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First structural evidence for complexes containing arsadiphospholyl anions. Crystal structure of the iron(II) complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2AsP_2)W(CO)_5]$

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Abstract

The preparation of novel 1-arsa-3,4-diphospholyl and 3-arsa-1,4-diphospholyl anions of the type $(C_2{}^tBu_2AsP_2)^-$ is described. Spectroscopic and structural characterisation of mono-and bi-metallic complexes of these anions are also reported.

Key words: Phosphorus; Arsenic; Tungsten; Crystal structure; Iron; Metallocene

1. Introduction

A recurring theme in the rapidly growing chemistry of compounds containing phosphorus–carbon multiple bonds has been the complexation of phosphorus-substituted unsaturated organic rings at transition metal centres [1]. Iron(II) complexes containing phosphorus-substituted cyclopentadienyl anions (phospholyl anions) of the type $C_nR_nP_{5-n}$ ($n = 0$–5) have received special attention owing to their similarities to ferrocene, and many compounds are known ranging from those containing monophospholyl anions [2] to the pentaphospholyl anion, P_5^- (**1a**) [3]. Especially relevant to the work reported here are the di- and tri-phospholyl anions $(C_3{}^tBu_3P_2)$ (**2**) and $(C_2{}^tBu_2P_3)$ (**3**), both of which coordinate an η^5 fashion to transition metals [4,5]. This chemistry has been extended to heavier Group 15 element where metal complexes of arsolyl, stibolyl and bismolyl anions are known [6], as are compounds containing the penta-arsolyl anion As_5^- (**1b**) [7,8]. Very recently, Mathey *et al.* [9] reported the synthesis of heterocycles containing one As and one P atom of type $C_3R_2HAsP^-$ (R = Me, Et, Ph) (**4a–c**) and structurally characterized an iron complex of 4b. We have briefly reported [10] the synthesis of the 1-arsa-3,4-diphospholyl anion $(C_2{}^tBu_2AsP_2)^-$(**5**) from the reaction of $LiAs(SiMe_3)_2 \cdot DME$ and the phosphaalkyne $P{\equiv}C^tBu$, but its structure was only assigned on the basis of NMR spectroscopic data. We now report the synthesis and full spectroscopic characterisation of the iron(II) complex $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2AsP_2)]$ (**7**) and the molecular structure of its $[W(CO)_5]$ adduct **9**, as determined by a single crystal X-ray diffraction study. Our results also provide evidence for the existence of the previously unknown 3-arsa-1,4-diphospholyl anion $(C_2{}^tBu_2PAsP)^-$ (**6**) in both its free and ligated state.

2. Results and discussion

The various reactions studied in this work are depicted in Scheme 1. Thus treatment of a DME solution of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-toluene})PF_6]$ [11] with **5** afforded, after column chromatography, a red oil which was shown by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy to contain one major and three minor products. The $^{31}P\{^1H\}$ NMR spectrum of the major product $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2AsP_2)]$ (**7**) (*ca.* 50%) (Table 1) shows a singlet shifted *ca.* 200 ppm upfield relative to the free ligand, suggesting that the ring is coordinated in an η^5 fashion to iron. The ^1H NMR spectrum shows, as expected, two singlets, which are assigned to cyclopentadienyl and tert-butyl protons, respectively. Two of

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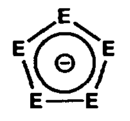
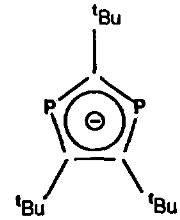


1a, E=P
1b, E=As



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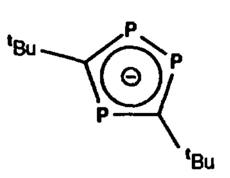

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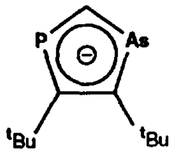
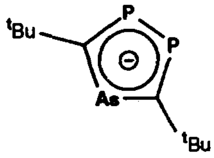


4a, R=Me
4b, R=Et
4c, R=Ph



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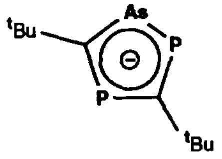

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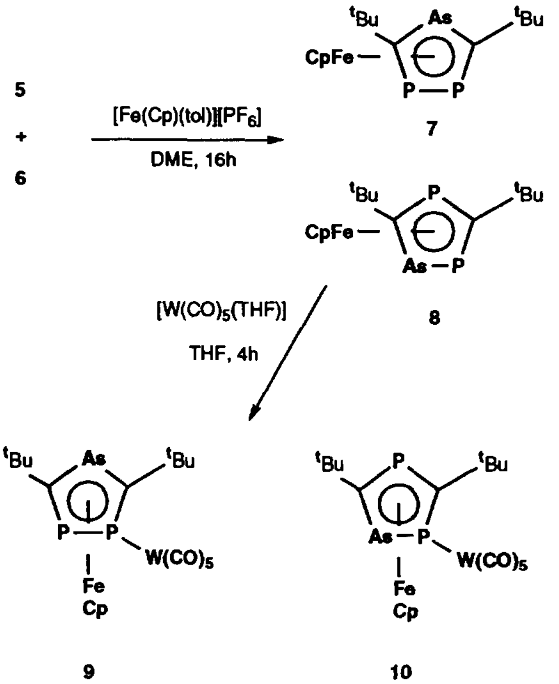

Scheme 1. Preparation of homo- and hetero-metallic arsadiphospholyl complexes **7**–**10**.

TABLE 1. Selected spectroscopic data [a] for the arsadiphospholyl anions **5** and **6** and their iron complexes **7**–**10**

5: $^{31}P\{^1H\}$ NMR δ: 246.0 (s) ppm.
6: $^{31}P\{^1H\}$ NMR δ: 284.2 (d); 250.2 (d) [$^2J_{P(A)P(X)} = 50$ Hz] ppm.
7: ^1H NMR δ: 1.37 (s, 18H); 4.32 (s, 5H) ppm.
$^{31}P\{^1H\}$ NMR δ: 41.1 (s) ppm.
8: ^1H NMR δ: 1.38 (s, 9H); 1.48 (s, 9H); 4.40 (s, 5H) ppm.
$^{31}P\{^1H\}$ NMR δ: 36.0 (d); 70.9 (d) [$^2J_{P(A)P(X)} = 43$ Hz] ppm.
9: ^1H NMR δ: 1.13 (s, 9H); 1.33 (s, 9H); 4.37 (s, 5H) ppm.
$^{31}P\{^1H\}$ NMR δ: 17.7, 25.4 (ABq) [$^1J_{P(A)P(B)} = 420$ Hz, $^1J_{P(A)W} = 212$ Hz] ppm.
10: ^1H NMR δ: 1.15 (s, 9H); 1.39 (s, 9H); 4.39 (s, 5H) ppm.
$^{31}P\{^1H\}$ NMR δ: 28.3 (d); 42.3 (d) [$^2J_{P(A)P(X)} = 51$ Hz, $^1J_{P(A)W} = 212$ Hz] ppm.

[a] ^1H NMR: C_6D_6, 250 MHz; $^{31}P\{^1H\}$ NMR: C_6D_6, 101.3 MHz.

the minor products, [Fe(η^5-C_5H_5)(η^5-$C_3{}^tBu_3P_2$)] and [Fe(η^5-C_5H_5)(η^5-$C_2{}^tBu_2P_3$)] (*ca.* 10% and 20% respectively), were identified by comparison of their spectra with those of authentic samples [5a]. Interestingly, the third product (*ca.* 20%) [Fe(η^5-C_5H_5)(η^5-$C_2{}^tBu_2PAsP$)] (**8**) shows an AX pattern in its $^{31}P\{^1H\}$ spectrum with $J_{P(A)P(X)} = 44$ Hz (Table 1), the latter value being comparable with that of $^2J_{PP'}$ observed for similar ($C_2{}^tBu_2P_3$) rings [2,4,5]. The ^1H NMR spectrum of **8** shows two tert-butyl and one cyclopentadienyl resonance, and thus **8** is identified as the cyclopentadienyliron complex of the novel 3-arsa-1,4-diphospholyl anion **6**. All three by-products are present as a result of their free anions also being formed during the synthesis of ($C_2{}^tBu_2AsP_2$)$^-$ (**5**). It appears that use of a large excess of phosphaalkyne in this synthesis results in the formation of larger amounts of **2** and **3**, but at present it is unclear what influences the formation of **6**.

When a THF solution of **7**, containing the by-products, is treated with [W(CO)$_5$(THF)] at room temperature, a red–orange solid is obtained after column chromatography of the product mixture, together with a red oil identified by its $^{31}P\{^1H\}$ NMR spectrum as unchanged [Fe(η^5-C_5H_5)(η^5-$C_3{}^tBu_3P_2$)]. This is in accord with previous work, which showed that the bulk of the three tert-butyl groups in ($C_3{}^tBu_3P_2$)$^-$ (**2**) prevents access of electron-deficient metals to the phosphorus lone pairs [5a]. Fractional crystallisation of the red–orange solid in hexane at −20°C separates two new products derived from the known complex [Fe(η^5-C_5H_5)(η^5-$C_2{}^tBu_2P_3$)W(CO)$_5$] [5a]. The major product is identified from its $^{31}P\{^1H\}$ NMR spectrum (Table 1) as [Fe(η^5-C_5H_5)(η^5-$C_2{}^tBu_2AsP_2$)W(CO)$_5$] (**9**) which exhibits an AB pattern, $^1J_{P(A),P(B)} = 420$ Hz, indicative of two directly bonded inequivalent phosphorus atoms. Additionally, one-half of the pattern exhibits, as expected, ^{183}W satellites with $^1J_{P(A)W} = 212$ Hz, this value being comparable with those previously observed for [W(CO)$_5$] adducts of related ($C_2{}^tBu_2P_3$) complexes [5a,12]. The ^1H NMR spectrum of **9** shows resonances for inequivalent tert-butyl groups and one cyclopentadienyl resonance. The $^{31}P\{^1H\}$ NMR spectrum of the minor product (Table 1) consists of an AX pattern, ${}^2J_{P(A)P(X)} = 51$ Hz, one-half of which exhibits ${}^{183}W$ satellites, ${}^1J_{P(A)W} = 212$ Hz. These data, together with those from the ${}^1H$ NMR spectrum, which shows two tert-butyl and one cyclopentadienyl resonance, suggest that the by-product is the $[W(CO)_5]$ adduct of **8**, *i.e.* $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2PAsP)W(CO)_5]$ (**10**). There is no evidence from ${}^{31}P\{{}^1H\}$ NMR spectroscopy to suggest that the W atom coordinates to the $(C_2{}^tBu_2AsP_2)^-$ or $(C_2{}^tBu_2PAsP)^-$ rings through the lone electron pair on the As atom.

The proposed formulations of **9** and **10** were confirmed by a single crystal X-ray diffraction study (Fig. 1). The molecular structure shows that the iron atom is sandwiched between two planar rings (dihedral angle 1.01°) with the W atom attached to one of the P atoms in the 1-arsa-3,4-diphospholyl ligand. Within this ligand the As atom is bonded, as expected, to two carbon atoms, and the P atoms are joined together. Of particular interest is the observation of a high disorder of occupancy between the As atom and the uncoordinated P atom, P(2), caused by the selection of a crystal containing two chemically distinct molecules disordered over a single crystallographic site. The disorder of occupancy, 56% As, 44%P for the site labelled As and 44% As, 56% P for the site labelled P(2), is the result of the presence of molecules of both **9** and **10** in the crystal; this interpretation was confirmed by ${}^{31}P\{{}^1H\}$ NMR spectroscopy. The disorder precludes the accurate assignment of bond lengths and angles (see Table 2) within the arsadiphospholyl rings. The fractional atomic coordinates and equivalent isotropic parameters are given in Table 3. The structural study also confirms the preference for the W atom to coordinate to the $(C_2{}^tBu_2AsP_2)^-$ ring through the P atom rather than the As atom. Further studies of the ligating behaviour of these interesting arsadiphospholyl anions, in particular their incorporation into 'triple-decker' sandwich complexes, are continuing [13].

3. Experimental details

3.1. Materials

Chromatographic purifications were performed with Keiselgel 60 GF_{254}, supplied by Merck. The BuLi was supplied by Aldrich Chemical Co. The starting materials, $As(SiMe_3)_3$ [14], ${}^tBuC{\equiv}P$ [15] and $[W(CO)_5 \cdot THF]$ [16], were prepared by published methods. Analytical grade solvents, THF, 1,2-dimethoxyethane (DME) and petroleum ether, b.p. 60–80°C, were dried over Na and distilled from Na/K alloy prior to use.

3.2. General

All reactions were performed under dry N_2 in freshly distilled solvents. NMR spectra were recorded on a Bruker AC-P250 spectrometer under the following conditions: ${}^1H$, 250.1 MHz, C_6D_6 internal reference; ${}^{31}P\{{}^1H\}$, 101.3 MHz 85% H_3PO_4 external reference. Infrared spectra were recorded as KBr discs, referenced to polystyrene, on a Perkin-Elmer 1710 infrared Fourier transform spectrometer. Melting points were

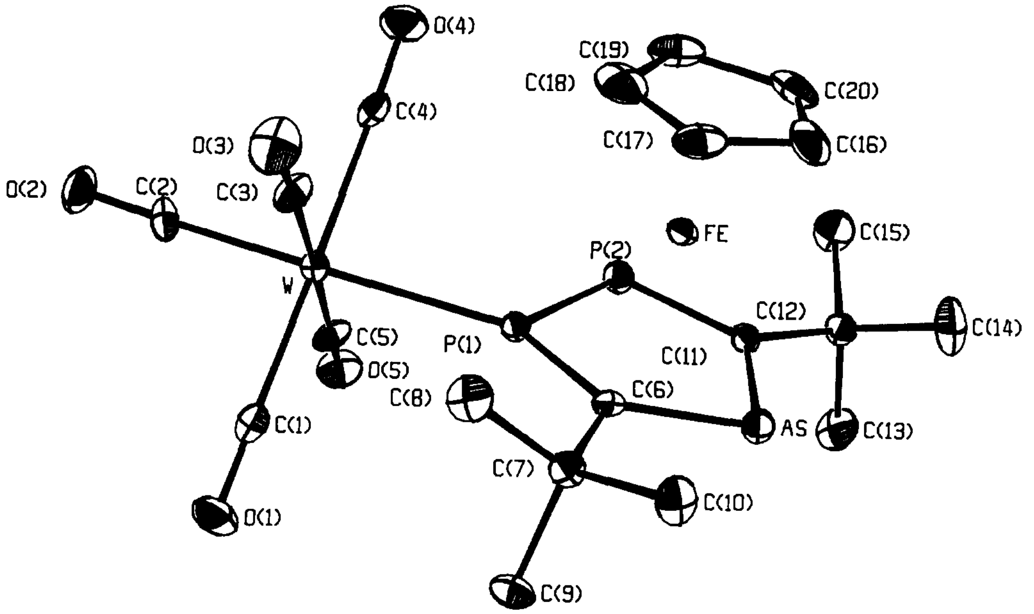

Fig. 1. The molecular structure of **9**.

determined on an Electrothermal melting point apparatus.

3.3. Preparation of $Li(C_2{}^tBu_2AsP_2)$ (5)

A DME solution (10 cm^3) of $As(SiMe_3)_3$ (1.0 g, 3.4 mmol) was cooled to −40°C and 2.2 cm^3 of a 1.6 M BuLi solution (3.5 mmol) was added dropwise. The mixture was slowly warmed to room temperature and stirred for 16 h. The solution was recooled to −40°C, $P{\equiv}C^tBu$ (0.7 g, 7.0 mmol) in DME (10 cm^3) was added slowly, and the solution warmed to room temperature. Stirring, for 16 h afforded a deep red solution from which volatiles were removed *in vacuo*. The resulting red oil was washed twice with petroleum ether and dried to leave $Li(C_2{}^tBu_2AsP_2)$ (**5**), together with small amounts of $Li(C_2{}^tBu_2PAsP)$ (**6**) (Table 1), $Li(C_2{}^tBu_2P_3)$ (**3**) [5a] and $Li(C_3{}^tBu_3P_2)$ (**2**) [5a] which were identified by $^{31}P\{^1H\}$ NMR spectroscopy. The oil was dissolved in 20 cm^3 DME to give a *ca.* 0.25 M solution which was used in further reactions.

TABLE 2. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Bonds			
W–P(1)	2.521(3)	W–C(1)	2.044(7)
W–C(2)	1.972(12)	W–C(3)	2.011(13)
W–C(4)	2.051(7)	W–C(5)	2.040(13)
As–Fe	2.385(2)	As–C(6)	1.846(9)
As–C(11)	1.832(9)	Fe–P(1)	2.317(3)
Fe–P(2)	2.408(3)	Fe–C(6)	2.171(6)
Fe–C(11)	2.159(11)	Fe–C(16)	2.081(15)
Fe–C(17)	2.062(15)	Fe–C(18)	2.024(15)
Fe–C(19)	2.058(10)	Fe–C(20)	2.069(10)
Fe–M(1)	1.64	Fe–M(2)	1.68
P(1)–P(2)	2.161(3)	P(1)–C(6)	1.766(11)
P(2)–C(11)	1.834(11)	O(1)–C(1)	1.162(10)
O(2)–C(2)	1.18(2)	O(3)–C(3)	1.16(2)
O(4)–C(4)	1.130(10)	O(5)–C(5)	1.14(2)
C(6)–C(7)	1.553(11)	C(7)–C(8)	1.52(2)
C(7)–C(9)	1.54(2)	C(7)–C(10)	1.53(2)
C(11)–C(12)	1.530(12)	C(12)–C(13)	1.51(2)
C(12)–C(14)	1.53(2)	C(12)–C(15)	1.520(12)
C(16)–C(17)	1.41(2)	C(16)–C(20)	1.36(2)
C(17)–C(18)	1.39(2)	C(18)–C(19)	1.37(2)
C(19)–C(20)	1.45(2)		
Angles			
P(1)–W–C(1)	92.0(3)	P(1)–W–C(2)	173.8(3)
P(1)–W–C(3)	94.5(3)	P(1)–W–C(4)	88.2(3)
P(1)–W–C(5)	86.3(3)	C(1)–W–C(2)	90.7(4)
C(1)–W–C(3)	90.6(4)	C(1)–W–C(4)	176.2(5)
C(1)–W–C(5)	88.7(4)	C(2)–W–C(3)	91.1(5)
C(2)–W–C(4)	89.4(4)	C(2)–W–C(5)	88.2(5)
C(3)–W–C(4)	85.6(4)	C(3)–W–C(5)	179.0(4)
C(4)–W–C(5)	95.1(4)	M(1)–Fe–M(2) [a]	178.8
C(6)–As–C(11)	96.9(4)	W–P(1)–P(2)	114.6(1)
W–P(1)–C(6)	141.7(3)	P(2)–P(1)–C(6)	103.7(3)
P(1)–P(2)–C(11)	95.3(3)	W–C(1)–O(1)	179.5(9)
W–C(2)–O(2)	176.1(8)	W–C(3)–O(3)	178 (1)
W–C(4)–O(4)	177(1)	W–C(5)–O(5)	178.4(8)
As–C(6)–P(1)	119.8(5)	As–C(6)–C(7)	117.7(7)
P(1)–C(6)–C(7)	122.2(7)	C(6)–C(7)–C(8)	114.5(7)
C(6)–C(7)–C(9)	106.2(9)	C(6)–C(7)–C(10)	111.0(8)
C(8)–C(7)–C(9)	107.8(8)	C(8)–C(7)–C(10)	109(1)
C(9)–C(7)–C(10)	107.8(8)	As–C(11)–P(2)	123.9(5)
As–C(11)–C(12)	119.5(7)	P(2)–C(11)–C(12)	116.2(7)
C(11)–C(12)–C(13)	106.9(8)	C(11)–C(12)–C(14)	111(1)
C(11)–C(12)–C(15)	113.5(8)	C(13)–C(12)–C(14)	108(1)
C(13)–C(12)–C(15)	109(1)	C(14)–C(12)–C(15)	108.5(9)
C(17)–C(16)–C(20)	109(1)	C(16)–C(17)–C(18)	107(1)
C(17)–C(18)–C(19)	111(1)	C(18)–C(19)–C(20)	106(1)
C(16)–C(20)–C(19)	108(1)		

[a] M(1) is the centre of As/C(11)/P(2)/P(1)/C(6); M(2) is the centre of C(16)/C(17)/C(18)/C(19)/C(20).

TABLE 3. Fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	U_{eq} [a]
W	0.35410(1)	0.09090(4)	0.62069(2)	0.030(1)
As	0.31364(5)	−0.34803(14)	0.71479(8)	0.038(1)
Fe	0.36987(5)	−0.17500(13)	0.79880(7)	0.030(1)
P(1)	0.3447(1)	−0.1071(2)	0.6712(1)	0.028(1)
P(2)	0.4301(1)	−0.2078(2)	0.7533(1)	0.037(1)
O(1)	0.2248(4)	0.0526(8)	0.4302(5)	0.077(4)
O(2)	0.3822(3)	0.3245(7)	0.5640(4)	0.073(4)
O(3)	0.2857(3)	0.2406(8)	0.6715(5)	0.073(4)
O(4)	0.4761(3)	0.1421(8)	0.8131(5)	0.071(4)
O(5)	0.4226(3)	−0.0515(8)	0.5660(5)	0.064(4)
C(1)	0.2718(4)	0.0660(9)	0.4992(6)	0.045(4)
C(2)	0.3695(4)	0.2386(9)	0.5835(6)	0.044(4)
C(3)	0.3107(4)	0.1837(9)	0.6539(6)	0.045(4)
C(4)	0.4335(4)	0.1219(9)	0.7446(6)	0.041(4)
C(5)	0.3973(4)	−0.0016(9)	0.5850(6)	0.042(4)
C(6)	0.2901(3)	−0.1990(8)	0.6636(5)	0.029(4)
C(7)	0.2204(3)	−0.1648(9)	0.6070(5)	0.036(4)
C(8)	0.2084(4)	−0.0328(11)	0.6076(7)	0.051(5)
C(9)	0.1908(4)	−0.1995(11)	0.5140(6)	0.050(5)
C(10)	0.1882(4)	−0.2369(11)	0.6328(6)	0.053(5)
C(11)	0.3963(3)	−0.3341(9)	0.7687(5)	0.031(4)
C(12)	0.4401(4)	−0.4384(9)	0.8225(6)	0.037(4)
C(13)	0.4347(5)	−0.5247(11)	0.7605(7)	0.061(5)
C(14)	0.4205(5)	−0.5032(12)	0.8689(8)	0.074(6)
C(15)	0.5076(4)	−0.4012(12)	0.8893(8)	0.063(6)
C(16)	0.3643(5)	−0.1940(13)	0.8964(6)	0.063(6)
C(17)	0.3325(4)	−0.0901(11)	0.8472(6)	0.056(5)
C(18)	0.3759(5)	−0.0183(13)	0.8539(6)	0.071(6)
C(19)	0.4329(4)	−0.0711(12)	0.9053(6)	0.062(6)
C(20)	0.4247(5)	−0.1845(13)	0.9316(6)	0.064(6)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

3.4. Preparation of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2AsP_2)]$ (7)

To a 5 cm^3 DME slurry of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}toluene)PF_6]$ (0.25 g, 0.73 mmol) was added 4 cm^3 of a 0.25 M solution of $[Li(C_2{}^tBu_2AsP_2)]$ (**5**) and the mixture stirred for 16 h. Evaporation *in vacuo* gave a brown residue which was extracted with petroleum ether. The extracts were chromatographed on a Kieselgel column with petroleum ether as eluent, and the red band was collected. Removal of the solvent gave a red oil which was shown by $^{31}P\{^1H\}$ NMR spectroscopy to contain $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2AsP_2)]$ (7) as the major product, along with $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2PAsP)]$ (8) (Table 1), $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2AsP_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_3{}^tBu_3P_2)]$ as minor products. Attempts to crystallise the oil from various solvents were unsuccessful.

3.5. Preparation of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_2{}^tBu_2AsP_2)W(CO)_5]$ (9)

A THF solution of $[W(CO)_6]$ (0.1 g, 0.3 mmol) was irradiated with UV light for 4 h. The resulting yellow solution was added to a THF solution of 7 containing the three by-products (0.10 g) and the mixture was stirred for 2 h. Work-up as above separated a small amount of red oil from a red–orange solid. Recrystallisation of the solid from petroleum ether at −20°C

TABLE 4. Crystal structure determination details [a]

Formula	$C_{20}H_{23}AsFeO_5P_2W$
Formula weight	720.0
Crystal system	monoclinic
Space group	$C2/c$ (No. 15)
Cell dimensions	
a/Å	28.005(9)
b/Å	11.188(3)
c/Å	20.151(7)
α(°)	90
β(°)	129.69(3)
γ(°)	90
Cell volume (Å^3)	4858.6
Z	8
D_{calc} (g cm^{-3})	1.97
$F(000)$	2768
Monochromated Mo Kα radiation	
λ (Å)	0.71069
μ (cm^{-1})	69.4
Crystal size (mm)	0.4 × 0.1 × 0.1
Diffractometer	Enraf-Nonius CAD4
Reflections for calculating cell number, θ_{min}, θ_{max}	25, 7, 8
Scan mode for data collection	θ–2θ
Data reflection ranges, θ_{min} and θ_{max} (°)	$0 \leqslant h \leqslant 33$, $0 \leqslant k \leqslant 13$, $-24 \leqslant l \leqslant 24$
Total reflections measured	4585
Unique reflections	4501
R_{int}	0.048
Significant reflections, $\lvert F^2 \rvert > 2\sigma(F^2)$	3456
Max. change in standard reflections	−1.9%
Decay correction	none
Absorption correction, max, min	1.63, 0.66 (DIFABS)

[a] *Structure solution and refinement:*

Non-H atoms located by	direct methods SHELXS-86
Refinement by	full matrix least-squares non-H atoms anisotropic Enraf-Nonius MOLEN programs
Hydrogen atoms	fixed calculated positions $U_{iso} = 1.3U_{eq}$ for parent atom
R	0.044
R'	0.060
S	2.5
No. variables	271
No. observed reflections	3456
$(\Delta/\sigma)_{max}$	0.02
$(\Delta\rho)_{max,min}$(e Å^{-3}	+1.48, −0.34 (close to W atom)

$\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$; $w = \sigma^{-2}(F)$; $\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$ minimised.

Disorder of occupancy of 56% As, 44% P for site labelled As and of 56% P, 44% As for site labelled P(2).

afforded red crystals of [Fe(η^5-C_5H_5)(η^5-$C_2{}^tBu_2AsP_2$)W(CO)$_5$] (**9**) and [Fe(η^5-C_5H_5)(η^5-$C_2{}^tBu_2PAsP$)W(CO)$_5$] (**10**) (mass, 0.072 g; m.p. 173°C). IR (KBr) $\nu_{(C-O)}$ (cm^{-1}): 2070; 1989; 1951; 1928. Analysis: Found: C, 33.4; H, 3.0%. $C_{20}H_{23}AsFeO_5P_2W$ requires: C, 33.3; H, 3.2%.

3.6. *Structure determination*

Suitable crystals were obtained from petroleum ether at −20°C. Crystal data and details of measurements and refinement are summarised in Table 4. Tables of hydrogen atom coordinates, thermal properties and torsion angles have been deposited at the Cambridge Crystallographic Data Centre.

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References

1 J.F. Nixon, *Chem. Rev., 88* (1988) 1327.
2 F. Mathey, *Coord. Chem. Rev.*, in press.
3 (a) O. Scherer and T. Bruck, *Angew. Chem., Int. Ed. Engl., 26* (1987) 59; (b) O.J. Scherer, T. Bruck and G. Wolmershäuser, *Chem. Ber., 121* (1988) 935.
4 R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1987) 1146; R. Bartsch, P.B. Hitchcock, T.J. Madden, M.F. Meidine, J.F. Nixon and H. Wang, *J. Chem. Soc., Chem. Commun.*, (1988) 1475; R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1990) 472.
5 (a) R. Bartsch, P.B. Hitchcock and J.F. Nixon, *J. Organomet. Chem., 340* (1988) C37; (b) C. Müller, R. Bartsch, A. Fischer and P.G. Jones, *J. Organomet. Chem., 453* (1993) C16.
6 A.P. Sadimenko, A.D. Garnovskii and N. Retta, *Coord. Chem. Rev., 126* (1993) 237.
7 O.J. Scherer, C. Blath and G. Wolmershäuser, *J. Organomet. Chem., 387* (1990) C21.
8 A.L. Rheingold, M.J. Foley and P.J. Sullivan, *J. Am. Chem. Soc. 104* (1982) 4727; (b) O.J. Scherer, W. Wiedemann and G. Wolmershäuser, *J. Organomet. Chem., 361* (1989) C11; (c) O.J. Scherer, W. Wiedemann and G. Wolmershäuser, *Chem. Ber., 123* (1990) 3.
9 M.L. Sierra, C. Charrier, L. Richard and F. Mathey, *Bull. Chim. Soc. Fr.*, (1993) 521.
10 R. Bartsch, P.B. Hitchcock, J.A. Johnson, R. Matos and J.F. Nixon, *Phosphorus, Sulfur, Silicon, Relat. Elem., 77* (1993) 45.
11 I.U. Khand, P.L. Pauson and W.E. Watts, *J. Chem. Soc. C*, (1968) 2257.
12 C. Müller, R. Bartsch, A. Fischer and P.G. Jones, *Polyhedron, 12* (1993) 1383.
13 P.B. Hitchcock, J.A. Johnson and J.F. Nixen, paper in preparation.
14 G. Becker, G. Gutekunst and H.J. Wessely, *Z. Anorg. Allg. Chem., 462* (1980) 113.
15 G. Becker, G. Gutekunst, G. Uhl and W. Uhl, *Inorg. Synth., 27* (1990) 243.
16 W. Strohmeier and F.-J. Müller, *Chem. Ber., 102* (1969) 3608.