

Polarity reversal in η^2 -phosphinocarbene and η^2 -arsinocarbene complexes of tungsten[☆]

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Abstract

Trichloro- and trifluoroacetic acids CF_3COOH and CCl_3COOH react with cationic η^2 -phosphino- $(\text{Cp}(\text{CO})(\text{PMe}_3)\text{-}\overline{\text{W}=\text{C}(\text{R})\text{-PPh}_2})(\text{BF}_4)$ as well as η^2 -arsinocarbene complexes of tungsten $(\text{Cp}(\text{CO})_2\overline{\text{W}=\text{C}(\text{R})\text{-AsPh}_2})(\text{PF}_6)$ to form the corresponding η^2 -phosphinomethanide $(\text{Cp}(\text{CO})(\text{PMe}_3)(\text{Y})\overline{\text{W}-\text{C}(\text{H})(\text{R})\text{-PPh}_2})(\text{BF}_4)$ ($\text{Y} = \text{CF}_3\text{COO}$, CCl_3COO) or η^2 -arsinomethanide compounds $(\text{Cp}(\text{CO})_2(\text{CF}_3\text{COO})\overline{\text{W}-\text{C}(\text{H})(\text{R})\text{-AsPh}_2})(\text{PF}_6)$, respectively. Next to spectroscopic investigations, the constitution of the new compounds is proved by X-ray single crystal structure determinations. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Transition metal complexes containing a metal carbon multiple bond can be classified as Fischer-type or Schrock-type carbene or carbyne complexes with respect to the metal ligand parameters and the chemical properties of the metal carbon multiple bond [1–6]. Although most of these compounds can be related to these two groups, some representatives show a pronounced amphiphilicity for the metal carbon multiple bond and therefore restrict a definite classification. Next to some acyclic carbene complexes like Ropers' $(\text{CO})_2(\text{PPh}_3)_2\text{Ru}=\text{CF}_2$ [7] or Caseys' $\text{Cp}(\text{CO})_2\text{Re}=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)_3$ [8] even a few cyclic

compounds e.g. η^2 -thiocarbene complexes $(\text{Cp}(\text{CO})\text{-}\overline{\text{LM}=\text{C}(\text{R})\text{-PPh}_2})(\text{BF}_4)$ [9–11] ($\text{R} = \text{alkyl, aryl}$) and trimethylphosphine substituted η^2 -phosphinocarbene complexes of molybdenum and tungsten $(\text{Cp}(\text{CO})\overline{\text{LM}=\text{C}(\text{R})\text{-PPh}_2})(\text{BF}_4)$ [12,13] ($\text{R} = \text{alkyl, aryl}$) are known.

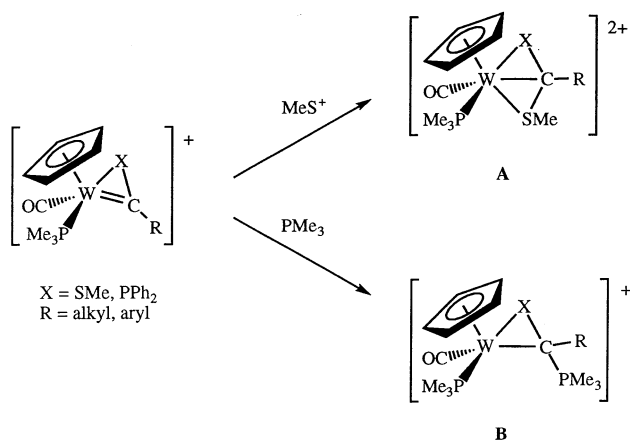
Thus, in the presence of electrophiles like MeS^+ dicationic tungsta-dithiabicyclo(1.1.0)butane [14] or tungsta-thia-phosphabicyclo(1.1.0)butane complexes [15] (**A**) are formed, whereas nucleophiles like phosphines add to the metal carbon double bond affording phosphoranylidene complexes [13] (**B**) (Scheme 1).

Further investigations have shown that other electrophiles like $\text{H}(\text{BF}_4)$ or sulfur do not afford any addition products. These observations diminish the amphiphilic character of the cyclic carbene complexes [16] and underline the fact that the nucleophilicity of the carbene carbon atom is not very significant, but could be increased by a modification of the ligand parameters.

[☆] Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

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Scheme 1.

2. Results

Surprisingly, in the presence of trihalogenated acetic acids like CF_3COOH and CCl_3COOH a (1,2)-addition reaction on the metal carbon double bond in cationic η^2 -phosphino-($\text{Cp}(\text{CO})(\text{PMe}_3)\overline{\text{W}}=\text{C}(\text{R})-\text{PPh}_2$)(BF_4) as well as η^2 -arsinocarbene complexes of tungsten ($\text{Cp}(\text{CO})_2\overline{\text{W}}=\text{C}(\text{R})-\text{AsPh}_2$)(PF_6) ($\text{R} = \text{Tol}, \text{Ph}, \text{Me}$) takes place providing yellow diamagnetic η^2 -phosphino-($\text{Cp}(\text{CO})(\text{PMe}_3)(\text{CF}_3\text{COO}/\text{CCl}_3\text{COO})\overline{\text{W}}-\text{C}(\text{H})-(\text{R})-\text{PPh}_2$)(BF_4) and η^2 -arsinomethanide complexes ($\text{Cp}(\text{CO})_2(\text{CF}_3\text{COO})\overline{\text{W}}-\text{C}(\text{H})(\text{R})-\text{AsPh}_2$)(PF_6) in high yields (Scheme 2).

In both type of complexes the proton of the acetic acid is located at the less nucleophilic carbene carbon atom. Therefore the (1,2)-addition reaction is accompanied probably by a significant ‘polarity reversal’ at the metal carbene carbon unit that could be induced by the electron-rich acetate ligand.

3. Spectroscopic investigations

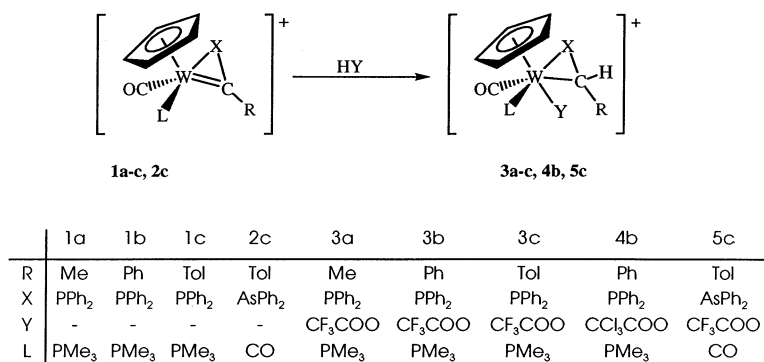
The IR spectra (Table 1) of **3a–4b** and **5c** in dichloromethane exhibit in the region of 1998–2092

Table 1
IR spectra of **3a–5c** in dichloromethane

	3a	3b	3c	4b	5c
ν_{CO}	2002 vs	2003 vs	1998 vs	2003 vs	2092 vs 2036 vs
ν_{OCO}	1716 vs 1703 vs	1717 vs 1760 vs	1717 vs 1701 vs	1696 vs	1718 s 1699w

cm^{-1} a characteristic absorption for the ν_{CO} -stretching vibrations of the carbonyl ligands. In comparison to the correspondent η^2 -phosphinocarbene complexes a significant decrease of the M–CO back donation is recognized due to electronic and sterical alterations at the metal center. The stretching frequencies of the ν_{OCO} -group in the acetic anion appear as characteristic ester double bands in the range of 1696–1760 cm^{-1} . In the ^1H -NMR spectra (Table 2) the addition of the trifluoro- or trichloroacetic acids to the η^2 -carbene complexes is reflected by a significant deshielding of all protons. The chemical shift of the added proton in the range of $\delta = 2.81$ – 3.01 ppm is comparable to η^2 -thiomethanide complexes described in the literature [17].

In the proton-decoupled ^{13}C -NMR spectra the former carbene carbon atoms are strongly shielded (Table 3). Within $\delta = 35$ and 46 ppm they are found in the range of well-known cationic phosphoranylidene complexes of tungsten ($\text{Cp}(\text{CO})(\text{PMe}_3)\overline{\text{W}}-\text{C}(\text{PMe}_3)(\text{R})-\text{PPh}_2$)(BF_4) [13] ($\delta = 7.8$ ppm) and tungsta-phospha-bicyclo(1.1.0)butanone complexes like ($\text{Cp}(\text{MeNC})(\text{PMe}_3)-\overline{\text{W}}-\text{C}(\text{O})-\text{C}(\text{Ph})-\text{PPh}_2$)(PF_6) [18] ($\delta = 6.2$ ppm). The possible formation of diastereomeric η^2 -phosphinomethanide complexes which formally result from the different side attack of the proton to the prochiral carbene carbon atom is not observed in the NMR studies, not even with temperature depending dynamic NMR investigations. Therefore, we suppose a not extensively studied conversion of both diastereomeric products via intramolecular rearrangements (see X-ray section below).



Scheme 2.

Table 2

¹H-NMR spectra of **3a–5c** in CDCl₃ (multiplicity and coupling constants in brackets)

	C ₆ H _{4/5}	C ₅ H ₅	C–H	C–CH ₃	P(CH ₃) ₃
3a	6.51–7.65 (14, m)	6.13 (5, s)	2.94 (1, dd, 2.9 ^a , 2.4 ^b)	2.32 (3, s)	1.50 (9, d, 10.3 ^a)
3b	6.64–7.66 (15, m)	6.16 (5, s)	2.96 (1, dd, 2.9 ^a , 2.4 ^b)	–	1.51 (9, d, 10.3 ^a)
3c	7.26–7.56 (10, m)	6.13 (5, s)	2.89 (1, m)	2.18 (3, d, 7.4 ^b)	1.78 (9, d, 10.1 ^a)
4b	6.21–7.67 (15, m)	6.21 (5, s)	3.01 (1, s)	– (9, d, 9.9 ^a)	1.55
5c	6.64–7.67 (14, m)	6.39 (5, s)	2.81 (1, s)	2.38 (3, s)	–

^a ²*J*(³¹P–¹H).^b ³*J*(³¹P–¹H).

The chemical shifts as well as the corresponding intramolecular spin–spin interactions in the proton decoupled phosphorus NMR spectra of **3a–4b** confirm the assigned structure with a W–P–C ring system (Table 4). The significant strong shielding of the phosphorus atom ($\delta = -31.3$ and -35.2 ppm) and the small metal–phosphorus coupling constants ¹*J*(¹⁸³W–³¹P) of the endocyclic phosphorus atoms within 163–165 Hz are in agreement with three-membered metal–phosphorus–carbon ring systems [13,19–21] (e.g. (Cp(CO)₂W=C(Ph)–PPh₂)(PF₆): $\delta = -114.4$ ppm, ¹*J*(¹⁸³W–³¹P) = 113 Hz, (Cp(CO)(PMe₃)W–C(Me)–(PMe₃)–PPh₂)(PF₆) $\delta = -1.6$ ppm, ¹*J*(¹⁸³W–³¹P) = 171 Hz). With the more deshielded exocyclic PMe₃ ligand ($\delta = -26.1$ to -26.5 ppm) both signals split into a doublet due to ²*J*(³¹P–³¹P) interactions.

The X-ray single crystal structure determinations of **3a** (Fig. 1) and **5c** (Fig. 2) display the tungsten atom in both complexes in a distorted octahedral ligand sphere. The cyclopentadienyl, the trimethylphosphine and the carbonyl ligand in **3a** as well as the cyclopentadienyl and the two carbonyl functions in **5c** are in a facial arrangement.

The W(1)–C(4) (231.8(11) pm), W(1)–P(1) (240.4(3) pm) and the P(1)–C(4) (173.9(11) pm) bond lengths (Tables 5 and 6) within the W–P–C ring as well as the W(1)–C(3) (234.0(5) pm), W(1)–As(1) (250.47(7) pm) and the As(1)–C(3) (190.7(6) pm) bond distances within the W–As–C ring are typical for single bonds and comparable to those described in literature [22] (e.g. (Cp(CO)(PMe₃)W–C(Me)(PMe₃)–PPh₂)(PF₆) W–C: 234.7 pm, W–P_{cycle}: 238.2 ppm, P_{cycle}–C: 178.3 ppm (13), Cp(CO)W–S–As(ⁱBu)₂ W–As: 254.7 pm [23].

We note that in **3a** the added proton is located in a favored *syn*-orientation (68%) as well as in an *anti*-orien-

tation (32%) with respect to the position of the acetic anion.

4. Experimental details

Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. All solvents were dried according to conventional methods and stored under nitrogen over molecular sieves (4 Å). IR spectra were recorded on a Perkin–Elmer FT-JR 1600 spectrometer. ¹H-, ¹³C-, and ³¹P-NMR spectra were taken in CDCl₃ and CD₂Cl₂ on a Jeol JNM-GX 270 (¹H, 270.27; ¹³C, 67.94; ³¹P, 109.37 MHz) spectrometer. Chemical shifts are quoted as δ in ppm with respect to the deuterated solvents (¹³C) and its residual proton resonances (¹H), and to aqueous 85% H₃PO₄ for ³¹P-NMR, respectively. Mass spectra were recorded on a Finnigan MAT90 spectrometer (molecular mass relative to ¹⁸⁴W). The starting materials **1a–c** [24] and **2** [22] were prepared as described in the literature. CF₃COOH and CCl₃COOH were commercial products from Aldrich (Scheme 3).

4.1. Synthesis of (Cp(CO)(PMe₃)(CF₃COO)–W–C(H)(Me)–PPh₂)(BF₄) (**3a**)

To a solution of 0.37 g (0.46 mmol) of **1a** in 10 ml dichloromethane was added 0.04 ml (0.52 mmol) of trifluoroacetic acid at -10°C . The solution was stirred for 5 h at room temperature. Recrystallization from dichloromethane/diethylether afforded a yellowish microcrystalline powder. Yield 0.28 g (80%). Element. Anal. Found: C, 38.55, H, 4.00, W, 24.08. C₂₅H₂₈BF₇O₃P₂W. Calc.: C, 39.20, H, 3.68, W, 24.00%. MS (FAB): 679 (K)⁺, 603 (K–PMe₃)⁺, 575 (K–CO–

Table 3

 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of **3a–5c** in CD_2Cl_2 (multiplicity and coupling constants in brackets)

	3a	3b	3c	4b	5c
W–CO	214.8 (d, 4.6 ^b)	214.5 (d, 4.6 ^b)	217.0	212.7 (d, 4.7 ^b)	202.6
CF_3COO	162.3 (q, 38.6 ^d)	162.4 (q, 38.6 ^d)			(q, 38.6 ^d)
CCl_3COO	–	–	–	166.2	–
$\text{C}_6\text{H}_{4/5}$	124.8–137.7	124.6–136.9	129.5–135.7	121.9–137.4	123.8–139.1
CF_3COO	113.8 (q, 289.6 ^c)	113.8 (q, 289.6 ^c)	n.f.	–	115.2
CCl_3COO	–	–	–	118.9	–
C_5H_5	92.5	92.5	92.0	92.7	94.9
W–C–H	46.3 (dd, 8.3 ^a , 7.4 ^b)	46.2 (dd, 8.3 ^a , 7.4 ^b)	35.3 (11.2 ^a)	46.8	49.6
CH_3	20.7	–	29.5	–	20.9
$\text{P}(\text{CH}_3)_3$	16.2 (d, 33.1 ^a)	16.2 (d, 33.1 ^a)	16.6 (d, 26.8 ^a)	16.4 (d, 34.2 ^a)	–

^a $^1J(^{31}\text{P}-^{13}\text{C})$.^b $^2J(^{31}\text{P}-^{13}\text{C})$.^c $^1J(^{19}\text{F}-^{13}\text{C})$.^d $^2J(^{19}\text{F}-^{13}\text{C})$.

PMe_3^+ , 565 ($\text{K}-\text{CF}_3\text{COOH}^+$), 489 ($\text{K}-\text{CO}-\text{PMe}_3-\text{CF}_3\text{COOH}^+$).

4.2. Synthesis of $(\text{Cp}(\text{CO})(\text{PMe}_3)(\text{CF}_3\text{COO})-\text{W}-\text{C}(\text{H})(\text{Ph})-\text{PPh}_2)(\text{BF}_4)$ (**3b**)

By the method used in Section 4.1, 0.41 g (0.47 mmol) of **1b** and 0.04 ml (0.52 mmol) of trifluoroacetic acid provides the yellow product **3b**.

3b. Yield: 0.35 g (90%). Element. Anal. Found: C, 43.03, H, 3.80, W, 21.17. $\text{C}_{30}\text{H}_{30}\text{BF}_7\text{O}_3\text{P}_2\text{W}$. Calc.: C, 43.47, H, 3.65, W, 22.21%. MS (FAB): 741 (K^+), 665 ($\text{K}-\text{PMe}_3^+$), 637 ($\text{K}-\text{CO}-\text{PMe}_3^+$), 627 ($\text{KCF}_3\text{COOH}^+$), 523 ($\text{K}-\text{CO}-\text{PMe}_3-\text{CF}_3\text{COOH}^+$).

4.3. Synthesis of $(\text{Cp}(\text{CO})(\text{PMe}_3)(\text{CF}_3\text{COO})-\text{W}-\text{C}(\text{H})(\text{Tol})-\text{PPh}_2)(\text{BF}_4)$ (**2c**)

This compound was prepared analogously to **3a** using 0.37 g (0.42 mmol) of **1c** and 0.04 ml (0.52 mmol) of trifluoroacetic acid. Yield: 0.33 g (94%). Element. Anal. Found: C, 43.77, H, 3.96, W, 21.77. $\text{C}_{31}\text{H}_{32}\text{BF}_7\text{O}_3\text{P}_2\text{W}$. Calc.: C, 44.21, H, 3.83, W, 21.83%. MS (FAB): 755 (K^+), 679 ($\text{K}-\text{PMe}_3^+$), 651 ($\text{K}-\text{CO}-\text{PMe}_3^+$), 641 ($\text{K}-\text{CF}_3\text{COOH}^+$), 565 ($\text{K}-\text{CO}-\text{PMe}_3-\text{CF}_3\text{COOH}^+$).

4.4. Synthesis of $(\text{Cp}(\text{CO})(\text{PMe}_3)(\text{CCl}_3\text{COO})-\text{W}-\text{C}(\text{H})(\text{Ph})-\text{PPh}_2)(\text{BF}_4)$ (**4b**)

The procedure employed was analogous to that for Section 4.1 using 0.16 g (0.22 mmol) of **1b** and 0.06 g (0.37 mmol) of trichloroacetic acid. Yield: 0.18 g (92%). Element. Anal. Found: C, 40.51, H, 3.40. $\text{C}_{30}\text{H}_{30}\text{BCl}_3\text{F}_4\text{O}_3\text{P}_2\text{W}$. Calc.: C, 41.09, H, 3.45, W, 21.83%. MS (FAB): 789 (K^+), 713 ($\text{K}-\text{PMe}_3^+$), 627 ($\text{K}-\text{CCl}_3\text{COOH}^+$), 599 ($\text{K}-\text{CO}-\text{CCl}_3\text{COOH}^+$).

4.5. Synthesis of $(\text{Cp}(\text{CO})(\text{PMe}_3)(\text{CCl}_3\text{COO})-\text{W}-\text{C}(\text{H})(\text{Tol})-\text{AsPh}_2)(\text{BF}_4)$ (**4c**)

To a solution of 0.42 g (0.54 mmol) of **2c** in 10 ml dichloromethane was added the amount of 0.05 ml (0.65 mmol) of trifluoroacetic acid at -50°C . The solution was stirred for 2 h at room temperature. Recrystallization from dichloromethane/diethylether afforded a yellowish brown microcrystalline powder. Yield 0.37 g (80%). Element. Anal. Found: C, 40.58, H, 3.23. $\text{C}_{29}\text{H}_{23}\text{AsF}_7\text{O}_4\text{PW}$. Calc.: C, 40.56, H, 2.70%. MS (FAB): 751 (K^+), 723 ($\text{K}-\text{CO}^+$), 695 ($\text{K}-2\text{CO}^+$), 609 ($\text{KCO}-\text{CF}_3\text{COOH}^+$).

4.6. X-ray structure determination of **3a** and **5c**

X-ray crystallographic data (Table 7) were collected by a Siemens P4 diffractometer with graphite-monochromatized $\text{Mo}-\text{K}_\alpha$ radiation ($\lambda = 71.073$ pm). The unit cell parameters were determined and refined from 25 (**3a**) and 29 (**5c**) randomly selected reflections, obtained by P4 automatic routines. Data were measured via ω -scan and corrected for Lorentz and polar-

Table 4

 $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **3a–5c** in CDCl_3 (multiplicity and coupling constants in brackets)

	3a	3b	3c	4b
$\text{P}(\text{CH}_3)_3$	–26.2 (d, 15.7 ^a) (263.8 ^b)	–26.1 (d, 17.1 ^a) (263.8 ^b)	–26.5 (d, 19.9 ^a) (262.4 ^b)	–26.3 (d, 17.4 ^a) (264.1 ^b)
PPh_2	–35.2 (d, 15.7 ^a) (162.6 ^b)	–33.8 (d, 17.1 ^a) (164.0 ^b)	–31.1 (d, 19.9 ^a) (165.4 ^b)	–33.8 (d, 17.4 ^a) (164.9 ^b)

^a $^2J(^{31}\text{P}-^{31}\text{P})$.^b $^1J(^{183}\text{W}-^{31}\text{P})$.

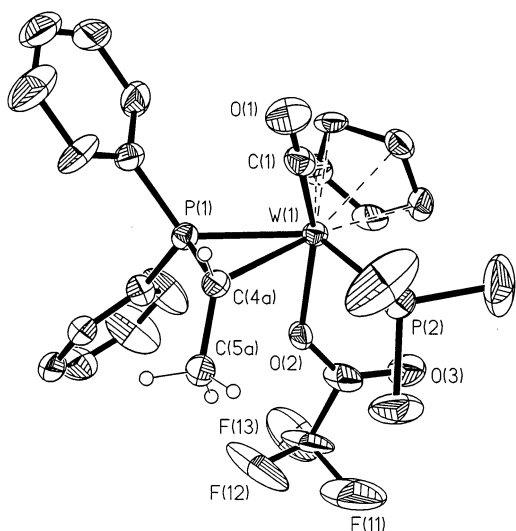


Fig. 1. ORTEP plot for the molecular structure of **3a**. The thermal ellipsoids are correspondent to 30% probability (hydrogen atoms of phenyl, cyclopentadienyl and PMe_3 -groups are omitted for clarity).

ization effects, an empirical absorption correction, based on ω -scans, was applied. The structures were solved by direct methods (SHELXS-86) [25] and refined by a full matrix least-squares procedure using F^2 (SHELXL-93) [26]. The function minimized was $\Sigma(w(F_o^2 - F_c^2)^2)$ with the weight defined as $w^{-1} = (\sigma^2(F_o^2) = (xP)^2 + yP)$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located by difference Fourier methods, but in the refinement they were included in calculated positions and refined with isotropic displacement parameters 1.2 times and

Table 5

Selected bond lengths (pm) and bond angles ($^\circ$) for **3a**

Bond lengths (pm)			
W(1)–P(1)	240.4(3)	O(1)–C(1)	113.7(13)
W(1)–P(2)	252.3(3)	O(2)–C(2)	125(2)
W(1)–O(2)	212.2(8)	O(3)–C(2)	123(2)
W(1)–C(1)	199.3(14)	F(11)–C(3)	133(2)
W(1)–C(4)	231.8(11)	F(12)–C(3)	127(2)
P(1)–C(4)	173.9(11)	F(13)–C(3)	126(2)
P(1)–C(6)	179.3(12)	C(4)–C(5)	155(2)
P(1)–C(12)	179.6(12)	C(2)–C(3)	153(2)
Bond angles ($^\circ$)			
W(1)–P(1)–C(4)	65.8(4)	P(1)–C(4)–C(5)	124.0(9)
W(1)–P(1)–C(6)	124.6(4)	P(2)–W(1)–O(2)	85.4(2)
W(1)–P(1)–C(12)	120.7(4)	P(2)–W(1)–C(1)	83.1(3)
W(1)–O(2)–C(2)	132.3(8)	P(2)–W(1)–C(4)	84.9(3)
W(1)–C(4)–P(1)	71.1(4)	O(2)–W(1)–C(4)	77.4(3)
W(1)–C(4)–C(5)	126.6(8)	O(2)–C(2)–O(3)	128.6(13)
P(1)–W(1)–P(2)	127.9(10)	O(2)–C(2)–C(3)	113.2(14)
P(1)–W(1)–O(2)	80.1(2)	O(3)–C(2)–C(3)	118(2)
P(1)–W(1)–C(1)	85.8(3)	C(6)–P(1)–C(12)	110.0(5)
P(1)–W(1)–C(4)	43.2(3)		

1.5 (for methyl hydrogen atoms) higher than U_{eq} of the attached carbon atoms, except for the hydrogen atom at C(4) of **5c**, which was refined isotropically with fixed distance of 94(1) pm.

Both single crystals had disordered groups in the asymmetric unit. For compound **3a** the methyl group has two conformations C(5a) and C(5b) with refined occupation factors of 0.68 and 0.32. C(5a) and C(5b) can be transferred to each other by reflection through the plane W (1), P (1) and C(4a) (=C(4b)). C(4a) and C(4b) with occupancy 0.68 and 0.32 have equivalent

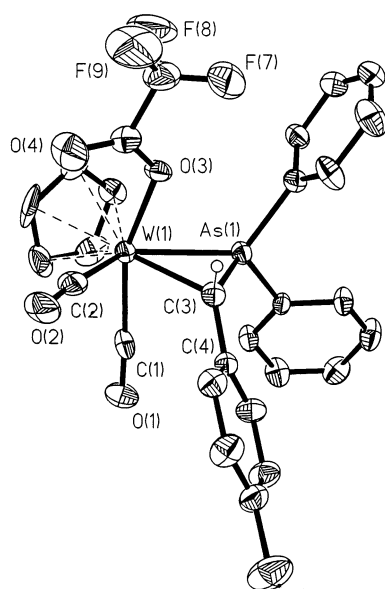
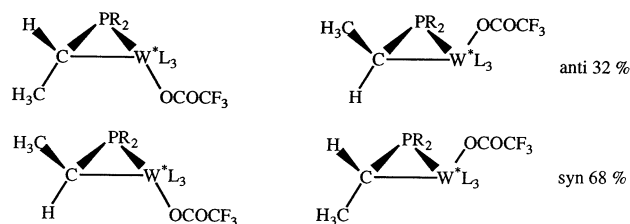


Fig. 2. ORTEP plot for the molecular structure of **5c**. The thermal ellipsoids are correspondent to 30% probability (only the hydrogen atom at C(3) is shown for clarity).

Table 6

Selected bond lengths (pm) and bond angles ($^\circ$) for **5c**

Bond lengths (pm)			
W(1)–As(1)	250.47(7)	O(1)–C(1)	113.5(7)
W(1)–O(3)	212.5(4)	O(2)–C(2)	113.0(7)
W(1)–C(1)	202.4(6)	O(3)–C(11)	127.9(6)
W(1)–C(2)	205.5(7)	O(4)–C(11)	119.4(7)
W(1)–C(3)	234.0(5)	F(7)–C(12)	126.8(8)
As(1)–C(3)	190.7(6)	F(8)–C(12)	133.6(9)
As(1)–C(13)	192.9(6)	F(9)–C(12)	129.9(8)
As(1)–C(19)	192.2(5)	C(3)–C(4)	148.9(8)
Bond angles ($^\circ$)			
W(1)–As(1)–C(3)	62.3(2)	O(3)–W(1)–C(1)	151.6(2)
W(1)–As(1)–C(13)	122.4(2)	O(3)–W(1)–C(2)	87.8(2)
W(1)–As(1)–C(19)	126.4(2)	O(3)–W(1)–C(3)	75.8(2)
W(1)–O(3)–C(11)	125.7(4)	O(3)–C(11)–O(4)	127.7(6)
W(1)–C(3)–As(1)	71.5(2)	O(3)–C(11)–C(12)	112.7(5)
W(1)–C(3)–C(4)	129.0(4)	C(1)–W(1)–C(2)	83.0(2)
As(1)–W(1)–O(3)	76.58(9)	C(1)–W(1)–C(3)	76.4(2)
As(1)–W(1)–C(1)	88.2(2)	C(2)–W(1)–C(3)	82.4(2)
As(1)–W(1)–C(2)	128.4(2)	C(3)–As(1)–C(13)	111.4(2)
As(1)–W(1)–C(3)	46.20(13)	C(3)–As(1)–C(19)	116.4(2)
As(1)–C(3)–C(4)	128.2(4)	C(13)–As(1)–C(19)	108.1(2)



Scheme 3.

coordinates and temperature parameters to calculate the disordered hydrogen atom. For compound **5c** the fluorine atoms of the anion PF_6^- have two possible positions F(1)–F(6) and F(1a)–F(6a) with refined occupancy of 0.57 and 0.43.

Table 7
Crystal data and structure refinement for **3a** and **5c**

Empirical formula	$\text{C}_{25}\text{H}_{28}\text{BF}_7\text{O}_3\text{P}_2$ $\text{W} \times 0.5\text{CH}_2\text{Cl}_2$	$\text{C}_{29}\text{H}_{23}\text{AsF}_9\text{O}_4$ $\text{PW} \times \text{C}_4\text{H}_4\text{O}$
Formula weight (g mol^{-1})	808.54	964.29
Crystal form/color	Yellow plates	Yellow plates
Temperature (K)	213(2)	218(2)
Radiation	Mo– K_α (71.073 pm)	Mo– K_α (71.073 pm)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Unit cell dimensions		
<i>a</i> (pm)	1029.7(4)	1500.3(3)
<i>b</i> (pm)	2430.6(3)	1185.6(2)
<i>c</i> (pm)	1355.1(1)	2091.6(3)
β (°)	109.19(12)	104.20(1)
<i>V</i> (nm^3)	3.2031(13)	3.6068(11)
<i>Z</i>	4	4
<i>D</i> _{calc.} (g cm^{-3})	1.677	1.776
Absorption coefficient (mm^{-1})	3.856	4.242
<i>F</i> (000)	1580	1872
Crystal dimensions (mm^3)	$0.3 \times 0.21 \times 0.19$	$0.3 \times 0.3 \times 0.14$
Theta range for data collection (°)	3.13–20.49	2.57–21.00
Index ranges	$0 \leq h \leq 9,$ $0 \leq k \leq 25,$ $-13 \leq l \leq 10$	$0 \leq h \leq 15,$ $-1 \leq k \leq 12,$ $-22 \leq l \leq 21$
Reflections collected	3092	4172
Independent reflections	2978 [$R_{\text{int}} = 0.0268$]	3839 [$R_{\text{int}} = 0.0328$]
Reflections observed [$I > 2\sigma(I)$]	2292	2863
Absorption correction	Ψ -scan	Ψ -scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2786/0/391	3557/1/511
Goodness-of-fit on F^2	1.066	1.040
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0362,$ $wR_2 = 0.0796$	$R_1 = 0.0360,$ $wR_2 = 0.0636$
<i>R</i> indices (all data)	$R_1 = 0.0582,$ $wR_2 = 0.0905$	$R_1 = 0.0648,$ $wR_2 = 0.0788$
Largest difference peak and hole (e nm^{-1})	564 and –492	477 and –395

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-408821 (**3a**) and CSD-408821 (**5c**), the names of authors, and the journal citation.

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