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Conversion of η^2-phosphinocarbene complexes into tungstaphosphabicyclo[1.1.0]butanone units

Th. Lehotkay [a], K. Wurst [b], P. Jaitner [b], F.R. Kreißl [a,*]

[a] *Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany*
[b] *Institut für Anorganische, Allgemeine und Theoretische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

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Abstract

Cationic η^2-phosphinocarbene complexes $[\eta^2\text{-}C_5H_5(CO)(PMe_3)\overline{W{=}C(R)\text{-}P}Ph_2][PF_6]$ (R = Me, Ph, Tol) react at -78°C with alkyl isonitriles R′NC (R′ = Me, ^{t}Bu) to provide tungstaphosphabicyclo[1.1.0]butanone complexes $[\eta^5\text{-}C_5H_5(R'NC)(PMe_3)\overline{W\text{-}C(O)\text{-}C}(R)\text{-}PPh_2][PF_6]$ in high yields. The constitution of the yellow bicyclic compounds was determined by spectroscopic investigations and, in the case of the 4-methylphenyl substituted compound **2c**, additionally by X-ray single crystal structure analysis. Crystal data for **2c** are as follows: space group $P2_1/n$ (No. 14), $a = 907.80(10)$, $b = 3658.1(6)$, $c = 1085.2(2)$ pm, $\alpha = 90°$, $\beta = 106.27(1)°$, $\gamma = 90°$, $Z = 4$. © 1998 Elsevier Science S.A.

Keywords: η^2-Phosphinocarbene complex; Tungstaphosphabicyclo[1.1.0]butanone complex; Metalla–phospha–carbon ring system

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1. Introduction

The structural and chemical properties of transition metal complexes with three-membered metalla–phospha–carbon ring systems have been studied for more than twenty years. Next to the large group of phosphinomethanide complexes with different metal-ligand parameters L_nM [1–4], few examples of η^2-phosphinocarbene complexes have been synthesized and characterized so far [5–9].

The reactivity of the η^2-phosphinocarbene complexes of tungsten $[\eta^5\text{-}C_5H_5(CO)(PMe_3)\overline{W{=}C(R)\text{-}P}R'_2]X$(R, R′ = alkyl, aryl; X = $[BF_4]$, $[PF_6]$) is comparable to well-known acyclic carbene complexes of tungsten in lower oxidation state [10–13]. In the presence of electrophiles like MeS^+ dicationic tungstaphosphathiabicyclo[1.1.0]butane complexes **A** are formed [14]. On the other hand, selected nucleophiles like trialkyl phosphines or the cyclopentadienyl anion $C_5H_5^-$ add at the carbene carbon atom providing phosphoranylidene complexes **B** [15] or tungstaphosphacyclopropane complexes **C** [16], respectively.

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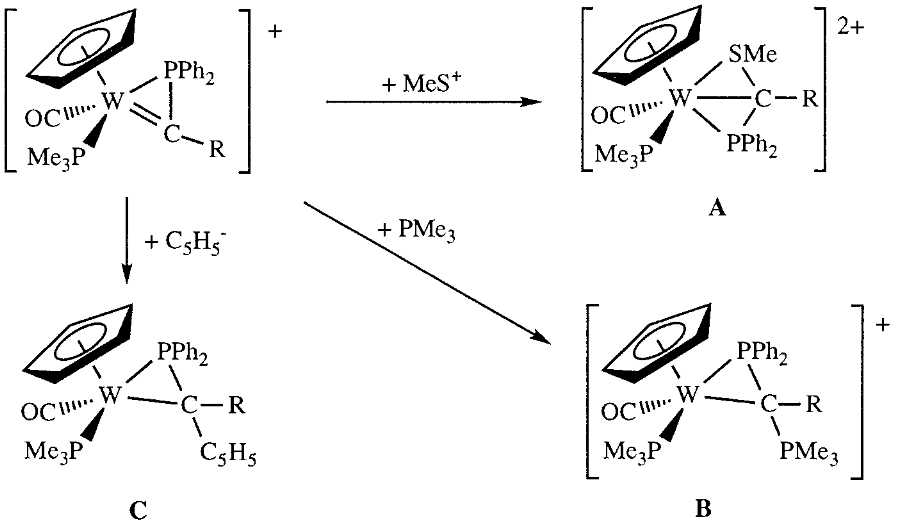
[*] Corresponding author.

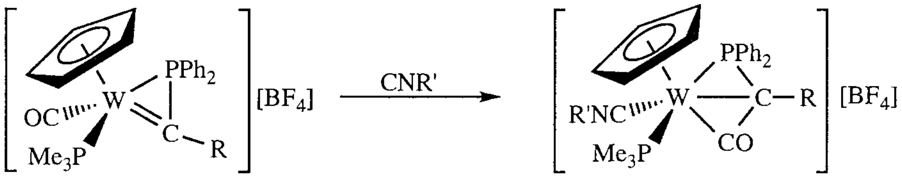


R = Me, Ph, Tol

In contrast, simple substitution reactions of the adjacent carbonyl or phosphine ligands have not been reported so far. For the structurally related neutral tantalum complexes η^5-$C_5H_5(PMe_3)(H_2)\overline{Ta=C(H)\text{-}P}Me_2Me_2$, different addition and substitution reactions are known. With olefins or substituted isocyanides [17], insertion into the Ta–H bond takes place without any modification of the M–P–C ring system. Thus, with neohexene dimerization as well as oligomerization is observed [18,19].

2. Results and discussion

We now report the conversion of η^2-phosphinocarbene complexes of tungsten with selected isonitriles into cationic tungstaphosphabicyclo[1.1.0]butanone complexes. The addition of both MeNC and more bulky isonitriles like ^{t}BuNC to $[\eta^5$-$C_5H_5(CO)(PMe_3)\overline{W=C(R)\text{-}P}Ph_2][PF_6]$ (R = Me, Ph, Tol) generates at −78°C the cationic species **2a**–**3c** in excellent yields.



1a-c **2a-3c**

	1a	1b	1c	2a	2b	2c	3a	3c
R	Me	Ph	Tol	Me	Ph	Tol	Me	Tol
R'				Me	Me	Me	^{t}Bu	^{t}Bu

The deep yellow, diamagnetic compounds are insoluble in nonpolar solvents like diethylether or pentane but slightly soluble in dichloromethane. The constitution and structure of **2a**–**3c** are confirmed by elemental analysis, infrared, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and, in the case of **2c**, additionally by an X-ray single crystal structure analysis.

The infrared spectra of **2a**–**3c** in dichloromethane exhibit in the region of 2126 to 2167 cm^{-1} characteristic absorptions for the ν_{CN} stretching vibrations of the isocyanide ligand and in the range of 1639 to 1659 cm^{-1} the ν_{CO} stretching frequencies for the bridging carbonyl group.

In the phosphorus NMR spectra the significant strong shielding of the endocyclic phosphorus nucleus together with the relatively small metal–phosphorus coupling constant $^1J(^{183}W-^{31}P)$ of about 195 Hz indicate the retention of the tungsten–phosphorus–carbon ring system [20–23].

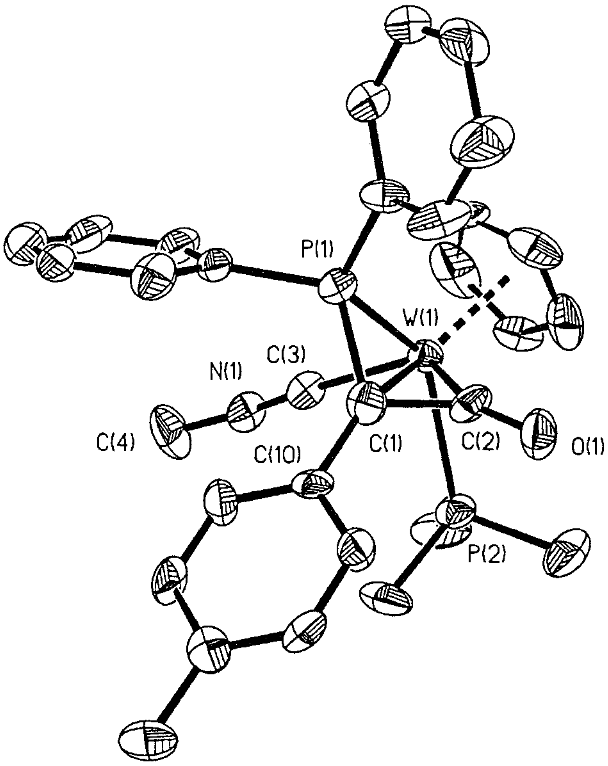
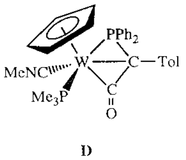


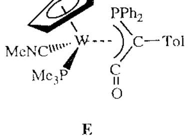
Fig. 1. ORTEP plot of **2c** (50% probability).

The ^{13}C NMR spectra also agree with the proposed structure of **2a**–**3c**. Of special interest are the data of both ring carbon atoms. Thus, the extreme shielding of the bridgehead carbon within $\delta = 3$ to 7 ppm and the downfield shift of the ring carbonyl carbon atom are good indications for the tungstaphosphabicyclo[1.1.0]butanone ring structure [24]. Both signals split into a doublet of doublets due to spin–spin interactions with the endo- and the exocyclic phosphorus atoms.

The X-ray single crystal structure determination reveals further details on the structural properties of **2c** (Fig. 1). The cation shows a tungsten–phosphorus–carbon ring that is fused to a second tungsten–carbon–carbon ring, affording a tungstaphosphabicyclo[1.1.0]butanone system. The distances from tungsten to the cyclopentadienyl, the trimethylphosphine, and to the isonitrile ligands are comparable to those found for other tungsten complexes. Within the tungsten–phosphorus–carbon ring the W(1)–P(1) [238.3(3) pm] and the P(1)–C(1) [175.9(13) pm] bond distances are similar to those reported for cationic η^2-phosphinocarbene complexes [20] and other metalla–phospha–heterocyclic systems [24]. The W(1)–C(1) distance [236.6(13) pm] is significantly elongated and is to be regarded as a W–C single bond [24,25]. The PPh$_2$-group is obviously bent away from the cyclopentadienyl ligand indicating sterical hindrance to the bulky phenyl rings. Within the second fused three-membered ring the significantly shortened W(1)–C(2) bond distance lies within 211.2(13) pm still in the range of a tungsten carbene unit. The ligand sphere around the tungsten atom could be described as a distorted octahedral polyeder with the cyclopentadienyl, the PPh$_2$- and the CO-fragments in a facial arrangement. Besides the description as a bicyclic system **D** the canonical form of an η^3-allylic arrangement **E** can also be taken into account due to the fact that the four atoms P(1), C(1), C(2) and C(10) are coplanar.



D

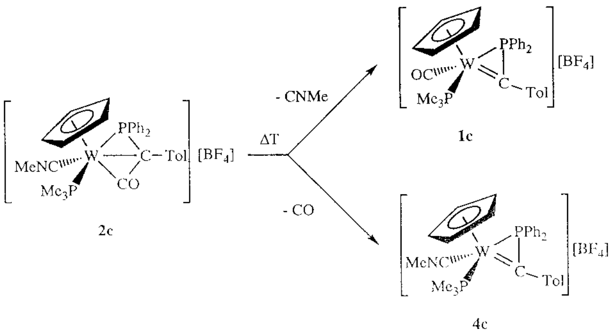


E

The linear conformation of the C-coordinated isonitrile ligand with slightly shortened W(1)–C(3) distance [210.2(14) pm], as well as the N(1)–C(3) [113.9(14) pm] triple- and N(1)–C(4) single-bond character [142(2) pm] reflect only little back donation from the metal to the isocyanide ligand.

2.1. Chemical properties

In comparison to isostructural trimethylphosphine-substituted tungstaphosphabicyclo[1.1.0]butanone compounds [η^5-C_5H_5(CO)(PMe_3)$\overline{\text{W-C(O)-C(R)-P}}$$Ph_2$][$BF_4$] (R = alkyl, aryl) [24] the isonitrile substituted representatives **2a**–**3c** are thermally more stable. Carbonyl extrusion is restricted even at room temperature. On refluxing a solution of **2c** in tetrahydrofurane the trimethylphosphine-substituted η^2-phosphinocarbene complex **1c** as well as the isonitrile-substituted η^2-phosphinocarbene complex **4c** are formed in a temperature-dependent ratio. As both cationic species show comparable solubility in most common solvents, a separation has not been successful.



3. 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). Infrared spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were taken in $CDCl_3$, CD_3CN, and CD_2Cl_2 on a Jeol JNM-GX 270 (^1H, 270.27; ^{13}C, 67.94; ^{31}P, 109.37 MHz) spectrometer. Chemical shifts are quoted as δ in ppm with respect to the deuterated solvents (^{13}C) and its residual proton resonances (^1H), and to aqueous 85% H_3PO_4 for ^{31}P NMR, respectively. Mass spectra were recorded on a Finnigan MAT 90 spectrometer (molecular mass relative to ^{184}W). The starting materials **1a**–**1c** as well as the isonitriles MeNC and ^{t}BuNC were prepared as described in the literature [26].

3.1. Synthesis of [η^5-C_5H_5(MeNC)(PMe_3)$\overline{\text{W-C(O)-C(Me)-P}}$$Ph_2$][$BF_4$] (2a)

To a solution of 0.41 g (0.63 mmol) of **1a** in 20 ml dichloromethane were added the stoichiometric amounts of 0.03 g of methylisonitrile at −78°C. The solution immediately turned to bright yellow and was stirred for 1 h at −78°C. Recrystallization from CH_2Cl_2/Et_2O/pentane afforded a bright microcrystalline powder. Yield 0.39 g (89%) of **2a**. Element. Anal. Found: C, 42.72; H, 4.37; N, 1.91; W, 26.90. $C_{25}H_{30}BF_4NOP_2W$, calcd.: C, 43.28; H, 4.36; N, 2.02; W, 26.54%. ^1H NMR ($CDCl_3$): 7.56–6.83 (m, 10H, C_6H_5); 4.61 (s, 5H, C_5H_5); 3.15 (s, 3H, CH_3NC); 1.41 (d, 3H, $^3J(PH) = 8.6$, C–CH_3); 1.20 (d, 9H, $^2J(PH) = 8.4$, PMe_3). $^{13}C\{^1H\}$ NMR (CD_3CN): 249.1 (dd, $^2J(PC) = 9.2$, $^2J(PC) = 9.2$, W–CO); 135.5–125.9 (C_6H_5); 90.9 (CH_3NC); 87.9 (C_5H_5); 31.6 (t, $^1J(CN) = 3.7$, CH_3NC); 18.1 (PMe_3, $^1J(PC) = 33.1$); 10.9 (C–CH_3); 3.9 (d, $^1J(PC) = 24.8$, W–C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −25.1 (d, $^2J(PP) = 2.9$, $^1J(^{183}W–^{31}P) = 251.0$, PMe_3); −35.4 (d, $^2J(PP) = 4.3$, $^1J(^{183}W–^{31}P) = 198.2$ PPh_2). IR (CH_2Cl_2): ν_{CN} 2165 vs; ν_{CO} 1659 s, 1606 w cm^{-1}. MS (FAB): 606 $[K]^+$, 578 $[K - CO]^+$, 565 $[K - CH_3NC]^+$, 537 $[K - CO–CH_3NC]^+$.

3.2. Synthesis of [η^5-C_5H_5(MeNC)(PMe_3)$\overline{\text{W-C(O)-C(Ph)-P}}$$Ph_2$][$BF_4$] (2b)

According to Section 3.1, 0.39 g (0.55 mmol) of **1b** and 0.03 g of methylisonitrile yielded 0.37 g (90%) of **2b**. Element Anal. Found: C, 46.87; H, 4.22; N, 1.77. $C_{30}H_{32}BF_4NOP_2W$, calcd.: C, 47.67; H, 4.27; N, 1.85; W, 24.36%. ^1H NMR ($CDCl_3$): 7.57–7.10 (m, 15H, C_6H_5); 5.08 (t, 5H, $^4J(NH) = 3.4$, C_5H_5); 3.69 (s, 3H, CH_3NC); 1.20 (d, 9H, $^2J(PH) = 9.3$, PMe_3). $^{13}C\{^1H\}$ NMR (CD_3CN): 246.1 (dd, $^2J(PC) = 9.2$, $^2J(PC) = 7.4$, W–CO); 133.5–116.7 (C_6H_5); 94.0 (C_5H_5); 90.0 (CH_3NC); 32.1 (CH_3NC); 17.0 (PMe_3, $^1J(PC) = 33.0$); 6.2 (dd, $^1J(PC) = 24.8$, $^2J(PC) = 7.4$, W–C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −27.1 (d, $^2J(PP) = 4.3$, $^1J(^{183}W–^{31}P) = 248.0$, PMe_3); −40.2 (d, $^2J(PP) = 4.3$, $^1J(^{183}W–^{31}P) = 191.1$ PPh_2). IR (CH_2Cl_2): ν_{CN} 2167 vs; ν_{CO} 1652 s cm^{-1}. MS (FAB): 668 $[K]^+$, 640 $[K - CO]^+$, 627 $[K - CH_3NC]^+$, 599 $[K - CO–CH_3NC]^+$, 564 $[K - PMe_3–CH_3NC]^+$.

3.3. Synthesis of $[\eta^5\text{-}C_5H_5(MeNC)(PMe_3)\overline{\overline{W\text{-}C(O)\text{-}C}(Tol)\text{-}P}Ph_2][BF_4]$ **(2c)**

The procedure employed was analogous to that in Section 3.1. using 0.46 g (0.63 mmol) of **1c** and 0.03 g of methylisonitrile. Recrystallization from $CH_2Cl_2/Et_2O/$pentane afforded a bright yellow microcrystalline powder. Yield 0.44 g (91%) of **2c**. Element anal. found: C, 47.66; H, 4.43; N, 1.83; W, 23.69. $C_{31}H_{34}BF_4NOP_2W$. calcd.: C, 48.36; H, 4.45; N, 1.82; W, 23.92%. ^1H NMR ($CDCl_3$): 7.82–6.94 (m, 14H, $C_6H_{4/5}$); 5.06 (t, 5H, $^4J(NH) = 3.4$, C_5H_5); 3.67 (t, 3H, $^2J(NH) = 3.9$, CH_3NC); 2.26 (s, 3H, Tol–CH_3); 1.20 (d, 9H, $^2J(PH) = 9.3$, PMe_3). $^{13}C\{^1H\}$ NMR (CD_3CN): 246.3 (W–CO); 137.6–129.1 ($C_6H_{5/4}$); 94.1 (C_5H_5); 89.9 (CH_3NC); 31.7 (CH_3NC); 21.2 (Tol–CH_3); 17.0 (PMe_3, $^1J(PC) = 33.1$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -27.0 (d, $^2J(PP) = 4.3$, $^1J(^{183}W-^{31}P) = 249.6$, PMe_3); -41.4 (d, $^2J(PP) = 4.3$, $^1J(^{183}W-^{31}P) = 192.5$, PPh_2). IR(CH_2Cl_2): ν_{CN} 2165 vs; ν_{CO} 1639 s, 1697 w cm^{-1}. MS (FAB): 682 $[K]^+$, 654 $[K - CO]^+$, 641 $[K - CH_3NC]^+$, 613 $[K - CO\text{–}CH_3NC]^+$, 578 $[K - CO\text{–}PMe_3]^+$.

3.4. Synthesis of $[\eta^5\text{-}C_5H_5(^tBuNC)(PMe_3)\overline{\overline{W\text{-}C(O)\text{-}C}(Me)\text{-}P}Ph_2][BF_4]$ **(3a)**

According to Section 3.1, 0.38 g (0.58 mmol) of **1a** and 0.05 g of *tert*-butylisonitrile yielded 0.35 g (82%) of **3a**. Element anal. found: C, 44.88; H, 4.73; N, 1.5; W, 22.04. $C_{28}H_{36}BF_4NOP_2W$. calcd.: C, 45.70; H, 4.94; N, 1.90; W, 25.02%. ^1H NMR ($CDCl_3$): 7.96–7.19 (m, 10H, C_6H_5); 5.02 (t, 5H, $^4J(NH) = 3.9$, C_5H_5); 1.80 (d, 3H, $^3J(PH) = 7.8$, C–CH_3); 1.61 (d, 9H, $^2J(PH) = 9.3$, PMe_3); 1.24 (s, 9H, ^tBuNC);. $^{13}C\{^1H\}$ NMR (CD_3CN): 247.8 (dd, $^2J(PC) = 11.0$, $^2J(PC) = 10.1$, W–CO); 135.4–129.0 (C_6H_5); 88.7 (Me_3CNC); 87.9 (C_5H_5); 59.9 (Me_3CNC); 30.2 (Me_3CNC); 18.0 (PMe_3, $^1J(PC) = 33.1$); 10.6 (C–CH_3); 3.5 (dd, $^1J(PC) = 24.8$, $^2J(PC) = 6.4$, W–C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -19.4 (d, $^2J(PP) = 4.3$, $^1J(^{183}W-^{31}P) = 245.3$, PMe_3); -29.5 (d, $^2J(PP) = 2.9$, $^1J(^{183}W-^{31}P) = 195.4$ PPh_2). IR(CH_2Cl_2): ν_{CN} 2127 vs; ν_{CO} 1659 s cm^{-1}. MS (FAB): 648 $[K]^+$, 620 $[K - CO]^+$, 565 $[K - {}^tBuNC]^+$, 537 $[K - CO\text{–}{}^tBuNC]^+$.

3.5. Synthesis of $[\eta^5\text{-}C_5H_5(^tBuNC)(PMe_3)\overline{\overline{W\text{-}C(O)\text{-}C}(Tol)\text{-}P}Ph_2][BF_4]$ **(3c)**

This compound was prepared analogously to **2a** using 0.45 g (0.62 mmol) of **1c** and 0.06 g of *tert*-butylisonitrile. Recrystallization from $CH_2Cl_2/Et_2O/$pentane afforded a bright microcrystalline powder. Yield 0.40 g (80%) of **3c**. Element anal. found: C, 49.01; H, 4.99; N, 1.37; W, 20.52. $C_{34}H_{40}BF_4NOP_2W$, calcd.: C, 50.30; H, 4.97; N, 1.73; W, 22.68%. ^1H NMR ($CDCl_3$): 7.82–6.92 (m, 14H, $C_6H_{4/5}$); 5.28 (s, 5H, C_5H_5); 2.27 (s, 3H Tol–CH_3); 1.40 (s, 9H, ^tBuNC); 1.23 (d, 9H, $^2J(PH) = 9.8$, PMe_3). $^{13}C\{^1H\}$ NMR (CD_3CN); 245.4 (dd, $^2J(PC) = 11.0$, $^2J(PC) = 11.0$, W–CO); 137.4–127.1 ($C_6H_{4/5}$); 93.2 (Me_3CNC); 88.5 (C_5H_5); 60.3 (Me_3CNC); 30.3 (Me_3CNC); 21.2 (Tol–CH_3); 17.0 (PMe_3, $^1J(PC) = 32.2$); 5.6 (d, $^1J(PC) = 22.4$, W–C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): -26.5 (d, $^2J(PP) = 4.3$, $^1J(^{183}W-^{31}P) = 241.0$, PMe_3); -40.3 (d, $^2J(PP) = 4.3$, $^1J(^{183}W-^{31}P) = 191.1$ PPh_2). IR(CH_2Cl_2): ν_{CN} 2126 vs; ν_{CO} 1640 s cm^{-1}. MS (FAB): 696 $[K]^+$, 613 $[K - {}^tBuNC]^+$.

3.6. Thermal treatment of $[\eta^5\text{-}C_5H_5(MeNC)(PMe_3)\overline{\overline{W\text{-}C(O)\text{-}C}(Tol)\text{-}P}Ph_2][BF_4]$ **(2c)**

A suspension of 0.32 g (0.42 mmol) of **2c** in 5 ml of tetrahydrofurane was refluxed for 1 h. After several minutes the suspension turned to an orange-brown solution. The formation of both η^2-phosphinocarbene complexes **1c** and **4c** could be observed by infrared spectroscopy.

1c: ^1H NMR ($CDCl_3$): 7.57–6.97 (m, $C_6H_{4/5}$); 5.83 (s, 5H, C_5H_5); 2.29 (s, 3H Tol–CH_3); 1.30 (d, 9H, $^2J(PH) = 9.9$, PMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): -24.2 (d, $^2J(PH) = 6.7$, $^1J(^{183}W-^{31}P) = 385.2$); -111.3 (d, $^2J(PP) = 6.7$, PPh_2). IR(CH_2Cl_2): ν_{CO} 1979 s, 1930 vs cm^{-1}. MS (FAB): 641 $[K]^+$, 613 $[K - CO]^+$.

4c: ^1H NMR ($CDCl_3$): 7.57–6.97 (m, $C_6H_{4/5}$); 5.30 (s, 5H, C_5H_5); 3.68 (s, 3H, $MeNC$); 2.29 (s, 3H Tol–CH_3); 1.22 (m, 9H, PMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): -28.3 (d, $^2J(PP) = 10.7$); -116.4 (d, $^2J(PP) = 10.7$, $^1J(^{183}W-^{31}P) = 131.4$ PPh_2). IR(CH_2Cl_2): ν_{CN} 2155 vs cm^{-1}. MS (FAB): 654 $[K]^+$, 613 $[K - MeNC]^+$.

4. X-ray structure determination of 2c

Suitable crystals of **2c** were grown from dichloromethane/diethyl ether at −30°C. Crystal data together with details of the data collection and structure refinement are listed in Table 1. A platelet of dimension 0.3 × 0.3 × 0.04 mm was measured on a Siemens P4 diffractometer with graphite-monochromatized Mo Kα-radiation. The unit cell parameters were determined and refined from 32 randomly selected reflections in the 2Θ range of 10.5 to 22.0°,

Table 1
Crystal data and structure refinement for **2c**

Molecular formula	$C_{31}H_{34}BF_4NOP_2W \cdot CH_2Cl_2$
Formula weight (g mol^{-1})	854.12
Temperature (K)	213(2)
Radiation	Mo Kα (71.073 pm)
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions	
a (pm)	907.80(10)
b (pm)	3658.1(6)
c (pm)	1085.2(2)
β (deg)	106.27(1)
Volume (nm^3)	3.4594(9)
Z	4
r_{calcd} (g cm^{-3})	1.640
absorption coefficient (mm^{-1})	3.634
F(000)	1688
Crystal dimension (mm^3)	$0.3 \times 0.3 \times 0.04$
θ range for data collection (deg)	10.5 to 22.0
Index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 37$, $-10 \leq l \leq 9$
Reflections collected	4267
Independent reflections	3972 ($R_{\text{int}} = 0.0418$)
Reflections with $I > 2\sigma(I)$	2797
Absorption correction	Ψ-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3971/0/399
Goodness-of-fit on F^2	1.057
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0476$, $wR_2 = 0.0977$
R indices (all data)	$R_1 = 0.0868$, $wR_2 = 0.1173$
Largest different peak and hole (e nm^{-3})	931 and -965

obtained by P4 automatic routines. Diffraction intensities were collected up to $2\Theta < 43°$ via ω-scans and corrected for Lorentz and polarisation effects. An empirical absorption correction [27] based on a series of ψ-scans was applied to the data (max. and min. transmission: 1.000 and 0.611). The structure was solved by direct methods (SHELXS-86) [28] and refined by full matrix least-squares against F^2 (SHELXL-93) [29]. The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^1 = [\sigma_2(F_o^2) + (xP)^2 + yP]$ with $P = (F_o^2 + 2F_c^2)/3$ ($x = 0.047$ and $y = 20.143$). All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in

Table 2
Selected bond lengths (pm) and angles (deg) for **2c**

W(1)–P(1)	238.3(3)	W(1)–C(2)–C(1)	80.1(8)
W(1)–P(2)	248.9(3)	W(1)–C(3)–N(1)	176.3(11)
W(1)–C(1)	236.6(13)	P(1)–W(1)–P(2)	132.48(12)
W(1)–C(2)	211.2(13)	P(1)–W(1)–C(1)	43.5(3)
W(1)–C(3)	210.2(14)	P(1)–W(1)–C(2)	68.8(3)
P(1)–C(1)	175.9(13)	P(1)–W(1)–C(3)	86.3(3)
P(1)–C(17)	181.1(12)	P(1)–C(1)–C(2)	103.1(8)
P(1)–C(23)	183.3(13)	P(1)–C(1)–C(10)	132.6(9)
O(1)–C(2)	119.3(14)	P(2)–W(1)–C(1)	90.6(3)
N(1)–C(3)	113.9(14)	P(2)–W(1)–C(2)	81.1(3)
N(1)–C(4)	142(2)	P(2)–W(1)–C(3)	80.5(3)
C(1)–C(10)	148(2)	O(1)–C(2)–C(1)	135.9(12)
C(1)–C(2)	149(2)	C(1)–W(1)–C(3)	89.1(4)
W(1)–P(1)–C(1)	67.8(4)	C(1)–W(1)–C(2)	38.4(4)
W(1)–P(1)–C(17)	126.5(5)	C(1)–P(1)–C(17)	113.8(6)
W(1)–P(1)–C(23)	123.5(4)	C(1)–P(1)–C(23)	113.3(6)
W(1)–C(1)–P(1)	68.8(4)	C(2)–C(1)–C(10)	123.2(11)
W(1)–C(1)–C(2)	61.5(6)	C(3)–W(1)–C(2)	123.5(5)
W(1)–C(1)–C(10)	140.2(9)	C(3)–N(1)–C(4)	174.7(13)
W(1)–C(2)–O(1)	143.2(9)	C(17)–P(1)–C(23)	105.3(6)

idealized positions and were refined with isotropic displacement parameters 1.2 and 1.5 times higher than U_{eq} of the attached carbon atoms. Selected bond lengths and angles for **2c** are shown in Table 2.

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Supporting Information Available: Tables of crystallographic and structure refinement data, atomic coordinates and isotropic displacement parameters, bond lengths and angels, anisotropic displacement parameters, and hydrogen coordinates (11 pages). Ordering information is given on any current masthead page. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-407342, the names of the authors, and the journal citation.

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