Syntheses and molecular structures of η^3-[(η^5-Cp*)(CO)$_2$Fe–AsPC(SiMe$_3$)$_2$]M(CO)$_2$(η^5-Cp) (M = Mo, W): the first complexes featuring η^3-arsaphosphaallyl ligands†

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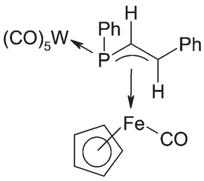
Received (in Cambridge, UK) 23rd September 2004, Accepted 21st December 2004
First published as an Advance Article on the web 27th January 2005
DOI: 10.1039/b414621b

Reaction of (η^5-Cp)(CO)$_2$M=P=C(SiMe$_3$)$_2$ 4a (M = Mo) and 4b (M = W) with (η^5-Cp*)(CO)$_2$Fe–As=C(NMe$_2$)$_2$ 5 affords the η^3-1-arsa-2-phosphaallyl complexes [(η^5-Cp*)(CO)$_2$Fe–AsPC(SiMe$_3$)$_2$]M(CO)$_2$(η^5-Cp) 6a and 6b, the molecular structures of which were determined by X-ray analyses.

The search for novel ligand systems remains an important target for both academic and industrial reasons. Prominent examples are *N*-heterocyclic carbenes which, as ancillary ligands in transition metal complexes, have significantly improved the efficiency of a number of catalysed processes.[1] Other remarkable examples concern phosphaalkenes, phospholyls and phosphinines which recently have emerged from laboratory curiosities to valuable ligands in complex catalysis.[2] Compared to a plethora of synthetically useful η^3-allyl complexes only a few coordination compounds with η^3-1-phosphaallyl ligands such as **1**[3] or η^3-1,3-diphosphaallyl ligands such as **2**[4a] and **3**[4b] are described. The latter complex exhibits catalytic activity in ethylene polymerisation. Complexes of the isomeric η^3-1,2-diphosphaallyl ligand or arsenic analogues thereof have not been reported in the literature as yet. This communication reports a convenient access to the first η^3-1-arsa-2-phosphaallyl complexes.



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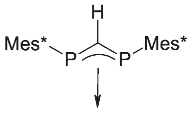

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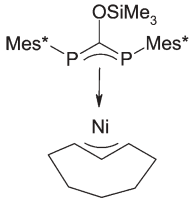

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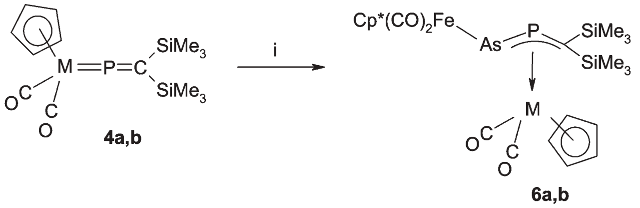
Reaction of (η^5-Cp*)(CO)$_2$FeAs=C(NMe$_2$)$_2$ (**5**)[5] with the phosphavinylidene complexes (η^5-Cp)(CO)$_2$M=P=C(SiMe$_3$)$_2$ **4a** (M = Mo) and **4b** (M = W)[6] in toluene in the temperature range −30 °C to room temperature (Scheme 1) led to the dark red crystalline η^3-1-arsa-2-phosphaallyl complexes **6a** (M = Mo, 35% yield) and **6b** (M = W, 52% yield). The products were isolated by column chromatography on Florisil with a mixture of hexane–diethyl ether 2 : 1 (v/v) (**6a**) or pentane–diethylether 5 : 1 (v/v) (**6b**) as eluents.



Scheme 1 *Reagents and conditions:* i, **4**, Cp*(CO)$_2$FeAs=C(NMe$_2$)$_2$ (**5**) (Cp* = C$_5$Me$_5$) (1 mol equiv.), toluene, −30 °C to 20 °C, 48 h (**a**: M = Mo; **b**: M = W).

The composition and constitution of the complexes **6a** and **6b** are proven by satisfactory elemental analyses, spectroscopic data‡ and X-ray structural analyses.§

A singlet at δ = 4.1 in the ^{31}P NMR spectrum of **6a**, a doublet in the ^{13}C{^{1}H} NMR spectrum at δ 49.9 ($^1J_{PC}$ = 105 Hz), and singlets in the ^{1}H NMR spectrum for two different trimethylsilyl groups (δ = 0.26, 0.61), the pentamethylcyclopentadienyl (δ = 1.46) and the cyclopentadienyl ligands (δ = 5.10) as well as the absence of resonances due to the C(NMe$_2$)$_2$-fragment indicate the combination of the phosphavinylidene unit of **4a** and the arsanediyl group of **5** to a novel ligand system in complex **6a**. Accordingly, the tungsten analogue **6b** displays a singlet at δ = −18.7 in the ^{31}P NMR spectrum. This high-field position is typical for the ^{31}P NMR resonances of η^3-phosphaallyl complexes of tungsten as evident from η^3-{2,4,6-tBu$_3$C$_6$H$_2$~PCHCH$_2$}W(CO)$_2$Cp (δ = −48.9 and −28 for both isomers).[7] In the ^{13}C {^{1}H} spectrum of **6b** the carbon atom of the 1-arsa-2-phosphaallyl ligand appears as a doublet at δ = 35.7 ($^1J_{PC}$ = 101.2 Hz).

The asymmetry of complexes **6a** and **6b** is mirrored by discrete resonances in the low field region of the ^{13}CO groups [**6a**: δ Mo(CO) = 234.3 s, 236.8 s; δ Fe(CO) = 216.7 s, 218.65 (d, $^3J_{PC}$ = 11.5 Hz); **6b**: δ W(CO) = 222.7 s, 224.6 s; δ Fe(CO) = 217.1 s, 219.0 s]. Inspection of the (CO)-stretching bands in the IR spectrum of **6a** (Fe(CO) = 1977, 1929 cm^{-1}, Mo(CO) = 1929, 1850 cm^{-1}), and **6b** (Fe(CO) = 1975, 1923 cm^{-1}, W(CO) = 1923, 1843 cm^{-1}) indicates the improved donor capacity of the 1-arsa-2-phosphaallyl ligand when compared with the η^3-1-phosphaallyl complex {2,4,6-tBu$_3$C$_6$H$_2$PCHCH$_2$}W(CO)$_2$Cp ((CO) = 1935, 1850 cm^{-1}).[7]

The X-ray analyses of **6a** (Fig. 1) and **6b** (Fig. 2) reveal the molecules as complexes where an η^3-ligand is unsymmetrically coordinated to the metal atom of an M(CO)$_2$(Cp) moiety *via* the arsenic atom [**6a**: *d*(Mo–As) = 2.7644(3) Å; **6b**:

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† Electronic supplementary information (ESI) available: details of the refinement and crystal structure of **6a**. See http://www.rsc.org/suppdata/cc/b4/b414621b/
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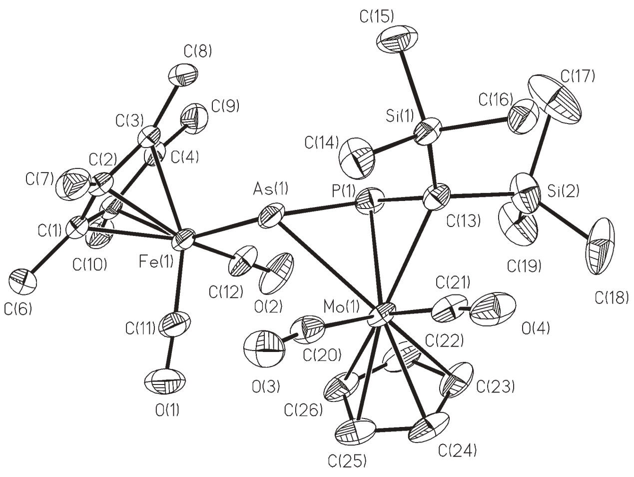

Fig. 1 ORTEP view of the structure of **6a** in the crystal. Important bond lengths (Å) and angles (°) are: Mo(1)–As(1) 2.7644(3), Mo(1)–P(1) 2.4940(6), Mo(1)–C(13) 2.420(2), Fe(1)–As(1) 2.4098(4), As(1)–P(1) 2.2507(7), P(1)–C(13) 1.791(2); Fe(1)–As(1)–P(1) 106.59(2), As(1)–P(1)–C(13) 99.15(7), P(1)–C(13)–Si(1) 120.88(12), P(1)–C(13)–Si(2) 108.67(11).

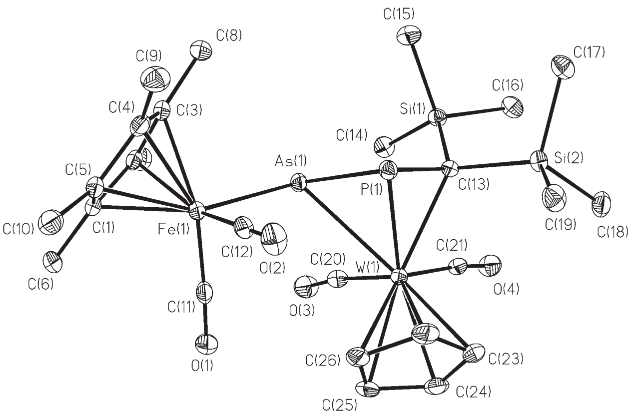

Fig. 2 ORTEP view of the structure of **6b** in the crystal. Important bond lengths (Å) and angles (°) are: W(1)–As(1) 2.7854(2), W(1)–P(1) 2.4955(5), W(1)–C(13) 2.411(2), Fe(1)–As(1) 2.4157(3), As(1)–P(1) 2.2543(5), P(1)–C(13) 1.797(2); Fe(1)–As(1)–P(1) 108.14(2), As(1)–P(1)–C(13) 97.87(6), P(1)–C(13)–Si(1) 121.51(10), P(1)–C(13)–Si(2) 107.92(10).

d(W–As) = 2.7854(2) Å], the central phosphorus atom [**6a**: *d*(Mo–P) = 2.4940(6) Å; **6b**: *d*(W–P) = 2.4955(5) Å] and the carbon atom of the former phosphavinylidene ligand of precursors **4a** and **4b** [**6a**: *d*(Mo–C) = 2.420(2) Å; **6b**: *d*(W–C) = 2.411(2) Å].

The W–As π-bonds in [η^1:η^2-PhAs=AsPh][$(W(CO)_5]_2$ [2.728(4) and 2.769(4) Å] are comparable to the W–As bond length in **6b**.[8] The Mo–P π-bond distance in {η^3-PhP[$W(CO)_5$]CH=CH_2}-$Mo(CO)_2Cp$ [2.533(8) Å][3c] as well as the W–P π-bond length in η^3-{2,4,6-$t$$Bu_3C_6H_2$–P(O)$CHCH_2$}$W(CO)_2Cp$ [2.488(1) Å] is also in good agreement with the respective atom distances in **6a** and **6b**.[9] The Mo–C(13) bond in **6a**, and the W–C(13) bond in **6b**, however, are markedly lengthened in comparison to those in [η^3-PhP{$W(CO)_5$}$CHCH_2$]$Mo(CO)_2Cp$ [2.251(3), 2.357(3) Å][3c] and η^3-{2,4,6-$t$$Bu_3C_6H_2$P(O)$CHCH_2$}$W(CO)_2Cp$ [2.344(5), 2.335(4)].[9]

Due to the π-interaction with a metal atom the As–P distances within the 1-arsa-2-phosphaallyl ligand in **6a** [2.2507(7) Å] and **6b** [2.2543(5) Å] are longer than the unsupported As=P double bonds in the structurally characterised compounds [$(Me_3Si)_2CH$]As=P(2,4,6-$t$$Bu_3C_6H_2$) [2.124 Å][10] or ($\eta^5$-$C_5Me_5$)$(CO)_2$As[$Cr(CO)_5$]=P(2,4,6-$t$$Bu_3C_6H_2$) [2.155(1) Å].[11]

The same is true with the ligated PC bonds in **6a** [1.791(2) Å] and **6b** [1.797(2) Å] which are even longer than those in [η^3-PhP{$W(CO)_5$}CH=CH_2]$Mo(CO)_2Cp$ [1.755(3) Å][3c] or in [η^3-2,4,6-$t$$Bu_3C_6H_2$P(O)$CHCH_2$]$W(CO)_2Cp$ [1.762(4) Å].[9]

The atoms Fe(1) and Si(2) in both complexes are directed towards the phosphorus atom enclosing angles Fe(1)–As(1)–P(1) [**6a**: 106.59(2)°; **6b**: 108.14(2)°], As(1)–P(1)–C(13) [**6a**: 99.15 (7); **6b**: 97.87(6)°] and P(1)–C(13)–Si(2) [**6a**: 108.67(11)°, **6b**: 107.92(10)°]. Substituent Si(1)$(CH_3)_3$ at C(13) is located above the plane defined by the atoms As(1),P(1) and C(13) with P(1)–C(13)–Si(1) angles of 120.88(12)° (**6a**) and 121.51(10)° (**6b**).

From the view-point of the Wade–Mingos rules molecules **6a** and **6b** possess four skeleton atoms and 14 skeleton electrons and thus have to be regarded as arachno-clusters.[12] Despite the presence of 4 chiral centers only one pair of enantiomers were obtained in each case.

Previously, transition metal-induced cleavages of inversely polarized arsaalkenes to cyclotriarsanes[13] or an η^2-diarsene ligand[14] were observed. Obviously, such arsaalkenes serve as convenient sources for the generation of highly reactive arsanediyls under mild conditions.

Investigations on the chemical properties of **6a** and **6b** are under way.

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Notes and references

‡ *Selected spectroscopic data*: for **6a**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.1 (s); ^1H NMR (C_6D_6): δ 0.26 (s, 9H, $SiMe_3$), 0.61 (s, 9H, $SiMe_3$), 1.46 (s, 15H, C_5Me_5), 5.10 (s, 5H, C_5H_5); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 236.8 (s, MoCO), 234.3 (s, MoCO), 218.65 (d, $^3J_{PC}$ = 11.5 Hz, FeCO), 216.7 (s, FeCO), 95.6 (s, $C_5(CH_3)_5$), 91.2 (s, C_5H_5), 49.9 (d, $^1J_{PC}$ = 105 Hz, $PCSi_2$), 9.4 (s, $C_5(CH_3)_5$), 4.35 (s, $SiCH_3$), 4.27 (s, $SiCH_3$); IR (KBr): 1850, 1929, 1977 cm^{-1} [ν(CO)]. Anal. calcd. for $C_{26}H_{38}AsFeMoO_4PSi_2$ (**6a**) : C 42.87, H 5.26; found C 43.17, H 5.29% for **6b**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ −18.7 (s); ^1H NMR (C_6D_6): δ 0.25 (s, 9H, $SiMe_3$), 0.66 (s, 9H, $SiMe_3$), 1.47 (s, 15H, C_5Me_5), 5.13 (s, 5H, C_5H_5); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 224.6 (s, WCO), 222.7 (s, WCO), 219.0 (s, FeCO), 217.1 (s, FeCO), 95.6 (s, $C_5(CH_3)_5$), 89.6 (s, C_5H_5), 35.7 (d, $^1J_{PC}$ = 101.2 Hz, $PCSi_2$), 10.1 (s, $SiCH_3$), 9.5 (s, $C_5(CH_3)_5$), 4.4 (d, $^3J_{PC}$ = 9.2 Hz, $SiCH_3$); IR (KBr): 1843, 1923, 1975 cm^{-1} [ν(CO)]. Anal. calcd. for $C_{26}H_{38}AsFeO_4PSi_2W$ (**6b**) : C 38.26, H 4.49; found C 38.68, H 4.90%.

§ *Crystal data*: $C_{26}H_{38}AsFeMoO_4PSi_2$ **6a**, M = 728.4, monoclinic space group $P2_1/n$, a = 12.9620(1), b = 18.3280(2), c = 13.7430(2) Å, β = 104.246(1)°, V = 3164.49(6) Å^3, Z = 4, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 2.047 mm^{-1}, D_c = 1.529 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current R_F = 0.032 based on 7859 reflections with $I_o \geqslant 2\sigma(I)$. $C_{26}H_{38}AsFeO_4PSi_2W$ (**6b**) + C_7H_{14}: M = 914.5, triclinic space group $P\bar{1}$, a = 9.5380(1), b = 14.0420(1), c = 14.3110(2) Å, α = 100.3140(7), β = 100.0740(7), γ = 92.4090(8)°, V = 1851.33(3) Å^3, Z = 2, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 4.525 mm^{-1}, D_c = 1.641 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares refinement to a current R_F = 0.018 based on 8006 reflections with $I_o \geqslant 2\sigma(I)$. CCDC 250373 (**6a**) and CCDC 255257 (**6b**).

See http://www.rsc.org/suppdata/cc/b4/b414621b/ for crystallographic data in .cif or other electronic format.

1 Review: W. A. Herrmann, *Angew. Chem.*, 2002, **114**, 1342, *Angew. Chem., Int. Ed.*, 2002, **41**, 1363.
2 Review: L. Weber, *Angew. Chem.*, 2002, **114**, 583, *Angew. Chem., Int. Ed.*, 2002, **41**, 563.
3 (*a*) F. Mercier, J. Fischer and F. Mathey, *Angew. Chem.*, 1986, **98**, 347, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 357; (*b*) F. Mercier, C. Hugel-Le Goff and F. Mathey, *Organometallics*, 1988, **7**, 955; (*c*) C. Hugel-LeGoff, F. Mercier, L. Ricard and F. Mathey, *J. Organomet. Chem.*, 1989, **363**, 325.
4 (*a*) R. Appel, W. Schuhn and F. Knoch, *Angew. Chem.*, 1985, **97**, 421, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 420; (*b*) W. Keim, R. Appel, S. Gruppe and F. Knoch, *Angew. Chem.*, 1987, **99**, 1042, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1012.
5 L. Weber, O. Kaminski, H.-G. Stammler and B. Neumann, *Chem. Ber.*, 1996, **129**, 223.
6 (*a*) A. M. Arif, A. H. Cowley, C. M. Nunn, S. Quashie, N. C. Norman and A. G. Orpen, *Organometallics*, 1989, **8**, 1878; (*b*) E. Niecke, H.-J. Metternich, M. Nieger, D. Gudat, P. Wenderoth, W. Malisch, C. Hahner and W. Reich, *Chem. Ber.*, 1993, **126**, 1299.
7 F. Mercier and F. Mathey, *Organometallics*, 1990, **9**, 863.
8 H. Lang, G. Huttner, B. Sigwarth, U. Weber, L. Zsolnai, I. Jibril and O. Orama, *Z. Naturforsch. B: Anorg. Chem. Org. Chem.*, 1986, **B41**, 191.
9 F. Mercier, L. Ricard and F. Mathey, *Polyhedron*, 1990, **9**, 2859.
10 A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski and B. R. Whittlesey, *J. Chem. Soc., Chem. Commun.*, 1983, 881.
11 L. Weber, D. Bungardt and R. Boese, *Chem. Ber.*, 1988, **121**, 1535.
12 (*a*) K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; (*b*) D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311.
13 L. Weber, G. Dembeck, P. Lönnecke, H.-G. Stammler and B. Neumann, *Organometallics*, 2001, **20**, 2288.
14 L. Weber, M. H. Scheffer, H.-G. Stammler and B. Neumann, *Inorg. Chim. Acta*, 1999, **291**, 311.