Chemistry of 2*H*-Azaphosphirene Complexes, 16[+]

Syntheses, Structures, and Reactions of *C*-Methoxycarbonyl-Functionalized Small- and Medium-Sized P-Heterocycle Complexes

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday

Keywords: Phosphorus heterocycles / 2*H*-Azaphosphirene complexes / Water-soluble P ligands / Tungsten / Cyclizations

Thermal ring-opening of [{2-bis(trimethylsilyl)methyl-3-phenyl-2*H*-azaphosphirene-κ*P*}pentacarbonyltungsten(0)] (**8a**) in the presence of dimethyl acetylenedicarboxylate (DMAD) led to the 2,3-bifunctionalized 1*H*-phosphirene complex **9a** and the 4-phenyl-substituted 2*H*-1,2-azaphosphole complex **10a**, the latter as a by-product. If a small amount of benzonitrile was added, complex **10a** was obtained as the main product, along with a small amount of the decomplexed 2*H*-1,2-azaphosphole **11**, which could not be isolated. Reaction of complex **10a** with elemental sulfur furnished the corresponding P^V sulfide **13**. When the ring-opening of complex **8a** was performed in the presence of two equivalents of DMAD and two equivalents of dimethyl cyanamide, we obtained the 4-dimethylamino-substituted 2*H*-1,2-azaphosphole complex **10b**, together with the diastereomeric Δ^3-1,3,2-oxazaphospholene complexes **14a**,**b**. On reaction of [{2-pentamethylcyclopentadienyl-3-phenyl-2*H*-azaphosphirene-κ*P*}pentacarbonyltungsten(0)] (**8b**) and DMAD in toluene, the corresponding 1*H*-phosphirene complex **9b** was only formed as a transient species and the *P*-coordinated P,C-cage compound **15** was the final product. Using benzonitrile as solvent, the 4-phenyl-substituted 2*H*-1,2-azaphosphole complex **10c** was obtained, together with the 7-aza-1-phosphanorbornadiene complex **16**, the latter through partial decomposition of **10c** coupled with rearrangement and a Diels–Alder reaction; the ratio **10c/16** was found to depend strongly on the molar ratio of complex **8b** to DMAD. A cycloaddition reaction of the 2,3-bifunctionalized 1*H*-phosphirene complex **9a** with 2,3-dimethylbutadiene furnished the bicyclic phosphirane complex **19**, along with a small amount of the noncoordinated bicyclic phosphirane **20**. Reaction of complex **9a** with diethylamine yielded the phosphirane complex **21** as a 1,2-addition product, the diorganophosphane complex **22** through ring-opening of **9a**, and the 3,4-functionalized 1,2-dihydro-1-phosphet-2-one complex **23** through an unprecedented ring-expansion reaction; the products **21**, **22**, **23** were formed in a ratio of ca. 1:1:1. The structures of the 1*H*-phosphirene complex **9a**, the 4-dimethylamino-substituted 2*H*-1,2-azaphosphole complex **10b**, the bicyclic phosphirane complex **19**, the phosphirane complex **21**, and the 1,2-dihydro-1-phosphet-2-one complex **23** have been determined by single-crystal X-ray diffraction analysis.

Introduction

The success of biphasic homogeneous catalytic reactions currently being achieved[2] using transition metals with triorganophosphane ligands has led to a great demand for ligands with enhanced water solubility.[3] Various concepts have been developed to satisfy this prerequisite, e.g. phosphanes bearing hydroxy-functionalized organic substituents such as the well-known tris(hydroxymethyl)phosphane **1**,[4] phosphanes bearing sodium *p*-phenylsulfonate groups as in triphenylphosphane trisodium sulfonate (TPPTS) **2**,[5] or sodium carboxylate groups as in **3**.[6] Moreover, water-soluble derivatives of P-heterocycles such as the 1-phosphanorbornadiene NORBOS **4**[7] have been successfully employed in catalytic processes, while others, such as the 1-phosphanorbornene **5**, seem likely to follow suit.[8] Apart from a very recent report on the catalytic use of complexes with polycyclic phosphane ligands having a phosphirane subunit,[9] knowledge of applications of small- and medium-sized P-heterocycle complexes as catalysts is still very limited. Equally apparent is the fact that unsaturated P^{III} heterocycles of different ring size with one or more *C*-methoxycarbonyl groups attached to the ring system are accessible only with difficulty,[10] although such systems are promising precursors for the respective carboxylic acid derivatives. This is in contrast to the situation for P^V phospholes such as **6**, which is accessible by reaction of trimethyl phosphite with dimethyl acetylenedicarboxylate (DMAD).[11] Unfortunately, the corresponding P^{III} derivative is still unknown. Apart from reactions of triorgano-

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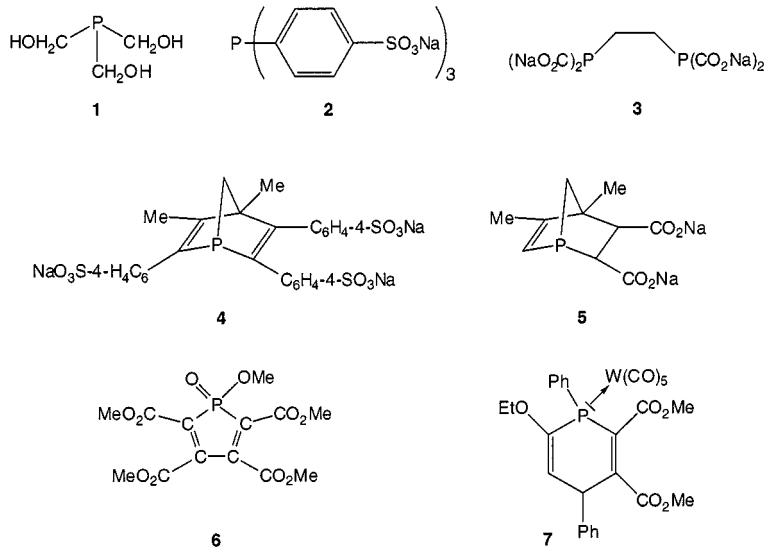


Scheme 1. Water-soluble phosphanes (**1**−**5**) and phosphorus heterocycles bearing methoxycarbonyl groups (**6**,**7**)

phosphanes with DMAD, which are often unselective,[12] some more useful reactions exist, relying on DMAD as trapping reagent and leading, e.g., to complexes such as **7** with six-membered P^{III} heterocyclic ring systems.[13]

In view of the aforementioned factors, and bearing in mind that ring size variations could be a valuable additional instrument for tuning the attributes of the ligands, we decided to seek new routes to small- and medium-sized P-heterocycle complexes having *C*-methoxycarbonyl groups attached to the ring system. These, in turn, could give rise to the uncoordinated P-heterocycles by applying standard decomplexing methodologies.

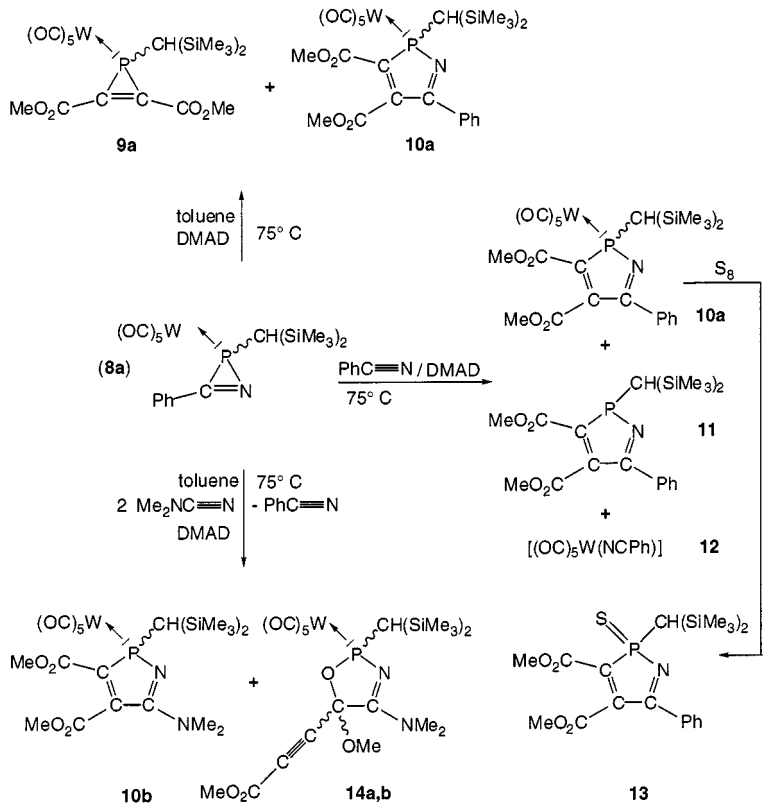
Recently, we demonstrated that ring-opening reactions of 2*H*-azaphosphirene complexes offer access to a wide variety of small- and medium-sized P-heterocycle complexes.[14−16] We also briefly reported on the syntheses of mono-,[17][18] bi-, and polycyclic P-heterocycles[1] with *C*-methoxycarbonyl-functionalized ring systems, using this methodology with dimethyl acetylenedicarboxylate (DMAD) as the trapping reagent.

In this paper, we show that the general reaction course to such *C*-methoxycarbonyl-functionalized heterocycle complexes depends largely on the solvent employed, and that the formation of the final products depends on the phosphorus substituent. Additionally, preliminary investigations of the reactivity of a 2,3-bifunctionalized 1*H*-phosphirene complex towards 2,3-dimethylbutadiene and diethylamine are presented. The latter reaction demonstrates how initial nucleophilic attack on the 1*H*-phosphirene ring system can give rise to three different reaction pathways, namely 1,2-addition to the C,C-double bond, ring-opening, and ring-expansion. The latter represents the first access to a ring-functionalized 1,2-dihydro-1-phosphet-2-one complex.

Results

A. Syntheses of *C*-Methoxycarbonyl-Functionalized Mono-, Bi-, and Polycyclic P-Heterocycles by Ring Opening of 2*H*-Azaphosphirene Complexes and Subsequent Trapping Reactions with DMAD

Apart from P^{V} phosphole derivatives such as **6**[11] and related compounds,[12] little is known about five-membered unsaturated P-heterocycles with one or more carboxylate groups bonded to the ring system.[13] Therefore, we became interested in developing a new synthetic methodology leading to such heterocycles. As we have already described in brief, thermally induced ring-opening of the 2*H*-azaphosphirene complex **8a**[19] in toluene and in the presence of DMAD leads to the 1*H*-phosphirene complex **9a** along with minor amounts of the 2*H*-1,2-azaphosphole complex **10a**.[17,18a] The yield of complex **10a** is significantly increased if the reaction is carried out in a mixture of toluene and benzonitrile. Under these reaction conditions, complex **10a** undergoes partial decomplexation leading to the benzonitrile−tungsten complex **12** and two other uncharacterized products exhibiting ^{31}P-NMR resonances at $\delta = 85.5$ and $\delta = 42.1$. Because of the $\Delta\delta$ value of the order of 25,[20] the former resonance would seem to be indicative of the 2*H*-1,2-azaphosphole **11**. Upon heating in benzonitrile with elemental sulfur, complex **10a** reacted selectively to give the 2*H*-1,2-azaphosphole *P*-sulfide **13**. When **8a** was heated in toluene in the presence of DMAD and two equivalents of dimethyl cyanamide, the reaction course was significantly altered; under these conditions the 2*H*-1,2-azaphosphole complex **10b**, along with the two diastereomeric Δ^3-1,3,2-oxazaphospholene complexes **14a**, **b** were formed.[18b] In this case, the transient formation of the nitrilium betaine-type complex



Scheme 2. Thermal ring-opening of 2*H*-azaphosphirene tungsten complex **8a** under various conditions in the presence of DMAD

$\{Me_2NCNP[CH(SiMe_3)_2]W(CO)_5\}$ via transylidation of **17a** seems to be operative (cf. Scheme 4).

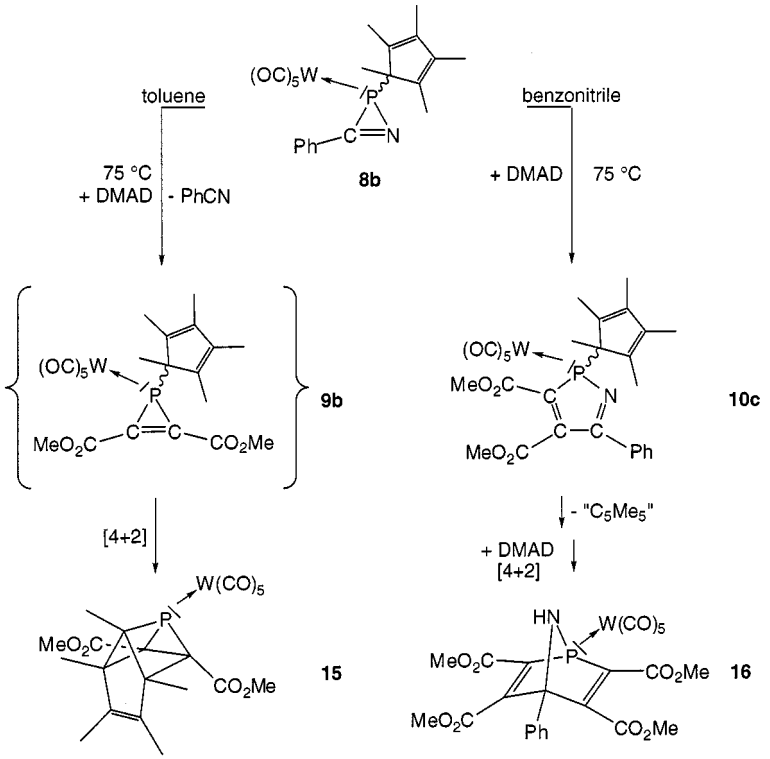
That the reaction course depends not only on the solvent, but also on the phosphorus substituent, was impressively demonstrated by investigations of the ring-opening of the 2*H*-azaphosphirene complex **8b**[20] in toluene and benzonitrile, both with DMAD as the trapping reagent (Scheme 3). In the first case, complex **15** was obtained as final product, whereas in the second case, the 7-aza-1-phosphanorbornadiene complex **16** was obtained.[1] The thermal instabilities of the transiently formed 1*H*-phosphirene complex **9b** and the 2*H*-1,2-azaphosphole complex **10c** were quite unexpected. Whereas the existence of the former is merely a plausible assumption, complex **10c** could be obtained using a different stoichiometry.

An explanation of these reaction pathways should take into account the roles of $[PhCNP(C_5Me_5)W(CO)_5]$ (**17c**) and the terminal phosphanediyl complex $[(OC)_5WPC_5Me_5]$ (**18b**) as intermediates (cf. Scheme 4). The fate of such intermediates seems to depend mainly on the solvent used for the reactions. The 1*H*-phosphirene complex **9b**, formed by [2+1] cycloaddition of **18b** to DMAD, undergoes rapid intramolecular [4+2] cycloaddition leading to the tungsten-coordinated P,C-cage compound **15**. In benzonitrile, complex **17b** reacts with the C,C π-system of DMAD to form the 2*H*-1,2-azaphosphole complex **10c** through a [3+2] cycloaddition. The next step could be an exocyclic P−C bond cleavage in complex **10c** with subsequent proton addition (the origin of which is still under investigation), to give a short-lived 1*H*-1,2-azaphosphole complex. This could then undergo rapid [4+2] cycloaddition with a second equivalent of DMAD, thereby yielding the 7-aza-1-phosphanorbornadiene complex **16**. Such a hypothesis of the intermediacy of a short-lived 1*H*-1,2-azaphosphole complex is further supported by an earlier observation by Mathey and co-workers that transiently formed 2*H*-phospholes undergo rapid [4+2] cycloaddition reactions leading to 1-phosphanorbornadienes[22] or 1-phosphanorbornenes[23] depending on the trapping reagent used.

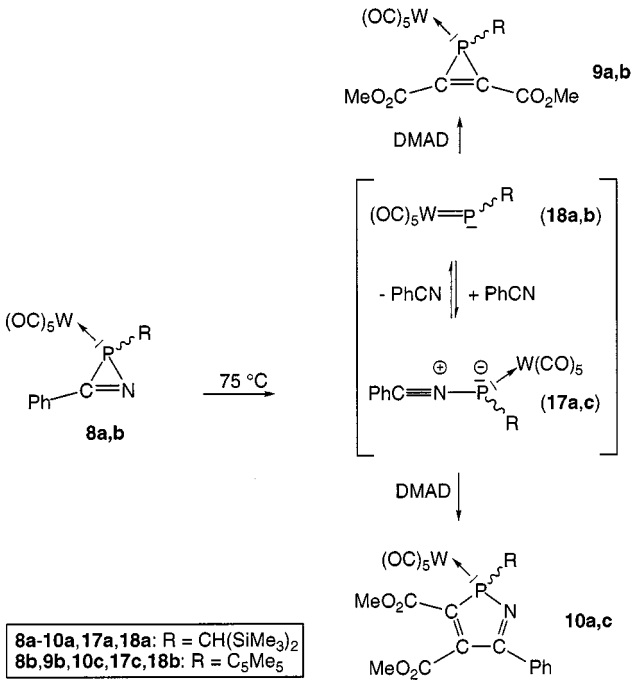
The main aspects of the aforementioned ring-opening reactions can be summarized as shown in Scheme 4. In all cases, the first step seems to be the transient formation of nitrilium phosphane−ylide complexes **17a**, **c**, which can decompose to give benzonitrile and the terminal phosphanediyl complexes **18a**, **b**. In toluene, complexes **18a**, **b** undergo subsequent [2+1] cycloaddition reactions to give complexes **9a**,**b**. In benzonitrile, however, reversion to the nitrilium phosphane−ylide complexes **17a**, **c** occurs preferentially, which show a tendency to undergo [3+2] cycloaddition reactions leading to the formation of 2*H*-1,2-azaphosphole complexes **10a**, **c**.

B. Cycloaddition, 1,2-Addition, Ring-Opening, and Ring-Expansion Reactions of *C*,*C*′-Methylcarboxylate-Functionalized 1*H*-Phosphirene Complex 9a

It has been demonstrated by Mathey and co-workers that a monofunctionalized *C*-carboxylate 1*H*-phosphirene com-



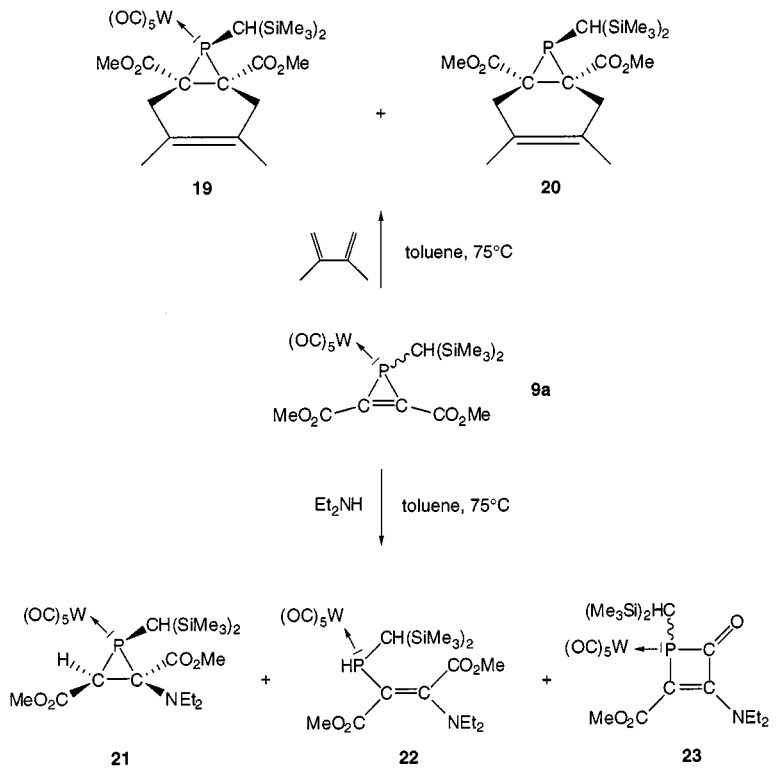
Scheme 3. Thermal ring-opening of 2*H*-azaphosphirene tungsten complex **8b** in various solvents in the presence of DMAD



Scheme 4. Proposed explanation for the generation and reactions of transiently formed nitrilium phosphane−ylide complexes

plex may react either with 1,3-dimethylbutadiene to give a bicyclic phosphirane complex through [4+2] cycloaddition, or with a secondary amine such as morpholine to yield a secondary vinylphosphane complex through ring-opening of the phosphirane ring.[24] These observations prompted us to investigate the reactivity of the bifunctionalized 1*H*-phosphirene complex **9a** towards 1,3-dimethylbutadiene and diethylamine. At 75°C, complex **9a** underwent a diastereoselective reaction with 1,3-dimethylbutadiene to give the [4+2] cycloadduct **19** together with a small amount of the bicyclic phosphirane **20**, the latter probably arising from partial decomplexation of complex **19** (Scheme 5). In both compounds, the six-membered ring moiety and the bis(trimethylsilyl)methyl substituent reside on the same side of the phosphirane ring plane, implying that the cycloaddition reaction is sterically controlled. In contrast to this relatively unsurprising reaction, the outcome of the reaction of complex **9a** with diethylamine at ambient temperature was unexpected: three phosphorus-containing products in a ratio of ca. 1:1:1 were formed, namely the 1,2-addition product **21**, the secondary vinylphosphane complex **22**, and the 1,2-dihydro-1-phosphet-2-one complex **23** (Scheme 5). In comparison to the other example mentioned above (PR = PPh),[24] the greater steric demand of the substituent at phosphorus in this case seems to increase the lifetime of the various intermediates, thus making possible three competing reaction pathways. Although the first 1,2-dihydro-1-phosphet-2-one complex[25] was also obtained by means of an insertion reaction (of carbon monoxide), the present example represents an unprecedented ring-expansion reaction in 1*H*-phosphirene chemistry.[26] A related ring-expansion has been reported for the reaction of a cyclopropene carboxylic acid derivative with $SOCl_2$.[27]

This reaction of complex **9a** can be rationalized by assuming the initial step to be a nucleophilic attack of the diethylamine nitrogen lone-pair on one carbon atom of the 1*H*-phosphirene ring, leading to the zwitterionic phosphir-



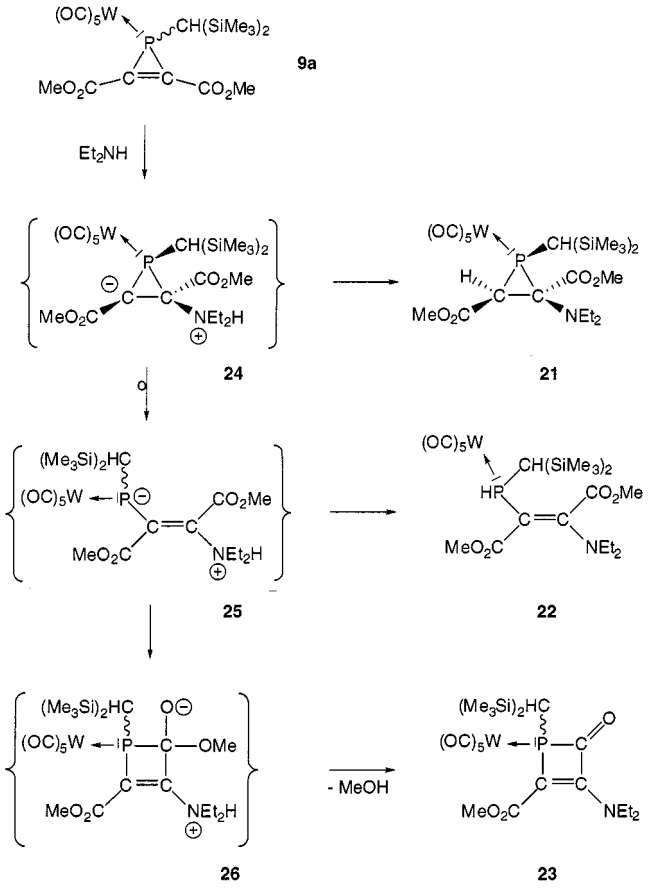
Scheme 5. Reactions of 1*H*-phosphirene tungsten complex **9a** with dimethylbutadiene and with diethylamine

ane complex **24**, which can either give rise to the 1,2-addition product **21** or undergo ring-opening to give **25** (Scheme 6). The latter can add a proton to furnish **22** or undergo ring-closure to yield **26** through an intramolecular attack of the phosphorus anion on the methoxycarbonyl carbon atom; the transient complex **26** subsequently eliminates methanol to give the 1,2-dihydro-1-phosphet-2-one complex **23**. The first step of this reaction cascade, i.e. the nucleophilic attack, also proceeds under steric control, leading exclusively to the phosphirane complex **21** with the pentacarbonyltungsten and diethylamino groups in a *trans* arrangement. The stereochemistry of the C−C double bond in **22** has not been determined but is expected to be *trans* (cf. ref.[25]). It should also be noted that no transformation of complex **21** into **22** (and vice versa) via prototropic rearrangement was observed.

C. Discussion of Selected NMR-Spectroscopic Data

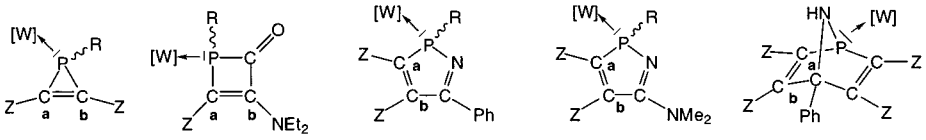
All of the reported complexes have been characterized by heteronuclear NMR experiments, IR spectroscopy, and mass spectrometry (see Experimental Section). Selected NMR data of the complexes are collected in Tables 1 and 2 and are discussed here; for X-ray data see Section D, Tables 1−3, and the Experimental Section.

A comparison of selected NMR data of the variously sized heterocycles of complexes **9a**, **10a**, **b**, **16**, and **23** (Table 1) shows, in all cases, significant resonances of the carbon nuclei of the C−C double bond units. Thus, the resonances of the carbons directly bonded to phosphorus appear at



Scheme 6. Proposed reaction course for the formation of complexes **21**−**23**

Table 1. Selected NMR [only absolute values of J(P,C) are given] and X-ray data of complexes **9a**, **23**, **10a**, **b**, and **16** (in order of ring-size); [W] = $W(CO)_5$, R = $CH(SiMe_3)_2$ and Z = CO_2Me; the X_3 plane in PR_3 units is defined by the three X atoms directly bonded to phosphorus

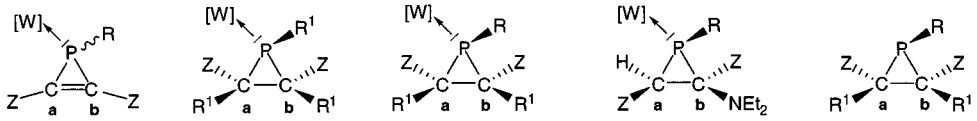


	9a	**23**	**10a**	**10b**	**16**
δ^{13}C-NMR [ppm]	C_a/C_b:	C_a/C_b:	C_a: 142.7 (25.9)	C_a: 139.2 (21.2)	C_a: 148.5 (13.3)
(J(P,C) [Hz])	143.2 (17.0)	119.4 (41.6)	C_b: 162.0 (1.4)	C_b: 161.8 (7.3)	C_b: 162.3 (16.3)
δ^{13}C-NMR [ppm]	C_a-CO_2Me:	C_a-CO_2Me:	C_a-CO_2Me:	C_a-CO_2Me:	C_a-CO_2Me:
(J(P,C) [Hz])	160.6 (8.5)	165.0 (14.5)	167.2 (11.5)	163.3 (7.3)	166.7 (2.1)
δ^{13}C-NMR [ppm]	C_b-CO_2Me:	C_b-CO_2Me:	C_b-CO_2Me:	C_b-CO_2Me:	C_b-CO_2Me:
(J(P,C) [Hz])	-	-	165.1 (14.2)	166.1 (14.6)	164.4 (9.7)
δ^{31}P-NMR [ppm]	-74.7	71.7	102.8	85.6	63.0
(^1J(W,P) [Hz])	(281.1)	(241.2)	(237.9)	(249.7)	(294.8)
P-atom/X_3-plane distance (Å)	0.9562	0.8737	0.785	0.7438	1.034
$\Sigma\,°(P_{PR3})(\pm2)$	265	293	306	310	272
d P-W (Å)	2.4749 (11)	2.5351 (13)	2.5045 (12)	2.5237 (11)	2.4525 (13)

higher field, while for the vicinal carbon atoms the opposite is true. All of the C_a carbons of **9a**, **10a**, **b**, **16**, and **23** exhibit absolute values of the carbon−phosphorus coupling constants in excess of 17 Hz, which depend specifically on the different scalar couplings (**9a** and **23**: $|^1J + {}^2J|$; **10a**, **b** and **16**: $|^1J + {}^4J|$). According to the ring size, the situation concerning the C_b carbons of **10a**, **b** and **16** is quite different from that in **23**; the former have absolute coupling constant values between 1.1 and 5.3 Hz ($|^2J + {}^3J|$), whereas for the latter the value is 56.2 Hz ($|^2J + {}^2J|$). Because of the approximately constant substitution pattern at phosphorus [with the exception of complex **16**, which has no $CH(SiMe_3)_2$ group] and the only slight variations at the other neighbouring atoms, the influence of the ring size on the phosphorus resonance can be delineated. The fact that the phosphorus nucleus becomes deshielded with increasing ring size has been widely documented for other P-heterocycles with different substitution patterns.[28] The magnitudes of the phosphorus−tungsten coupling constants show a marked dependence on the electronegativities of the phosphorus substituents[29] and, more surprisingly, on the ring size as well.

The 7-aza-1-phosphanorbornadiene complex **16** exhibits a phosphorus resonance δ = 63.0 with a large phosphorus−tungsten coupling constant of 294.8 Hz, indicating that the nitrogen fragment is directly bonded to the phosphorus. Compared to [pentacarbonyl(1,3,4-triphenyl-1,2-dihydro-1-phosphet-2-one)tungsten(0)][25a] [**27**; δ(^{31}P) = 86.9, ^1J(P,W) = 231.9 Hz], complex **23** shows similar ^{31}P-NMR data [δ = 71.7, ^1J(P,W) = 241.2 Hz]. Nevertheless, the π-donation of the diethylamino group is quite apparent throughout the ^{13}C-NMR resonances of the four-membered ring {δ = 119.4, [$^{(1+3)}J$(P,C) = 41.6 Hz, P*C*CO_2Me], 152.9 [$^{(2+2)}J$(P,C) = 56.2 Hz; PC*C*NEt_2]}, although the P*C*O carbon resonance seems to be largely unaffected {δ = 198.7, [$^{(1+3)}J$(P,C) = 35.7 Hz]; cf. **27:** δ = 190.72, [$^{(1+3)}J$(P,C) = 34.2 Hz]}. A comparison of the NMR data of the five-membered heterocycles **10a**, **b** and **13** reveals some noteworthy details. The phosphorus nuclei of **10a**, **b** and **13** exhibit resonances in the range δ = 85.6 to 103, whereas that in **10c** is significantly more deshielded (δ = 119.6). In these 2*H*-1,2-azaphosphole derivatives, the magnitudes of the phosphorus−tungsten coupling constants show a marked dependence on the nature of the substituents at phosphorus and the C^5-carbon; those in **10b** (J = 249.7 Hz) and **10c** (J = 248.1 Hz) are thus considerably greater than that in **10a** (237.9 Hz). Considering further the phosphorus−tungsten coupling constants, the effect of the oxygen atom directly bonded to phosphorus in the diastereoisomeric Δ^3-1,3,2-oxazaphospholene complexes **14a**, **b** is dominant (J = 303.1 and 305.9 Hz). Astonishingly, the imino carbon resonances of **10a**−**c**, **13**, and **14a**, **b** are hardly affected by variations in the bonding situation at the phosphorus atom. A comparison of selected NMR data of the three-membered heterocycle complexes having a mono- or polycyclic ring system (Table 2) shows that the phosphirane complexes **15**, **19**, and **21** exhibit phosphorus resonances in the same region as the 1*H*-phosphirene complex **9a**, which is not unexpected.[30] Complexes **9a**, **19**, and **21** show only slightly different phosphorus−tungsten coupling constants, whereas that of complex **15** is markedly smaller. Moreover, the nuclei of the three-membered ring of **15** are more deshielded. Taken together, the above results point to the dominating effect of the electronegativity of the phos-

Table 2. Selected NMR [only absolute values of *J*(P,C) are given] and X-ray data of complexes **9a, 15**, **19** and **21**; [W] = $W(CO)_5$, R = $CH(SiMe_3)_2$, R^1 = organic fragment and Z = CO_2Me; #: not determined; the X_3 plane in PR_3 units is defined by the three X atoms directly bonded to phosphorus



	9a	**15**	**19**	**21**	**20**
δ^{13}C-NMR [ppm]	C_a/C_b:	C_a/C_b:	C_a/C_b:	C_a: 41.4 (14.2)	C_a/C_b:
(J(P,C) [Hz])	143.2 (17.0)	70.4 (5.2)	40.2 (18.1)	C_b: 66.6 (16.0)	41.5 (47.7)
δ^{13}C-NMR [ppm]	C_a/C_b-CO_2Me:	C_a/C_b-CO_2Me:	C_a/C_b-CO_2Me:	C_a-CO_2Me: 167.1 (s)	C_a/C_b-CO_2Me:
(J(P,C) [Hz])	160.6 (8.5)	168.7 (s)	171.2 (3.7)	C_b-CO_2Me: 172.2 (s)	173.3 (14.2)
δ^{31}P-NMR [ppm]	-74.7	-67.2	-87.1	-81.1	-105.8
(^{1}J(W,P) [Hz])	(281.1)	(242.0)	(269.9)	(274.7)	(s)
P-atom/X_3-plane distance (Å)	0.9562	1.448	1.0131	1.0225	#
Σ °(P_{PR3}))(±2)	265	195	264	263	#
d P-W (Å)	2.4749 (11)	2.4569 (8)	2.5539 (7)	2.5351 (11)	#

phorus substituents (especially with regard to the hybridization of the carbon atoms) on the phosphorus−tungsten coupling constants. In this context, the very small bond angle sums of these complexes are of particular interest (see Section D).

D. Discussion of Selected X-ray Structural Data

The molecular structures of the complexes **9a**, **10b**, **19**, **21**, and **23** were confirmed in the solid state by X-ray crystallography (Figures 1−5); further details of the crystal data and structure refinement are given in Table 3.[31] Comparison of the structure of complex **9a** (Figure 1) with that of other 1*H*-phosphirene complexes[17b] having the same phosphorus fragment, [{$(Me_3Si)_2HCP$}$W(CO)_5$], reveals slightly shortened endo- and exocyclic carbon−carbon and phosphorus−carbon distances and a significantly shortened tungsten−phosphorus distance of 2.4749(11) Å (vs. ca. 2.50 Å)[17b] as the most interesting features. The latter is combined with a widened W−P−C(12) angle of 121.27(24)° (vs. ca. 118−119.5°)[17b] and an increased W−C(5) distance [2.001(5) Å] of the *trans* CO ligand, thus indicating weaker W−C and stronger W−P π-back bonding. The fact that there are no extended P−C distances (bonds) within the *P*-ligand is quite remarkable and is inconsistent with the current π-acceptor orbital bonding model, for which a substantial participation of σ*-orbitals has been proposed.[32][33]

For complex **10b**, the asymmetric unit contains two independent molecules, which are not significantly different from one another. The structure consists of discrete molecules with no unusual intermolecular distances. The heterocyclic ring of complex **10b** (Figure 2) is approximately planar, with the dimethylamino group subtending an interplanar angle to the five-membered ring of 11.4°. Apart

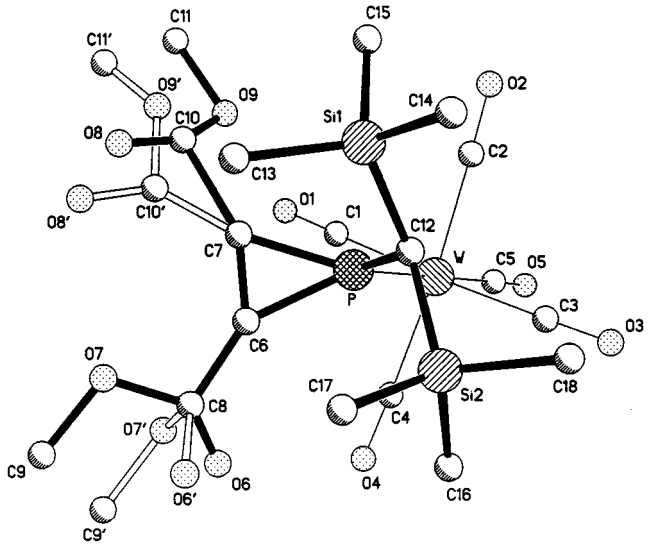


Figure 1. Molecular structure of **9a** in the crystal (both positions of the two disordered methoxycarbonyl groups are shown; hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: W−C(5) 2.001(5), W−C(4) 2.054(6), W−P 2.4749(11), P−C(12) 1.808(4), P−C(6) 1.791(5), P−C(7) 1.795(5), C(6)−C(7) 1.294(7); W−P−C(12) 121.27(14), C(6)−P−C(7) 42.3(2), C(6)−C(7)−P 68.7(3), C(7)−C(6)−P 69.0(3)

from localized endocyclic nitrogen−carbon and carbon−carbon double-bond lengths of 1.312(5) and 1.338(6) Å, respectively, the ring also has a substantially shortened exocyclic nitrogen−carbon bond length of 1.346(5) Å (cf. ref.[34]). Together with the angle sum of 360° at the N(2) nitrogen atom, this provides evidence for a $p_\pi-p_\pi$ electron interaction of the nitrogen lone-pair and the C−N π-bond. It is also noteworthy that this also affects the W−P distance, which amounts to 2.5237(11) Å in **10b** and 2.505(12) Å in **10a**.[18a]

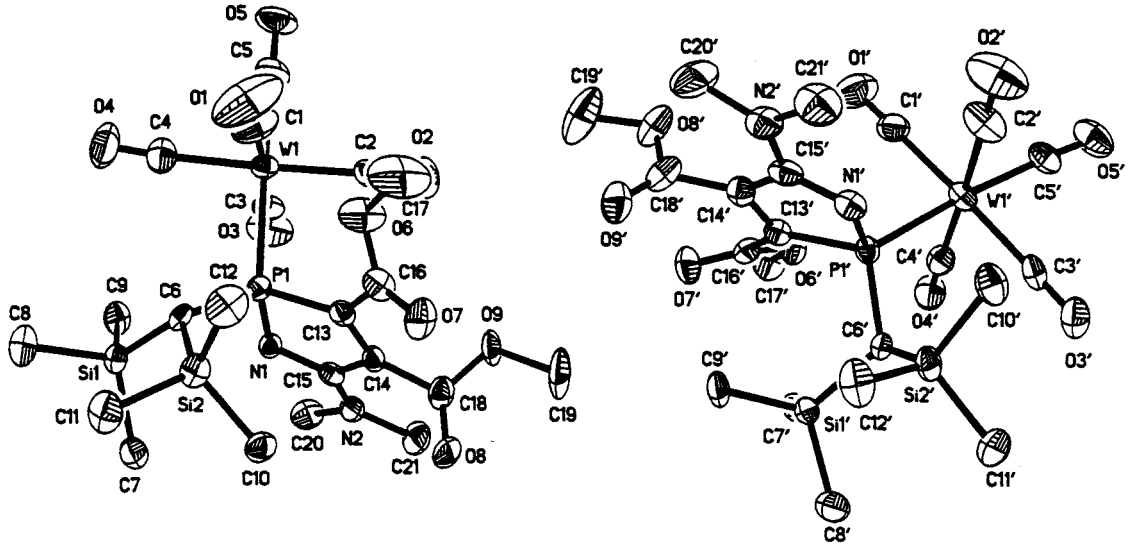


Figure 2. Two independent molecules of **10b** in the crystal (only one data set is given; ellipsoids represent 30% probability levels, hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: W(1)−C(5) 1.999(5), W(1)−C(1) 2.019(6), W(1)−C(2) 2.053(5), W(1)−P(1) 2.5237(11), P(1)−C(6) 1.836(4), P(1)−N(1) 1.674(4), N(1)−C(15) 1.312(5), N(2)−C(15) 1.346(5), C(15)−C(14) 1.492(6), C(14)−C(18) 1.338(6), C(13)−P(1) 1.839(4); W(1)−P−C(6) 119.26(14), C(13)−P(1)−N(1) 92.51(19), P(1)−N(1)−C(15) 112.1(3), N(1)−C(15)−C(14) 114.9(4), C(15)−C(14)−C(13) 111.6(4), C(14)−C(13)−P(1) 108.0(3)

Comparison of the structures of complexes **19** and **21** (Figures 3 and 4) with that of **9a** shows that the former have both significantly lengthened endocyclic bond lengths and slightly widened W−P−C(6) angles of 122.62(9) and 124.10(10)°, respectively. Detailed comparison between **19** and **21** cannot be made as the $CH(SiMe_3)_2$ groups adopt opposite orientations with respect to the $W(CO)_5$ fragment, which is very unusual in such P-heterocycle complexes. All three complexes have comparable angle sums [$\Sigma°(P_{PR3})$ values, Table 2] of ca. 264°, but distinctly different W−P distances. This finding most probably stems from different cone angles[35] of these P-ligands; unfortunately, much less data is currently available for such P-heterocycle ligands than for acyclic triorganophosphane ligands.[32][33] Comparing these findings to those for complex **15**,[1] for which a smaller bond angle sum [$\Sigma°(P_{PR3})$ value] and W−P distance were observed [ca. 195° and 2.4569(8) Å], this situation seemingly results from a reduction in the steric strain and an increase in the pyramidalization of the PR_3 ligand, as shown by the increasing distance of the phosphorus atom from the plane defined by the α-atoms of the three substituents (cf. Tables 2 and 3).[32][33] The latter aspect in particular merits further study. Although complexes **15**, **19**, **21** (and even **9a**) are quite similar, it is noteworthy that there is no simple correlation between X-ray structural parameters such as the $\Sigma°(P_{PR3})$ value and the W−P distance on one hand, and an NMR parameter such as the magnitude of the phosphorus−tungsten coupling constant on the other (cf. Table 2).

The molecular structure of the 1,2-dihydro-1-phosphet-2-one complex **23** (Figure 5) is characterized by an unsymmetrical, planar, four-membered ring system. Compared to the structure of complex **27**,[25a] the carbon−carbon bond length of the double bond unit is longer in **23** [1.399(5) vs. 1.36(1) Å (**27**)]. Moreover, it forms part of a

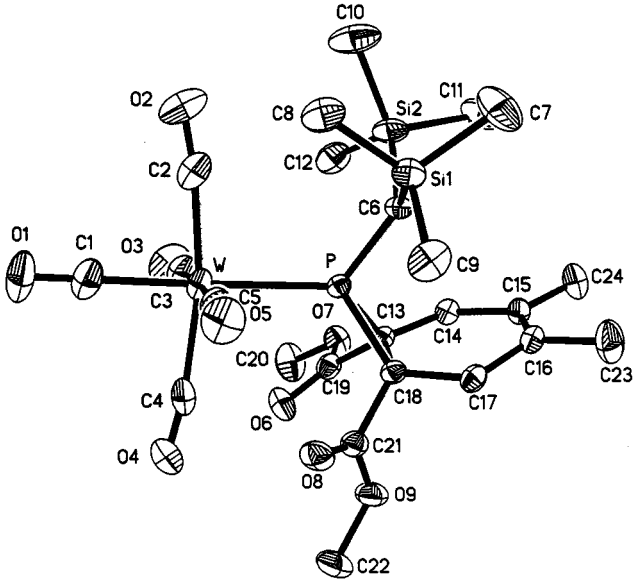


Figure 3. Molecular structure of **19** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: W−C(1) 1.982(3), W−C(4) 2.063(3), W−C(5) 2.035(3), W−P 2.5539(7), P−C(6) 1.822(3), P−C(13) 1.908(3), P−C(18) 1.846(3), C(13)−C(18) 1.533(3), C(13)−C(19) 1.491(4), C(18)−C(21) 1.514(3); C(5)−W−P 87.95(8), C(4)−W−P 96.47(8), W−P−C(6) 122.62(9), C(13)−P−C(18) 48.18(10), P−C(13)−C(18) 63.78(13), C(13)−C(18)−P 68.03(13)

delocalized π-system consisting of the planar N−C(16)−C(13)−C(14) subunit [$\Sigma°(N_{NR3})$ value: 360; interplanar angle between the plane C(17)−N−C(19) and that of the four-membered ring 3.8°] and the planar N−C(16)−C(21)−O(8) subunit, which has significantly shortened exocyclic single bond lengths (cf. ref.[34]), [N−C(16) 1.328(5) Å and C(13)−C(14) 1.458(5) Å] for the

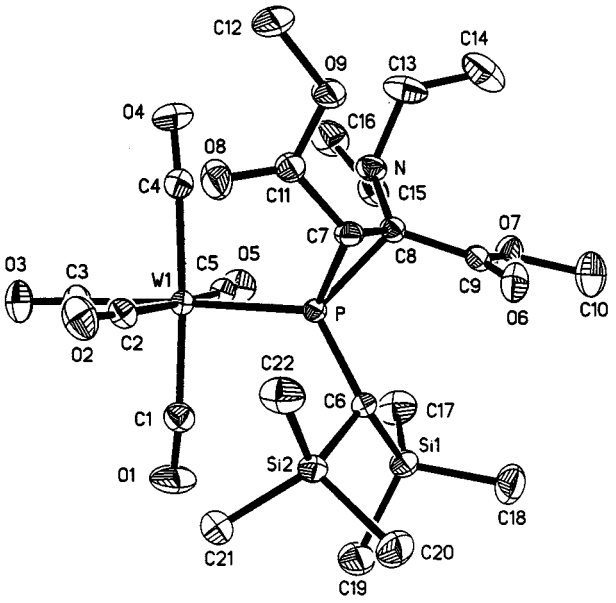


Figure 4. Molecular structure of **21** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: W(1)−C(3) 1.987(3), W(1)−C(4) 2.057(3), W(1)−P 2.5351(11), P−C(6) 1.819(3), P−C(7) 1.816(3), P−C(8) 1.903(3), C(7)−C(8) 1.542(4), C(7)−C(11) 1.505(4), C(8)−C(9) 1.511(4), C(8)−N 143.1(4); C(2)−W(1)−P 88.43(9), C(5)−W(1)−P 98.29(9), W(1)−P−C(6) 124.10(10), C(7)−P−C(8) 48.91(12), P−C(7)−C(8) 68.5(2), C(7)−C(8)−P 62.60(14)

former and an increased carbon−oxygen distance for the latter [C(21)−O(8) 1.197(5) Å; **27**: 1.16(1) Å].

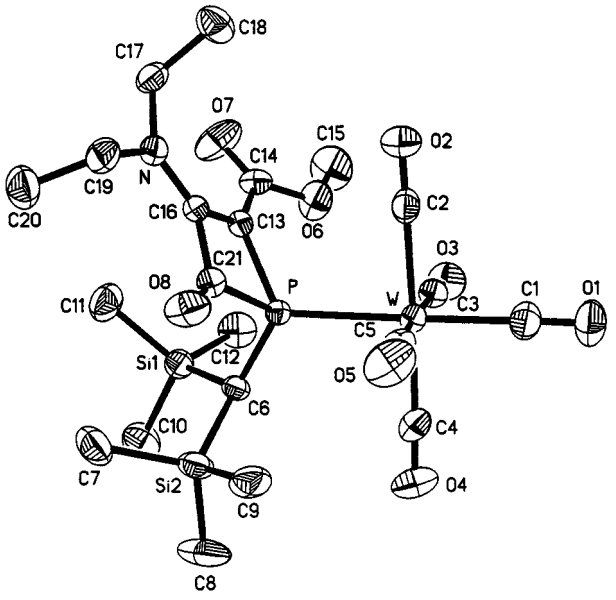


Figure 5. Molecular structure of **23** in the crystal (ellipsoids represent 50% probability levels, hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: W−C(1) 2.012(4), W−C(2) 2.044(4), W−P 2.4995(1), P−C(6) 1.836(4), P−C(13) 1.834(4), C(13)−C(16) 1.399(5), C(16)−C(21) 1.511(5), P−C(21) 1.880(4), C(13)−C(14) 1.458(5), N−C(16) 1.328(5), C(21)−O(8) 1.197(5); C(2)−W−P 85.91(11), C(3)−W(1)−P 92.57(11), W−P−C(6) 119.34(12), C(13)−P−C(21) 72.0(2), P−C(21)−C(16) 92.5(2), C(21)−C(16)−C(13) 97.2(3), C(16)−C(13)−P 98.3(2)

Experimental Section

General Procedures: All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen, 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 ^{1}H; 50.3 MHz for ^{13}C; 81.0 MHz for ^{31}P) with [D]chloroform and [D_6]benzene as solvents and internal standards; shifts are given relative to ext. tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). − Mass spectra were recorded on a Finnigan MAT 8430 (70 eV); apart from the *m*/*z* values of the molecular ions, only those peaks having intensities > 20% of the base-peak are listed. − Infrared spectra were recorded on a Biorad FT-IR 165 spectrometer (selected data given). − Melting points were measured on a Büchi 535 capillary apparatus. − Elemental analyses were performed using a Carlo Erba analytical gas chromatograph. − The κ*P* notation in the nomenclature is intended to differentiate between *P*- and *N*-coordination of the relevant heterocycle to the metal.

Pentacarbonyl[2-bis(trimethylsilyl)methyl-3,4-bis(methoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (10a): To a solution of the 2*H*-azaphosphirene tungsten complex **8a** (1.5 g, 2.4 mmol) in toluene (7.5 mL) and benzonitrile (2 mL) was added dimethyl acetylenedicarboxylate (0.6 mL, 5 mmol) and the mixture was heated at 75°C for 1.5 h under slow stirring. The solvent was then removed in vacuo and the product was separated by low-temperature column chromatography (SiO_2, −20°C, 10 × 4 cm, hexane/diethyl ether, 90:10). Evaporation of the solvent from the second fraction yielded **10a** as dark-red crystals. Yield: 680 mg (43%). − M.p. 121°C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 0.39 (s, 9 H, $SiMe_3$), 1.35 [d, ^{2}J(P,H) = 2.4 Hz, 1 H, C*H*($SiMe_3$)$_2$], 3.87 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 7.50 (m_c, 3 H, C$H_{arom.}$), 7.79 (m_c, 2 H, C$H_{arom.}$). − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 2.6 [d, ^{3}J(P,C) = 1.9 Hz, $SiMe_3$], 3.2 [d, ^{3}J(P,C) = 2.4 Hz, $SiMe_3$], 18.9 [s, *C*H($SiMe_3$)$_2$], 53.0 (s, O*C*H$_3$), 53.2 (s, O*C*H$_3$), 128.4 (s, Ph), 128.8 (s, Ph), 131.7 (s, Ph), 134.4 [d, ^{3}J(P,C) = 16.6 Hz, Ph], 142.7 [d, ^{1}J(P,C) = 25.9 Hz, P*C*C], 162.0 [d, $^{(2+3)}J$(P,C) = 1.4 Hz, PC*C*], 162.7 [d, ^{3}J(P,C) = 13.1 Hz, *C*O$_2$Me], 165.1 [d, ^{3}J(P,C) = 14.2 Hz, *C*O$_2$Me], 167.7 [d, $^{(2+3)}J$(P,C) = 11.5 Hz, PN*C*], 196.7 [d, ^{2}J(P,C) = 6.5 Hz, *cis*-*C*O], 198.0 [d, ^{2}J(P,C) = 23.1 Hz, *trans*-*C*O]. − $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 102.8 [s, ^{1}J(P,W) = 237.9 Hz]. − IR (KBr): $\tilde{\nu}$ = 2073 (s), 1992 (s), 1953 (vs), 1926 (vs), 1913 (vs) cm^{-1} (CO); 1745 (s), 1719 (s) cm^{-1} (CO_2); 1596 (m, sh), 1546 (m) cm^{-1} (C=N). − MS (70 eV, EI), (^{184}W); *m*/*z* (%): 759 (4) [M^+], 647 (50) [(M − 4 CO)$^+$·], 631 (100) [(M − 3 CO)$^+$·], 603 (40) [(M − 4 CO)$^+$·], 575 (35) [(M − 5 CO)$^+$·], 73 (100) [$SiMe_3^+$·]. − $C_{25}H_{30}NO_9PSi_2W$ (759.5): calcd. C 39.54, H 3.98, N 1.84; found C 39.73, H 3.85, N 1.76.

[2-Bis(trimethylsilyl)methyl-3,4-bis(methoxycarbonyl)-5-phenyl-2*H*-1,2-azaphosphole] *P*-Sulfide (13): A mixture of the 2*H*-1,2-azaphosphole tungsten complex **10a** (0.2 g, 0.25 mmol) and sulfur (0.08 g, 0.25 mmol) in benzonitrile (3 mL) was heated for 1.5 h at 75°C under slow stirring. The solvent was then removed in vacuo and the product was separated by low-temperature column chromatography of the residue (SiO_2, −20°C, 4 × 4 cm, dichloromethane). Crystallization from a small amount of pentane at −20°C afforded **13** as red crystals. Yield: 80 mg (65%). − M.p. 79°C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 0.09 (s, 9 H, $SiMe_3$), 0.43 (s, 9 H, $SiMe_3$), 1.33 [d, ^{2}J(P,H) = 21.2 Hz, 1 H, C*H*($SiMe_3$)$_2$], 3.85 [d, ^{6}J(P,H) = 0.5 Hz, 3 H, OCH_3], 3.89 [d, ^{5}J(P,H) = 0.6 Hz, 3 H, OCH_3], 7.46 (m_c, 3 H, C$H_{arom.}$), 7.79 (m_c, 2 H, C$H_{arom.}$). − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 2.2 [d, ^{3}J(P,C) = 3.2 Hz, $SiMe_3$], 3.3 [d, ^{3}J(P,C) = 2.9 Hz, $SiMe_3$], 19.9 [d, ^{1}J(P,C) = 32.9 Hz, *C*H($SiMe_3$)$_2$], 53.0 (s, O*C*H$_3$),

53.1 (s, OCH_3), 128.6 (s, Ph), 128.8 (s, Ph), 133.2 (s, Ph), 134.0 [d, ^3J(P,C) = 23.7 Hz, Ph], 151.0 [d, ^1J(P,C) = 53.1 Hz, P*C*C], 161.3 [d, $^{(2+3)}J$(P,C) = 13.8 Hz, PN*C*], 164.8 [d, ^2J(P,C) = 22.4 Hz, PC*C*], 167.7 (s, *C*O_2Me), 170.7 [d, ^3J(P,C) = 7.5 Hz, *C*O_2Me]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 101.0 (s). − IR (KBr): ṽ = 1737 (vs), 1718 (vs) cm^{-1} (CO_2); 1610 (m), 1528 (m) cm^{-1} (C=N). − MS (70 eV, EI); *m/z* (%): 467 (25) [M^+·], 452 (50) [(M − CH_3)$^+$·], 408 (100) [(M − $C_2H_3O_2$)$^+$·]. − $C_{20}H_{30}NO_4PSi_2$ (467.7): calcd. C 51.37, H 6.47, N 3.00, S 6.86; found C 51.35, H 6.60, N 2.90, S 6.60.

Procedure for the Synthesis of 2*H*-1,2-Azaphosphole Tungsten Complex 10b and Δ^3-1,3,2-Oxazaphospholene Tungsten Complexes 14a, b: To a solution of 2*H*-azaphosphirene tungsten complex **8a** (1.5 g, 2.4 mmol) in toluene (3 mL), dimethylcyanamide (0.2 mL, 0.2 mmol), and dimethyl acetylenedicarboxylate (0.4 mL, 3 mmol) were added and the mixture was heated at 75°C for 1.5 h under slow stirring. After concentration to dryness, the products were separated by low-temperature column chromatography of the residue (SiO_2, −20°C, 10 × 2 cm, hexane/diethyl ether, 90:10) and subsequently crystallized from pentane at −20°C.

Pentacarbonyl[2-{bis(trimethylsilyl)methyl}-5-dimethylamino-3,4-bis(methoxycarbonyl)-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (10b): Yield: 130 mg (14%). − M.p. 123°C (dec.). − ^1H NMR ($CDCl_3$): δ = 0.05 (s, 9 H, $SiMe_3$), 0.35 (s, 9 H, $SiMe_3$), 1.13 [d, ^2J(P,H) = 5.6 Hz, 1 H, C*H*($SiMe_3$)$_2$], 3.13 [s, 6 H, N(CH_3)$_2$], 4.55 (s, 3 H, OCH_3), 4.76 (s, 3 H, OCH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.7 [d, ^3J(P,C) = 2.0 Hz, $SiMe_3$], 3.4 [d, ^3J(P,C) = 2.6 Hz, $SiMe_3$], 22.6 [s, *C*H($SiMe_3$)$_2$], 39.7 [s, N(*C*H_3)$_2$], 52.6 (s, O*C*H_3), 53.3 (s, O*C*H_3), 139.2 [d, ^1J(P,C) = 21.2 Hz, P*C*C], 158.4 [d, $^{(2+3)}J$(P,C) = 5.3 Hz, PN*C*], 161.8 [d, $^{(2+3)}J$(P,C) = 7.3 Hz, PC*C*], 163.2 [d, ^3J(P,C) = 7.3 Hz, *C*O_2Me], 166.1 [d, ^2J(P,C) = 14.6 Hz, *C*O_2Me], 197.7 [d, ^2J(P,C) = 7.2 Hz, *cis*-*C*O], 199.7 [d, ^2J(P,C) = 22.6 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 85.6 [s, ^1J(P,W) = 249.7 Hz]. − IR (KBr): ṽ = 2069 (s), 1983 (s), 1929 (vs sh) cm^{-1} (CO); 1742 (m), 1735 (m), 1720 (s) cm^{-1} (CO_2); 1596 (m), 1546 (m) cm^{-1} (C=N). − MS (70 eV, EI), (^{184}W); *m/z* (%): 726 (20) [M^+·], 698 (50) [(M − 1 CO)$^+$·], 614 (60) [(M − 4 CO)$^+$·], 586 (50) [(M − 5 CO)$^+$·], 558 (100) [M − 6 (CO)$^+$], 73 (80) [$SiMe_3^+$]. − $C_{21}H_{31}N_2O_9PSi_2W$ (726.5): calcd. C 34.72, H 4.30, N 3.86; found C 34.61, H 4.32, N 3.55.

Pentacarbonyl[2-{bis(trimethylsilyl)methyl}-5-dimethylamino-4-methoxy-4-(2-methoxycarbonylacetylenyl)-Δ^3-1,3,2-oxazaphospholene-κ*P*]tungsten(0) (14a,b): Compound **14a**: Yield: 125 mg (13%). − M.p. 164°C (dec.). − ^1H NMR ($CDCl_3$): δ = 0.17 (s, 9 H, $SiMe_3$), 0.29 (s, 9 H, $SiMe_3$), 1.49 [s, 1 H, C*H*($SiMe_3$)$_2$], 3.16 [s, 6 H, N(CH_3)$_2$], 3.63 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.5 (s, $SiMe_3$), 2.6 (s, $SiMe_3$), 37.8 [d, ^1J(P,C) = 5.9 Hz, *C*H($SiMe_3$)$_2$], 38.1 [s, N(*C*H_3)$_2$], 40.0 [s, N(*C*H_3)$_2$], 53.2 (s, O*C*H_3), 53.8 (s, O*C*H_3), 77.8 (s, C*C*CO_2Me), 79.9 (s, *C*CCO_2Me), 99.2 [d, $^{(2+3)}J$(P,C) = 4.0 Hz, PO*C*], 152.7 (s, *C*O_2Me), 158.0 [d, $^{(2+3)}J$(P,C) = 1.3 Hz, PN*C*], 197.1 [d, ^2J(P,C) = 8.8 Hz, ^1J(C,W) = 117.8 Hz, *cis*-*C*O], 201.1 [d, ^2J(P,C) = 29.1 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 191.6 [s, ^1J(P,W) = 305.9 Hz]. − IR (KBr): ṽ = 2073 (s), 1986 (s), 1952 (vs), 1930 (vs), 1919 (vs) cm^{-1} (CO); 1629 (s) cm^{-1} (CO_2). − MS (70 eV, EI), (^{184}W); *m/z* (%): 726 (50) [M^+·], 642 (30) [(M − 3 CO)$^+$·], 586 (40) [(M − 5 CO)$^+$·], 571 (50) [(M − 5 CO − CH_3)$^+$·], 558 (100) [(M − 6 CO)$^+$], 543 (60) [(M − 6 CO − CH_3)$^+$·], 73 (60) [$SiMe_3^+$].

Compound **14b**: Yield: 70 mg (8%). − M.p. 164°C (dec.). − ^1H NMR ($CDCl_3$): δ = 0.17 (s, 9 H, $SiMe_3$), 0.32 (s, 9 H, $SiMe_3$), 1.46 [s, 1 H, C*H*($SiMe_3$)$_2$], 3.16 [s, 3 H, N(CH_3)$_2$], 3.19 [s, 3 H, N(CH_3)$_2$], 3.61 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.1 [d, ^3J(P,C) = 2.9 Hz, $SiMe_3$], 2.3 [d, ^3J(P,C) = 1.3 Hz, $SiMe_3$], 36.8 [m_c, *C*H($SiMe_3$)$_2$], 38.5 [s, N(*C*H_3)$_2$], 39.9 [s, N(*C*H_3)$_2$], 52.9 (s, O*C*H_3), 53.2 (s, O*C*H_3), 74.6 (s, C*C*CO_2Me), 79.8 (s, *C*CCO_2Me), 99.1 [d, $^{(2+3)}J$(P,C) = 6.9 Hz, PO*C*], 152.7 (s, *C*O_2Me), 158.1 [d, $^{(2+3)}J$(P,C) = 1.1 Hz, PN*C*], 197.2 [d, ^2J(P,C) = 8.7 Hz, ^1J(C,W) = 126.1 Hz, *cis*-*C*O], 200.1 [d, ^2J(P,C) = 29.4 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 198.6 [s, ^1J(P,W) = 303.1 Hz]. − IR (KBr): ṽ = 2071 (s), 1983 (s), 1940 (vs), 1918 (vs) cm^{-1} (CO); 1726 (s) cm^{-1} (CO_2); 1618 (s) cm^{-1} (C=N). − MS (70 eV, EI), (^{184}W); *m/z* (%): 726 (40) [M^+·], 614 (30) [(M − 4 CO)$^+$·], 586 (100) [(M − 5 CO)$^+$·], 571 (80) [(M − 5 CO − CH_3)$^+$·], 543 (60) [(M − 6 CO − CH_3)$^+$·], 73 (35) [$SiMe_3^+$]. − $C_{21}H_{31}N_2O_9PSi_2W$ (726.5): calcd. C 34.72, H 4.30, N 3.86; found C 34.98, H 4.20, N 3.57.

Pentacarbonyl[3,4-bis(methoxycarbonyl)-2-pentamethylcyclopentadienyl-5-phenyl-2*H*-1,2-azaphosphole-κ*P*]tungsten(0) (10c): To a solution of 0.3 g (0.5 mmol) of the 2*H*-azaphosphirene tungsten complex **8b** in 3 mL of benzonitrile was added 0.5 mL (0.6 mmol) of dimethyl acetylenedicarboxylate and the mixture was stirred for 95 min at 62°C. The solution was then concentrated to dryness in vacuo (ca. 0.01 mbar) and the residue was subjected to low-temperature column chromatography on silica (−35°C, hexane/diethyl ether, 99:1). A red fraction was concentrated to dryness in vacuo and the product was crystallized from pentane. Yield: 118 mg (32%). − M.p. 132°C (dec.). − ^1H NMR: δ = 1.10 [d, ^2J(P,H) = 16.0 Hz, 3 H, Cp*-C1-CH_3], 1.82 [pseudo t, ^3J(P,H) = 6.0 Hz, 6 H, Cp*-C3/6-CH_3], 2.21 (s, 6 H, Cp*-C4/5-CH_3), 3.84 (s, 6 H, CO_2CH_3), 7.51 (m_c, 2 H, C$H_{arom.}$), 7.90 (m_c, 2 H, C$H_{arom.}$). − $^{13}C\{^1H\}$ NMR: δ = 11.3 [d, ^3J(P,C) = 1.6 Hz, Cp*-*C*H_3], 11.9 (s, Cp*-*C*H_3), 12.6 (s, Cp*-*C*H_3), 14.1 [d, ^4J(P,C) = 2.6 Hz, Cp*-C1-*C*H_3], 52.1 (s, O*C*H_3), 56.5 [d, ^4J(P,C) = 9.2 Hz, O*C*H_3], 62.9 [d, *J*(P,C) = 7.4 Hz, Cp*-C1], 128.5 (s, *i*-Ph), 128.7 (s, *p*-Ph), 131.7 (s, *o*-Ph), 134.1 (s, *m*-Ph), 136.2 (s, Cp*), 136.7 [d, *J*(P,C) = 2.0 Hz, Cp*], 141.6 [d, *J*(P,C) = 3.1 Hz, Cp*], 141.8 [d, *J*(P,C) = 2.4 Hz, Cp*], 144.8 [d, $^{(1+4)}J$(P,C) = 21.8 Hz, *C*3], 159.6 [d, $^{(2+3)}J$(P,C) = 4.2 Hz, *C*5], 162.8 [d, $^{(2+3)}J$(P,C) = 12.3 Hz, *C*4], 164.9 [d, ^2J(P,C) = 13.3 Hz, C3-*C*O_2CH_3], 168.3 [d, ^3J(P,C) = 13.2, Hz, C4-*C*O_2CH_3], 195.3 [d, ^2J(P,C) = 6.6 Hz, *cis*-*C*O], 197.4 [d, ^2J(P,C) = 26.3 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 119.6 [s, ^1J(P,W) = 248.1 Hz]. − IR (KBr): ṽ = 2075 (s), 1939 (vs, br), (CO); 1734 (s), 1719 (s) cm^{-1} (CO_2). − MS (positive CI, NH_3), (^{184}W) (%): 736 (12) [(M + H)$^+$], 602 (10) [(M + H − $C_{10}H_{14}$)$^+$], 135 (100) [$C_{10}H_{15}^+$]. − $C_{28}H_{26}NO_9PW$ (735.3): calcd. C 45.74, H 3.56, N 1.90; found C 45.91, H 4.09, N 1.81.

Procedure for the Preparation of Complexes 15 and 16: A mixture of 0.3 g (0.5 mmol) of the 2*H*-azaphosphirene tungsten complex **8b** and 0.5 mL (0.6 mmol) of dimethyl acetylenedicarboxylate was stirred for 25 min in 3 mL of toluene (**15**) or 3 mL of benzonitrile (**16**) at 75°C. The solution was then concentrated to dryness in vacuo (ca. 0.01 mbar), and the residue was subjected to low-temperature column chromatography on silica (−20°C, hexane/diethyl ether, 99:1). The eluents were concentrated to dryness in vacuo and the products were crystallized from pentane at −20°C (pale-yellow crystals in both cases).

Pentacarbonyl[3,4,5,6,8-pentamethyl-1-phosphatetracyclo-[4.1.1.1^{3,6}0^{2,7}]-2,7-bis(methoxycarbonyl)hept-4-ene-κ*P*]tungsten(0) (15): Yield: 0.25 g (81%). − M.p. 98°C (dec.). − ^1H NMR: δ = 0.58 [d, ^3J(P,H) = 19.0 Hz, 3 H, C8-CH_3], 1.52 (s, 6 H, C3/6-CH_3), 1.71 (s, 6 H, C4/5-CH_3), 3.62 (s, 6 H, CO_2CH_3). − $^{13}C\{^1H\}$ NMR: δ = 5.9 [d, ^3J(P,C) = 5.8 Hz, C8-*C*H_3], 14.0 (s, C3/6-*C*H_3), 14.1 [d, ^4J(P,C) = 2.6 Hz, C4/5-*C*H_3], 52.1 (s, O*C*H_3), 56.5 [d, ^4J(P,C) = 9.2 Hz, *C*3/6], 66.5 [d, *J*(P,C) = 32.2 Hz, *C*8], 70.4 [d, *J*(P,C) = 5.2 Hz, *C*2/7], 141.7 [d, *J*(P,C) = 10.4 Hz, *C*4/5], 168.7 (s, *C*O_2CH_3),

193.6 [d, ^2J(P,C) = 8.1 Hz, *cis*-*C*O], 197.4 [d, ^2J(P,C) = 35.5 Hz, *trans*-*C*O]. − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −74.6 [s, ^1J(P,W) = 281.1 Hz]. − IR (KBr): $\tilde{\nu}$ = 2079 (s), 1996 (s), 1946 (vs), 1922 (vs) cm^{-1} (CO); 1725 (s) cm^{-1}, 1718 (s) cm^{-1} (CO_2). − MS (negative CI, NH_3), (^{184}W); *m*/*z* (%): 631 (42) [M − H], 324 (100) [(C_5O_5W)], 308 (16) [M − (C_5O_5W)]. − $C_{21}H_{21}O_9PW$ (632.2): calcd. C 39.92, H 3.35; found C 39.92, H 3.46.

Pentacarbonyl[2,3,5,6-tetrakis(methoxycarbonyl)-4-phenyl-7-aza-1-phosphanorbornadiene-κ*P*]tungsten(0) (16): The assignments for C_a and C_b given in ref.[1] were erroneous!

Yield: 0.21 g (58%). − M.p. 152°C (dec.). − ^{1}H NMR: δ = 3.72 (s, 6 H, OCH_3), 3.76 [d, ^2J(P,H) = 5.1 Hz, 1 H, N*H*], 3.85 (s, 6 H, OCH_3), 7.45 (m_c, 3 H, $H_{arom.}$), 7.62 (m_c, 2 H, $H_{arom.}$). − ^{13}C{^{1}H} NMR: δ = 52.8 (s, O*C*H$_3$), 53.0 (s, O*C*H$_3$), 88.6 [d, J(P,C) = 5.4 Hz, *C*4], 126.1 (s, Ph), 129.0 (s, Ph), 129.6 (s, Ph), 132.5 [d, J(P,C) = 5.3 Hz, *i*-Ph], 148.5 [d, ^1J(P,C) = 13.3 Hz, *C*2/6], 162.3 [d, ^2J(P,C) = 16.3 Hz, *C*3/5], 164.4 [d, ^3J(P,C) = 9.7 Hz, *C*3/5-*C*O$_2$Me], 166.7 [d, ^2J(P,C) = 2.1 Hz, C2/6-*C*O$_2$Me], 194.2 [d, ^2J(P,C) = 8.2 Hz, *cis*-*C*O], 196.6 [d, ^2J(P,C) = 32.9 Hz, *trans*-*C*O]. − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 63.0 [s, ^1J(P,W) = 294.8 Hz]. − IR (KBr): $\tilde{\nu}$ = 3432 (s, br) (NH), 2082 (s), 1942 (vs, br), (CO); 1735 (s), 1724 (s) cm^{-1} (CO_2). − MS (positive CI, NH_3), (^{184}W); *m*/*z* (%): 761 (1) [(M + NH_4)$^+$], 602 (3) [(M + H − $C_6H_6O_4$)$^+$], 278 (100) [$C_{13}H_{13}NO_4P^+$]. − $C_{24}H_{18}NO_{13}PW$ (743.2): calcd. C 38.79, H 2.44, N 1.88; found C 38.92, H 2.52, N 1.94.

Procedure for the Diels−Alder Reaction of 1*H*-Phosphirene Tungsten Complex 9a with 2,3-Dimethylbutadiene: To a solution of the 1*H*-phosphirene tungsten complex **8a** (3.6 g, 0.55 mmol) in toluene (1.8 mL) was added 2,3-dimethylbutadiene (0.27 g, 3.3 mmol) and the mixture was heated at 75°C for 90 h under slow stirring. After concentration to dryness, the products were separated by low-temperature column chromatography of the residue (SiO_2, −20°C, 12 × 2 cm, hexane/diethyl ether, 98:2) and subsequently crystallized from pentane at −20°C.

Pentacarbonyl[1-{bis(trimethylsilyl)methyl}-2,7-bis(methoxycarbonyl)-4,5-dimethyl-1-phosphabicyclo[4.1.0^{2,7}]hept-4-ene-κ*P*]tungsten(0) (19): Yield: 100 mg (25%). − M.p. 117°C (dec.). − ^{1}H NMR (C_6D_6): δ = 0.27 (s, 18 H, $SiMe_3$), 0.94 [d, ^2J(P,H) = 14.4 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 1.37 (s, 6 H, C*H*$_3$), 2.37 [dd, ^2J(H,H) = 17.1 Hz, ^3J(P,H) = 13.1 Hz, 2 H, C*H*$_2$], 2.87 [dd, ^2J(H,H) = 17.3 Hz, ^3J(P,H) = 10.6 Hz, 2 H, C*H*$_2$], 3.47 (s, 6 H, OCH_3). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 2.6 (s, $SiMe_3$), 2.7 (s, $SiMe_3$), 12.7 [d, ^1J(P,C) = 34.2 Hz, *C*H(SiMe$_3$)$_2$], 18.4 (s, CH_3), 33.1 [d, ^2J(P,C) = 3.7 Hz, *C*H$_2$], 40.2 [d, ^1J(P,C) = 18.1 Hz, P*C*], 52.5 (s, O*C*H$_3$), 124.4 (s, *C*CH$_3$), 171.2 [d, ^3J(P,C) = 3.7 Hz, *C*O$_2$Me], 197.3 [d, ^2J(P,C) = 33.9 Hz, *trans*-*C*O], 197.4 [d, ^2J(P,C) = 7.4 Hz, *cis*-*C*O]. − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −87.1 [s, ^1J(P,W) = 269.9 Hz]. − IR (KBr): $\tilde{\nu}$ = 2075 (s), 2001 (s), 1932 (vs), 1910 (vs) cm^{-1} (CO); 1742 (vs) cm^{-1} (CO_2). − MS (70 eV, EI), (^{184}W); *m*/*z* (%): 710 (5) [(M − CO)$^+$·], 682 (25) [(M − 2 CO)$^+$·], 73 (100) [$SiMe_3^+$]. − $C_{24}H_{35}O_9PSi_2W$ (738.5): calcd. C 39.03, H 4.88; found C 40.12, H 5.13.

1-[Bis(trimethylsilyl)methyl]-2,7-bis(methoxycarbonyl)-4,5-dimethyl-1-phosphabicyclo[4.1.0^{2,7}]hept-4-ene (20): Yield: 50 mg (22%). − ^{1}H NMR (C_6D_6): δ = 0.16 [d, ^4J(P,H) = 0.8 Hz, 18 H, $SiMe_3$], 1.33 [d, ^2J(P,H) = 10.0 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 1.57 (s, 6 H, C*H*$_3$), 2.25 [d, ^2J(H,H) = 19.2 Hz, 2 H, C*H*$_2$], 3.05 [dd, ^2J(H,H) = 17.6 Hz, 2 H, C*H*$_2$], 3.37 (s, 6 H, OCH_3). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 1.6 (s, $SiMe_3$), 1.8 (s, $SiMe_3$), 6.8 [d, ^1J(P,C) = 81.5 Hz, *C*H(SiMe$_3$)$_2$], 18.6 (s, CH_3), 33.5 [d, ^2J(P,C) = 2.3 Hz, *C*H$_2$], 41.5 [d, ^1J(P,C) = 47.7 Hz, P*C*], 51.9 (s, O*C*H$_3$), 125.5 (s, *C*CH$_3$), 173.3 [d, ^3J(P,C) = 14.2 Hz, *C*O$_2$Me]. − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −105.8 (s). − MS (70 eV, EI), (^{184}W); *m*/*z* (%): 414 (15) [M$^+$·], 193 (100) [(Me$_3$Si)$_2$HCPH_2^+·], 73 (50) [$SiMe_3^+$].

Procedure for the Reaction of 1*H*-Phosphirene Tungsten Complex 9a with Diethylamine: To a solution of the 1*H*-phosphirene tungsten complex **9a** (0.25 g, 0.4 mmol) in toluene (5 mL) was added diethylamine (1 mL, 9.6 mmol) and the mixture was slowly stirred for 18 h at room temp. ^{31}P-NMR spectroscopic control showed that **21**, **22**, and **23** were formed in a ratio of 1:1:1. After concentration to dryness, the products were separated by low-temperature column chromatography of the residue (SiO_2, −20°C, 10 × 2 cm, hexane/diethyl ether, 98:2) and subsequently crystallized from pentane at −20°C. The crystals of **21**, **22**, and **23** were resolved manually using the Pasteur selection method.

Pentacarbonyl[1-{bis(trimethylsilyl)methyl}-2-(diethylamino)-2,3-bis(methoxycarbonyl)phosphirane-κ*P*]tungsten(0) (21): Yield: 55 mg (20%). − M.p. 114°C (dec.). − ^{1}H NMR (C_6D_6): δ = 0.20 (s, 9 H, $SiMe_3$), 0.29 (s, 9 H, $SiMe_3$), 0.93 [t, ^3J(H,H) = 6.7 Hz, 3 H, CH_2CH_3], 1.19 (m_c, 3 H, CH_2CH_3), 1.19 [d, ^2J(P,H) = 14.9 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 2.70 (m_c, 2 H, CH_2CH_3), 3.18 (m_c, 1 H, CH_2CH_3), 3.35 [d, $^{(2+2)}J$(P,H) = 7.9 Hz, 1 H, PC*H*], 3.47 (m_c, 1 H, CH_2CH_3), 3.73 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3). − ^{13}C{^{1}H} NMR (C_6D_6): δ = 1.8 (s, $SiMe_3$), 2.0 (s, $SiMe_3$), 13.5 (s, CH_2CH_3), 14.0 (s, CH_2CH_3), 15.9 [d, ^1J(P,C) = 32.2 Hz, *C*H(SiMe$_3$)$_2$], 41.4 [d, $^{(1+2)}J$(P,C) = 14.2 Hz, P*C*HC], 46.6 [d, ^3J(P,C) = 5.4 Hz, *C*H$_2$CH$_3$], 49.5 (s, *C*H$_2$CH$_3$), 51.9 (s, O*C*H$_3$), 52.3 (s, O*C*H$_3$), 66.6 [d, $^{(1+2)}J$(P,C) = 16.0 Hz, P*C*N], 167.1 (s, *C*O$_2$Me), 172.2 (s, *C*O$_2$Me), 196.4 [d, ^2J(P,C) = 35.1 Hz, *trans*-*C*O], 197.1 [d, ^2J(P,C) = 7.0 Hz, *cis*-*C*O]. − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −81.1 [s, ^1J(P,W) = 274.7 Hz]. − IR (KBr): $\tilde{\nu}$ = 2038 (s), 1996 (s), 1935 (vs), 1911 (vs) cm^{-1} (CO); 1735 (s), 1700 (s) cm^{-1} (CO_2). − MS (70 eV, EI), (^{184}W); *m*/*z* (%): 729 (20) [M$^+$·], 486 (70) [(OC)$_4$WPCH(SiMe$_3$)$_2^+$·], 184 (100) [MeO$_2$C(H)CC(NEt$_2$)CO$^+$·]. − $C_{22}H_{36}NO_9PSi_2W$ (729.5): calcd. C 36.22, H 4.97, N 1.92; found C 36.36, H 5.08, N 1.98.

Pentacarbonyl{[bis(trimethylsilyl)methyl]-1-[2-(diethylamino)-1,2-bis(methoxycarbonyl)ethenyl]phosphane-κ*P*}tungsten(0) (22): Yield: 110 mg (40%). − M.p. 86°C (dec.). − ^{1}H NMR (C_6D_6): δ = 0.26 (s, 9 H, $SiMe_3$), 0.28 [d, ^4J(P,H) = 3.3 Hz, 9 H, $SiMe_3$], 0.77 [t, ^3J(H,H) = 7.0 Hz, 3 H, CH_2CH_3], 0.85 (m_c, 3 H, CH_2CH_3), 1.03 [dd, ^2J(P,H) = 11.1 Hz, ^3J(H,H) = 5.6 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 2.80 [q, ^3J(H,H) = 7.3 Hz, 2 H, CH_2CH_3], 2.95 (m_c, 2 H, CH_2CH_3), 3.42 (s, 3 H, OCH_3), 3.55 (s, 3 H, OCH_3), 5.82 [dd, ^1J(P,H) = 330.1 Hz, ^3J(H,H) = 5.6 Hz, 1 H, C*H*]. − ^{13}C{^{1}H} NMR (C_6D_6): δ = 1.9 [d, ^3J(P,C) = 3.5 Hz, $SiMe_3$], 2.5 [d, ^3J(P,C) = 2.8 Hz, $SiMe_3$], 13.3 (s, CH_2CH_3), 17.3 [d, ^1J(P,C) = 5.5 Hz, *C*H(SiMe$_3$)$_2$], 46.1 (s, *C*H$_2$CH$_3$), 47.4 (s, *C*H$_2$CH$_3$), 51.3 (s, O*C*H$_3$), 52.3 (s, O*C*H$_3$), 95.7 [d, ^1J(P,C) = 39.9 Hz, P*C*C], 155.6 [d, ^3J(P,C) = 2.4 Hz, *C*O$_2$Me], 166.4 [d, ^2J(P,C) = 2.8 Hz, *C*O$_2$Me], 166.8 [d, ^2J(P,C) = 16.1 Hz, PC*C*], 198.5 [d, ^2J(P,C) = 6.8 Hz, *cis*-*C*O], 201.0 (m_c, *trans*-*C*O). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −48.7 [s, ^1J(P,W) = 235.2 Hz]. − IR (KBr): $\tilde{\nu}$ = 2067 (s), 1975 (s), 1915 (vs) cm^{-1} (CO); 1730 (s), 1693 (s) cm^{-1} (CO_2). − MS (70 eV, EI), (^{184}W); *m*/*z* (%): 729 (2) [M$^+$·], 674 (50) [(M − 2 CO)$^+$·], 362 (100) [$C_{16}H_{31}NO_3Si_2P^+$·], 73 (80) [$SiMe_3^+$]. − $C_{22}H_{36}NO_9PSi_2W$ (729.5): calcd. C 36.22, H 4.97, N 1.92; found C 36.41, H 5.03, N 1.88.

Pentacarbonyl[1-{bis(trimethylsilyl)methyl}-3-dimethylamino-4-methoxycarbonyl-1,2-dihydro-1-phosphet-2-one-κ*P*]tungsten(0) (23): Yield: 55 mg (20%). − M.p. 100°C (dec.). − ^{1}H NMR (C_6D_6): δ = 0.11 (s, 9 H, $SiMe_3$), 0.33 [d, ^4J(P,H) = 0.3 Hz, 9 H, $SiMe_3$], 0.78 [t, ^3J(H,H) = 7.1 Hz, 6 H, CH_2CH_3], 1.24 [d, ^2J(P,H) = 8.7 Hz, 1 H, C*H*(SiMe$_3$)$_2$], 2.78 [q, ^3J(H,H) = 7.1 Hz, 2 H, CH_2CH_3], 2.56 (m_c, 2 H, CH_2CH_3), 3.55 (s, 3 H, OCH_3), 3.56 (s, 3 H, OCH_3). −

Table 3. Crystal data and structure refinement of complexes **9a**, **10b**, **19**, **21**, and **23**

Complex	**9a**	**10b**	**19**	**21**	**23**
Empirical formula	$C_{18}H_{25}O_9PSi_2W$	$C_{21}H_{31}N_2O_9PSi_2W$	$C_{24}H_{35}O_9PSi_2W$	$C_{22}H_{36}NO_9PSi_2W$	$C_{21}H_{32}NO_8P_2Si_2W$
Formula weight M_r [g mol^{-1}]	656.38	726.48	728.52	729.52	697.48
Crystal size [mm]	0.50 × 0.35 × 0.20	0.40 × 0.24 × 0.14	0.70 × 0.50 × 0.40	0.50 × 0.35 × 0.20	0.60 × 0.50 × 0.25
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic
Space group	*C*2/*c*	*P*−1	*P*−1	*P*−1	*P*−1
a [Å]	33.558(3)	10.3286(14)	9.4580(10)	10.940(4)	10.050(4)
b [Å]	9.4981(10)	12.5475(16)	10.9450(10)	11.333(4)	10.239(4)
c [Å]	18.972(2)	23.393(2)	15.785(2)	13.579(5)	14.453(4)
α [°]	90	92.177(8)	75.416(10)	81.56(2)	100.64(4)
β [°]	120.544(5)	95.816(10)	88.493(10)	80.61(3)	94.53(4)
γ [°]	90	100.268(12)	73.844(10)	63.60(2)	98.98(4)
Volume [Å^3]	5207.9(9)	2962.9(6)	1517.3(3)	1482.6(9)	1434.8(9)
Z	8	4	2	2	2
Density D_X [Mg m^{-3}]	1.674	1.629	1.617	1.634	1.614
Absorption coefficient μ [mm^{-1}]	4.631	4.080	3.984	4.076	4.205
F(000)	2576	1440	736	728	692
Temperature *T* [°C]	−100	−100	−100	−130	−130
Data collection $2\theta_{max}$	50	50	50	50	50
Limiting indices (*h*, *k*, *l*)	−37/43, −12/9, −24/0	−12/12, −14/12, −27/27	−10/11, −12/12, −18/7	−13/12, −13/15, −15/16	−11/2, −12/12, −17/17
Reflections collected	11324	13786	8089	5518	6127
Independent reflections	5985	10415	5296	5219	5057
R_{int}	0.0312	0.0279	0.0135	0.0157	0.0271
Parameters	279	669	344	372	316
Restraints	103	36	169	150	123
Final $wR2(F^2)$ [all data]	0.071	0.053	0.044	0.046	0.064
Final $R1(F)$ [$I > 2\sigma(I)$]	0.032	0.028	0.019	0.019	0.025
Max. and min. Δρ [eÅ^{-3}]	1.143/−1.656	0.873/−0.714	0.658/−0.473	0.741/−0.364	1.110/−1.124

$^{13}C\{^1H\}$ NMR (C_6D_6): δ = 2.4 [d, ^3J(P,C) = 2.9 Hz, $SiMe_3$], 2.5 [d, ^3J(P,C) = 2.2 Hz, $SiMe_3$], 14.0 (m_c, CH_2CH_3), 27.8 [d, ^1J(P,C) = 21.0 Hz, $CH(SiMe_3)_2$], 45.5 (s, CH_2CH_3), 51.3 (s, OCH_3), 119.4 [d, $^{(1+3)}J$(P,C) = 41.6 Hz, $PCCO_2Me$], 152.9 [d, $^{(2+2)}J$(P,C) = 56.2 Hz, PC*C*], 165.0 [d, ^2J(P,C) = 14.5 Hz, CO_2Me], 197.7 [d, ^2J(P,C) = 6.9 Hz, *cis*-*C*O], 198.7 [d, $^{(1+3)}J$(P,C) = 35.7 Hz, P*C*O], 200.1 [d, ^2J(P,C) = 24.7 Hz, *trans*-*C*O]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 71.7 [s, ^1J(P,W) = 241.2 Hz]. − IR (KBr): $\tilde{\nu}$ = 2069 (s), 1942 (vs, br) cm^{-1} (CO); 1742 (s), 1693 (s) cm^{-1} (CO_2). − MS (70 eV, EI), (^{184}W); *m*/*z* (%): 698 (30) [M$^+$·], 557 (100) [(M − 4 CO − C_2H_5)$^+$·], 362 (100) [$C_{16}H_{31}NO_3Si_2P^+$], 73 (80) [$SiMe_3^+$]. − $C_{22}H_{36}NO_9PSi_2W$ (697.5): calcd. C 36.16, H 4.62, N 2.01; found C 36.35, H 4.79, N 1.91.

Data Collection, Structure Solution, and Refinement of 9a, 10b, 19, 21, and 23: Crystal data for all the structures are presented in Table 3. Structure determination of **9a**, **10b**, and **19**: A yellow prism (**9a**), a yellow tablet (**10b**), or a pale-yellow block (**19**) was mounted in inert oil and measured by ω-scans using Mo-K_α radiation (graphite monochromator) on a Siemens P4 diffractometer. After an absorption correction (ψ-scans), all unique data were used for the calculations (**9a**, **19**: program SHELXL-93;[37] **10b**: program SHELXL-97[38]). The structures were solved by direct methods (**9a**, **10b**) or the heavy-atom method (**19**) and refined anisotropically by full-matrix least-squares on F^2. All hydrogen atoms (except rigid methyl groups) were refined as a riding model. Structure determination of **21** and **23**: A colourless tablet (**21**) or an orange tablet (**23**) was mounted in inert oil and measured by ω/θ-scans using Mo-K_α radiation (graphite monochromator) on a Stoe STADI-4 diffractometer. Structure solution: heavy-atom method. Other details were as for **10b** above.

Acknowledgments

Support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, and MS measurements by Dr. Hans-Martin Schiebel (Technische Universität Braunschweig) are gratefully acknowledged.

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Received March 12, 1999
[I99093]