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Stereochemically defined metal carbene complexes as chemical probes for studies of the ring formation of 2*H*-azaphosphirene complexes

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Dedicated to Professor Ernst Otto Fischer on the occasion of his 80th birthday

Abstract

Strong evidence for a strictly intramolecular rearrangement process leading to 2*H*-azaphosphirene complex **4** was obtained by reactions of {[amino(phenyl)carbene]pentacarbonyltungsten(0)} (**1**) with [bis(trimethylsilyl)methylene]chlorophosphane (**2**) and triethylamine under CO atmosphere; the byproducts, dinuclear carbene complexes **3a**,**b**, were obtained and characterized as *E*,*E*- and *E*,*Z*-isomers. Reaction of a 5:2 mixture of complexes **3a**,**b** with triethylamine in dichloromethane afforded 2*H*-azaphosphirene complex **4** and another product **5**, which could not be isolated, but showed ^{31}P-NMR characteristics of a $\sigma^4\lambda^5$-phosphorus center possessing a P–H function. {*cis*-[ethoxy/amino(aryl)carbene](triorganylphosphane)chromium(0)} and -tungsten(0) complexes **6a**,**b**, **7a**,**b** and **11**, **12** were synthesized, **6a** and **7b** additionally characterized by X-ray crystallography, and reacted also with methylene(chloro)phosphane **2** in the presence of triethylamine, thus yielding *cis*-2*H*-azaphosphirene triorganylphosphane complexes **8a**,**b** and **13a**,**b**, which were unambiguously confirmed by NMR spectroscopy. The latter reactions proceeded with *cis*-stereospecificity. Significant chiral induction was not observed in the reaction leading to **13a**,**b**, and racemization occured, most probably, at the phosphorus of the 2*H*-azaphosphirene complex. These results provide strong evidence for non-participation of the metal atom center in the ring-closure process giving the three-membered 2*H*-azaphosphirene ring system.

Keywords: Aminocarbene complexes; 2*H*-Azaphosphirene complexes; Phosphorus; Ring-closure; Tungsten

1. Introduction

Since the discovery of stable carbene complexes by Fischer [1], alkoxycarbene metal complexes have received widespread interest as powerful synthons in organic and organometallic synthesis [2]. In recent years we have studied the reaction of metal carbene complexes with various organophosphorus halides, which, depending on the organic substituents, led to stable or unstable *O*- [3] **I** or *N*-organophosphorus-substituted [4] **II** metal carbene complexes, bearing $\sigma^3\lambda^3$- and/or $\sigma^2\lambda^3$-phosphorus centers. Unexpectedly, complex derivatives of type **III**, formed as reactive intermediates, rearranged to 2*H*-azaphosphirene metal complexes **IV** (Scheme 1) [5]. Quite recently, we observed that this rearrangement was hindered in the case of a chromium [6] complex or when bulky substituted aryl groups were bonded to the carbene center [7] and, therefore, we suggested that steric protection should enhance the lifetime of such metallaheterobutadiene intermediates of type **III**.

These observations increased our interest in two important questions: (1) is the rearrangement truly intramolecular, meaning the ligand does not dissociate prior to the formation of the three-membered ring, and (2) is the P–C-bond formation directed by the transition metal center as in reductive elimination reactions?

Here, we report on the influence of CO and ^{13}CO atmosphere on the product formation and also on preliminary investigations of stereochemical aspects of

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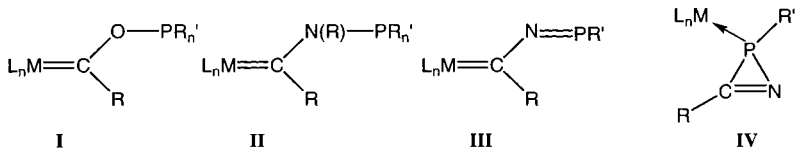
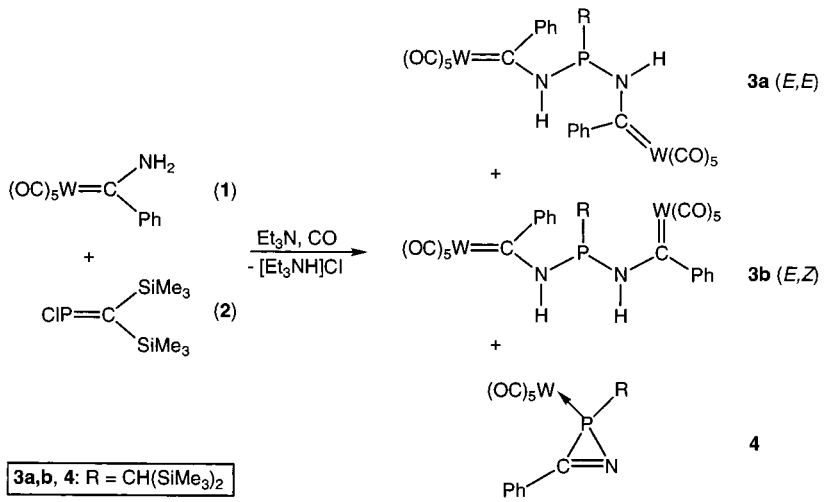


Scheme 1. Fischer-type carbene complexes with various C, O, P and C, N, P linkages **I**–**III** and 2*H*-azaphosphirene complexes **IV** ([M] = metal complex fragment, R denotes ubiquitous organic substituents).



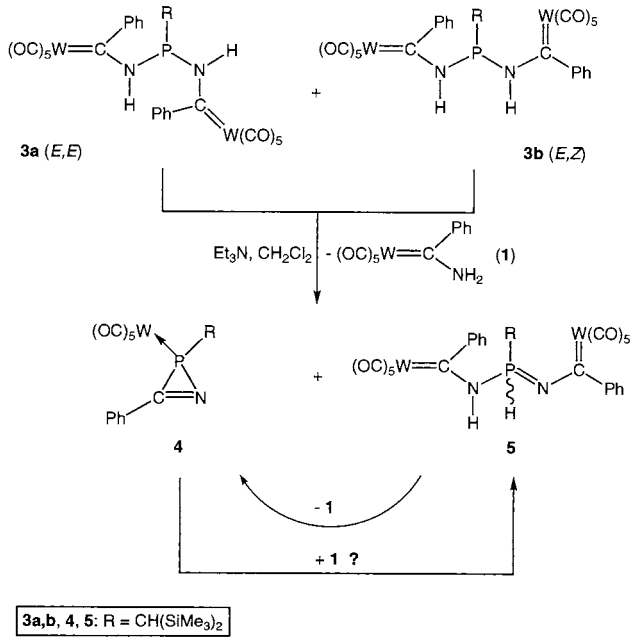
Scheme 2. Reaction of complex **1** with **2** under CO atmosphere.

the formation of 2*H*-azaphosphirene metal complexes; the latter was studied by employing various *cis*-[amino(aryl)carbene] triorganylphosphane metal(0) complexes.

2. Results and discussion

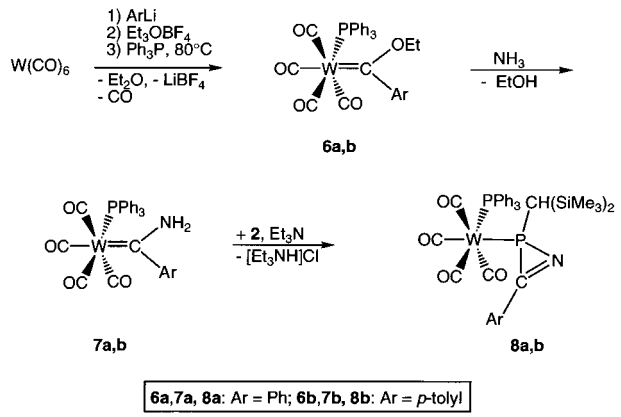
Amino(phenyl)carbene tungsten complex **1** [8] was reacted with the methylene(chloro)phosphane **2** [9] at −15°C, −30°C and −50°C (slow warm-up) in the presence of triethylamine under CO atmosphere under otherwise standard conditions [10] giving, in all cases, the two dinuclear tungsten carbene complexes **3a**,**b** as *E*,*E*- and *E*,*Z*-isomers and the 2*H*-azaphosphirene complex **4** [10] as main products (Scheme 2). Together with **3a**,**b** (ca. 35%) and **4** (ca. 40%), other products were formed at −50°C in very low quantities at $\delta =$ 357.5, 353.3 349.8, 330.9, 328.2 and 26.2 (ca. 1–3%; complete reaction after 19 h); the formation of $W(CO)_6$ could not be detected. This result has several interesting aspects. First, the 2*H*-azaphosphirene complex formation seems to proceed entirely intramolecularly without dissociation of phosphorus-containing ligands at any step of the rearrangement. Secondly, the formation of the complexes **3a**,**b** points, once more, to the intermediacy of a complex of type **III** with a P–N double bond, having an increased lifetime at lower temperature, thus forming the complexes **3a**,**b** by addition of the N–H function of the carbene complex **1** to the P–N double bond. A remarkable finding is also that at −50°C (19 h) the isomers **3a**,**b** were formed in ca. 25:1-ratio, whereas at higher temperature (−15°C, 1 h) the **3a**,**b**-ratio was ca. 3:1 (^{31}P-NMR monitoring). Furthermore, the product at $\delta = 26.2$ is of interest because of its phosphorus-proton couplings of 535.6 and 19.5 Hz, thus pointing to the dinuclear carbene complex **5** with a $\sigma^4\lambda^5$-phosphorus center, possessing a P–H function, as a bridging unit. The reaction of tungsten carbene complex **1** and methylene(chloro)phosphane **2** under a N_2 atmosphere (−50°C, 19 h, otherwise the same reaction conditions) needed longer reaction times – probably because of solvent-like effects of dissolved CO in the other case – (ca. 15% of **2** was unreacted at that time) and yielded complexes **3a**,**b** as main products (60%, **3a**,**b**-ratio 14:1; **4** (16%)). Finally, ^{13}C-NMR studies on the ratio of the CH–, the *cis*-CO and the *trans*-CO resonances of 2*H*-azaphosphirene complex **4** formed under CO *or* N_2 atmosphere revealed that, in the former case, no significant amounts of ^{13}CO (uncertainty: < 5%) had been incorporated into the $W(CO)_5$ group [11].

By changing the solvent to dichloromethane, complexes **3a**,**b** were obtained, after rapid work-up and low-temperature column chromatography, by reacting complex **1** with methylene(chloro)phosphane **2** at 0°C in the presence of triethylamine. Examination of the reactivity of a pure 5:2 mixture of complexes **3a**,**b**



Scheme 3. Reaction of a 3:2 mixture of complexes **3a**,**b** with triethylamine.

towards triethylamine in dichloromethane showed the formation of complexes **4** and **5** (Scheme 3); unfortunately complex **5** decomposed during column chromatography. The ^{31}P-NMR monitoring showed a fast decrease of complex **3a** during the first 90 min. (as compared to **3b**) and a predominant formation of complex **5** (4:5-ratio: 1:6). The situation changed significantly after 90 min, because the amounts of 2*H*-azaphosphirene complex **4** started to increase,



Scheme 4. Synthesis and reactions of tungsten carbene complexes **7a**,**b** with **2** and triethylamine.

whereas that of complex **5** decreased, thus reaching a **4**:**5**-ratio of 1:1 after 48 h (Fig. 1); the **4**:**5**-ratio remained unchanged for a longer period of time. Therefore, we conclude that complex **5** plays a role as reactive intermediate for formation of the 2*H*-azaphosphirene complex, under these conditions [10]. There seems however to be also a reaction pathway from complex **4** to **5**, which is not understood at present.

The *cis*-amino(aryl)carbene triphenylphosphane tungsten complexes **7a**,**b**, synthesized by heating the ethoxy(aryl)carbene tungsten complexes [10] and triphenylphosphane in toluene [12] and subsequent ammonolysis of complexes **6a**,**b**, were reacted with methylene(chloro)phosphane **2** in dichloromethane at room temperature, thus giving selectively the *cis*-2*H*-azaphosphirene triphenylphosphane tungsten com-

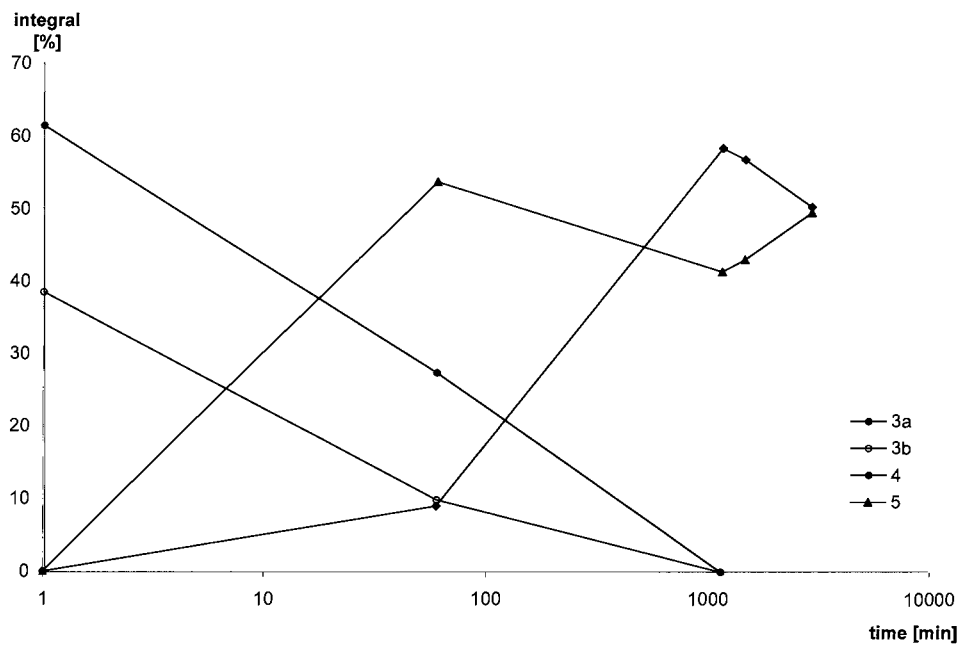
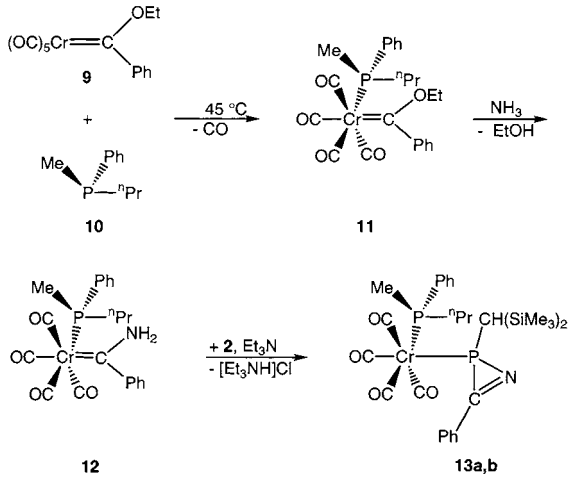


Fig. 1. ^{31}P-NMR monitoring of the reaction of complexes **3a**,**b** with triethylamine.



Scheme 5. Synthesis and reactions of chiral chromium carbene complex **12** with **2** and triethylamine.

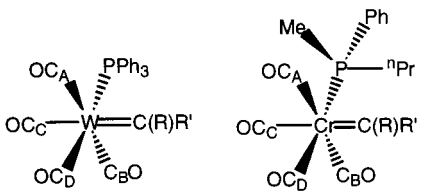
plexes **8a**,**b** in good yields (Scheme 4). The formation of *trans*-isomers, which should exhibit greater values of the ^2J(P,P) coupling constants [13], or triphenylphosphane-substituted analogs of **3a**,**b** was not observed. Apart from the *cis*-stereospecifity of the reaction **7**→**8**, the latter aspects provide further evidence for a truly intramolecular rearrangement cascade without dissociation of ligands.

To examine the possibility of chiral induction, we reacted the (−)(*R*)-*cis*-[amino(phenyl)carbene]methyl-(phenyl)-*n*-propylphosphane chromium complex **12**, synthesized by heating the ethoxy(phenyl)carbene chromium complex **9** [14] and (−)(*R*)-methyl(phenyl)-*n*-propylphosphane [15] (**10**) in toluene [16] and subsequent ammonolysis of complex **11**, with methylene-(chloro)phosphane **2** in dichloromethane at room temperature, thus giving the diastereomeric *cis*-2*H*-azaphosphirene methyl(phenyl)-*n*-propylphosphane chromium complexes **13a**,**b** and an unknown product at $\delta = 351.9$ (ca. 10%) (Scheme 5). After purification, the former were characterized by NMR spectroscopy as a 1:1 mixture. As in the previous case for **8**, the formation of **13a**,**b** proceeded with *cis*-stereospecifity (*trans*-isomers were not detected), but only a very small diastereomeric excess was observed by ^{31}P-NMR spectroscopy after 1.5 h (ca. 10%). Therefore, we conclude that the metal atom fragment is *not* directly involved in the P–C bond formation. Interestingly, the diastereomeric excess changed within the next few hours, reaching an equilibrium after ca. 20 h. This racemization of the 2*H*-azaphosphirene phosphorus centers in **13a**,**b** occurs probably via an intermediate ring-opening/ring-closure process.

2.1. Discussion of NMR and X-ray data

The composition of all complexes was confirmed by elemental analyses and mass spectrometry and the structural formulation of the complexes is based on their characteristic NMR spectral data in solution. Proof for the structures of the carbene complexes **3a**,**b** and the triorganophosphane-substituted carbene complexes **6a**,**b**, **7a**,**b**, **11** and **12** is given through the carbene and carbonyl carbon atom resonances (Table 1); the latter were tentatively assigned. The numerical values are in the typical range of related Fischer-type carbene complexes [17]. It is very interesting that the complexes **3a**,**b** display an *E*,*E*- (**3a**) and *E*,*Z*-isomerism (**3b**) at the C–N bond, thus representing the first examples of such an isomerism of dinuclear *N*-phosphanyl aminocarbene complexes [7]. The phosphorus nuclei of

Table 1
Selected ^{13}C- and ^{31}P-NMR data of the carbene complexes **6a**,**b**, **7a**,**b**, **11** and **12** [a]



6a,b 7a,b **11,12**

δ ^{13}C	C_AO	$^2J_{CP}$	C_BO	$^2J_{CP}$	C_CO	$^2J_{CP}$	C_DO	$^2J_{CP}$	M=CR_2	$^2J_{CP}$	δ ^{31}P	$^1J_{PW}$
6a	202.8	7.0	202.8	7.0	211.8	7.4	205.6	21.8	318.3	7.5	26.4	238.0
6b	203.0	7.1	203.0	7.1	211.7	6.3	205.8	22.0	317.7	7.3	26.5	237.1
7a	204.1	7.4	204.1	7.4	211.3	6.9	208.5	25.1	269.6	6.9	27.1	235.1
7b	203.7	7.2	203.7	7.2	210.8	6.2	208.2	22.8	269.0	7.1	27.3	233.2
11	220.9	14.9	221.0	14.8	226.1	8.3	231.5	12.9	347.7	13.8	28.0	–
12	221.1	14.7	221.3	14.5	228.0	6.6	229.3	12.6	293.4	12.6	30.8	–

[a] δ (ppm), J (Hz), $CDCl_3$; assignment and notation of the carbonyl groups according to the formulae.

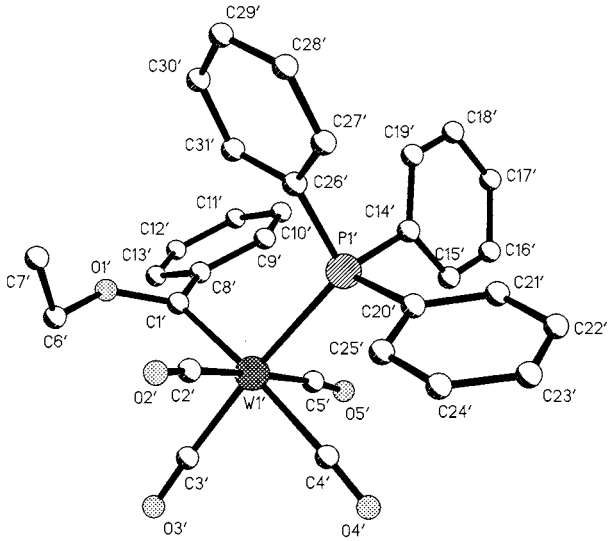


Fig. 2. Structure of one independent molecule of complex **6a** (denoted as **6a**′ in Table 4) (hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (°) of the two independent molecules of complex **6a**: W(1)–C(2) 203.1(8), W(1′)–C(2′) 202.6(9), W(1)–C(5) 204.9(9), W(1′)–C(5′) 206.2(9), C(1)–C(8) 152.2(10), C(1′)–C(8′) 148.3(11); C(1)–W(1)–C(2) 97.7(3), C(1′)–W(1′)–C(2′) 96.4(3), C(1)–W(1)–C(5) 87.2(3), C(1′)–W(1′)–C(5′) 86.9(3).

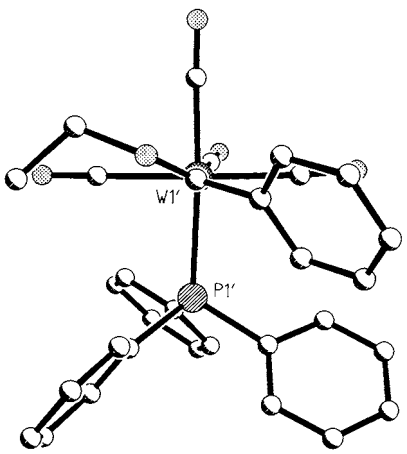


Fig. 3. View of complex **6a** along the axis C1′–W1′ (hydrogen atoms are omitted for clarity).

3a,**b** display resonances at $\delta = 93.5$ (**3a**) and 109.0 (**3b**); the deshielding of the latter resonance probably stems from an increased steric repulsion in the *E*,*Z*-isomer **3b**. It is also remarkable that, in the case of the triphenylphosphane-substituted complexes, the carbonyl atom resonances differentiate completely only if bulky 2*H*-azaphosphirenes are ligated (**8a**,**b**) (Table 2), thus pointing to an increased hindrance of the rotation about the P–W axes. The carbonyl carbon atoms of complexes **8a**,**b**, which are in *trans*-position to 2*H*-azaphosphirenes, showed significantly larger phosphorus–carbon couplings. The triphenylphosphane phosphorus nuclei of **8a**,**b** display slightly upfield-shifted resonances to those of **6a**,**b** and **7a**,**b**, whereas the 2*H*-azaphosphirene phosphorus nuclei of **8a**,**b** remain unchanged as compared to their pentacarbonyltungsten complexes [5,10]. The latter finding is in contrast to the situation of complexes **13a**,**b**, because the 2*H*-azaphosphirene phosphorus nuclei appear at $\delta = -46.1$ and -45.1, respectively, whereas the resonance of the related pentacarbonylchromium complex was observed at $\delta = -54.3$ [6].

The molecular structures of complexes **6a** (Figs. 2 and 3) and **7b** (Fig. 4, Table 3) were established by X-ray diffraction analyses.[1] In both cases, two independent molecules were found in the unit cell (together with one molecule of diethyl ether in the case of **6a**); in neither case were significant differences in bond distances or angles observed. Like {*cis*-(*N*-methyl-1,2-dihydro - benzoxazole - 2 - ylidene)(triphenylphosphane)-tetracarbonyltungsten(0)} [19] (**14**), complexes **6a** and **7b** show distorted octahedral coordination of the tungsten atoms and approximately ecliptic conformation of the carbene group and the neighboring CO groups, as shown in Fig. 3 for **6a** (the shown independent molecule of **6a** is denoted as **6a**′ in Table 4). A compari-

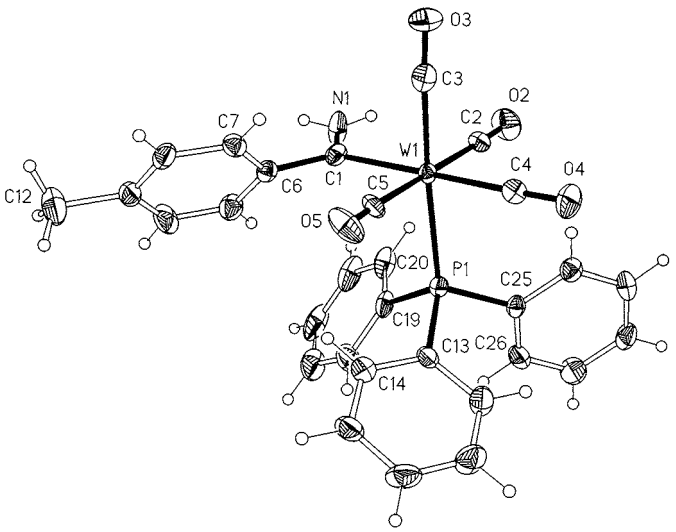
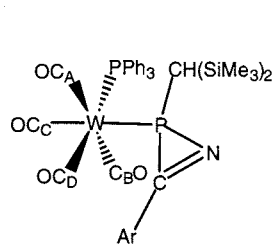


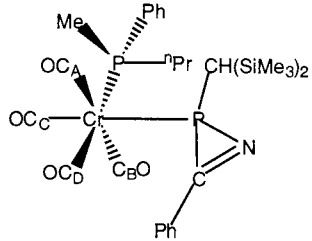
Fig. 4. Structure of one independent molecule of complex **7b** (ellipsoids represent 50% probability level). Selected bond lengths (pm) and angles (°) of the two independent molecules of complex **7b**: W(1)–C(2) 201.0(4), W(1′)–C(2′) 199.4(5), W(1)–C(5) 203.1(4), W(1′)–C(5′) 204.8(5), C(1)–C(6) 149.4(6), C(1′)–C(6′) 149.8(6); C(1)–W(1)–C(2) 90.48(17), C(1′)–W(1′)–C(2′) 87.80(17), C(1)–W(1)–C(5) 91.49(17), C(1′)–W(1′)–C(5′) 88.47(18).

[1] Structure analysis of **6a** and **7b**: crystals were mounted in a perfluoropolyether oil at -100°C on a Siemens P4 diffractometer. Intensities were registered to 2θ 50°. Absorption corrections were based on psi-scans. The structures were solved by the heavy-atom method and refined against F^2 [18]. Methyl H atoms were included using rigid groups, all other H atoms with a riding model (exceptions: solvent methyl for **6a** riding, N–H for **7b** free with N–H distance restraints). For further details see Table 3.

Table 2
Selected ^{13}C- and ^{31}P-NMR data of the 2*H*-azaphosphirene complexes **8a**,**b** and **13a**,**b** [a]



8a,b



13a,b

δ ^{13}C	C_AO	$^2J_{CP}$	C_BO	$^2J_{CP}$	C_CO	$^2J_{CP}$	C_DO	$^2J_{CP}$	δ $^{31}P^{PR3}$ ($^2J_{PP}$)	$^1J_{PW}$	δ $^{31}P^{PCN}$	$^1J_{PW}$
8a	200.8	10.8, 7.6	201.8,	10.0, 6.9	203.5	40.5, 5.3	205.6	23.6, 4.6	22.9 (33.4)	237.2	−108.8	284.3
8b	200.8	10.6, 7.6	201.8,	10.2, 7.2	203.6	40.8, 5.7	205.6	23.7, 4.4	22.9 (33.5)	235.9	−111.9	283.0
13a,**b** [b]	220.6	m_c	224.3	m_c	226.1	m_c	231.0	m_c	26.6/27.2 (47.4)/(46.3)		−46.1/−45.1 (47.4)/(46.3)	

[a] δ (ppm), *J* (Hz), $CDCl_3$; assignment and notation of the carbonyl groups according to the formulae.
[b] No assignment possible.

Table 3
Crystal structure analyses of complexes **6a** and **7b**

Complex	**6a**·1/2$C_4H_{10}O$	**7b**
Formula	$C_{33}H_{30}O_{5.5}PW$	$C_{30}H_{24}NO_4PW$
M_r	729.39	677.32
Crystal habit	Red prism	Yellow prism
Crystal size (mm)	0.40×0.30×0.30	0.50×0.25×0.10
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (pm)	2503.6(2)	915.2(2)
b (pm)	1246.09(14)	1668.5(2)
c (pm)	2069.7(2)	2023.8(3)
α (°)	90	112.843(8)
β (°)	110.893(6)	92.344(12)
γ (°)	90	105.543(12)
V (nm^3)	6.0321(10)	2.7071(7)
Z	8	4
D_X (Mg m^{-3})	1.595	1.662
μ (mm^{-1})	3.924	4.362
Transmissions	0.67–0.97	0.56–1.0
F(000)	2848	1328
T (K)	173	173
$2\theta_{max}$	50	50
No. of reflections		
Measured	14 757	13 947
Unique	10 588	9179
R_{int}	0.0502	0.0222
Parameters	712	681
Restraints	584	498
wR (F^2, all reflections)	0.0783	0.0535
R (F, $>4\sigma(F)$)	0.0425	0.0247
S	0.851	0.906
Max $\Delta\rho$ (e nm^{-3})	1267	904

son of selected bond lengths and angles of complexes **6a**, **7b** and **14** (Table 4) highlights the most important stereoelectronic effects on the bonding situations, thus showing for example the variability of the phosphorus–tungsten bond length, which decreases upon lengthening of the W1–C1 bond, or of the C4–W1–C1 angles.

In the packing of compound **6a**, the (ordered) ether molecule accepts a C–H···O hydrogen bond from C17′–H17′, with C–H···O 162° (Table 5). The NH_2 group of complex **7b** form hydrogen bonds to carbonyl groups (Table 6).

Table 5
Hydrogen bonds (Å and °) for compound **6a** [a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
C(17′)–H(17′)···O(99) # 1	0.95	2.49	3.409(11)	161.8
C(18)–H(18)···O(1) # 2	0.95	2.57	3.499(10)	167.5
C(97)–H(97B)···O(3′) # 2	0.99	2.60	3.437(13)	141.9

[a] Symmetry transformations used to generate equivalent atoms: # 1, $x-1$, y, z; # 2, $-x+1$, $y+1/2$, $-z+3/2$.

Table 6
Hydrogen bonds (Å and °) for compound **7b**[a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(01)···O(2′) # 1	0.84(2)	2.41(4)	3.004(5)	128(4)
N(1)–H(02)···O(4) # 2	0.85(2)	2.14(3)	2.980(5)	169(5)
N(1′)–H(01′)···O(2) # 1	0.84(2)	2.35(4)	3.027(5)	138(4)
N(1′)–H(02′)···O(4′) # 2	0.84(2)	2.21(3)	3.002(5)	158(4)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x+1$, $-y+1$, $-z$; # 2 $x-1$, y, z.

3. Experimental

3.1. General

All operations were carried out under an inert atmosphere of deoxygenated dry nitrogen. Solvents were dried according to standard procedures. NMR spectra

Table 4
Selected bond lengths (pm) and angles (°) of the two independent molecules of complexes **6a**, **7b** and **14** [a] [19]

Compound	W1–C1	W1–P1	O1–C1	N1–C1	W1–C4	W1–C3
6a	214.6(8)	255.02(19)	133.0(9)	–	205.3(10)	198.8(8)
6a′	217.0(9)	255.7(2)	133.8(9)	–	204.7(9)	199.8(9)
7b	221.7(5)	251.99(12)	–	130.9(6)	198.1(5)	202.5(5)
7b′	221.8(4)	252.39(12)	–	131.1(5)	198.4(5)	199.9(5)
14	219.6(6)	254.2(2)	137.3(8)	133.4(9)	198.6(7)	199.8(8)
	C4–W1–C1	C3–W1–P1	C1–W1–P1	O1–C1–W1	N1–C1–W1	X–C1–Y
6a	170.4(3)	173.1(2)	99.1(2)	131.4(6)	–	103.2(6)
6a′	169.9(3)	172.9(2)	100.1(2)	131.4(6)	–	104.5(7)
7b	179.1(2)	176.59(13)	92.86(12)	–	119.8(4)	109.6(4)
7b′	176.61(17)	176.37(13)	93.00(11)	–	122.2(3)	110.9(4)
14	176.12(3)	179.0(2)	88.8(2)	119.8(4)	135.2(5)	105.1(5)

[a] For the notation see Figs. 2 and 4.

were recorded on a Bruker AC-200 spectrometer (200 MHz for ^{1}H; 50.3 MHz for ^{13}C; 81 MHz for ^{31}P) using [d_6]chloroform and [d_6]benzene as solvents, the latter as internal standard; shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P); only coupling constant magnitudes are given. MS: Finnigan Mat 8430 (70 eV); selected data given. Elemental analyses: Carlo Erba analytical gas chromatograph. IR: Biorad FT-IR-165; selected data given.

The following compounds were synthesized by the literature methods: {[amino(phenyl)-carbene]pentacarbonyltungsten(0)} [8] (**1**), [bis(trimethylsilyl)methylene]chlorophosphane [9] (**2**), {[ethoxy(phenyl)carbene]-pentacarbonylchromium(0)} [14] (**9**) and (−)(*R*)-methyl(phenyl)*n*-propyl-phosphane [15] (**10**).

3.2. Procedure for the reaction of complexes **1** and **2** in diethyl ether under CO atmosphere

In an apparatus, consisting of two flasks connected via a bridge, a solution of 0.43 g (1.0 mmol) of complex **1** and 0.22 g (1.0 mmol) of **2** in 10 ml of diethyl ether transferred to one and 3.3 ml of triethylamine to the second flask. The solutions were cooled to −196°C and the N_2 atmosphere was removed at 0.01 mbar and replaced by CO atmosphere (1 atm). Thereafter the triethylamine was added to the solution of complexes **1** and **2** at −15°C, −30°C or −50°C and the reaction mixtures were stirred. After (a) 50 min, (b) 240 min, (c) 940 min, 4 ml of the reaction mixtures were taken, immediately evaporated to dryness, the residues redissolved in 1 ml of diethyl ether and the ^{31}P-NMR spectra of the samples immediately recorded. As a control, the same experiments were carried out simultaneously under N_2 atmosphere.

3.3. Procedure for the reaction of complexes **1** and **2** in diethyl ether under ^{13}CO atmosphere

In an apparatus consisting of two flasks connected via a bridge, a solution of 0.86 g (2.0 mmol) of complex **1** and 0.45 g (2.0 mmol) of **2** in 20 ml of diethyl ether transferred to one and 6.6 ml of triethylamine to the second flask. The solutions were cooled to −196°C and the N_2 atmosphere was removed at 0.01 mbar and replaced by a ^{13}CO atmosphere (1 atm). Afterwards the triethylamine was added to the solution of complexes **1** and **2** at ambient temperature and the reaction mixture was stirred for 20 h. The resulting yellow–orange mixture was evaporated to dryness under reduced pressure (0.01 mbar) and the residue extracted twice with 40 ml of *n*-pentane and filtered. The filtration residue was washed twice with 5 ml of *n*-pentane, the organic phases combined and the solvent removed under reduced pressure. ^{13}C-NMR spectra were measured of one sample of the residue dissolved in 0.5 ml of [d_6]benzene and another sample dissolved in 0.5 ml [*d*]chloroform.

3.4. Synthesis of *N*,*N*′-bis{amino[(phenyl)carbene]-pentacarbonyltungsten(0)}bis(trimethylsilyl)-methyl-phosphane (**3a**,**b**)

To a solution of 2.15 g (5 mmol) {[amino(phenyl)-carbene]pentacarbonyltungsten(0)} (**1**) in 5 ml of dichloromethane, 0.63 g (2.8 mmol) of [bis(trimethylsilyl)methylene]chlorophosphane (**2**) and 1.66 ml (22 mmol) of triethylamine was added at 0°C and stirred at 0°C for 10 min (^{31}P-NMR). The solvent was removed under reduced pressure (0.01 mbar), and the residue extracted with 10 ml of *n*-pentane (three times) and subjected to low-temperature column chromatography (SiO_2, −10°C, *n*-hexane–diethyl ether, 1:1). Removing the solvents under reduced pressure of the first yellow–orange fraction yielded complexes **3a**,**b** as an orange solid. Yield: 1.83 g (1.75 mmol, 70%). M.p. 140°C (decomp.). IR (KBr) $\bar{\nu} = 3300$ (w), 3252 (w) (NH); 2066 (s), 1987(m), 1917(vs) (CO) cm^{-1}. MS (CI, (NH_3, pos), (^{184}W): *m*/*z* (%): 1047 (7) [$(M+H)^+$], 991 (3) [$(M+H-2CO)^+$], 914 (42) [$(M+H-2CO-Ph)^+$], 723 (81) [$(M+H-W(CO))^+$], 620 (100) [$M^+-(CO)_5W{=}C(C_6H_5)(NH))^+$], 428 (96) [$(M-(CO)_5W{=}C(C_6H_5)(NH)-PCH(SiMe_3)_2)^+$]. Calc. for $C_{31}H_{31}N_2O_{10}PSi_2W_2$ (1046.4): C, 35.58; H, 2.99; N, 2.68. Anal. Found: C, 35.58; H, 2.98; N, 2.56%.

3a: ^{1}H-NMR ($CDCl_3$): $\delta = 0.21$ (d, 18H, $^4J_{HP} = 0.4$ Hz, Si(CH_3)$_3$), 0.48 (d, 1H, $^2J_{PH} = 4.1$ Hz, PC*H*), 6.55 (m_c, 4H, Ph–*H*), 7.35 (m_c, 6H, Ph–*H*), 9.66 (s, br, 2H, N*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 2.4$ (s br, Si(*C*H$_3$)$_3$), 21.2 (d, $^1J_{CP} = 48.3$ Hz, P*C*H), 120.1 (s, Ph–*C*3/3′), 128.0 (s, Ph–*C*4), 128.2 (s, Ph–*C*2/2′), 152.7 (d, $^3J_{CP} = 11.2$ Hz, Ph–*C*1), 197.8 (s, $^1J_{CW} = 128.0$ Hz, *cis*-*C*O), 203.8 (s, *trans*-*C*O), 285.8 (d, $^2J_{CP} = 5.8$ Hz, W=*C*R$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 93.5$ (s).

3b: ^{1}H-NMR ($CDCl_3$): $\delta = 0.31$ (pt, 18H, $^4J_{HP} = 0.9$ Hz, $^4J_{HP} = 1.1$ Hz, Si(CH_3)$_3$), 0.83 (d, 1H, $^2J_{PH} = 2.9$ Hz, PC*H*), 7.03 (m_c, 4H, Ph–*H*), 7.35 (m_c, 6H, Ph–*H*), 9.12 (s, br, 1H, N*H*), 9.69 (s, br, 1H, N*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 2.2$ (s, Si(*C*H$_3$)$_3$), 2.3 (s, Si(*C*H$_3$)$_3$), 20.5 (d, $^1J_{CP} = 47.9$ Hz, P*C*H), 120.1 (s, Ph–*C*3/3′), 120.7 (s, Ph–*C*3/3′), 128.6 (s, Ph–*C*4), 128.8 (s, Ph–*C*2/2′), 128.9 (s, Ph–*C*2/2′), 129.2 (s, Ph–*C*4), 152.9 (d, $^3J_{CP} = 9.7$ Hz, Ph–*C*1), 158.3 (d, $^3J_{CP} = 8.6$ Hz, Ph–*C*1), 197.9 (s, $^1J_{CW} = 127.9$ Hz, *cis*-*C*O), 197.9 (s, $^1J_{CW} = 127.9$ Hz, *cis*-*C*O), 203.7 (s, *trans*-*C*O), 281.1 (s, W=*C*R$_2$), 282.3 (s, W=*C*R$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 109.0$ (s).

*3.4.1. Reaction of a 5:2 mixture of E,E- and E,Z-N,N′-bis{amino[(phenyl)carbene]-pentacarbonyl-tungsten(0)}bis(trimethylsilyl)-methylphosphane (**3a**,**b**) with triethylamine*

To 26 mg (0.025 mmol) of **3a**,**b**, dissolved in 0.5 ml of dichloromethane, 0.2 ml of triethylamine was added at ambient temperature with stirring. ^{31}P-NMR monitoring showed the formation of complexes **4** and **5** (Fig. 1).

*3.5. General procedure for the preparation of {cis-[ethoxy(aryl)carbene]tetracarbonyl-(triphenylphosphane)tungsten(0)} complexes **6a**,**b***

Solutions of 5 mmol of the ethoxy(aryl)carbene tungsten complexes and 2.19 g (5.5 mmol) of triphenylphosphane in 20 ml of toluene were stirred at 80°C for 6 h until triphenylphosphane was consumed (^{31}P-NMR). The solvent was removed under reduced pressure (0.01 mbar), and the residues purified by low-temperature column chromatography. Phenyl groups at phosphorus are denoted hereafter as Ph_A and those at the carbene atom as Ph_B.

*3.5.1. {cis-[Ethoxy(phenyl)carbene]-tetracarbonyl(triphenylphosphane)tungsten(0)} (**6a**)*

A total of 1.66 g of **6a** (48%) was obtained as a dark-red powder after chromatography (SiO_2, −10°C; *n*-hexane/diethyl ether, 10:1). M.p. 108°C (decomp.). ^{1}H-NMR ($CDCl_3$): $\delta = 1.36$ (t, $^3J_{HH} = 7.2$ Hz, 3H, C*H*$_3$), 4.47 (q, $^3J_{HH} = 7.2$ Hz, 2H, C*H*$_2$), 7.08 (m_c, 2H, Ph–*H*), 7.36 (m_c, 18H, Ph-*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 14.8$ (s, *C*H$_3$), 77.5 (s, *C*H$_2$), 125.2 (s, Ph_B–*C*), 127.3 (s, Ph_B–*C*), 128.4 (d, $^2J_{CP} = 9.8$ Hz, Ph_A-*C*2/2′), 129.4 (s, Ph_B–*C*4), 130.1 (d, $^4J_{CP} = 1.8$ Hz, Ph_A–*C*4), 133.3 (d, $^3J_{CP} = 12.0$ Hz, Ph_A–*C*3/3′), 135.7 (d, $^1J_{CP} = 38.7$ Hz, Ph_A–*C*1), 157.1 (s, Ph_B–*C*1), 202.8 (d, $^2J_{CP} = 7.0$ Hz, *cis*-*C*O), 205.6 (d, $^2J_{CP} = 21.8$ Hz, (*trans*-PPh$_3$)–*C*O), 211.8 (d, $^2J_{CP} = 7.4$ Hz, (*trans*-CR$_2$)–*C*O), 318.3 (d, $^2J_{CP} = 7.5$ Hz, W=*C*R$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 26.4$ (s, $^1J_{PW} = 238.0$ Hz). MS (70 eV), (^{184}W); *m*/*z* (%): 692 (1) [M$^+$], 664 (4) [(M–CO)$^+$], 608 (3) [(M–3CO)$^+$], 262 (100) [Ph$_3$P$^+$]. Calc. for $C_{31}H_{25}O_5PW$ (692.4): C, 53.77; H, 3.65. Anal. Found: C, 53.75; H, 3.85%.

*3.5.2. {cis-[Ethoxy(p-methylphenyl)carbene]-tetracarbonyl(triphenylphosphane)tungsten(0) (**6b**)*

A total of 6.19 g of **6b** (62%) was obtained as a red powder after chromatography (SiO_2, −10°C; *n*-hexane/diethyl ether, 10:1). M.p. 111°C (decomp.). IR (KBr) $\tilde{\nu} = 2020$ (m) cm^{-1}, 1917 (m), 1903 (s), 1885 (s) (CO). ^{1}H-NMR ($CDCl_3$): $\delta = 1.38$ (t, 3H, $^3J_{HH} = 7.1$ Hz, CH$_2$–C*H*$_3$), 2.31 (s, 3H, *p*-Ar–C*H*$_3$), 4.52 (q, 2H, $^3J_{HH} = 7.1$ Hz, O–C*H*$_2$), 6.94 (d, 2H, $^3J_{HH} = 7.3$ Hz, *p*-Tol–*H*3/3′), 7.01 (d, 2H, $^3J_{HH} = 7.5$ Hz, *p*-Tol–*H*2/2′), 7.37 (m_c, 15H, Ph–*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 14.8$ (s, CH$_2$–*C*H$_3$), 21.4 (s, *p*-Ar–*C*H$_3$), 77.6 (s, O–*C*H$_2$), 126.3 (s, *p*-Tol–*C*2/2′),128.0 (s, *p*-Tol–*C*3/3′), 128.4 (d, $^3J_{CP} = 9.4$ Hz, Ph_A–*C*3/3′), 130.1 (d, $^4J_{CP} = 1.7$ Hz, Ph_A–*C*4), 133.3 (d, $^2J_{CP} = 12.1$ Hz, Ph_A–*C*2/2′), 135.8 (d, $^1J_{CP} = 37.2$ Hz, Ph_A–*C*1), 140.3 (s, *p*-Tol–*C*4), 154.5 (s, *p*-Tol–*C*1), 203.0 (d, $^2J_{CP} = 7.1$ Hz, *cis*-(PPh$_3$, CR$_2$)–*C*O), 205.8 (d, $^2J_{CP} = 22.0$ Hz, (*cis*-CR$_2$, *trans*-PPh$_3$)–*C*O), 211.7 (d, $^2J_{CP} = 6.3$ Hz, (*trans*-CR$_2$, *cis*-PPh$_3$)–*C*O), 317.7 (d, $^2J_{CP} = 7.3$ Hz, W=*C*R$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 26.5$ (s, $^1J_{PW} = 237.1$ Hz). MS (70 eV), (^{184}W); *m*/*z* (%): 706 (2) [M$^+$], 678 (2) [(M–CO)$^+$], 622 (1) [(M–3CO)$^+$], 594 (1) [(M–4CO)$^+$], 444 (3) [(M–PPh$_3$)$^+$], 387 (2) [(M–PPh$_3$–CO–C$_2$H$_5$)$^+$], 275 (3) [(M–PPh$_3$–5CO–C$_2$H$_5$)$^+$], 262 (100) [PPh$_3^+$]. Calc. for $C_{32}H_{27}O_5PW$ (706.4): C, 54.41; H, 3.85. Anal. Found: C, 54.32; H, 3.78%.

*3.6. General procedure for the preparation of {cis-[amino(aryl)carbene]tetracarbonyl-(triphenylphosphane)tungsten(0)} complexes **7a**,**b***

A gentle flow of ammonia was bubbled through a solution of 5 mmol of the complexes **6a**,**b** in 60 ml of THF (100 ml three-necked flask) until a yellow colour persisted and thin liquid chromatography (SiO_2, *n*-hexane/Et_2O, 2:1) indicated that all the starting material had reacted. All volatile compounds were removed under reduced pressure (0.01 mbar) and the yellow residues were purified by low-temperature column chromatography.

*3.6.1. {cis-[Amino(phenyl)carbene]-tetracarbonyl(triphenylphosphane)tungsten(0)} (**7a**)*

A total of 2.6 g of **7a** (79%) was obtained as a yellow powder. M.p. 180°C (decomp.). ^{1}H-NMR ($CDCl_3$): $\delta = 7.06$ (m_c, 2H, Ph–*H*), 7.36 (m_c, 18H, Ph–*H*), 7.76 (s, br, 1H, N*H*), 7.92 (s, br, 1H, N*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 124.7$ (s, Ph_B–*C*), 128.6 (s, Ph_B–*C*), 128.7 (d, $^2J_{CP} = 7.2$ Hz, Ph_A–*C*2/2′), 129.9 (s, Ph_B–*C*4), 130.2 (s, Ph_A–*C*4), 133.7 (d, $^3J_{CP} = 12.0$ Hz, Ph_A–*C*3/5), 136.1 (d, $^1J_{CP} = 37.7$ Hz, Ph_A–*C*1), 153.5 (s, Ph_B–*C*1), 204.1 (d, $^2J_{CP} = 7.4$ Hz, *cis*-*C*O), 208.5 (d, $^2J_{CP} = 25.1$ Hz, (*trans*-PPh$_3$)–*C*O), 211.3 (d, $^2J_{CP} = 6.9$ Hz, (*trans*-CR$_2$)–*C*O), 269.6 (d, $^2J_{CP} = 6.9$ Hz, W=*C*R$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 27.1$ (s, $^1J_{PW} = 235.1$ Hz, *P*Ph$_3$). MS (70 eV), (^{184}W); *m*/*z* (%): 663 (2) [M$^+$], 635 (10) [(M–CO)$^+$], 607 (8) [(M–2CO)$^+$], 551 (17) [(M–4CO)$^+$], 262 (100) [Ph$_3$P$^+$]. Calc. for $C_{29}H_{22}NO_4PW$ (663.3): C, 52.51; H, 3.35; N, 2.11. Anal. Found: C, 52.11; H, 3.32; N, 2.03%.

*3.6.2. {cis-[Amino(p-methylphenyl)carbene]-tetracarbonyl(triphenylphosphane)tungsten(0)} (**7b**)*

A total of 2.95 g of 7b (87%) was obtained as a yellow powder. M.p. 169°C (decomp.). IR (KBr) $\tilde{\nu} =$ 3437 (m) cm^{-1}, 3331 (m), 3270 (m) (NH), 2004 (m),

1931 (m), 1911 (s), 1876 (s), 1852 (s), 1839 (s) (CO). ^{1}H-NMR ($CDCl_3$): $\delta = 2.35$ (s, 3H, *p*-Ar–CH_3), 7.03 (d, 2H, $^3J_{HH} = 7.3$ Hz, *p*-Tol–*H*3/3′), 7.12 (d, 2H, $^3J_{HH} =$ 7.5 Hz, *p*-Tol–*H*2/2′), 7.33 (m_c, 15H, Ph–*H*), 7.65 (s, br, 1H, NH_2), 7.89 (s, br, 1H, NH_2). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 21.3$ (s, *p*-Aryl–*C*H_3), 124.9 (s, Tolyl–*C*2/2′), 128.3 (d, $^3J_{CP} = 9.5$ Hz, Ph_A–*C*3/3′), 129.0 (s, Tol–*C*3/3′), 129.8 (s, Ph_A–*C*4), 133.4 (d, $^2J_{CP} = 12.0$ Hz, Ph_A–*C*2/2′), 135.7 (d, $^1J_{CP} = 37.2$ Hz, Ph_A–*C*1), 140.2 (s, Tol–*C*4), 150.3 (s, Tol–*C*1), 203.7 (d, $^2J_{CP} = 7.2$ Hz, *cis*-(PPh_3, CR_2)–*C*O), 208.2 (d, $^2J_{CP} = 2.8$ Hz, (*cis*-CR_2, *trans*-PPh_3)–*C*O), 210.8 (d, $^2J_{CP} = 6.2$ Hz, (*trans*-CR_2, *cis*-PPh_3)–*C*O), 269.0 (d, $^2J_{CP} = 7.1$ Hz, W=*C*R_2).-^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 27.3$ (s, $^1J_{PW} = 233.2$ Hz, *P*Ph_3). MS (70 eV), (^{184}W); *m*/*z* (%): 677 (1) [M^+], 649 (1) [(M–CO)$^+$], 621 (1) [(M–2CO)$^+$], 586 (1) [(M–C_7H_7)$^+$], 565 (3) [(M–4CO)$^+$], 415 (2) [(M–PPh_3)$^+$], 262 (100) [PPh_3^+]. Calc. for $C_{30}H_{24}NO_4PW$ (677.4): C, 53.19; H, 3.57; N, 2.07. Anal. Found: C, 53.38; H, 3.57; N, 2.03%.

3.7. General procedure for the preparation of *cis*-(2H-azaphosphirene)(triphenylphosphane) complexes **8a**,**b**

To a solution of 1.5 mmol of complexes **7a**,**b** and 0.34 g (1.5 mmol) of [bis(trimethylsilyl)methylene]-chlorophosphane (**2**) in 15 ml of dichloromethane, 5 ml of NEt_3 was added at 0°C. The reaction mixture was stirred at ambient temperature until **2** was consumed (^{31}P-NMR). The yellow–orange reaction mixture was evaporated to dryness under reduced pressure (0.1 mbar). The residue was extracted with 5×50 ml of *n*-pentane and filtered. The filtration residue was washed twice with 5 ml of pentane, the organic phases combined and the solvent removed under reduced pressure. The residue was purified, if necessary, by low-temperature column chromatography (SiO_2, −20°C; *n*-hexane/diethyl ether, 15:1).

3.7.1. {*cis*-[2-Bis(trimethylsilyl)-methyl-3-phenyl-2H-azaphosphirene-κP]-tetracarbonyl(triphenyl-phosphane)tungsten(0)} (**8a**)

A total of 0.87 g of **8a** (68%) was obtained as a yellow powder after chromatography (SiO_2, −20°C; *n*-hexane/diethyl ether, 15:1). M.p. 122°C (decomp.). IR (KBr) $\tilde{\nu} = 2021$ (s) cm^{-1}, 1936 (m), 1926 (s), 1909 (vs), 1889 (vs) (CO). ^{1}H-NMR ($CDCl_3$): $\delta = -0.05$ (s, 9H, Si(CH_3)$_3$), 0.09 (s, 9H, Si(CH_3)$_3$), 0.85 (d, $^2J_{HP} = 2.7$ Hz, 1H, PC*H*), 7.15–7.69 (m_c, 20H, Ph–*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 1.3$ (d, $^3J_{CP} = 3.0$ Hz, Si(*C*H_3)$_3$), 2.4 (d, $^3J_{CP} = 3.0$ Hz, Si(*C*H_3)$_3$), 28.5 (dd, $^1J_{CP} = 22.1$, $^3J_{CP} =$ 2.0 Hz, P*C*H), 127.4 (d, $^1J_{CP} = 15.3$ Hz, Ph_B–*C*1), 128.2 (s, Ph_A–*C*4), 129.3 (d, $^3J_{CP} = 12.2$ Hz, Ph_A–*C*2/2′), 129.5, 129.7 (s, Ph_B–*C*2/2′, Ph_B–*C*3/3′), 133.2 (s, Ph_B–*C*4), 133.3 (d, $^3J_{CP} = 32.1$ Hz, Ph_A–*C*3/3′), 135.5 (dd, $^1J_{CP} = 38.1$, $^3J_{CP} = 2.2$ Hz, Ph_A–*C*1), 190.8 (d, $\Sigma J_{CP} =$ 1.5 Hz, P*C*N), 200.8 (dd, $^2J_{CP} = 10.8$, $^2J_{CP} = 7.6$ Hz, *cis*-(PPh_3, PCN)–*C*O), 201.8 (dd, $^2J_{CP} = 10.0$, $^2J_{CP} =$ 6.9 Hz, *cis*-(PPh_3, PCN)–*C*O), 203.5 (dd, $^2J_{CP} = 40.5$, $^2J_{CP} = 5.3$ Hz, (*cis*-PPh_3, *trans*-PCN)–*C*O), 203.5 (dd, $^2J_{CP} = 23.8$, $^2J_{CP} = 19.2$ Hz, (*trans*-PPh_3, *cis*-PCN)–*C*O). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 22.9$ (d, $^2J_{PP} = 33.4$ Hz, $^1J_{PW} = 237.2$ Hz, *P*Ph_3), −108.8 (d, $^2J_{PP} = 33.4$ Hz, $^1J_{PW} = 284.3$ Hz, *P*CN). MS (70 eV), (^{184}W); *m*/*z* (%): M^+ was not detected, 262 (100) [PPh_3^+], 103 (52) [$PhCN^+$], 73 (18) [Me_3Si^+]; (pos-FAB, *m*-NBA), (^{184}W); *m*/*z* (%): M^+ was not detected, 748 (6) [(M–PhCN)$^+$], 720 (56) [(M–PhCN–CO)$^+$], 692 (68) [(M–PhCN–2CO)$^+$], 262 (14) [PPh_3^+], 103 (18) [$PhCN^+$], 73 (100) [Me_3Si^+]. $C_{36}H_{39}NO_4P_2Si_2W$ (851.7): Calc. Anal.: C, 50.76; H, 4.63; N, 1.65; Anal. Found: C, 50.52; H, 4.80; N, 1.56%.

3.7.2. {*cis*-[2-Bis(trimethylsilyl)methyl-3-(4-methylphenyl)-2H-azaphosphirene-κP]tetracarbonyl (triphenylphosphane)tungsten(0)} (**8b**)

A total of 0.83 g of **8b** (64%) was obtained as a yellow powder after chromatography (SiO_2, −20°C; *n*-hexane/diethyl ether, 15:1). M.p. 118°C (decomp.). IR (KBr) $\tilde{\nu} = 2020$ (s) cm^{-1}, 1928 (s), 1899 (vs), 1886 (vs) (CO), 1618 (w) (CN). ^{1}H-NMR ($CDCl_3$): $\delta = 0.10$ (s, 9H, Si(CH_3)$_3$), 0.23 (s, 9H, Si(CH_3)$_3$), 0.98 (d, 1H, $^2J_{HP}$ 2.3 Hz, PC*H*), 2.46 (s, 3H, *p*-Ar–CH_3), 7.36 (m_c, 19H, Ar–*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 1.3$ (d, $^3J_{CP} = 2.9$ Hz, Si(*C*H_3)$_3$), 2.3 (d, $^3J_{CP} = 2.4$ Hz, Si(*C*H_3)$_3$), 21.9 (s, *p*-Ar–*C*H_3), 28.3 (d, $^1J_{CP} = 22.7$ Hz, $^3J_{CP} = 1.5$ Hz, P*C*H), 124.2 (d, $^2J_{CP} = 15.3$ Hz, *p*-Tol–*C*1), 128.0 (d, $^3J_{CP} = 9.7$ Hz, Ph_A–*C*3/3′), 129.5 (d, $^4J_{CP} = 1.3$ Hz, Ph_A–*C*4), 129.58, 129.62 (s, *p*-Tol–*C*2/2′; s, *p*-Tol–*C*3/3′), 133.2 (d, $^2J_{CP} = 12.0$ Hz, Ph_A–*C*2/2′), 135.5 (dd, $^1J_{CP} = 38.6$ Hz, $^3J_{CP} = 2.0$ Hz, Ph_A–*C*1), 144.1 (s, *p*-Tol–*C*4), 189.9 (d, $^1J_{CP} = 1.0$ Hz, P*C*N), 200.8 (dd, $^2J_{CP} = 10.6$ Hz, $^2J_{CP} = 7.6$ Hz, *cis*-(PPh_3, PCN)–*C*O), 201.8 (dd, $^2J_{CP} = 10.2$ Hz, $^2J_{CP} = 7.2$ Hz, *cis*-(PPh_3, PCN)–*C*O), 203.6 (dd, $^2J_{CP} = 40.8$ Hz, $^2J_{CP} = 5.7$ Hz, (*cis*-PPh_3, *trans*-PCN)–*C*O), 205.6 (dd, $^2J_{CP} = 23.7$ Hz, $^2J_{CP} = 4.5$ Hz, (*trans*-PPh_3, *cis*-PCN)–*C*O). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 22.9$ (d, ^1J(PW) = 235.9 Hz, $^2J_{PP} =$ 33.5 Hz, *P*Ph_3), −111.9 (d, ^1J(PW) = 283.0 Hz, $^2J_{PP} = 33.5$ Hz, *P*CN). MS (pos.-CI, (NH_3), ^{184}W); *m*/*z* (%): M^+ was not detected, 837 (1) [M^+–CO], 751 (2) [(M–3CO–3CH_3)$^+$], 587 (3) [(M–C_7H_7CN–C_6H_5–3CO)$^+$], 263 (100) [(PPh_3 + H)$^+$]. Calc. for $C_{37}H_{41}NO_4P_2Si_2W$ (865.7): C, 51.33; H; 4.77; N, 1.62. Anal. Found: C, 51.56; H, 4.86; N, 1.78%.

3.8. {(−)(*R*)-*cis*-[Ethoxy(phenyl)carbene]-tetracarbonyl(methyl-phenyl-n-propylphosphane)-chromium(0)} (**11**)

A solution of 10.1 g (31.0 mmol) of chromium carbene complex **9** and 2.0 g (12.0 mmol) (−)(*R*)-

methyl(phenyl)-*n*-propylphosphane (**10**) in 60 ml of toluene was heated for 2 h at 45°C, until the phosphane was consumed (^{31}P-NMR). The toluene was evaporated under reduced pressure (ca. 0.01 mbar) and the residue was subjected to twofold low-temperature column chromatography (1: SiO_2, −10°C, *n*-hexane–diethyl ether (10:1); 2: SiO_2, −10°C, *n*-hexane/diethyl ether (10:1)). The first fraction contained mainly {[ethoxy(phenyl)-carbene]pentacarbonylchromium(0)} (**9**) and the second fraction (red–black) complex **11** (ca. 0.01 mbar); evaporation of the solvents yielded slightly impure complex **11** as a red–black oil. Yield approximately 60–65% (^{31}P-NMR). ^{1}H-NMR ($CDCl_3$): $\delta = 1.45$ (m_c, 13H, P–C*H*$_2$–C*H*$_2$–C*H*$_3$, P–C*H*$_3$, O–CH$_2$–C*H*$_3$), 4.09 (q, 2H, $^{3}J_{HH} = 6.9$ Hz, O–C*H*$_2$), 6.69 (m_c, 2H, C$_6$*H*$_5$), 7.24 (m_c, 8H, C$_6$*H*$_5$). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 13.6$ (d, $^{1}J_{CP} = 22.7$ Hz, P–*C*H$_2$–CH$_2$–CH$_3$), 15.0 (s, O–CH$_2$–*C*H$_3$), 15.7 (d, $^{2}J_{CP} = 12.1$ Hz, P–CH$_2$–*C*H$_2$–CH$_3$), 17.3 (d, $^{3}J_{CP} = 4.9$ Hz, P–CH$_2$–CH$_2$–*C*H$_3$), 34.7 (d, $^{1}J_{CP} = 21.1$ Hz, P–*C*H$_3$), 73.8 (s, O–*C*H$_2$–CH$_3$), 121.7 (s, C–Ph–*C*3/3′), 127.4 (s, C–Ph–*C*2/2′), 127.9 (s, C–Ph–*C*4), 128.4 (d, $^{3}J_{CP} = 8.6$ Hz, P–Ph–*C*3/3′), 128.8 (d, $^{4}J_{CP} = 1.7$ Hz, P–Ph–*C*4), 129.3 (d, $^{2}J_{CP} = 8.8$ Hz, P–Ph–*C*2/2′), 138.7 (d, $^{1}J_{CP} = 31.4$ Hz, P–Ph–*C*1), 153.7 (s, C–Ph–*C*1), 220.9 (d, $^{2}J_{CP} = 14.9$ Hz, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$), CR$_2$)–*C*O), 221.0 (d, $^{2}J_{CP} =$ 14.8 Hz, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$), CR$_2$)–*C*O), 226.1 (d, $^{2}J_{CP} = 8.3$ Hz, (*cis*-CR$_2$, *trans*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$)–*C*O), 231.5 (d, $^{2}J_{CP} = 12.9$ Hz, (*trans*-CR$_2$, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$)–*C*O), 347.7 (d, $^{2}J_{CP} = 13.8$ Hz, Cr=*C*R$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 28.0$ (s). $C_{23}H_{25}CrO_5P$ (464.4).

3.9. {(−)(R)-cis-[Amino(phenyl)carbene]-tetracarbonyl(methyl(phenyl)-n-propylphosphane)-chromium(0)} (12)

A gentle flow of ammonia was bubbled through a solution of 5.0 g (10.8 mmol) of complex **11** in 60 ml of THF (100 ml three-necked flask) until a bright red colour persisted and thin layer chromatography (SiO_2; *n*-hexane/Et$_2$O, 2:1) indicated that all starting material had reacted. All volatile compounds were removed under reduced pressure (ca. 0.01 mbar) and the red residue was purified by column chromatography (SiO_2, *n*-hexane/Et$_2$O, 2:1). Complex **12** was thus obtained as a red powder. Yield: 0.85 g (1.95 mmol) 18%. M.p. 118°C (decomp.). IR (KBr): $\tilde{\nu} = 3431$ (w), 3323 (w), 3249 (w) (NH), 1996 (s), 1896 (s, sh), 1871 (s) (CO) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 1.43$ (m_c, 13H, P–C*H*$_2$–C*H*$_2$–C*H*$_3$, P–C*H*$_3$), 7.19 (m_c, 10H, C$_6$*H*$_5$), 7.66 (s, br, 1H, N*H*), 8.10 (s, br, 1H, N*H*). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 13.4$ (d, $^{1}J_{CP} = 22.2$ Hz, P–*C*H$_2$–CH$_2$–CH$_3$), 15.7 (d, $^{2}J_{CP} = 12.0$ Hz, P–CH$_2$–*C*H$_2$–CH$_3$), 17.3 (d, $^{3}J_{CP} = 4.5$ Hz, P–CH$_2$–CH$_2$–*C*H$_3$), 34.6 (d, $^{1}J_{CP} = 21.3$ Hz, P–*C*H$_3$), 122.7 (s, C–Ph–*C*3/3′), 128.1 (s, C–Ph–*C*2/2′), 128.4 (d, $^{3}J_{CP} = 8.0$ Hz, P–Ph–*C*3/3′), 128.7 (s, C–Ph–*C*4, P–Ph–*C*4), 129.3 (d, $^{2}J_{CP} =$ 8.6 Hz, P–Ph–*C*2/2′), 137.9 (d, $^{1}J_{CP} = 28.8$ Hz, P–Ph–*C*1), 153.1 (s, C–Ph–*C*1), 221.1 (d, $^{2}J_{CP} = 14.7$ Hz, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$), CR$_2$)–*C*O), 221.3 (d, $^{2}J_{CP} = 14.5$ Hz, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$), CR$_2$)–*C*O), 228.0 (d, $^{2}J_{CP} = 6.6$ Hz, (*cis*-CR$_2$, *trans*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$)–*C*O), 229.3 (d, $^{2}J_{CP} = 12.6$ Hz, (*trans*-CR$_2$, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$)–*C*O), 293.4 (d, $^{2}J_{CP} = 12.6$ Hz, Cr=*C*R$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): $\delta = 30.8$ (s). Optical rotation (25°C, toluene): $[\alpha]_{578} = -87°$. MS (EI, ^{52}Cr): *m*/*z* (%): 435 (8) [M$^+$], 407 (4) [(M–CO)$^+$], 379 (4) [(M–2CO)$^+$], 351 (2) [(M–3CO)$^+$], 323 (100) [(M–4CO)$^+$], 218 (8) [(Cr(P(CH$_3$,C$_3$H$_7$,C$_6$H$_5$))$^+$], 166 (17) [P(CH$_3$,C$_3$H$_7$,C$_6$H$_5$)$^+$], 157 (47) [(M–4CO–(P(CH$_3$,C$_3$H$_7$,C$_6$H$_5$))$^+$], 124 (11) [(P(CH$_3$,C$_6$H$_5$)H)$^+$], 77 (5) [C$_6$H$_5^+$], 52 (16) [Cr$^+$]. $C_{21}H_{22}CrNO_4P$ (435.4), HR EI MS (res.: 10 000, 10% Tal-def.): 435.0691 (theor.), 435.0690 ± 3 (exp.).

3.10. Reaction of {(−)(R)-cis-[amino(phenyl)carbene]-tetracarbonyl(methyl(phenyl)-n-propylphosphane)-chromium(0)} (12) with [bis(trimethylsilyl)methylene]-chlorophosphane (2) in the presence of triethylamine

To a stirred solution of 600 mg (1.38 mmol) of {(−)(*R*) - *cis* - [amino(phenyl)carbene]tetracarbonyl-(methyl(phenyl)-*n*-propylphosphane)chromium(0)} (**12**) in 14 ml of dichloromethane 300 mg (1.38 mmol) of [bis(trimethylsilyl)methylene]chlorphosphane (**2**) and 6.6 ml (90 mmol) of triethylamine was added at −60°C and warmed up to room temperature within 17 h. All volatile compounds were removed under reduced pressure (ca. 0.01 mbar). The residue was extracted with 3 × 100 ml of *n*-pentane, filtered and all volatile compounds removed from the filtrate under reduced pressure. The residue was purified by column chromatography (SiO_2, −20°C, *n*-hexane/diethyl ether, 5:1). Complexes **13a**,**b** were thus obtained as a 1:1 mixture, which was slightly impurified by unknown compounds (< 5%). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 1.3$ (d, $^{3}J_{CP} = 2.7$ Hz, Si(*C*H$_3$)$_3$), 1.5 (d, $^{3}J_{CP} = 2.7$ Hz, Si(*C*H$_3$)$_3$), 2.37 (s, Si(*C*H$_3$)$_3$), 2.42 (s, Si(*C*H$_3$)$_3$), 12.4 (dd, $^{1}J_{CP} = 21.4$ Hz, $^{3}J_{CP} = 2.1$ Hz, P–*C*H$_2$–CH$_2$–CH$_3$), 13.8 (dd, $^{1}J_{CP} = 22.2$ Hz, $^{3}J_{CP} = 3.6$ Hz, P–*C*H$_2$–CH$_2$–CH$_3$), 15.6 (d, $^{2}J_{CP} = 12.5$ Hz, P–CH$_2$–*C*H$_2$–CH$_3$), 17.2 (d, $^{3}J_{CP} = 4.4$ Hz, P–CH$_2$–CH$_2$–*C*H$_3$), 29.2 (dd, $^{1}J_{CP} = 27.8$ Hz, $^{3}J_{CP} = 1.7$ Hz, P*C*H), 34.0 (dd, $^{1}J_{CP} = 20.9$ Hz, $^{3}J_{CP} = 2.8$ Hz, P–*C*H$_3$), 35.6 (dd, $^{1}J_{CP} = 21.9$ Hz, $^{3}J_{CP} = 5.5$ Hz, P–*C*H$_3$), 127.5 (d, $^{2}J_{CP} = 14.9$ Hz, Ph), 127.9 (d, $^{3}J_{CP} = 8.4$ Hz, P–Ph), 129.4 (d, $^{2}J_{CP} = 9.4$ Hz, P–Ph), 129.1 (s, Ph), 129.3 (s, Ph), 129.4 (s, Ph), 130.9 (s, Ph), 133.2 (s, Ph), 137.5 (d, $^{1}J_{CP} = 31.7$ Hz, P–Ph), 138.3 (d, $^{1}J_{CP} = 34.0$ Hz, P–Ph), 193.5 (d, $^{1}J_{CP} = 6.0$ Hz, P*C*N), 194.0 (d, $^{1}J_{CP} = 6.0$ Hz, P*C*N), 220.6 (m_c, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$), PCN)–*C*O), 224.3 (m_c, *cis*-(P(CH$_3$, C$_3$H$_7$, C$_6$H$_5$), PCN)

–*C*O), 226.1 (m_c, (*trans*-(P(CH_3, C_3H_7, C_6H_5), *cis*-PCN)–*C*O). $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 26.6$ (d, $^2J_{PP} = 47.4$ Hz, *P*(CH_3, C_3H_7, C_6H_5)), -46.1 (d, $^2J_{PP} = 47.4$ Hz, *P*CN) and 27.2 (d, $^2J_{PP} = 46.4$ Hz, *P*(CH_3, C_3H_7, C_6H_5)), -45.1 (d, $^2J_{PP} = 46.4$ Hz, *P*CN).

4. Supplemenary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147354 for compound **6a** and CCDC no. 147355 for compound **7b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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