

Catalytic and selective ring expansion reactions of *ortho*-phenyl-substituted 2*H*-azaphosphirene tungsten complexes

Christoph Neumann, Emanuel Ionescu, Udo Schiemann, Manuela Schlenker, Maren Bode, Frank Ruthe, Peter G. Jones, Rainer Streubel *

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

ortho-Phenyl-substituted ethoxy- and aminocarbene pentacarbonyltungsten complexes **2a–c** and **3a–c** are synthesized and the latter are reacted with chloromethylenephosphane **4** in diethyl ether in the presence of triethylamine to yield the *ortho*-phenyl-substituted 2*H*-azaphosphirene complexes **6a–c** via elimination of triethylammonium chloride; remarkable are the prolonged reaction times in the case of the methoxy- and dimethylamino-substituted complexes **6b,c**. The 2*H*-azaphosphirene complexes **6a–c** and **7d** are reacted with benzonitrile in dichloromethane in the presence of ferrocenium hexafluorophosphate to furnish the 2*H*-1,2,4-diazaphosphole complexes **8a–d** (**8a**: R = Me, **8b**: R = OMe, **8c**: R = NMe₂, **8d**: R = H); the reaction course will be discussed. All complexes were unambiguously confirmed by NMR spectroscopy and elemental analysis and, additionally complexes **2b**, **5** and **6b** by X-ray analysis. © 2002 Elsevier Science B.V. All rights reserved.

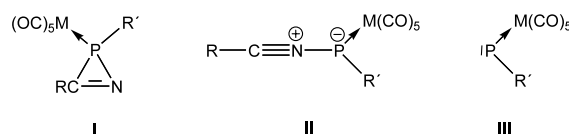
Keywords: Azaphosphirene complexes; Carbene complexes; Diazaphospholes; Ring formation; Phosphorus; Tungsten

1. Introduction

Transition-metal promoted synthesis of P-heterocycles has attracted attention over the years, because of the frequently outstanding reaction selectivities and product yields [1]. Recently, we demonstrated the widespread applicability of 2*H*-azaphosphirene metal complexes **I** [2] in heterocyclic ligand synthesis using ring cleavage [3] and ring expansion reactions. In the latter case intermediately formed nitrilium phosphanylid metal complexes **II** were trapped and thus proved to be the reactive species [4,5]. By using this new building block in [3 + 2]-cycloaddition reactions we gained access to a variety of five-membered P-heterocycle complexes [6–8]. More generally, the formation of nitrilium phosphanylid metal complexes **II** can be achieved via end-on [1,1]-addition reactions of terminal phosphanediyl complexes **III** [9,10] to carbonitriles, which is

a weakly exothermic process according to DFT-calculations [11] (Scheme 1).

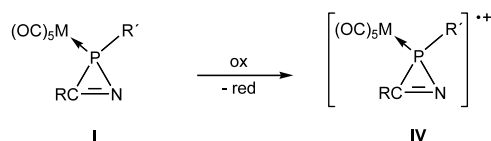
More recently, we presented a novel application of 2*H*-azaphosphirene complexes **I** in heterocycle synthesis through P–N bond-selective ring expansion reactions, which do not proceed via the intermediates **II** and/or **III** and which have to be induced by catalytical amounts of typical one-electron oxidants such as tetracyanoethylene [12] and/or ferrocenium hexafluorophosphate [13]. Besides the presence of such oxidants in these reactions, the following factors are important: (1) polar solvents such as dichloromethane or carbonitriles; (2) π -systems that additionally possess a lone pair at one terminal atom; and (3) the nucleophiles should



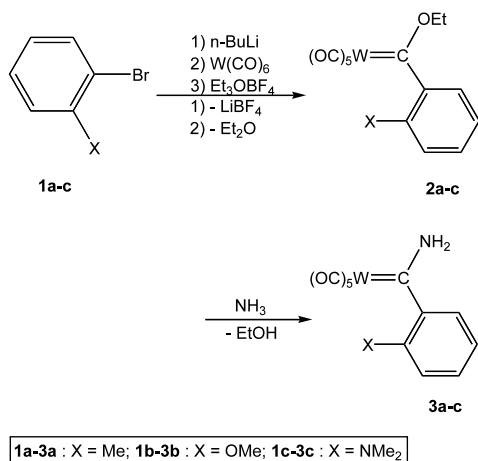
Scheme 1. 2*H*-Azaphosphirene complexes **I** as precursors for nitrilium phosphanylid complexes **II** and terminal phosphanediyl complexes **III** (M = Cr, Mo, W; R, R' = organic substituents).

* Corresponding author. Tel.: +49-531-3917350; fax: +49-531-3915387.

E-mail address: r.streubel@tu-bs.de (R. Streubel).



Scheme 2. Assumed formation of 2*H*-azaphosphirene complex radical cations **IV** from 2*H*-azaphosphirene complexes **I** via one-electron oxidation reaction in solution ($M = \text{Cr}, \text{Mo}, \text{W}$; $R, R' = \text{organic substituents}$).



Scheme 3. Synthesis of ethoxy- and aminocarbene complexes **2a–c** and **3a–c**.

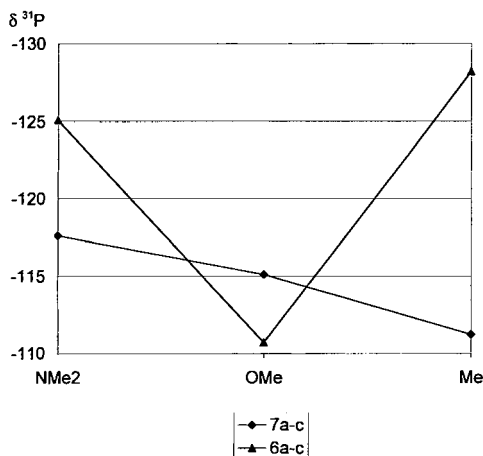


Fig. 1. ^{31}P -NMR resonances of **6a–c** and **7a–c** (CDCl_3) ($c = 0.25 \text{ mol l}^{-1}$).

possess substituents that are not bulky. All aspects taken together indicate primary formation and subsequent reaction of a 2*H*-azaphosphirene complex radical cation **IV** (Scheme 2), although we have so far not succeeded in obtaining evidence of this by spectroscopic means. In order to obtain more information about stereoelectronic factors that might affect the reaction course, we decided to synthesize *ortho*-phenyl-substituted 2*H*-azaphosphirene tungsten complexes using our metal carbene complex rearrangement route [14]. Here,

Table 1

Selected ^{13}C -NMR data ^a of carbene complexes **2a**, **2b** [16], **2c** and **3a–c**

Compounds	$\delta\text{-}^{13}\text{C}$ ($[\text{W}]=\text{C}$)	$\delta\text{-}^{13}\text{C}$ (<i>cis</i> -CO)	$\delta\text{-}^{13}\text{C}$ (<i>trans</i> -CO)
2a	329.4	196.6	203.0
2b [16]	325.3	197.3	205.4
2c	330.4	196.4	203.6
3a	272.4	197.9	203.7
3b	264.5	198.4	203.9
3c	268.8	198.2	204.1

^a CDCl_3 .

we report synthesis and catalytic reactions of such 2*H*-azaphosphirene complexes with benzonitrile and ferrocenium hexafluorophosphate.

2. Results and discussion

2.1. Synthesis and NMR spectroscopic data of *ortho*-phenyl-substituted aminocarbene complexes **2a–c** and **3a–c**

The *ortho*-phenyl-substituted aminocarbene tungsten complexes were synthesized analogously to the procedure described by Fischer and Kollmeier (Scheme 3) [15]. The reactions proceeded smoothly for the carbene complexes **3a,b**. Only in the case of the ethoxycarbene complex **2c** [16], slight decomposition was observed in solution, thus leading to reduced yields of complex **3c**. The molecular structure of complex **2b**, obtained by single crystal X-ray analysis [17], shows a *Z*-configured C–O unit with otherwise common structural features and parameters (Fig. 1) [18].

The ^{13}C -NMR spectroscopic data of the carbene atoms of complexes **2a–c** and **3a–c** were observed in the typical range [18] of such compounds (Table 1). Apart from their *E,Z*-isomerism, which has been already recognized and investigated in detail for complex **2b** [16] and related complexes, complexes **2a,b** displayed no unusual NMR data. Complexes **3a,c** showed lowfield-shifts of the carbene carbon atoms of ca. 8–14 ppm as compared to the corresponding *para*-phenyl-substituted aminocarbene complexes [19], whereas for complex **3b** no significant deviation of the chemical shift value was observed.

2.2. Synthesis and spectroscopic data of *ortho*-phenyl-substituted 2*H*-azaphosphirene complexes **6a–c**

The 2*H*-azaphosphirene complexes **6a–c** were obtained by reacting the aminocarbene complexes **3a–c** with [bis(trimethylsilyl)methylene]chlorophosphane (**4**)

Table 2
Selected NMR data ^a of 2*H*-azaphosphirene complexes **6a–c** and **7d** [19]

Compounds	δ - ³¹ P (¹ J(W, P))	δ - ¹³ C (PCN) (¹⁺² J(P, C))	δ - ¹³ C (<i>cis</i> -CO) (² J(P, C))	δ - ¹³ C (<i>trans</i> -CO) (² J(P, C))
6a	–128.3 (293.2)	191.9 ^b	196.4 (9.0)	197.7 (35.8)
6b	–110.7 (295.2)	189.6 ^b	196.1 (8.7)	198.5 (35.9)
6c	–125.1 (292.8)	187.7 (2.1)	196.6 (8.8)	198.4 (35.0)
7d [19]	–111.0 (293.8)	192.4 (1.7)	196.4 (8.8)	197.9 (36.1)

^a CDCl₃.

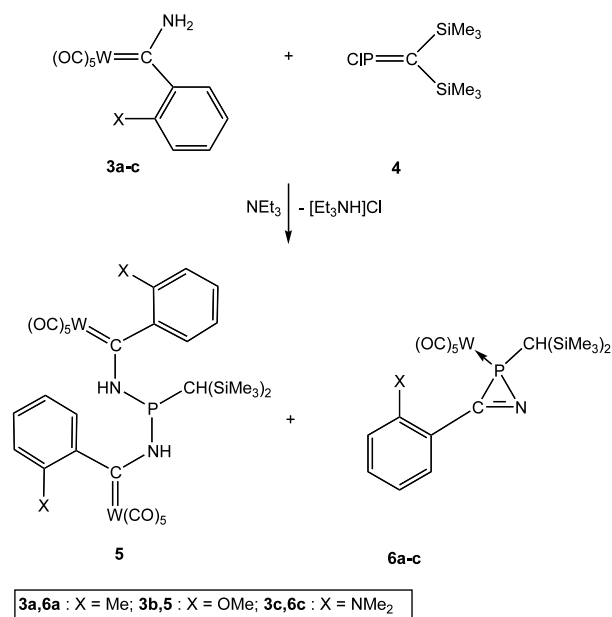
^b Not resolved.

[20] in diethyl ether in the presence of triethylamine (Scheme 4). Exclusively in the case of complex **3a**, the reaction proceeded smoothly to the 2*H*-azaphosphirene complex **6a**. In the cases of complexes **3b** and **3c** longer reaction times than those of the *para*-phenyl-substituted 2*H*-azaphosphirene complexes were observed [19]. Furthermore, the final products exhibited an enhanced reactivity towards triethylammonium chloride at ambient temperature, thus leading to a cleavage of the three-membered ring, whereby the phosphorus-containing product was identified by its typical ³¹P-NMR resonance [19]. The ring cleavage could be significantly suppressed by using acetonitrile as solvent and lower temperatures, thus also diminishing the reaction times for **6b,c**. It was also remarkable that the intermediately formed *ortho*-methoxy-substituted dinuclear bis-carbene complex **5** displayed a longer lifetime than the corresponding *para*-substituted complex [19]. We were thus enabled to isolate complex **5** and to get structural information via an X-ray analysis of suitable single crystals of **5** (Fig. 2, Table 3 and Table 6) [17]. Complex **5** displayed the typical *E,E*-configuration at the C–N bonds, which had already been observed for related complexes [19]. In general, C–N bonds of aminocarbene complexes have enhanced bond orders, thus leading to *E,Z*-isomeric forms [18].

From the NMR spectroscopic data of the 2*H*-azaphosphirene complexes **6a–c**, the phosphorus resonances are the most significant (Table 2), whereby a very surprising observation was made for complex **6b**. Whereas, the ³¹P resonances of **6a,c** appeared significantly highfield-shifted as compared to the corresponding *para*-phenyl-substituted complexes **7a–c** [19] (Fig. 3), this was not the case for complex **6b**. In contrast, the ³¹P resonance of complex **7c** showed a highfield-shift as compared to complex **6b**. Furthermore, we, at first thought that the solvent dependence of the phosphorus–tungsten coupling constant magnitude of **6b** was exceptionally great, but this behavior was strictly paralleled by complex **7b**, albeit the magnitude was found to be generally higher for complex **6b** (Fig. 4). The origins of these special effects of the *ortho*-bonded methoxy group are not yet understood.

The X-ray structure analysis [17] of 2*H*-azaphosphirene complex **6b**, which crystallizes with two inde-

pendent molecules, revealed that the methoxy-substituent is on the phosphorus side (Fig. 5, Tables 3 and 7) rather than the nitrogen side of the 2*H*-azaphosphirene ring [21]. This outcome was surprising with respect to steric repulsion between the methoxy group, on one hand, and the pentacarbonyltungsten fragment and the bis(trimethylsilyl)methyl group, on the other hand, which was expected to be significant. The interplanar angle between the two ring systems of 12.3° (19.8°) would enable an interaction between the methoxy oxygen atom and the phosphorus atom. Furthermore, the C14–C19–O6 angle of 116.0(2) Å (115.5 Å) deviates slightly from the expected 120° value and would also be consistent with such an interaction, but the O–P distance of 3.576(2) Å (3.486 Å) is greater than the sum of the oxygen–phosphorus van der Waals-radii of 3.4 Å. The other structural features of complex **6b** are normal for aryl-substituted 2*H*-azaphosphirene complexes.



Scheme 4. Synthesis of dinuclear bis-carbene complex **5** and 2*H*-azaphosphirene complexes **6a–c**.

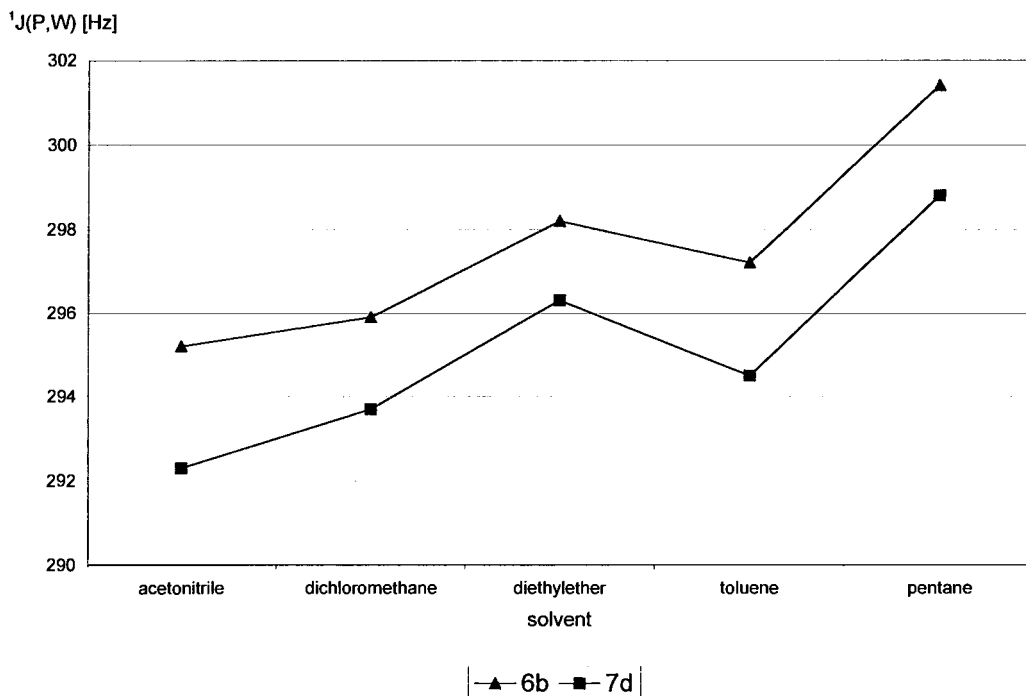


Fig. 2. Tungsten–phosphorus coupling constants of **6b** and **7d** in different solvents (CDCl_3) ($c = 0.25 \text{ mol l}^{-1}$).

2.3. Synthesis and spectroscopic data of *ortho*-phenyl-substituted 2*H*-1,2,4-diazaphosphole complexes **8a–c**

2*H*-Azaphosphirene complexes **6a–c** and **7d** [19] reacted with benzonitrile (two equivalents) in dichloromethane in the presence of ferrocenium hexafluorophosphate (0.2 equivalents) to 2*H*-1,2,4-diazaphosphole complexes **8a–c** and **8d** [6] (Scheme 5), which were isolated in moderate to good yields by column chromatography at low temperature. Apart from ferrocene, which was isolated in ca. 10% yield, and the hexafluorophosphate, which was easily identified by its ^{31}P -NMR data, we could neither detect nor identify the cation formed in this reaction. The reaction rate decreased significantly from complex **7d** > **6a** > **6b** > **6c** (0.8, 1, 12 h, 5 days; ca. 20% conversion of **6c**), which corresponds to the increase in electron donor abilities of the aryl substituents [22] of the 2*H*-azaphosphirene complexes along the series **6c** > **6b** > **6a** > **7d**. Because complex **6c** showed almost no reaction under these conditions, we used neat benzonitrile as solvent. But even under these conditions the reaction was slow (5 days). Furthermore, only in the case of complex **6c** did we observe a reactive intermediate by ^{31}P -NMR spectroscopy (186.5 ppm, $^1J(W, P) = 305.5 \text{ Hz}$), which unfortunately could not be isolated. Some characteristic NMR data of complexes **8a–c** and **8d** are collected in Table 4. Whereas, the ^{13}C -NMR chemical shifts of the C^5 atom resonances are stunningly invariant at 169 ppm,

the C^3 atoms in **8a–c** are more shielded than in **8d** and display greater variations. The ^{31}P -NMR spectra showed also some substituent effects on the resonances, although not as expected for electron-donating groups.

2.3.1. Conclusions

Two interpretations of our findings presented are plausible, which depend on the charge partitioning within the 2*H*-azaphosphirene complex radical cations **IV** — which are still undetected and which are assumed to be produced via one-electron oxidation with the ferrocenium salt (Scheme 2). If the charge is mostly localized on the phosphorus atom then intramolecular donor adducts of type **V** might be reactive intermediates during the ring expansion (Fig. 6). The adduct formation would significantly decrease the electrophilicity of the phosphorus atom of the 2*H*-azaphosphirene complexes in the case of complexes **6b,c**, and, in consequence, slow down the reaction rate. As an alternative, if the charge is mostly localized on the tungsten atom, intramolecular chelate complexes **VI**, via coordination of the methoxy- or dimethylamino group to the tungsten complex fragment, might be formed intermediately, thus also pushing electron density into the system. A related bonding situation concerning the phosphorus atom in **V** has been proposed to occur in reactions of 1*H*-phosphirene complexes with nucleophiles [23].

Currently, further investigations are under way, which aim at the elucidation of the reaction mechanism.

3. Experimental

3.1. General procedures

All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen,

Table 3
Crystal data and structure refinement of complexes **2b**, **5** and **6b**

Complex	2b	5	6b
Empirical formula	C ₁₅ H ₁₂ O ₇ W	C ₃₃ H ₃₅ N ₂ O ₁₂ ⁻	C ₂₀ H ₂₆ NO ₆ ⁻
<i>M_r</i>	488.10	1106.48	647.42
Crystal system	Monoclinic	Monoclinic	Triclinic
Crystal habit	Red block	Orange tablet	Colorless tablet
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>T</i> (K)	143(2)	173(2)	133(2)
Unit cell dimensions			
<i>a</i> (pm)	706.9(3)	1137.1(3)	1240.007(8)
<i>b</i> (pm)	1006.9(3)	1835.1(2)	1414.34(11)
<i>c</i> (pm)	1137.5(4)	1960.9(3)	1483.74(11)
α (°)	90	90	85.421(3)
β (°)	104.06(4)	93.992(18)	86.244(3)
γ (°)	90	90	87.831(3)
<i>V</i> (nm ³)	0.7854(4)	4.0818(12)	2.5870(3)
<i>Z</i>	2	4	4
<i>D</i> _{calc} (mg m ⁻³)	2.064	1.801	1.662
μ (mm ⁻¹)	7.387	5.788	4.653
Transmissions	0.71–0.85	0.51–0.99	0.61–0.86
<i>F</i> (000)	464	2136	1272
Crystal size (mm)	0.7 × 0.4 × 0.4	0.40 × 0.25 × 0.08	0.24 × 0.17 × 0.12
2 θ _{max}	50	50	60
Reflections			
Measured	3001	7565	59 025
Unique	2771	7182	15 086
<i>R</i> _{int}	0.0282	0.028	0.0595
Parameters	147	485	573
Restraints	210	35	45
Flack-parameter	-0.03(2)		
<i>wR</i> (<i>F</i> ² , all reflections)	0.0704	0.0533	0.0561
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0280	0.0540	0.0305
<i>S</i>	1.031	0.950	0.875
Max $\Delta\rho$ (e nm ⁻³)	1061	1631	695

Table 4
Selected NMR data^a of 2*H*-1,4,2-diazaphosphole complexes **8a–d**

Compounds	δ - ³¹ P (¹ <i>J</i> (W, P))	δ - ¹³ C ³ (¹ <i>J</i> (P, C))	δ - ¹³ C ⁵ (²⁺³ <i>J</i> (P, C))
8a	115.8 (229.2)	198.3 (22.6)	169.0 (4.3)
8b	111.7 (222.0)	196.5 (24.5)	168.0 (4.3)
8c	114.4 (236.7)	198.2 (22.1)	169.3 (4.6)
8d	110.6 (227.9)	202.3 (22.9)	169.5 (5.1)

^a CDCl₃.

Table 5
Bond lengths (Å) and angles (°) for complex **2b**

Bond lengths	
W–C(1)	2.0199(73)
W–C(3)	2.0206(72)
W–C(2)	2.0301(72)
W–C(4)	2.0393(74)
W–C(5)	2.0734(75)
W–C(6)	2.1724(74)
C(1)–O(1)	1.1509(84)
C(2)–O(2)	1.1584(86)
C(3)–O(3)	1.1500(82)
C(4)–O(4)	1.1418(86)
C(5)–O(5)	1.1339(84)
C(6)–O(7)	1.3106(84)
C(6)–C(7)	1.5114(96)
C(7)–C(12)	1.3719(114)
C(7)–C(8)	1.3987(106)
C(8)–O(6)	1.3671(90)
C(8)–C(9)	1.3762(107)
C(9)–C(10)	1.3867(128)
C(10)–C(11)	1.3841(127)
C(11)–C(12)	1.3979(120)
O(6)–C(13)	1.4207(96)
O(7)–C(14)	1.4633(86)
C(14)–C(15)	1.4931(120)
Bond angles	
C(1)–W–C(3)	86.7(3)
C(1)–W–C(2)	86.4(3)
C(3)–W–C(2)	173.1(3)
C(1)–W–C(4)	89.8(3)
C(3)–W–C(4)	88.2(3)
C(2)–W–C(4)	91.3(3)
C(1)–W–C(5)	90.2(3)
C(3)–W–C(5)	88.9(3)
C(2)–W–C(5)	91.6(3)
C(4)–W–C(5)	177.1(3)
C(1)–W–C(6)	174.7(3)
C(3)–W–C(6)	96.5(2)
C(2)–W–C(6)	90.4(3)
C(4)–W–C(6)	94.5(3)
C(5)–W–C(6)	85.6(3)
O(1)–C(1)–W	179.4(7)
O(2)–C(2)–W	175.4(7)
O(3)–C(3)–W	176.1(6)
O(4)–C(4)–W	177.6(7)
O(5)–C(5)–W	179.1(6)
O(7)–C(6)–C(7)	106.5(6)
O(7)–C(6)–W	133.7(5)
C(7)–C(6)–W	119.8(4)
C(12)–C(7)–C(6)	120.4(7)
C(12)–C(7)–C(8)	122.3(7)
C(8)–C(7)–C(6)	117.4(7)
O(6)–C(8)–C(9)	125.2(7)
O(6)–C(8)–C(7)	115.0(6)
C(9)–C(8)–C(7)	119.7(7)
C(8)–C(9)–C(10)	120.1(8)
C(11)–C(10)–C(9)	120.2(7)
C(10)–C(11)–C(12)	119.7(8)
C(7)–C(12)–C(11)	119.8(8)
C(8)–O(6)–C(13)	117.7(6)
C(6)–O(7)–C(14)	121.3(6)
O(7)–C(14)–C(15)	108.2(7)

Table 6
Bond lengths (Å) and angles (°) for complex 5

<i>Bond lengths</i>	
W(1)–C(4)	2.018(6)
W(1)–C(1)	2.019(6)
W(1)–C(3)	2.046(7)
W(1)–C(5)	2.054(7)
W(1)–C(2)	2.061(6)
W(1)–C(18)	2.167(5)
W(2)–C(6)	1.996(7)
W(2)–C(7)	2.030(7)
W(2)–C(8)	2.032(7)
W(2)–C(10)	2.047(7)
W(2)–C(9)	2.068(7)
W(2)–C(26)	2.185(5)
P–N(1)	1.756(5)
P–N(2)	1.781(5)
P–C(11)	1.827(5)
Si(1)–C(14)	1.858(6)
Si(1)–C(12)	1.859(6)
Si(1)–C(13)	1.877(7)
Si(1)–C(11)	1.895(6)
Si(2)–C(15)	1.850(7)
Si(2)–C(17)	1.852(7)
Si(2)–C(16)	1.858(7)
Si(2)–C(11)	1.917(5)
O(1)–C(1)	1.155(7)
O(2)–C(2)	1.131(6)
O(3)–C(3)	1.142(7)
O(4)–C(4)	1.141(7)
O(5)–C(5)	1.128(7)
O(6)–C(6)	1.153(7)
O(7)–C(7)	1.139(7)
O(8)–C(8)	1.144(7)
O(9)–C(9)	1.131(7)
O(10)–C(10)	1.145(7)
O(11)–C(24)	1.363(9)
O(11)–C(25)	1.412(8)
O(12)–C(32)	1.400(7)
O(12)–C(33)	1.411(7)
C(18)–N(1)	1.363(7)
C(18)–C(19)	1.436(7)
C(19)–C(24)	1.395(9)
C(19)–C(20)	1.407(8)
C(20)–C(21)	1.375(9)
C(21)–C(22)	1.350(13)
C(22)–C(23)	1.396(13)
C(23)–C(24)	1.402(10)
C(26)–N(2)	1.314(7)
C(26)–C(27)	1.514(7)
C(27)–C(28)	1.370(7)
C(27)–C(32)	1.376(8)
C(28)–C(29)	1.380(8)
C(29)–C(30)	1.380(9)
C(30)–C(31)	1.382(8)
C(31)–C(32)	1.374(7)
<i>Bond angles</i>	
C(4)–W(1)–C(1)	86.1(2)
C(4)–W(1)–C(3)	90.8(3)
C(1)–W(1)–C(3)	90.1(2)
C(4)–W(1)–C(5)	86.4(3)
C(1)–W(1)–C(5)	91.1(2)
C(3)–W(1)–C(5)	176.8(2)
C(4)–W(1)–C(2)	175.0(3)
C(1)–W(1)–C(2)	90.3(2)

Table 6 (Continued)

C(3)–W(1)–C(2)	92.8(2)
C(5)–W(1)–C(2)	90.2(2)
C(4)–W(1)–C(18)	95.6(2)
C(1)–W(1)–C(18)	178.0(2)
C(3)–W(1)–C(18)	90.9(2)
C(5)–W(1)–C(18)	88.0(2)
C(2)–W(1)–C(18)	87.9(2)
C(6)–W(2)–C(7)	88.0(3)
C(6)–W(2)–C(8)	89.8(3)
C(7)–W(2)–C(8)	88.9(3)
C(6)–W(2)–C(10)	91.7(3)
C(7)–W(2)–C(10)	89.8(3)
C(8)–W(2)–C(10)	178.0(2)
C(6)–W(2)–C(9)	85.3(3)
C(7)–W(2)–C(9)	172.9(3)
C(8)–W(2)–C(9)	88.7(3)
C(10)–W(2)–C(9)	92.7(3)
C(6)–W(2)–C(26)	174.8(2)
C(7)–W(2)–C(26)	97.2(2)
C(8)–W(2)–C(26)	90.5(2)
C(10)–W(2)–C(26)	88.1(2)
C(9)–W(2)–C(26)	89.6(2)
N(1)–P–N(2)	97.8(2)
N(1)–P–C(11)	100.7(2)
N(2)–P–C(11)	105.3(2)
C(14)–Si(1)–C(12)	107.8(3)
C(14)–Si(1)–C(13)	107.8(3)
C(12)–Si(1)–C(13)	108.8(3)
C(14)–Si(1)–C(11)	112.0(3)
C(12)–Si(1)–C(11)	108.9(3)
C(13)–Si(1)–C(11)	111.4(3)
C(15)–Si(2)–C(17)	110.2(4)
C(15)–Si(2)–C(16)	108.6(4)
C(17)–Si(2)–C(16)	108.6(4)
C(15)–Si(2)–C(11)	110.6(3)
C(17)–Si(2)–C(11)	110.7(3)
C(16)–Si(2)–C(11)	108.1(3)
C(24)–O(11)–C(25)	117.9(7)
C(32)–O(12)–C(33)	115.6(5)
O(1)–C(1)–W(1)	178.2(5)
O(2)–C(2)–W(1)	178.0(5)
O(3)–C(3)–W(1)	179.5(6)
O(4)–C(4)–W(1)	174.9(6)
O(5)–C(5)–W(1)	178.5(6)
O(6)–C(6)–W(2)	178.1(7)
O(7)–C(7)–W(2)	174.0(6)
O(8)–C(8)–W(2)	177.6(6)
O(9)–C(9)–W(2)	172.4(6)
O(10)–C(10)–W(2)	178.2(7)
P–C(11)–Si(1)	123.0(3)
P–C(11)–Si(2)	105.3(3)
Si(1)–C(11)–Si(2)	118.7(3)
N(1)–C(18)–C(19)	112.0(5)
N(1)–C(18)–W(1)	124.2(4)
C(19)–C(18)–W(1)	123.7(4)
C(24)–C(19)–C(20)	118.1(6)
C(24)–C(19)–C(18)	120.9(6)
C(20)–C(19)–C(18)	120.9(6)
C(21)–C(20)–C(19)	120.5(8)
C(22)–C(21)–C(20)	121.9(9)
C(21)–C(22)–C(23)	119.3(8)
C(22)–C(23)–C(24)	120.3(9)
O(11)–C(24)–C(19)	114.2(6)
O(11)–C(24)–C(23)	125.8(8)
C(19)–C(24)–C(23)	120.0(8)

Table 6 (Continued)

N(2)–C(26)–C(27)	110.3(5)
N(2)–C(26)–W(2)	129.7(4)
C(27)–C(26)–W(2)	119.8(4)
C(28)–C(27)–C(32)	117.9(5)
C(28)–C(27)–C(26)	121.0(5)
C(32)–C(27)–C(26)	121.1(5)
C(27)–C(28)–C(29)	123.0(6)
C(30)–C(29)–C(28)	116.7(6)
C(29)–C(30)–C(31)	122.5(6)
C(32)–C(31)–C(30)	117.9(6)
C(31)–C(32)–C(27)	122.0(6)
C(31)–C(32)–O(12)	122.6(5)
C(27)–C(32)–O(12)	115.4(5)
C(18)–N(1)–P	123.8(4)
C(26)–N(2)–P	124.8(4)

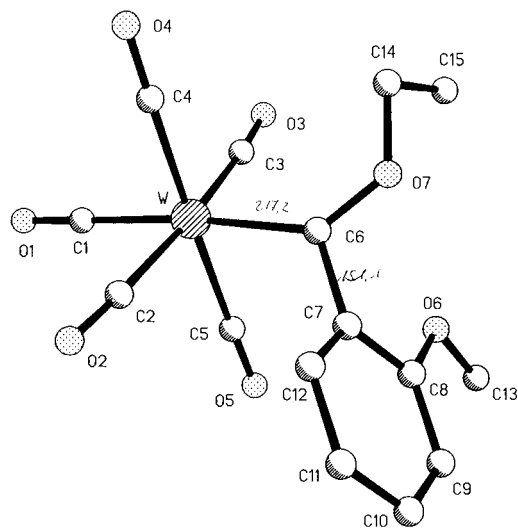


Fig. 3. Molecular structure of **2b** in the crystal (ellipsoids represent 30% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): W–C1, 2.020(7); W–C6, 2.172(7); C6–C7, 1.511(10); O6–C8–C7, 115.0(6); O7–C6–C7, 106.5(6) (Table 5).

using standard Schlenk techniques with conventional glassware. Solvents were dried according to standard procedures. — NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for ^1H ; 50.3 MHz for ^{13}C ; 81.0 MHz for ^{31}P) using $[d_6]\text{CHCl}_3$ and $[d_6]\text{C}_6\text{H}_6$ as solvent and internal standard; shifts are given relative to ext. Me_4Si (^1H , ^{13}C) and 85% H_3PO_4 (^{31}P). — Mass spectra were recorded on a Finigan Mat 8430 (70 eV); apart from m/z -values of the molecule ions, only m/z -values having intensities of more than 20% are given. — IR spectra were recorded on a Biorad FT-IR 165 (selected data given). — M.p. were obtained on a Büchi 535 capillary apparatus. —

Elemental analyses were performed using a Carlo Erba analytical gas chromatograph. — All products were separated by column chromatography at low temperature. — The κP -notation in the nomenclature is

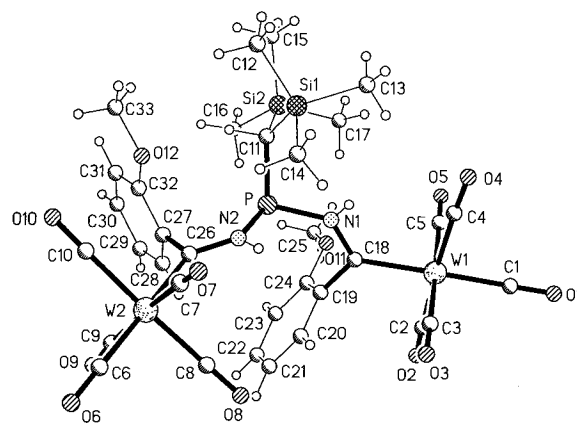


Fig. 4. Molecular structure of **5** in the crystal (ellipsoids represent 30% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): W1–C1, 2.019(6); W1–C18, 2.167(5); C18–N1, 1.363(7); N1–P, 1.756(5); P–C11, 1.827(5); P–N2, 1.781(5); N2–C26, 1.314(7); C26–W2, 2.185(5); W2–C6, 1.996(7); N1–C18–W1, 124.2(4); N1–P–N2, 97.8(2); N2–C26–W2, 129.7(4) (Table 6).

intended to differentiate between P- and N-coordination of the appropriate heterocycle to the metal.

3.2. General procedure for the synthesis of the *o*-phenyl-substituted ethoxycarbene tungsten complexes **2a,c**

A mixture of Et_2O (40 ml), 15 mmol of *o*-bromoarenes **1a–c** and 15 mmol *n*-BuLi (10 ml of a *n*- C_6H_{14} 1.6 M solution) were added via a dropping funnel to a suspension of 15 mmol (5.2 g) $\text{W}(\text{CO})_6$ in 15 ml Et_2O in a three-necked flask. The resulting solutions were stirred for 1/2 h and then reduced in vacuo (ca. 0.01 mbar) to dryness, thus obtaining the pentacarbonyl-

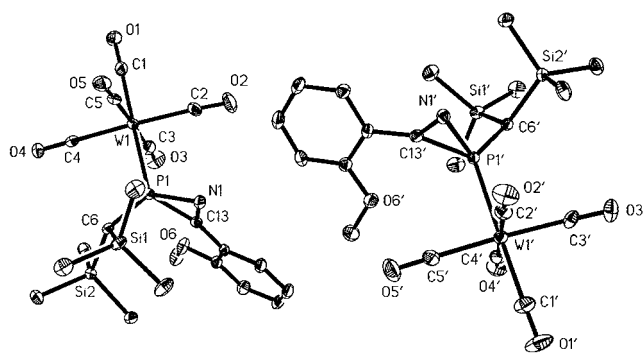


Fig. 5. Molecular structure of **6b** in the crystal (ellipsoids represent 30% probability levels; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): W–C1, 2.016(3); W–P, 2.4741(7); P–C13, 1.763(3); P1–N1, 1.796(2); C13–N1, 1.276(3); C13–C14, 1.454(3); C13–P1–N1, 42.01(10); C14–C19–O6, 116.0(2); W1–P1–C6, 122.34(8); N1–P1–C6, 109.12(11); N1–P1–W1, 119.30(8); W–C1', 2.022(3); W–P', 2.4785(7); P'–C13', 1.759(3); P1'–N1', 1.808(2); C13'–N1', 1.286(3); C13'–P1'–N1', 42.22(10); C14'–C19'–O6', 115.50(2); W1'–P1'–C6', 121.21(8); N1'–P1'–C6', 107.37(11); N1'–P1'–W1', 122.20(8) (Table 7).

Table 7
Bond lengths (Å) and angles (°) for complex **6b**

<i>Bond lengths</i>	
W(1)–C(1)	2.016(3)
W(1)–C(4)	2.029(3)
W(1)–C(5)	2.039(3)
W(1)–C(3)	2.056(3)
W(1)–C(2)	2.061(3)
W(1)–P(1)	2.4741(7)
P(1)–C(13)	1.763(3)
P(1)–N(1)	1.796(2)
P(1)–C(6)	1.813(3)
Si(1)–C(9)	1.860(3)
Si(1)–C(8)	1.867(3)
Si(1)–C(7)	1.870(3)
Si(1)–C(6)	1.908(2)
Si(2)–C(11)	1.863(3)
Si(2)–C(10)	1.870(3)
Si(2)–C(12)	1.871(3)
Si(2)–C(6)	1.911(2)
N(1)–C(13)	1.276(3)
O(1)–C(1)	1.141(3)
O(2)–C(2)	1.138(4)
O(3)–C(3)	1.136(4)
O(4)–C(4)	1.139(3)
O(5)–C(5)	1.145(3)
O(6)–C(19)	1.356(3)
O(6)–C(20)	1.439(3)
C(13)–C(14)	1.454(3)
C(14)–C(15)	1.392(3)
C(14)–C(19)	1.411(4)
C(15)–C(16)	1.371(4)
C(16)–C(17)	1.386(4)
C(17)–C(18)	1.385(4)
C(18)–C(19)	1.385(3)
W(1')–C(1')	2.022(3)
W(1')–C(3')	2.026(3)
W(1')–C(4')	2.037(3)
W(1')–C(2')	2.046(3)
W(1')–C(5')	2.049(3)
W(1')–P(1')	2.4785(7)
P(1')–C(13')	1.759(3)
P(1')–N(1')	1.808(2)
P(1')–C(6')	1.814(3)
Si(1')–C(7')	1.854(3)
Si(1')–C(9')	1.865(3)
Si(1')–C(8')	1.868(3)
Si(1')–C(6')	1.902(2)
Si(2')–C(11')	1.858(3)
Si(2')–C(12')	1.864(3)
Si(2')–C(10')	1.864(3)
Si(2')–C(6')	1.909(2)
N(1')–C(13')	1.286(3)
O(1')–C(1')	1.133(3)
O(2')–C(2')	1.138(3)
O(3')–C(3')	1.148(3)
O(4')–C(4')	1.138(3)
O(5')–C(5')	1.148(4)
O(6')–C(19')	1.359(3)
O(6')–C(20')	1.431(3)
C(13')–C(14')	1.460(3)
C(14')–C(15')	1.395(3)
C(14')–C(19')	1.406(4)
C(15')–C(16')	1.376(4)
C(16')–C(17')	1.383(4)
C(17')–C(18')	1.374(4)

Table 7 (Continued)

C(18')–C(19')	1.389(4)
<i>Bond angles</i>	
C(1)–W(1)–C(4)	89.98(11)
C(1)–W(1)–C(5)	89.85(12)
C(4)–W(1)–C(5)	87.09(11)
C(1)–W(1)–C(3)	89.73(12)
C(4)–W(1)–C(3)	90.99(12)
C(5)–W(1)–C(3)	178.03(12)
C(1)–W(1)–C(2)	93.49(12)
C(4)–W(1)–C(2)	175.93(11)
C(5)–W(1)–C(2)	90.81(13)
C(3)–W(1)–C(2)	91.13(14)
C(1)–W(1)–P(1)	178.95(9)
C(4)–W(1)–P(1)	90.94(7)
C(5)–W(1)–P(1)	90.69(8)
C(3)–W(1)–P(1)	89.76(8)
C(2)–W(1)–P(1)	85.60(8)
C(13)–P(1)–N(1)	42.01(10)
C(13)–P(1)–C(6)	111.31(12)
N(1)–P(1)–C(6)	109.12(11)
C(13)–P(1)–W(1)	125.29(9)
N(1)–P(1)–W(1)	119.30(8)
C(6)–P(1)–W(1)	122.34(8)
C(9)–Si(1)–C(8)	109.65(15)
C(9)–Si(1)–C(7)	108.40(15)
C(8)–Si(1)–C(7)	108.60(15)
C(9)–Si(1)–C(6)	108.88(12)
C(8)–Si(1)–C(6)	112.61(12)
C(7)–Si(1)–C(6)	108.61(13)
C(11)–Si(2)–C(10)	107.23(13)
C(11)–Si(2)–C(12)	109.95(13)
C(10)–Si(2)–C(12)	109.49(13)
C(11)–Si(2)–C(6)	109.82(12)
C(10)–Si(2)–C(6)	108.85(11)
C(12)–Si(2)–C(6)	111.40(12)
C(13)–N(1)–P(1)	67.60(15)
C(19)–O(6)–C(20)	116.8(2)
O(1)–C(1)–W(1)	178.4(3)
O(2)–C(2)–W(1)	176.9(3)
O(3)–C(3)–W(1)	178.4(3)
O(4)–C(4)–W(1)	178.2(2)
O(5)–C(5)–W(1)	177.5(3)
P(1)–C(6)–Si(1)	113.57(13)
P(1)–C(6)–Si(2)	112.36(12)
Si(1)–C(6)–Si(2)	118.59(12)
N(1)–C(13)–C(14)	132.8(2)
N(1)–C(13)–P(1)	70.39(15)
C(14)–C(13)–P(1)	156.8(2)
C(15)–C(14)–C(19)	119.1(2)
C(15)–C(14)–C(13)	117.7(2)
C(19)–C(14)–C(13)	123.2(2)
C(16)–C(15)–C(14)	121.4(3)
C(15)–C(16)–C(17)	118.9(3)
C(18)–C(17)–C(16)	121.3(3)
C(17)–C(18)–C(19)	119.9(3)
O(6)–C(19)–C(18)	124.6(2)
O(6)–C(19)–C(14)	116.0(2)
C(18)–C(19)–C(14)	119.4(2)
C(1')–W(1')–C(3')	87.42(13)
C(1')–W(1')–C(4')	90.42(12)
C(3')–W(1')–C(4')	88.68(12)
C(1')–W(1')–C(2')	92.88(12)
C(3')–W(1')–C(2')	90.59(12)
C(4')–W(1')–C(2')	176.58(11)

Table 7 (Continued)

C(1')–W(1')–C(5')	91.01(13)
C(3')–W(1')–C(5')	178.27(11)
C(4')–W(1')–C(5')	90.62(13)
C(2')–W(1')–C(5')	90.20(13)
C(1')–W(1')–P(1')	179.51(11)
C(3')–W(1')–P(1')	92.10(8)
C(4')–W(1')–P(1')	89.60(8)
C(2')–W(1')–P(1')	87.09(8)
C(5')–W(1')–P(1')	89.47(9)
C(13')–P(1')–N(1')	42.22(10)
C(13')–P(1')–C(6')	112.65(12)
N(1')–P(1')–C(6')	107.37(11)
C(13')–P(1')–W(1')	124.85(9)
N(1')–P(1')–W(1')	122.20(8)
C(6')–P(1')–W(1')	121.24(8)
C(7')–Si(1')–C(9')	109.36(15)
C(7')–Si(1')–C(8')	108.86(14)
C(9')–Si(1')–C(8')	107.92(14)
C(7')–Si(1')–C(6')	107.71(12)
C(9')–Si(1')–C(6')	109.27(13)
C(8')–Si(1')–C(6')	113.66(12)
C(11')–Si(2')–C(12')	112.22(15)
C(11')–Si(2')–C(10')	106.86(13)
C(12')–Si(2')–C(10')	108.91(15)
C(11')–Si(2')–C(6')	107.96(12)
C(12')–Si(2')–C(6')	110.45(12)
C(10')–Si(2')–C(6')	110.37(12)
C(13')–N(1')–P(1')	66.83(14)
C(19')–O(6')–C(20')	118.0(2)
O(1')–C(1')–W(1')	178.5(3)
O(2')–C(2')–W(1')	177.6(3)
O(3')–C(3')–W(1')	177.9(3)
O(4')–C(4')–W(1')	178.6(3)
O(5')–C(5')–W(1')	178.9(3)
P(1')–C(6')–Si(1')	115.14(13)
P(1')–C(6')–Si(2')	111.89(12)
Si(1')–C(6')–Si(2')	118.29(13)
N(1')–C(13')–C(14')	133.4(2)
N(1')–C(13')–P(1')	70.95(16)
C(14')–C(13')–P(1')	155.7(2)
C(15')–C(14')–C(19')	119.6(2)
C(15')–C(14')–C(13')	119.0(2)
C(19')–C(14')–C(13')	121.4(2)
C(16')–C(15')–C(14')	120.7(3)
C(15')–C(16')–C(17')	118.8(3)
C(18')–C(17')–C(16')	122.0(3)
C(17')–C(18')–C(19')	119.6(3)
O(6')–C(19')–C(18')	125.2(2)
O(6')–C(19')–C(14')	115.5(2)
C(18')–C(19')–C(14')	119.3(2)

(acyl)tungstates. The residues were then resolved in a two-phase system of water (50 ml) and *n*-C₅H₁₂ (100 ml) and 16.5 mmol (3.13 g) Meerwein salt was then added in small portions. The thus resulting ethoxycarbene complexes were filtered using a short column containing SiO₂ and a layer of MgSO₄ on top (4:1 ratio). Evaporating of all volatile compounds in vacuo (ca. 0.01 mbar) and recrystallization from *n*-C₅H₁₂ yielded the ethoxycarbene complexes as red solids.

3.2.1. {[Ethoxy-(2-methylphenyl)carbene]penta-carbonyltungsten(0)} (2a)

Yield: 5.23 g (74%), m.p. 48 °C; ¹H-NMR (CDCl₃): 1.56 (t, ³J_{H,H} = 7.1 Hz, 3H, O–CH₂CH₃), 2.09 (s, 3H, CH₃), 4.91 (q, ³J_{H,H} = 7.1 Hz, 2H, O–CH₂CH₃), 7.10 (m_c, 4H, Ar); ¹³C{¹H}-NMR (CDCl₃): 14.4 (s, O–CH₂CH₃), 18.6 (s, CH₃), 95.1 (s, O–CH₂CH₃), 124.8 (s, Ar), 127.9 (s, Ar), 130.2 (s, Ar), 196.6 (s, *cis*-CO), 203.0 (s, *trans*-CO); MS (70 eV, EI) (¹⁸⁴W): *m/z* (%) = 472 (40) [M⁺], 444 (60) [M⁺ – CO], 359 (65) [M⁺ – 4CO], 330 (100) [M⁺ – 5CO]; Anal. Calc. for C₁₅H₁₂O₆W (472.0): C, 38.16; H, 2.56. Found: C, 38.39; H, 2.58%.

3.2.2. {[Ethoxy-(2-*N,N*-dimethylaminophenyl)carbene]penta-carbonyltungsten(0)} (2c)

Yield: 5.2 g (71%); ¹H-NMR (CDCl₃): 0.81 (t, ³J_{H,H} = 7.1 Hz, 3H, O–CH₂CH₃), 2.13 (s, 6H, NCH₃), 4.14 (q, ³J_{H,H} = 7.1 Hz, 2H, O–CH₂CH₃), 7.10 (m_c, 4H, Ar); ¹³C{¹H}-NMR (CDCl₃): 13.1 (s, O–CH₂CH₃), 43.2 (s, NCH₃), 78.1 (s, O–CH₂CH₃), 117.2 (s, Ar), 128.6 (s, Ar), 145.7 (s, Ar), 196.6 (s, *cis*-CO), 203.0 (s, *trans*-CO); 330.5 (W=C).

3.3. General procedure for the synthesis of the *o*-phenyl-substituted aminocarbene tungsten complexes 3a–c

The ethoxycarbene complexes **2a–c** were dissolved in Et₂O and NH₃ and was bubbled for 1/2 h through the solution until the color turned from red to orange. After removing the solvent in vacuo (ca. 0.01 mbar) and washing the residues with *n*-C₅H₁₂, the aminocarbene tungsten complexes **3a–c** were obtained as yellow crystals.

3.3.1. {[Amino(2-methylphenyl)carbene]penta-carbonyltungsten(0)} (3a)

Yield: 4.8 g (72%), m.p. 108 °C; ¹H-NMR (CDCl₃): 2.26 (s, 3H, Ar–CH₃), 6.90 (m_c, 1H, *o*-Ar), 7.18 (m_c, 3H, *m,p*-Ar), 8.53 (s, 1H, NH), 8.82 (s, 1H, NH); ¹³C{¹H}-NMR (CDCl₃): 19.2 (s, Ar–CH₃), 121.3 (s, Ar), 126.8 (s, *o*-Ar), 127.9 (s, Ar), 130.8 (s, Ar), 153.1 (s, *i*-Ar), 197.9 (s, ¹J_{C,W} = 128.4 Hz, *cis*-CO), 203.7 (s, ¹J_{C,W} = 125.4 Hz, *trans*-CO), 272.3 (s, ¹J_{C,W} = 88.5 Hz, W=C); MS (70 eV, EI) (¹⁸⁴W): *m/z* (%) = 443 (55) [M⁺], 331 (100) [M⁺ – 4CO], 303 (90) [M⁺ – 5CO]; IR (KBr, ν (CO)) $\tilde{\nu}$ = 2066 (m), 1943 (s), 1895 (s), 1870 (s) cm⁻¹; Anal. Calc. for C₁₃H₉NO₅W (443.1): C, 35.24; H, 2.15; N, 3.16. Found: C, 34.48; H, 2.03; N, 3.05%.

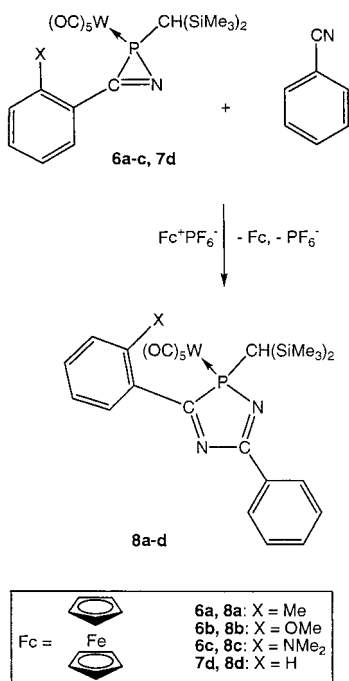
3.3.2. {[Amino(2-methoxyphenyl)carbene]penta-carbonyltungsten(0)} (3b)

Yield: 5.27 g (77%), m.p. 104 °C; ¹H-NMR (CDCl₃): 3.85 (s, 3H, OCH₃), 7.09 (m_c, 3H, Ar), 7.31 (m_c, 1H, Ar), 8.54 (s, 1H, NH), 8.96 (s, 1H, NH); ¹³C-NMR

(CDCl₃): 55.4 (s, OCH₃), 111.3 (s, Ar), 120.7 (s, Ar), 126.1 (s, Ar), 130.5 (s, Ar), 140.5 (s, Ar), 151.7 (s, Ar), 198.4 (s, *cis*-CO), 203.9 (s, *trans*-CO), 264.5 (s, W=C); MS (70 eV, EI) (¹⁸⁴W): *m/z* (%) = 459 (10) [M⁺], 347 (80) [M⁺ - 4CO], 317 (100) [M⁺ - 5CO]; IR (KBr, $\nu(\text{CO})$) $\tilde{\nu}$ = 2064 (m), 1980 (s), 1937 (s), 1890 (vs) cm⁻¹.

3.3.3. {[Amino(2-*N,N*-dimethylaminophenyl)carbene]-pentacarbonyltungsten(0)} (3c)

Yield: 4.82 g (68%), m.p. 103 °C; ¹H-NMR (CDCl₃): 2.72 (s, 6H, NCH₃), 7.06 (m_c, 2H, Ar), 7.29 (m_c, 2H, Ar), 8.74 (s, 1H, NH), 9.87 (s, 1H, NH); ¹³C-NMR (CDCl₃): 44.7 (s, NCH₃), 119.3 (s, Ar), 124.8 (s, Ar), 130.2 (s, Ar), 132.4 (s, Ar), 142.4 (s, Ar), 148.3 (s, *i*-Ar), 199.9 (s, *cis*-CO), 207.2 (s, *trans*-CO), 268.8 (s, W=C); MS (70 eV, EI) (¹⁸⁴W): *m/z* (%) = 472 (5) [M⁺], 444



Scheme 5. Catalytic ring expansion reactions of 2*H*-azaphosphirene complexes **6a–c** and **7d** using ferrocenium hexafluorophosphate and benzonitrile.

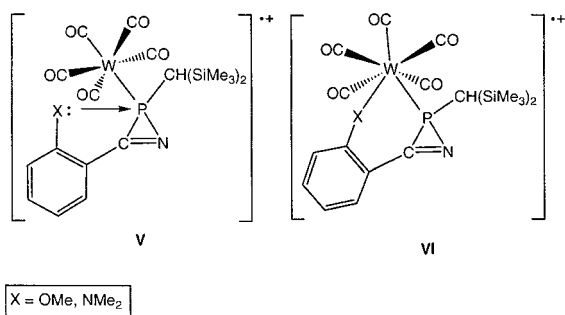


Fig. 6. Possible reactive intermediates of the reactions of complexes **6b,c** with benzonitrile.

(50) [M⁺ - 1CO], 416 (40) [M⁺ - 2CO], 388 (35) [M⁺ - 3CO], 386 (33) [M⁺ - 2CO - 2CH₃], 360 (40) [M⁺ - 4CO], 358 (40) [M⁺ - 3CO - 2CH₃], 332 (80) [M⁺ - 5CO], 330 (100) [M⁺ - 4CO - 2CH₃]; IR (KBr, $\nu(\text{CO})$) $\tilde{\nu}$ = 2058 (w), 1917 (s), 1894 (s) cm⁻¹; Anal. Calc. for C₁₄H₁₂N₂O₅W (471.5): C, 35.62; H, 2.56; N, 5.93. Found: C, 34.39; H, 2.57; N, 5.21%.

3.4. General procedure for the synthesis of *o*-phenyl-substituted 2*H*-azaphosphirene tungsten complexes **6a–c**

Appropriate carbene complexes **3a–c** (1 mmol) and [bis(trimethyl-silyl)methylene]chlorophosphane (**4**) (1 mmol) were dissolved in MeCN (10 ml) and 4 ml Et₃N was added. The solution was stirred for 3 h at ambient temperature, whereby the reactions were controlled by ³¹P-NMR spectroscopy. At the end of the reaction the solvent was evaporated in vacuo (ca. 0.01 mbar). The residues were dissolved in ether, the precipitated Et₃NHCl filtered off and the filtrates were reduced in vacuo (ca. 0.01 mbar) to dryness. The residue was purified by low temperature column chromatography (neutral SiO₂, 8 × 2 cm, -10 °C, petrol ether (50/70)–Et₂O 95/5).

3.4.1. {[2-Bis(trimethylsilyl)methyl-3-(2-methylphenyl)-2*H*-azaphosphirene- κ P]pentacarbonyl tungsten(0)} (**6a**)

Yield: 630 mg (92%), m.p. 107 °C (dec.); ¹³C-NMR (CDCl₃): 1.2 (d, ³J_{P,C} = 3.1 Hz, SiCH₃), 2.1 (d, ³J_{P,C} = 3.1 Hz, SiCH₃), 20.7 (s, Ar-CH₃), 26.8 (d, ¹J_{P,C} = 23.8 Hz, CH), 125.0 (d, J_{P,C} = 14.1 Hz, Ar), 126.6 (s, Ar), 128.5 (s, Ar), 131.8 (s, Ar), 133.4 (d, J_{P,C} = 9.5 Hz, Ar), 140.8 (d, J_{P,C} = 2.7 Hz, Ar), 191.9 (s, PCN), 196.4 (d, ²J_{P,C} = 9.0 Hz, *cis*-CO), 197.7 (s, ²J_{P,C} = 35.8 Hz, *trans*-CO); ³¹P{¹H}-NMR (CDCl₃): -128.3 (s, ¹J_{W,P} = 292.8 Hz); MS (70 eV, EI) (¹⁸⁴W): *m/z* (%) = 631 (5) [M⁺], 73 (100) [Si(CH₃)₃⁺]; IR (KBr, $\nu(\text{CO})$) $\tilde{\nu}$ = 2072 (m), 1987 (w), 1963 (s), 1943 (s), 1923 (vs) cm⁻¹; Anal. Calc. for C₂₀H₂₆NO₅PSi₂W (631.02): C, 38.04; H, 4.15; N, 2.22. Found: C, 37.60; H, 4.26; N, 2.21%.

3.4.2. {[2-Bis(trimethylsilyl)methyl-3-(2-methoxyphenyl)-2*H*-azaphosphirene- κ P]pentacarbonyl tungsten(0)} (**6b**)

Yield: 616 mg (76%), m.p. 92 °C; ¹H-NMR (CDCl₃): 0.05 (s, 9H, SiCH₃), 0.31 (s, 9H, SiCH₃), 0.64 (d, ²J_{H,H} = 2.9 Hz, 1H, CH), 3.99 (s, 3H, OCH₃), 6.85 (m_c, 1H, Ar), 7.10 (m_c, 1H, Ar) 7.60 (m_c, 1H, Ar), 7.95 (m_c, 1H, Ar); ¹³C-NMR (CDCl₃): 1.2 (d, ³J_{P,C} = 3.1 Hz, SiCH₃), 2.1 (d, ³J_{P,C} = 3.1 Hz, SiCH₃), 27.3 (d, ¹J_{P,C} = 13.1 Hz, CH), 55.8 (s, OCH₃), 111.9 (s, Ar), 115.5 (d, J_{P,C} = 13.1 Hz, Ar), 121.7 (s, Ar), 130.0 (s, Ar), 135.8 (s, Ar), 158.9 (s, Ar), 189.6 (s, PCN), 196.1 (d, ²J_{P,C} = 8.7 Hz, *cis*-CO), 198.5 (d, ²J_{P,C} = 35.9 Hz, *trans*-CO); ³¹P{¹H}-NMR (CDCl₃): -110.2 (s, ¹J_{W,P} = 294.6 Hz);

MS (70 eV, EI) (^{184}W): m/z (%) = 647 (5) [M^+], 574 (10) [$\text{M} - \text{SiMe}_3^+$], 486 (80) [(OC) $_4$ WPCNCH(SiMe $_3$) $_2^+$], 430 (100) [(OC) $_2$ WPCNCH(SiMe $_3$) $_2^+$], 133 (25) [$\text{C}_4\text{H}_4(\text{OMe})\text{CN}^+$], 73 (100) [$\text{Si}(\text{CH}_3)_3^+$].

3.4.3. {[2-Bis(trimethylsilyl)methyl-3-(2-*N,N*-dimethylaminophenyl)-2*H*-azaphosphirene- κ P]-pentacarbonyltungsten(0)} (6c)

Yield: 269 mg (41%), m.p. 92 °C; $^1\text{H-NMR}$ (CDCl_3): 0.02 (s, 9H, SiCH $_3$), 0.29 (s, 9H, SiCH $_3$), 0.68 (d, $^2J_{\text{H,H}} = 1.7$ Hz, 1H, CH), 2.54 (s, 6H, NCH $_3$), 6.58 (d, $^3J_{\text{H,H}} = 8.33$ Hz, 1H, Ar), 6.78 (ddd, br, 1H, Ar), 7.04 (ddd, $J_{\text{H,H}} = 8.78$, 1.72 Hz, 1H, Ar), 8.09 (dd, $J_{\text{H,H}} = 7.72$, 1.67 Hz, 1H, Ar); $^{13}\text{C-NMR}$ (CDCl_3): 1.3 (d, $^3J_{\text{P,C}} = 2.8$ Hz, SiCH $_3$), 2.1 (d, $^3J_{\text{P,C}} = 2.9$ Hz, SiCH $_3$), 27.3 (d, $^1J_{\text{P,C}} = 24.3$ Hz, CH), 44.3 (s, NCH $_3$), 112.8 (s, Ar), 118.4 (s, Ar), 120.5 (s, Ar), 128.3 (s, Ar), 135.7 (s, Ar), 154.2 (d, $J_{\text{P,C}} = 2.5$ Hz, Ar), 187.8 (s, PCN), 196.6 (d, $^2J_{\text{P,C}} = 8.8$ Hz, *cis*-CO), 198.1 (d, $^2J_{\text{P,C}} = 35.1$ Hz, *trans*-CO); $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): -125.1 (s, $^1J_{\text{W,P}} = 292.8$ Hz); MS (70 eV, EI) (^{184}W): m/z (%) = 660 (5) [M^+], 486 (80) [(OC) $_4$ WPCNCH(SiMe $_3$) $_2^+$], 458 (25) [(OC) $_3$ WPCNCH(SiMe $_3$) $_2^+$], 430 (45) [(OC) $_2$ WPCNCH(SiMe $_3$) $_2^+$], 146 (25) [$\text{C}_4\text{H}_4(\text{NMe}_2)\text{CN}^+$], 73 (100) [$\text{Si}(\text{CH}_3)_3^+$]; IR (KBr, $\nu(\text{CO})$) $\tilde{\nu} = 1920.5$ (vs), 1951.2 (s), 1987 (w), 2071 (m); Anal. Calc. for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_5\text{PSi}_2\text{W}$ (660.1): C, 38.19; H, 4.43; N, 4.24. Found: C, 37.51; H, 4.56; N, 3.83%.

3.5. General procedure for the synthesis of the 2*H*-1,4,2-diazaphosphole complexes 8a–d

To solutions of 1 mmol each of the 2*H*-azaphosphirene complexes 6a–c and 7d [19], dissolved in 4 ml of CH_2Cl_2 , 0.2 mmol (61 mg) of ferrocenium hexafluorophosphate and 2 mmol (0.2 ml) benzonitrile were added. The reaction mixtures were stirred at ambient temperature for 3 h (reaction monitoring by $^{31}\text{P-NMR}$ spectroscopy). Evaporation of the solvent in vacuo (ca. 0.01 mbar), low temperature column chromatography (neutral SiO_2 , 8 × 2 cm, -15 °C, petrol ether (50/70)– Et_2O 95/5) and evaporation of the solvent yielded the 2*H*-1,4,2-diazaphosphole complexes 8a–c and 8d [6] as orange solids.

3.5.1. {[2-Bis(trimethylsilyl)methyl-3-(2-methylphenyl)-5-phenyl-2*H*-1,4,2-diazaphosphole- κ P]-pentacarbonyltungsten(0)} (8a)

Yield: 640 mg (86%), m.p. 55 °C (dec.); $^1\text{H-NMR}$ (CDCl_3): 0.01 (s, 9H, SiCH $_3$), 0.61 (s, 9H, SiCH $_3$), 1.31 (d, $^2J_{\text{P,H}} = 5.2$ Hz, 1H, CH), 2.99 (s, 3H, CH $_3$), 7.51 (m_c, 3H, Ar), 7.64 (m_c, 3H, Ar), 8.05 (d, $^3J_{\text{H,H}} = 7.49$ Hz, 1H, Ar), 8.56 (dd, $J_{\text{H,H}} = 7.23/1.77$ Hz, 2H, Ar); $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 2.9 (d, $^3J_{\text{P,C}} = 1.9$ Hz, SiCH $_3$), 3.7 (d, $^3J_{\text{P,C}} = 2.6$ Hz, SiCH $_3$), 18.4 (d, $^1J_{\text{P,C}} = 7.1$ Hz, CH), 24.2 (s, CH $_3$), 125.63 (s, Ar), 128.7 (s, Ar), 130.6

(s, Ar), 130.8 (s, Ar), 130.9 (s, Ar), 131.2 (s, Ar), 132.3 (s, Ar), 132.4 (s, Ar), 136.2 (d, $J_{\text{P,C}} = 3.8$ Hz, Ar), 140.8 (d, $J_{\text{P,C}} = 4.4$ Hz, Ar), 169.0 (d, $^{2+3}J_{\text{P,C}} = 4.3$ Hz, PNC), 197.2 (d, $^2J_{\text{P,C}} = 6.1$ Hz, *cis*-CO), 198.3 (d, $^{1+4}J_{\text{P,C}} = 22.6$ Hz, PCN), 203.6 (d, $^2J_{\text{P,C}} = 25.7$ Hz, *trans*-CO); $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): 115.8 (s, $^1J_{\text{W,P}} = 229.2$ Hz); MS (70 eV, EI) (^{184}W): m/z (%) = 734 (10) [M^+], 706 (25) [$\text{M}^+ - \text{CO}$], 678 (70) [$\text{M}^+ - 2\text{CO}$], 547 (15) [$\text{M}^+ + \text{H}^+ - \text{PhCN} - 3\text{CO}$], 293 (20) [$\text{M}^+ - \text{W}(\text{CO})_5 - \text{PhCN} - \text{CH}_3$], 73 (100) [SiMe_3^+]; Anal. Calc. for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}_5\text{PSi}_2\text{W}$ (734.2): C, 44.15; H, 4.25; N, 3.81. Found: C, 43.51; H, 4.08; N, 3.42%.

3.5.2. {[2-Bis(trimethylsilyl)methyl-3-(2-methoxyphenyl)-5-phenyl-2*H*-1,4,2-diazaphosphole- κ P]-pentacarbonyltungsten(0)} (8b)

Yield: 247 mg (33%), m.p. 70 °C (dec.); $^1\text{H-NMR}$ (CDCl_3): -0.17 (s, 9H, SiCH $_3$), 0.58 (s, 9H, SiCH $_3$), 1.28 (d, $^2J_{\text{P,H}} = 4.1$ Hz, 1H, CH), 4.02 (s, 3H, OCH $_3$), 7.02 (d, $^3J_{\text{H,H}} = 8.32$ Hz, 1H, Ar), 7.17 (m_c, 1H, Ar), 7.53 (m_c, 1H, Ar), 8.56 (m_c, 2H, Ar), 8.73 (dd, br, $^3J_{\text{H,H}} = 7.91$ Hz, 1H, Ar); $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 2.7 (d, $^3J_{\text{P,C}} = 1.9$ Hz, SiCH $_3$), 3.8 (d, $^3J_{\text{P,C}} = 3.1$ Hz, SiCH $_3$), 13.8 (d, $^1J_{\text{P,C}} = 3.7$ Hz, CH), 54.6 (s, OCH $_3$), 111.3 (s, Ar), 121.7 (s, Ar), 122.4 (s, Ar), 122.9 (s, Ar), 128.6 (s, Ar), 130.4 (s, Ar), 130.5 (d, $J_{\text{P,C}} = 3.6$ Hz, Ar), 131.8 (s, Ar), 135.6 (s, Ar), 158.8 (d, $J_{\text{P,C}} = 2.3$ Hz, Ar), 167.9 (d, $^{2+3}J_{\text{P,C}} = 4.1$ Hz, PNC), 196.5 (d, $^{1+4}J_{\text{P,C}} = 24.5$ Hz, PCN), 197.8 (d, $^2J_{\text{P,C}} = 6.8$ Hz, *cis*-CO), 198.2 (d, $^2J_{\text{P,C}} = 22.3$ Hz, *trans*-CO); $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): 111.8 (s, $^1J_{\text{W,P}} = 222.6$ Hz); MS (70 eV, EI) (^{184}W): m/z (%) = 750 (10) [M^+], 722 (30) [$\text{M}^+ - \text{CO}$], 694 (50) [$\text{M}^+ - 2\text{CO}$], 666 (25), [$\text{M}^+ - 3\text{CO}$], 563 (40) [$\text{M}^+ + \text{H}^+ - \text{PhCN} - 3\text{CO}$], 507 (20) [$\text{M}^+ + \text{H}^+ - \text{PhCN} - 5\text{CO}$], 411 (20) [$\text{M}^+ - \text{W}(\text{CO})_5 - \text{CH}_3$], 293 (25) [$\text{M}^+ - \text{W}(\text{CO})_5 - \text{PhCN} - \text{OCH}_3$], 73 (100) [SiMe_3^+].

3.5.3. {[2-Bis(trimethylsilyl)methyl-3-(2-*N,N*-dimethylaminophenyl)-5-phenyl-2*H*-1,4,2-diazaphosphole- κ P]-pentacarbonyltungsten(0)} (8c)

Yield: 247 mg (33%), m.p. 73 °C (dec.); $^1\text{H-NMR}$ (CDCl_3): -0.02 (s, 9H, SiCH $_3$), 0.58 (s, 9H, SiCH $_3$), 1.28 (d, $^2J_{\text{P,H}} = 4.1$ Hz, 1H, CH), 2.58 (s, 6H, NCH $_3$), 7.21 (m_c, 2H, Ar), 7.54 (m_c, 5H, Ar), 8.54 (m_c, 2H, Ar); $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 2.8 (d, $^3J_{\text{P,C}} = 2.8$ Hz, SiCH $_3$), 3.6 (d, $^3J_{\text{P,C}} = 3.7$ Hz, SiCH $_3$), 22.5 (d, $^1J_{\text{P,C}} = 14.3$ Hz, CH), 46 (s, NCH $_3$), 124.3 (s, Ar), 128.7 (s, Ar), 130.6 (s, Ar), 130.8 (s, Ar), 130.9 (s, Ar), 132.4 (s, Ar), 132.8 (s, Ar), 132.4 (s, Ar), 134.9 (d, $J_{\text{P,C}} = 1.8$ Hz, Ar), 154.3 (s, Ar), 169.0 (d, $^{2+3}J_{\text{P,C}} = 4.3$ Hz, PNC), 197.2 (d, $^2J_{\text{P,C}} = 6.1$ Hz, *cis*-CO), 198.2 (d, $^{1+4}J_{\text{P,C}} = 22.1$ Hz, PCN), 199.9 (d, $^2J_{\text{P,C}} = 20.7$ Hz, *trans*-CO); $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): 114.4 (s, $^1J_{\text{W,P}} = 236.7$ Hz); MS (70 eV, EI) (^{184}W): m/z (%) = 766 (10) [M^+], 738 (30) [$\text{M}^+ - \text{CO}$], 710 (50) [$\text{M}^+ - 2\text{CO}$], 73 (100) [SiMe_3^+].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 174447 (**2b**), 174448 (**5**), 174449 (**6b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

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- [17] Solution and refinement of **2b**, **5** and **6b**: Crystal data for all structures are presented in Table 3. *Structure determination of 2b* (Acorn): A cut orange block was mounted in inert oil and measured by ω - θ -scans using Mo-K $_{\alpha}$ radiation (graphite monochromator) on a Stoe STADI-4 diffractometer. After absorption correction (ψ -scans) all unique data were used for calculations (program SHELXL-93 [24]). The structure was solved by direct methods and refined anisotropically by full-matrix least-squares on F^2 . All methyl groups were refined as rigid groups, all other protons with a riding model. *Structure determination of 5* (praktin): A orange tablet was mounted in inert oil and measured by ω -scans using Mo-K $_{\alpha}$ radiation (graphite monochromator) on a Siemens P4 diffractometer. After absorption correction (ψ -scans) all unique data were used for calculations (program SHELXL-97 [25]). The structure was solved by the heavy atom method and refined as above. Hydrogen atoms were refined with a riding model, except rigid methyl groups and free refined NH protons. *Structure determination of 6b* (neander): An irregular colorless tablet was mounted in inert oil and measured by ω -scans using Mo-K $_{\alpha}$ radiation (graphite monochromator) on a Bruker SMART 1000 CCD diffractometer. After absorption correction (multiple scans) all unique data were used for calculations (program SHELXL-97 [25]). The structure was solved by the heavy atom method and refined as above. All hydrogen atoms (except rigid methyl groups) were refined with a riding model.
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