–Fe–C(1) 46.7(1), P–Fe–C(2) 76.1(1), P–Fe–C(3) 46.6(1), C(1)–Fe–C(2) 37.8(2), C(1)–Fe–C(3) 77.2(2), C(2)–Fe–C(3) 80.7(2), W–P–Fe 133.93(5), W–P–C(1) 123.4(1), W–P–C(3) 137.8(1), Fe–P–C(1) 61.4(1), Fe–P–C(3) 63.0(1), C(1)–P–C(3) 98.7(2), Fe–C(1)–P 71.9(1), Fe–C(3)–P 70.5(1) and P–C(3)–C(4) 119.5(3)

phorus is a better acceptor ‡ and a better ligand toward iron when located in the central than in the terminal position of the diene.

Experimental

All reactions were carried out under argon. Chromatographic separations were performed on a silica gel column (70–230 mesh, Merck). NMR spectra were recorded on a Brucker AC 200 SY spectrometer operating at 200.13 MHz for ¹H and 50.32 MHz for ¹³C and on a Brucker WP 80 SY spectrometer operating at 32.44 MHz for ³¹P. Chemical shifts are expressed in

^{*} The synthesis of compound 11 and the organic chemistry of 12 will be reported elsewhere.

[†] The ionization potential of the π system is 10.3 eV in CH₂=PH, 10.5 eV in CH₂=CH₂.¹³

 $[\]ddagger The^{-1}J(P-W)$ coupling increases with the electronegativity of the phosphorus substituents.¹⁴

ppm downfield from internal SiMe₄ (¹H and ¹³C) and external 85% H₃PO₄ (³¹P). Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct-inlet method. Infrared spectra were recorded with a Perkin-Elmer model 297 spectrometer. Elemental analyses were performed by the service d'Analyse du CNRS, Gif-sur-Yvette, France.

Synthesis of the 1-Phosphabutadiene Complexes 2 and 3.— The complexes $[Fe(CO)_4(EtCH=CHCHO)]$ and $[Fe(CO)_4-{(MeO)_2CHCH=CHCHO}]$ are prepared as usual from diiron nonacarbonyl and the corresponding aldehyde in benzene at 40 °C. For the synthesis of *trans*-4,4-dimethoxybut-2-enal see ref. 15.

Butyllithium (1.3 cm³, 1.6 mol dm⁻³ solution in hexane) was added at -78 °C to a solution of complex 1 (1.14 g, 2.0 mmol) in thf. After a few minutes a solution of the [Fe(CO)₄(aldehyde)] complex (2.2 mmol) in thf was added. The solution was allowed to warm to room temperature and stirred for about 1 h. After hydrolysis and evaporation, the final product was purified by chromatography on silica gel column with hexane–diethyl ether (98:2) as eluent.

Complex 2: yield 0.72 g (56%); yellow-orange solid, m.p. 118 °C; IR (decalin) v[Fe(CO)₃] 2055s, 2005s, 2000(sh), v[W(CO)₅] 2075m and 1945vs cm⁻¹; ³¹P NMR (C₆D₆) δ -27.3 [¹J(¹⁸³W-³¹P)232Hz]; ¹H NMR (C₆D₆) δ 0.98 [t, ³J(H-H) 7.3 Hz, CH₃] and 1.5 (m, 2 H, CH₂); ¹³C NMR (C₆D₆) δ 16.33 (s, CH₃), 28.19 (s, CH₂), 74.94 [d, ³J(C-P) 19.1, HC₉], 76.95 [d, ¹J(C-P) 13.6, HC_a], 95.36 [d, ²J(C-P) 8.6, HC₉], 196.74 [d, ²J(C-P) 7.0 Hz, *cis* CO, W(CO)₅], 198.58 ppm [d, ²J(C-P) 27.7 Hz, *trans* CO, W(CO)₅], Fe(CO)₃ unresolved; mass spectrum (¹⁸⁴W) *m*/*z* 640 (*M*⁺, 6), 500 (*M* - 5CO, 55) and 414 (100%).

Complex 3: yield 0.82 g (60%); yellow solid, m.p. 130 °C (hexane); IR (decalin) v[Fe(CO)₃] 2060s, 2015(sh), 2005s, v[W(CO)₅] 2075m and 1945vs cm⁻¹; ³¹P NMR (C₆D₆) δ -27.7 [¹J(¹⁸³W-³¹P) 234 Hz]; ¹H NMR (C₆D₆) δ 3.11 (s, OCH₃) and 4.39 [d, ³J(H-H) 3.2 Hz, CH(OMe)₂]; ¹³C NMR (C₆D₆) δ 52.67 (s, OCH₃), 54.15 (s, OCH₃), 68.51 [d, ³J(C-P) 19.1, HC_γ], 77.69 [d, ¹J(C-P) 14.1, HC_α], 93.36 [d, ²J(C-P) 8.1 Hz, HC_β] and 102.74 ppm [s, CH(OMe)₂]; mass spectrum (¹⁸⁴W) *m*/*z* 685 (*M* - 1, 13), 602 (*M* - 3CO, 57), 462 (*M* - 8CO, 61) and 446 (100%) (Found: C, 35.05; H, 2.05. Calc. for C₂₀H₁₅FeO₁₀PW: C, 35.00; H, 2.20%).

Hydrolysis of the Acetal group of Complex 3: Synthesis of Complex 4.—Water (three drops) was added with continuous magnetic stirring to a suspension of silica gel (0.9 g) in dichloromethane. Trichloroacetic acid (about 70 mg) and the acetal 3 (1.3 g, 2 mmol) were added and stirring was continued at room temperature for 1.5 h. The solid phase was separated by filtration. After evaporation the final product 4 was purified by chromatography with hexane-diethyl ether (90:10) as eluant: yield 1.24 g (97%); orange solid, m.p. 60 °C (decomposition); IR (decalin) v[Fe(CO)₃] 2065s, 2025m, 2018s, v[W(CO)₅] 2080m and 1950vs cm⁻¹; ³¹P NMR (C₆D₆) δ – 19.17 [¹J(¹⁸³W-³¹P) 239 Hz]; ¹H NMR (C₆D₆) δ 9.17 (s, CHO); ¹³C NMR (C₆D₆) δ 60.57 [d, ³*J*(C-P) 17.1, HC₇], 83.02 [d, ¹*J*(C-P) 14.1, HC₈], 93.35 [d, ²J(C-P) 8.1 Hz, HC_β] and 193.01 ppm (s, CHO); mass spectrum (¹⁸⁴W) m/z 639 (M - 1, 6), 556 (M - 3CO, 30), 416 (M - 8CO, 85) and 294 (100%) (Found: C, 33.80; H, 1.25. Calc. for C₁₈H₉FeO₉PW: C, 33.80; H, 1.40%).

Synthesis of Complexes **5a** and **5b**.—Methyllithium (1.4 cm³, 1.6 mol dm⁻³ solution in ether, 2.2 mmol) was added at -78 °C to a solution of complex **4** (1.3 g, 2 mmol) in thf. The solution was allowed to warm to room temperature and stirred for about 10 min. Hydrolysis with water–NH₄Cl and extraction in ether gave crude **5** which was purified by chromatography with hexane–diethyl ether (90:10): a small amount of the minor isomer **5a** was recovered first. Elution with hexane–diethyl ether (80:20) gave then the major isomer **5b**. Total yield: 1.26 g (96%).

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Complex 5a: orange solid; IR (decalin) v[Fe(CO)₃] 2060s, 2005s, v[W(CO)₅] 2075m and 1945vs cm⁻¹; ³¹P NMR (C₆D₆) δ -29.18 [¹J(¹⁸³W-³¹P) 234 Hz]; ¹H NMR (C₆D₆) δ 1.08 [d, ³J(H-H) 6.1 Hz, CH₃] and 3.68 (m, CHOH).

Complex **5b**: orange solid; m.p. 80 °C (decomposition); IR $(CH_2Cl_2) \vee [Fe(CO)_3] 2060s$, 2000s, $\nu [W(CO)_5] 2075m$ and 1940vs cm⁻¹; ³¹P NMR $(C_6D_6) \delta -27.3 [^1J(^{183}W-^{31}P) 234$ Hz]; ¹H NMR $(C_6D_6) \delta 0.97$ (OH), 1.16 [d, ³J(H-H) 6.4 Hz, CH₃] and 3.57 (m, CHOH); ¹³C NMR $(C_6D_6) \delta 25.99$ (s, CH₃), 68.39 (s, CHOH), 76.34 [d, ³J(C-P) 19.1, HC₇], 77.02 [d, ¹J(C-P) 12.6, HC₈], 92.23 ppm [d, ²J(C-P) 8.1 Hz, HC₈]; mass spectrum (¹⁸⁴W) *m*/z 655 (*M* - 1, 15), 572 (*M* - 3CO, 49), 460 (*M* - 7CO, 85) and 432 (*M* - 8CO, 100%).

Synthesis of Complexes **6a** and **6b**.—A solution of complex **4** (0.64 g, 1 mmol) and methyl (triphenylphosphoranylidene)acetate (0.33 g, 1 mmol) in thf was refluxed for 20 min. Chromatographic separation with hexane–diethyl ether (90:10) gave first the minor isomer **6a**. The major isomer **6b** was eluted then with hexane–diethyl ether (75:25). Total yield: 0.56 g (80%).

Complex 6a: yellow solid, m.p. 180 °C (decomposition); IR (decalin) v[Fe(CO)₃] 2055s, 2015s, 2000m, v[W(CO)₅] 2075m and 1945vs cm⁻¹; ³¹P NMR (C₆H₆) δ -25.11 [¹J(¹⁸³W-³¹P) 234 Hz]; ¹H NMR (C₆D₆) δ 3.37 (s, OCH₃) and 5.55 (m, 2 H, CH=CHCO₂Me).

Complex **6b**: orange solid, m.p. 156 °C (ether-pentane); IR $(CH_2Cl_2) \ \nu[Fe(CO)_3] 2060s, 2010s, \nu[W(CO)_5] 2080m, 1945vs, v(CO ester) 1710 cm⁻¹; ³¹P NMR (C_6D_6) \delta -23.08 [¹J(¹⁸³W-³¹P) 234 Hz]; ¹H NMR (C_6D_6) \delta 3.38 (s, OCH_3) and 6.39 (AB, ³J_{AB} 15.3 Hz, =CH); ¹³C NMR (C_6D_6) \delta 51.25 (s, OCH_3), 64.67 [d, ³J(C-P) 20.6, HC_7], 79.21 [d, ¹J(C-P) 14.6; HC_{a}], 95.23 [d, ²J(C-P) 7.6 Hz, HC_{b}], 122.06 (s, HCCO_2Me), 146.14 (s, CH=CHCO_2Me) and 166.13 ppm (s, CO_2Me); mass spectrum (¹⁸⁴W)$ *m*/*z*696 (*M*, 6), 612 (*M*- 3CO, 66), 556 (*M*- 5CO, 74) and 472 (*M*- 8CO, 100%) (Found: C, 36.00; H, 2.00. Calc. for C₂₁H₁₃FeO₁₀PW; C, 36.25; H, 1.90%).

Reduction of Complex 4 to the Alcohol 7.—A mixture of LiAlH₄ (50 mg, 0.8 mmol) and AlCl₃ (0.18 g, 1.3 mmol) in ether was cooled to -78 °C. Complex 4 (0.64 g, 1 mmol) was then added. The reaction mixture was allowed to warm slowly (0.5 h) to -50 °C and then hydrolysed with water–NH₄Cl. After extraction with ether and evaporation, the final product was purified by chromatography with hexane–diethyl ether (80:20). A small amount of the starting material was also recovered.

Complex 7: yield 0.46 g (72%); orange solid, m.p. 112 °C (CH₂Cl₂-pentane); IR (CH₂Cl₂) v[Fe(CO)₃] 2060s, 2005s, v[W(CO)₅] 2075m and 1940vs cm⁻¹; ³¹P NMR (C₆H₆) δ – 25.19 [¹J(¹⁸³W-³¹P) 232 Hz], ¹H NMR (C₆D₆) δ 0.82 (OH) and 3.39 (br s, CH₂OH); ¹³C NMR (C₆D₆) δ 62.68 (s, CH₂OH), 71.14 [d, ³J(C-P) 19.6, HC_γ], 77.17 [d, ¹J(C-P) 14.1, HC_α] and 93.19 ppm [d, ²J(C-P) 8.6 Hz, HC_β]; mass spectrum (¹⁸⁴W) *m*/z 642 (*M*, 13), 558 (*M* – 3CO, 34) and 418 (*M* – 8CO, 100%) (Found: C, 33.55; H, 1.95. Calc. for C₁₈H₁₁FeO₉PW: C, 33.70; H, 1.75%).

Synthesis of Complex 8.—Boron trifluoride etherate (two drops) was added to a mixture of complex 4 (1.3 g, 2 mmol) and propane-1,3-dithiol (0.20 cm³, 2 mmol) in CHCl₃. After stirring for 1 h at room temperature, the solvent was evaporated and the final product 8 was purified either by crystallization from an hexane–diethyl ether mixture or by chromatography with hexane–diethyl ether (90:10) as eluent: yield 1.7 g (88%); yellow solid, m.p. 172 °C (decomposition); IR (CH₂Cl₂) v[Fe(CO)₃] 2060s, 2010s, v[W(CO)₅] 2075m and 1945vs cm⁻¹; ³¹P NMR (C₆D₆) δ –25.2 [¹J(¹⁸³W–³¹P) 237 Hz]; ¹H NMR (C₆D₆) δ 1.2—1.6 (m, 2 H, CH₂), 2.2 (m, 4 H, SCH₂), 3.78 [d, ³J(H–H) 10.2 Hz, CHS]; ¹³C NMR (CDCl₃) δ 24.53 (s, CH₂), 31.11 (s, SCH₂), 31.43 (s, SCH₂), 50.45 (s, CHS), 69.07 [d, ³J(C–P) 20.1, HC_γ], 78.63 [d, ¹J(C–P) 15.1, HC_α], 94.65 ppm [d, ²J(C–P) 8.6 Hz, HC_β]; mass spectrum (¹⁸⁴W) *m/z* 730

 Table 2 Positional parameters and their estimated standard deviations

Atom	x	У	Ζ	Atom	x	у	Z
(a) Com	plex 12						
w	0.22212(2)	0.029 83(2)	0.830 65(3)	C(6)	-0.059 8(7)	0.207 5(6)	0.508(1)
Р	0.233 0(2)	0.155 8(1)	0.737 1(2)	C(7)	0.495 5(5)	0.264 1(4)	1.007 8(7)
O(13)	0.161 7(6)	-0.0253(3)	0.500 3(6)	C(8)	0.497 2(7)	0.338 6(4)	0.974 0(9)
O(14)	0.208 6(6)	-0.1301(3)	0.952 0(7)	C(9)	0.570 2(8)	0.386 2(5)	1.047(1)
O(15)	0.279 5(5)	0.083 9(4)	1.162 5(5)	C(10)	0.646 6(8)	0.363 8(5)	1.161(1)
O(16)	-0.0446(5)	0.051 0(4)	0.836 5(7)	C(11)	0.654 7(7)	0.290 6(6)	1.202 9(9)
O(17)	0.487 2(5)	0.001 7(4)	0.824 3(8)	C(12)	0.579 3(6)	0.242 6(5)	1.126 4(8)
C(1)	0.335 2(6)	0.224 0(4)	0.816 9(8)	C(13)	0.184 5(7)	-0.0051(4)	0.619 3(8)
C(2)	0.416 4(5)	0.210 0(4)	0.933 1(7)	C(14)	0.214 3(7)	-0.071 9(4)	0.907 7(8)
C(3)	0.150 5(6)	0.196 1(4)	0.601 0(8)	C(15)	0.260 3(6)	0.064 8(4)	1.044 3(8)
C(4)	0.045 2(6)	0.162 5(4)	0.504 8(8)	C(16)	0.052 4(7)	0.044 0(4)	0.835 2(9)
C(5)	0.064 0(9)	0.149 7(6)	0.347(1)	C(17)	0.393 7(7)	0.012 2(4)	0.828 2(9)
(b) Com	plex 13						
W	0.774 48(2)	0.353 53(1)	0.260 17(1)	C(6)	0.648 8(5)	0.756 8(6)	0.038 8(4)
Fe	1.007 24(6)	0.815 85(6)	0.198 19(4)	C(7)	1.157 0(5)	1.036 8(5)	0.414 2(3)
Р	0.834 3(1)	0.617 7(1)	0.268 15(8)	C(8)	1.164 2(6)	1.174 9(5)	0.422 4(4)
O(13)	0.723 5(4)	0.278 7(5)	0.016 9(3)	C(9)	1.294 7(6)	1.299 9(6)	0.478 4(5)
O(14)	1.136 0(4)	0.467 3(5)	0.260 7(3)	C(10)	1.410 1(7)	1.281 5(7)	0.527 4(4)
O(15)	0.811 0(4)	0.388 9(4)	0.503 0(3)	C(11)	1.401 6(7)	1.144 9(7)	0.519 3(5)
O(16)	0.411 6(4)	0.238 7(4)	0.246 8(3)	C(12)	1.279 7(6)	1.021 2(6)	0.463 7(4)
O(17)	0.717 9(5)	0.027 9(4)	0.269 1(4)	C(13)	0.742 3(5)	0.309 6(5)	0.104 4(4)
O(18)	0.941 7(4)	0.634 3(4)	-0.0004(3)	C(14)	1.007 3(5)	0.427 0(5)	0.262 0(4)
O(19)	1.022 8(5)	1.089 9(4)	0.132 8(3)	C(15)	0.799 1(5)	0.379 3(4)	0.415 5(4)
O(20)	1.336 2(4)	0.888 3(5)	0.220 0(4)	C(16)	0.542 2(5)	0.281 5(4)	0.253 5(3)
C(1)	0.989 4(4)	0.761 9(4)	0.349 1(3)	C(17)	0.738 3(5)	0.145 8(5)	0.266 4(4)
C(2)	1.016 0(4)	0.909 4(4)	0.356 7(3)	C(18)	0.969 3(4)	0.705 3(5)	0.077 4(3)
C(3)	0.762 3(4)	0.723 6(4)	0.206 9(3)	C(19)	1.019 5(5)	0.984 0(5)	0.147 7(4)
C(4)	0.634 0(4)	0.649 3(4)	0.117 9(3)	C(20)	1.209 0(5)	0.860 8(5)	0.211 6(4)
C(5)	0.477 8(5)	0.594 8(6)	0.158 6(4)				

(M, 13), 645 (M - 3CO - 1, 51), 506 (M - 8CO, 87) and 386 (100%).

Dehydration of the Alcohols 5 and 7 to Complexes 9 and 10.— Fluoroboric acid $(0.2 \text{ cm}^3, 54\% \text{ solution in ether})$ was added to a stirred solution of complex 5 or 7 (1 mmol) in ether at room temperature. After 1.5 h the solvent was evaporated and the final product was purified by chromatography with hexane for 9 and with hexane–diethyl ether (92:8) for 10.

Complex 9: yield 0.63 g (*ca.* 100%); yellow solid, m.p. 115 °C (pentane); IR (decalin) v[Fe(CO)₃] 2055s, 2010s, 2000(sh), v[W(CO)₅] 2075m and 1945vs cm⁻¹; ³¹P NMR (C₆D₆) δ – 26.6 [¹J(¹⁸³W-³¹P) 261 Hz]; ¹H NMR (C₆D₆) 4.9 (m, 1 H, =CH) and 5.5 (m, 2 H, =CH); ¹³C NMR (C₆D₆) δ 70.05 [d, ³J(C-P) 19.6, HC₇], 77.17 [d, ¹J(C-P) 14.1, HC₈], 93.43 [d, ²J(C-P) 9.1 Hz, HC₆], 118.69 (s, =CH₂) and 136.99 ppm (s, =CH); mass spectrum (¹⁸⁴W) *m*/z 637 (*M* – 1, 9), 554 (*M* – 3CO, 47), 414 (*M* – 8CO, 81) and 358 (100%).

Complex 10: yield 0.35 g (56%); yellow solid, mixture of two isomers; ³¹P NMR (C_6D_6) $\delta - 25.00$ [¹J(¹⁸³W-³¹P) 234] and -25.19 [¹J(¹⁸³W-³¹P) 234 Hz]; ¹H NMR (C_6D_6) $\delta 2.28$ [m, ³J(H₇-H_β) 8.9, ³J(H-H) 5.8, CH₇], 3.36 [*A*B, ²J_{AB} 11.4, 1 H, CH₂], 3.54 (*AB*, 1 H, CH₂) [and 3.43 (br s, CH₂)], 4.87 [d, ³J(H_a-H_β) 6.3 Hz, CH_a] and 5.4 (m, CH_β); ¹³C NMR (C_6D_6) δ 66.48 [d, ³J(C-P) 20.37, HC₇], 71.37 (s, CH₂O), 78.44 [d, ¹J(C-P) 13.9, HC_a] {and 78.32 [d, ¹J(C-P) 13.7, HC₃]}, 94.30 ppm [d, ²J(C-P) 8.0, HC_β] {and 94.46 [d, ²J(C-P) 8.5 Hz, HC_β]}.

Synthesis of Complex 12.—A solution of complex 11 (6.0 g, 10 mmol) in thf was cooled to -78 °C. Butyllithium (6.25 cm³, 1.6 mol dm⁻³ solution in hexane) was then added. After a few minutes, isobutyraldehyde (1.4 cm³, 15 mmol) was added. The reaction mixture was allowed to warm to room temperature. After evaporation and extraction with hexane, the final product 12 was purified by chromatography with pentane, followed by

crystallization in pentane at -20 °C: yield 2.36 g (46%); yellow solid, m.p. 89 °C (pentane); ³¹P NMR (C₆D₆) δ 185.2 [¹J(¹⁸³W-³¹P) 254 Hz]; ¹H NMR (C₆D₆) δ 0.99 [dd, ³J(H-H) 6.5, ⁴J(H-P) 1.3, CH₃], 2.94 (m, CHMe₂), 6.71 [AB, dd, ³J(H_A-H_B) 17.2, J(H-P) 3.2, =CH] and 7.50 [dd, ²J(H-P) 18.5, ³J(H-H) 11.9 Hz, P=CH]; ¹³C NMR (C₆D₆) δ 23.99 [d, ³J(C-P) 17.1, CH₃], 33.96 [d, ²J(C-P) 9.3, CHMe₂], 135.54 [d, J(C-P) 20.2, C(Ph)], 147.75 [d, J(C-P) 13.5, =CH], 179.26 [d, ¹J(C-P) 50.7, P=CH], 194.91 [d, ²J(C-P) 9.8, cis CO] and 198.68 [d, ²J(C-P) 27.8 Hz, trans CO]; mass spectrum (¹⁸⁴W) *m*/*z* 514 (*M*, 40), 374 (*M* – 5CO, 100%) (Found: C, 39.75; H, 3.05. Calc. for C₁₇H₁₅O₅PW: C, 39.70; H, 2.95%).

Reaction of Complex 12 *with* [Fe₂(CO)₉].—A mixture of complex 12 (0.51 g, 1 mmol) and [Fe₂(CO)₉] (0.44 g, 1.2 mmol) in thf was heated at 40 °C for 40 min. After evaporation of the solvent, the residue was dissolved in toluene and refluxed for 1.5 h. The final product 13 was purified by chromatography with hexane–diethyl ether (95:5) followed by crystallization from pentane at -20 °C: yield 0.15 g (23%); yellow solid, m.p. 139 °C (pentane); IR (decalin) v(CO) 2075m, 2050s, 2000s, 1980vs, 1955vs and 1935s cm⁻¹; ³¹P NMR (C₆D₆) δ -2.4 [¹J(¹⁸³W⁻³¹P) 264 Hz]; ¹H NMR (C₆D₆) δ 0.58 [dd, ³J(H–H) 11.6, ²J(H–P) 2.7, PCHCHMe₂], 0.89 [d, ³J(H–H) 6.2, 3 H, CH₃], 0.98 [d, ³J(H–H) 6.4, 3 H, CH₃], 1.55 (m, CHMe₂), 2.5, ³J(H–H) 11.2 Hz, PhCHCH–P]; ¹³C NMR (C₆D₆) δ 25.81 [d, ³J(C–P) 15.1, CH₃], 26.95 (s, CH₃), 32.70 [d, ²J(C–P) 9.2, CHMe₂], 68.12 [d, ¹J(C–P) 14.8, PCHCHMe₂], 75.71 [d, ¹J(C–P) 6.9, PCH–CH=CH], 89.67 [s, PhCH=CH] and 194.87 ppm [d, ²J(C–P) 7.9 Hz, cis CO]; mass spectrum (¹⁸⁴W) m/z 654 (M, 15), 486 (M – 6CO, 83) and 428 (100%).

X-Ray Structure Determ nations.—Complex 12. Crystals of 12 were grown at -18 °C from a pentane–dichloromethane solution of the compound. Data were collected at 18 ± 1 °C

on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf-Nonius SDP package.¹⁶

Crystal data. $C_{17}H_{15}O_5PW$, M = 514.13, monoclinic, space group $P2_1/c$, a = 11.730(1), b = 18.297(1), c = 9.237(1) Å, $\beta = 99.85(1)^\circ$, U = 1953.33(54) Å³, Z = 4; $D_c = 1.748$ g cm⁻³; graphite monochromatized Mo-K α radiation ($\lambda = 0.710$ 73 Å), $\mu = 61.4$ cm⁻¹, F(000) = 984. A total of 3419 unique reflections were recorded in the range

A total of 3419 unique reflections were recorded in the range $2 \le 2\theta \le 50.0^{\circ}$ of which 1153 were considered as unobserved $[F^2 < 3.0\sigma(F^2)]$. The structure was solved by Patterson methods, yielding positions for the tungsten and phosphorus atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement, and anisotropic thermal parameters for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor of 0.06 in $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$. The final agreement factors were R = 0.026, R' = 0.039, goodness of fit = 1.02.

Complex 13. Crystals of 13 were grown at -18 °C from a dichloromethane-pentane solution of the compound. Data were collected and the crystal structure solved and refined as above.

Crystal data. $C_{20}H_{15}FeO_8PW$, M = 654.01, triclinic, space group PI, a = 9.789(1), b = 10.205(1), c = 13.155(1) Å, $\alpha = 94.65(1)$, $\beta = 94.39(1)$, $\gamma = 117.52(1)^\circ$, U = 1151.93(48) Å³, Z = 2, $D_c = 1.890$ g cm⁻³, $\mu = 58.5$ cm⁻¹, F(000) = 628.

A total of 4052 unique reflections were recorded in the range $2 \le 2\theta \le 50.0^{\circ}$ of which 451 were considered as unobserved $[F^2 < 3.0\sigma(F^2)]$. The structure was solved by Patterson methods, yielding the position for the tungsten, iron and phosphorus atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement, and anisotropic thermal parameters for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor of 0.05 in $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$. The final agreement factors were R = 0.022, R' = 0.032, goodness of fit = 1.04.

Final atomic coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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