A New Concept for the Efficient Synthesis of Chiral Phosphorus−Nitrogen−Carbon Cage Compounds

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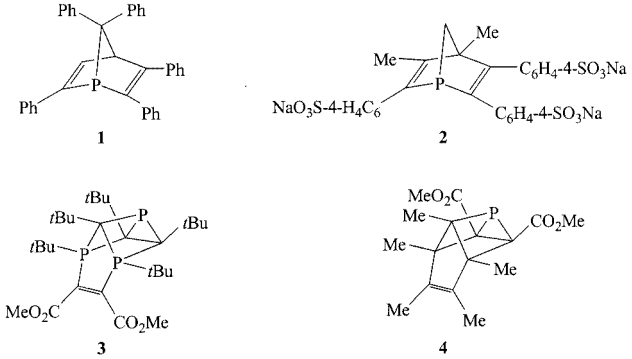
Keywords: Azaphospholes / Phosphorus / Cage compounds / Tungsten / Cyclization

A new concept for the efficient synthesis of a chiral phosphorus-nitrogen-carbon cage-compound is reported, which is comprised of a high-yield three-step procedure starting from a *P*-Cp*-substituted 2*H*-azaphosphirene complex. Thermolysis of a solution of the latter complex in the presence of Ph_3PNCN and DMAD afforded the *P*-Cp*-substituted 2*H*-1,2-azaphosphole complex **11** in a clean reaction; a further reaction at 75 °C with DMAD produced complex **12** via an *intermolecular* Diels–Alder reaction of the Cp* group. A subsequent *intramolecular* Diels–Alder reaction of **12**, at 120 °C, yielded the title compound, complex **13,** in quantitative yields. Elemental analyses and detailed (solution) NMR spectroscopic and MS investigations confirmed all complexes. Furthermore, solid state structures of complexes **11** and **13** were established by X-ray single crystal structure analyses.

Introduction

The development − or better, constant search − of new and effective synthetic methods of rigid chiral trivalent phosphorus(III) compounds, which might offer improved performance in asymmetric catalysis, is one of the current challenges in Organophosphorus Chemistry, as pointed out recently by Mathey.[1] Early findings by Shell scientists in 1966 showed that cyclic phosphanes perform better in hydroformylation processes than tributyl-phosphane.[2] Burk[3] then showed in 1990 that phospholane-based C_2-symmetric chelating ligands, dubbed as DuPHOS, are important in the catalytic hydrogenation of functional alkenes. Mathey[4] and Réau[5] reported the use of the 1-phosphanorbornadiene **1**, obtained by [4+2] cycloaddition reactions of a transient 2*H*-phosphole and tolane,[6] in hydrogenation[4] and hydroformylation[5] reactions. The same ligand system was modified by Herrmann and co-workers and introduced as NORBOS **2** in the biphasic hydroformylation of propene.[7] It was Mathey again, who developed BIPNOR[8] as a new bidentate ligand and employed it e.g. in the asymmetric isomerization of a cyclic diene, in which it proved to be far superior to BINAP.[9]

In view of this background and the great variety of established structures of polycyclic phosphanes[10] and phosphorus-carbon cage compounds[10,11] with a ring junction phosphorus atom, it is surprising − at first sight − that studies of their use as cocatalysts have remained scarce. The problem is that most often their synthesis relies, at one stage or another, on the employment of phosphaalkyne derivatives, which are not readily accessible, e.g. in the case of **3**,[12] and/or because of the lack of straightforward high-yield synthetic methodologies. One of the few exceptions may be **4** (Scheme 1), which was obtained by a ligand-centered reaction as a coordination compound in quantitative yields.[13]



Scheme 1. Unusual bicyclic phosphanes (**1**, **2**) and phosphorus−carbon cage compounds (**3**, **4**)

For the same aforementioned reasons the selective synthesis of phosphorus-nitrogen-carbon cage compounds such as **5**[14] and **6**[15] aroused interest (Scheme 2); the latter was obtained as a coordination compound. Grützmacher demonstrated that **5** is surprisingly stable under oxidative

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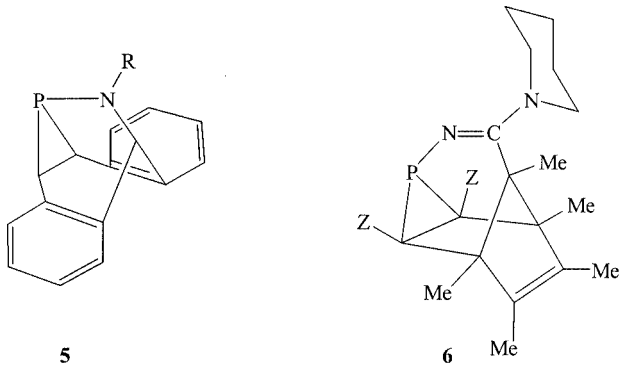
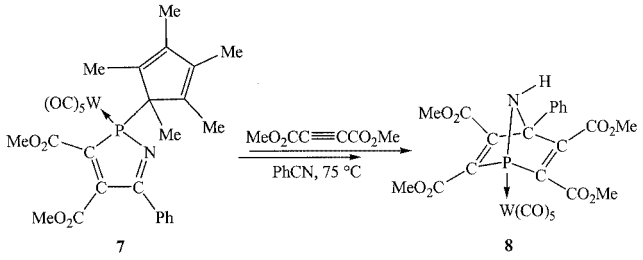
conditions and thus showed that such ligand systems might have additional advantageous properties associated with their unusual small valence bond angle sums at phosphorus (Σ°P), which are below 270°, e.g. Σ°P·255° (**5**) and Σ°P·263° (**6**). He also showed that **5** can be used successfully as a new ligand system in catalytic hydrosilylations.[16] It is also remarkable that unusual properties of phosphanes with valence bond angle sums at phosphorus below 270° were predicted theoretically by Orpen and Connely some years ago.[17]



Scheme 2. Unusual phosphorus−nitrogen−carbon cage compounds **5** and **6**

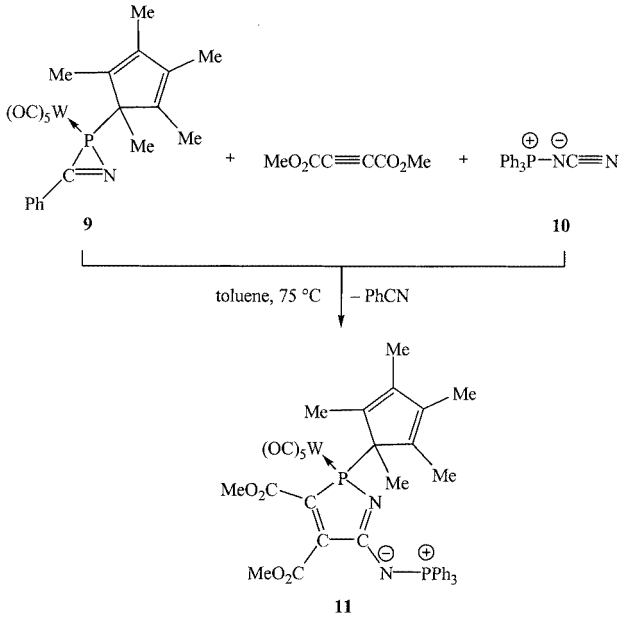
Because of our long-standing interest in the synthesis of new mono- and polycyclic unsaturated phosphorus-nitrogen heterocycles[18] using 2*H*-azaphosphirene complexes[19] as precursors, we recently decided to return to the unresolved problem of the surprising instability of the exocyclic P−C bond of the *P*-pentamethylcyclopentadienyl-substituted 2*H*-1,2-azaphosphole complex **7**.[20] Upon heating in benzonitrile, complex **7** decomposed in the presence of dimethyl acetylenedicarboxylate (DMAD), forming the bicyclic heterocycle **8**, the first 7-aza-1-phosphanorbornadiene complex (Scheme 3).



Scheme 3. Formation of 7-aza-1-phosphanorbornadiene complex **8** via thermolysis of the 2*H*-1,2-azaphosphole complex **7** in the presence of DMAD

Results and Discussion

In an attempt to synthesize new functional derivatives of **8**, we have now achieved selective synthesis of 2*H*-1,2-azaphosphole complex **11** using the *P*-Cp*-substituted 2*H*-azaphosphirene complex **9**[21] and Ph_3PNCN[22] (**10**) in *o*-xylene at 75 °C (Scheme 4). Surprisingly, complex **11** showed no signs of decomposition up to temperatures as high as 120 °C! Since the only difference between **7** and **11** is the replacement of a phenyl by the Ph_3PN group, clearly the new substituent is responsible for this dramatic effect − but the reason is not immediately apparent.



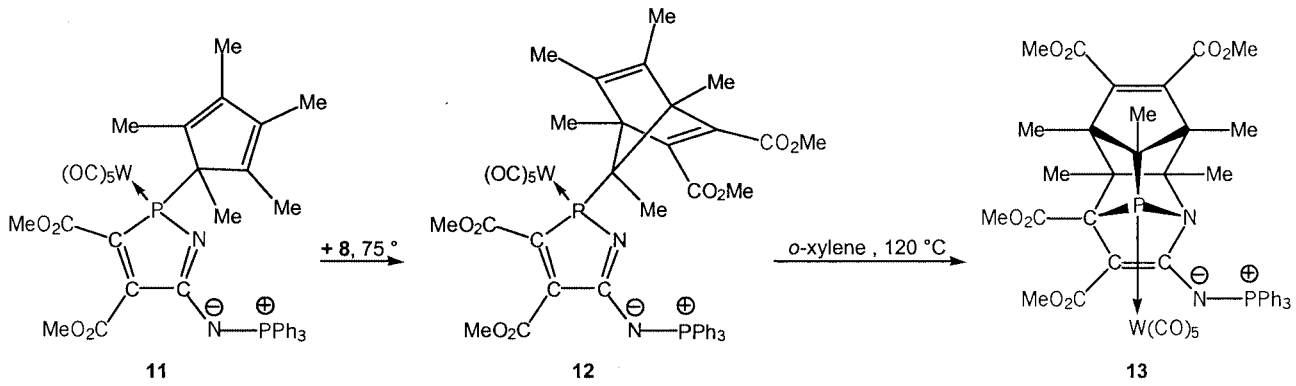
Scheme 4. Synthesis of 2*H*-1,2-azaphosphole complex **11**

We were also able to carry out a clean *intermolecular* Diels−Alder reaction of **11** with DMAD at 75 °C, which yielded complex **12** in high yields, just by strictly controlling the reaction times for the first (**9** → **11**) and the second chemical transformations (**11** → **12**). Further studies of the thermal stability of complex **12** led to another surprisingly high-yield and unprecedented cycloaddition reaction in azaphosphole chemistry. Upon heating an *o*-xylene solution of complex **12** at 120 °C an *intramolecular* Diels−Alder reaction of the aza-1,3-diene unit of the 2*H*-1,2-azaphosphole ring with the dimethyl-substituted ethylene unit of the norbornadiene substituent selectively furnished complex **13**, which contains a new phosphorus−nitrogen−carbon cage compound as the ligand system (Scheme 5).

It is remarkable that the ^{31}P resonance of the ring junction phosphorus atom in **13** at δ = 158.4 ppm [$J(^{183}W,P)$ = 269.9 Hz] is much more deshielded than the phosphorus nuclei in **11** and **12**, although it now has a more conventional chemical environment. Therefore, this deshielding might be explained in terms of ring strain in **13**.[23] Furthermore, the exocyclic phosphorus atom in **13** experiences a significant shielding in comparison with **11** and **12** and resonates at δ = 1.3 [**11**: δ(P) = 18.1 and **12**: δ(P) = 18.4 ppm].

Discussion of Selected ^1H and ^{13}C NMR Spectroscopic and Mass Spectrometric Data

The ^1H and ^{13}C NMR spectra of complexes **11**−**13** were assigned as fully as possible by the use of two-dimensional shift correlation experiments (HSQC and HMBC). One-di-



Scheme 5. Synthesis of complexes **12** and **13** using inter- and intramolecular Diels–Alder reactions

mensional ^{1}H and ^{13}C NMR spectra were recorded at magnetic field strengths of both 4.7 T and 9.4 T so that, for closely lying lines, one could unequivocally decide which line distances corresponded to coupling constants involving ^{31}P and which ones to small chemical shift differences.

The ^{1}H and ^{13}C NMR signals of the PPh_3 groups of **11–13** are assigned in a straightforward manner and need not be discussed. In the spectra of **11** the ^{13}C and ^{1}H signals belonging to the same ester groups can be identified by the correlation spectra. But as the ester nuclei do not show any correlations to 'outside' nuclei, it is not clear which ester group gives rise to which signals. Assignment of the signals of the Cp* moiety starts from the large $^{3}J_{P,H}$ coupling constant (15.0 Hz) of the protons of the methyl group at the quaternary sp^3 carbon (Cp*-C-1). By exploiting the $^{2}J_{C,H}$ and $^{3}J_{C,H}$ correlations, the ^{1}H and ^{13}C signals of the Cp* group are fully assigned. The vicinity of the chiral phosphorus atom causes chemical nonequivalence of C-2 and C-5, of C-3 and C-4 and of their attached methyl groups. It may be noted that three-bond C,H-correlations are found across the double bonds of the Cp* group but not across the C-3/C-4 single bond, i.e. there is no crosspeak for C-3/4-Me or C-4/3-Me. The carbon atoms of the 2*H*-1,2-azaphosphole ring show no HMBC correlations to any protons. They are tentatively assigned on account of their chemical shifts and coupling constants with phosphorus. Hence, the most deshielded carbon (δ_C = 166.5 ppm) is assumed to be C-5 because of its amidine character. Of the remaining ring carbon atoms, C-4 has $^{2}J_{P,C}$ and $^{3}J_{P,C}$ couplings, while C-3 experiences $^{1}J_{P,C}$ and $^{4}J_{P,C}$ interactions. The values of 18.9 or 26.1 Hz associated with δ_C = 149.4 ppm are believed to be too large for $^{4}J_{P,C}$. Thus C-3 is assigned to δ_C = 151.6 ppm with its *J* values of 4.4, 2.7 Hz.

The spectral assignments for **12** were similar to those described for **11**. The two ester groups at the 2*H*-1,2-azaphosphole ring are distinguished from those at the norbornadiene moiety by the coupling of their carbonyl carbon nuclei with the phosphorus atom. Assignment of the pentamethylnorbornadiene atoms started with the protons of the 7-methyl group which were again identified by their coupling with ^{31}P. The protons of one of the bridgehead methyl groups were found to be strongly shielded (δ = 0.08 ppm), while their counterparts show a more normal ^{1}H chemical shift of δ = 1.59 ppm. Possible causes for this shielding are the aromatic rings of the triphenylphosphane-iminyl group or one or several of the carbonyl groups of the $W(CO)_5$ substituent. The unknown geometry of **12** does not permit a definite conclusion. Finally, the extreme deshielding of the carbon C-7 from the norbornadiene bridge (δ = 90.5 ppm), an sp^3 carbon atom with a phosphorus atom as the only somewhat polar substituent, is in line with the large chemical shift in norbornadiene itself (δ = 75.1 ppm),[24] which is further increased by the presence of one α- and two β-methyl groups.

For compound **13**, all ^{13}C and ^{1}H chemical shifts of the central 1-aza-11-phosphatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene system were assigned from the crosspeaks in the HSQC and HMBC spectra. Apart from the methyl carbons (*C*-methyl and ester *O*-methyl) and the $W(CO)_5$ group, only the carbon nuclei of the 9,10-double bond showed no correlations with distant protons. These carbon atoms have widely different chemical shifts (δ = 159.8 ppm and 98.6) which are characteristic of a push-pull substituted double bond.

A common feature of the EI-mass spectra of **11**, **12** and **13** is the cleavage of the P,N ylidic bond, thus generating $[Ph_3P]^{+\cdot}$ and neutral species such as nitrenes. The further degradation of $[Ph_3P]^{+\cdot}$ has been reported previously[25] and was very recently observed in the case of *P*-bis(trimethylsilyl)methyl-substituted 2*H*-1,2-azaphosphole complexes.[26] Another important fragmentation process is the cleavage of the exocyclic P–C bond of the complexes **11** and **12.** Furthermore, all complexes lose the $W(CO)_5$ fragment upon ionization. In the case of complex **13** the main fragmentation includes a rearrangement of the polycyclic ring system by formation of a substituted pyridine radical cation.

Discussion of Selected Structural Data

We were able to confirm the molecular structures of complexes **11** (Figure 1) and **13** (Figure 3 and 4) for the solid state by X-ray single crystal structure analyses (Table 1). The almost planar 2*H*-1,2-azaphosphole ring of complex **11** (mean deviation of 0.02 Å) showed no unusual atom dis-

tances when compared to complex **14** (Figure 2),[15] the only known structure of a *P*-Cp*-substituted phosphole[27,28] or heterophosphole.[29] As a common structural motif in diester-substituted 2*H*-1,2-azaphosphole rings[25] the ester group at C16 almost shows an in-plane orientation, whereas the ester group at C-17 is oriented out-of-plane. The torsion angle of N(1)−C(18)−N(2)−P(2) is 0.3° and, therefore, should enable electronic interactions between the substituent and the ring system. The planes of the two five-membered rings in **11** are partially eclipsed, in contrast to **14**, where the respective planes adopt a conformation in which they have an opposite orientation along the exocyclic P−C bond. However, this does not greatly effect the corresponding P−C distances [**11**: P(1)−C(6) 1.886(3) Å and **14**: P(1)−C(8) 187.7(2) Å]. A comparison of the azaphospholene moiety of the molecular structure of complex **13** (Figure 3 and 4) with compounds **15**[30] and **16**[31] (Figure 5), which also have azaphospholene ring structures with a C−C double bond, reveals the uniqueness of **13**. The C(7)−C(8) distance of 1.373(2) Å is that of an elongated C-C double bond [**15**: 1.290(3) Å;[30] **16**: 1.329 Å[31]], which might be caused by the electronic interaction with the Ph_3PN group [N(1)−C(8)−N(2)−P(2): −29.8 °]. It is also remarkable that the P(1)−C(6) and P(1)−N(1) distances of 1.8925(15) and 1.7706(13) Å, respectively, are fairly long [**15**: 1.818(2) and 164.5(2) Å;[30] **16**: 180.0 and 171.6 pm[31]]. This is associated with a long P(1)−C(13) distance of 1.8968(15) Å and a short P(1)−W distance of 2.4744(4) Å. The valence bond angle sum of Σ°P(1)·273 °, which very much resembles the situation of compound **8** in its transition metal-coordinated form.

Table 1. Crystal data and structure refinement[34] of complexes **11** and **13**

Complex	**11**	**13**
Empirical formula	$C_{41}H_{46}N_3O_9P_2W$	$C_{47}H_{50}Cl_2N_2O_{13}P_2W$
M_r	970.60	1167.58
Crystal size (mm)	0.21 × 0.14 × 0.05	0.31 × 0.30 × 0.08
Crystal system	triclinic	monoclinic
Space group	$P(-1)$	$P2_1/n$
Unit cell dimensions		
a (Å)	11.9636(12)	17.4060(10)
b (Å)	13.8639(14)	12.3286(6)
c (Å)	14.5331(14)	22.1482(12)
α (°)	93.959(3)	90
β (°)	90.407(3)	101.746(3)
γ (°)	113.490(3)	90
V (Å^3)	2203.9(4)	4653.3(4)
Z	2	4
$D_{calcd.}$ (Mg·m^{-3})	1.463	1.667
μ (mm^{-1})	2.747	2.734
Transmissions	0.7119−0.8622	0.6192−0.8622
F(000)	978	2352
T (K)	133(2)	133(2)
$2\theta_{max}$	60	60
No. of reflections		
measured	47472	84792
unique	13346	14181
R_{int}	0.0434	0.0339
Parameters	541	613
Restraints	9	102
wR (F^2, all reflections)	0.0694	0.0564
R [F, $I > 2\sigma(I)$]	0.0313	0.0205
S	0.781	1.011
max. Δρ (e·Å^{-3})	2.161	1.153

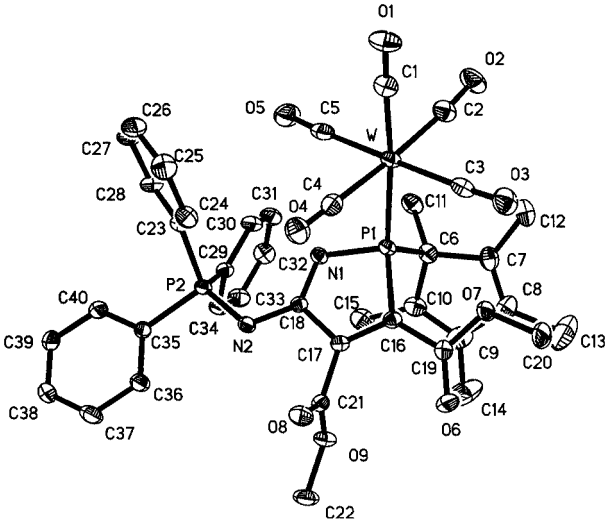
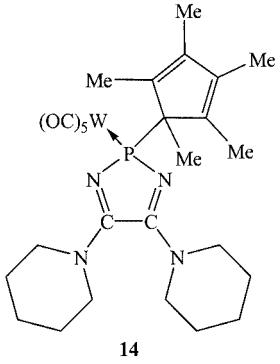


Figure 1. Molecular structure of **11** from the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°] (values for both molecules are given): W−C1 2.004(3), W−P1 2.5338(7), P1−N1 1.691(2), N1−C18 1.306(3), C16−C17 1.338(3); W−P1−C6 118.79(8), C18−N1−P1 111.15(17), C16−C17−C18 112.7(2). The following short contacts are observed in **11**: C37−H37···O8 Å (operator $-x$, $-y + 1$, $-z + 2$); C28−H28···O2 (operator $-x + 1$, $-y + 1$, $-z + 1$); C11−H11C···O99 (operator $-x + 1$, $-y + 1$, $-z + 1$); C26−H26···O99 (operator $-x + 1$, $-y + 1$, $-z + 1$)



14

Figure 2. 2*H*-1,2-azaphosphole complex **14**[15]

Because studies of a so called[31] "dimer" of compound **16** have shown an excellent performance (up to 95% *ee* at −70 °C) in hydrovinylation reactions of styrene,[32] we are currently trying to liberate the new polycyclic phosphane ligand of **13**.

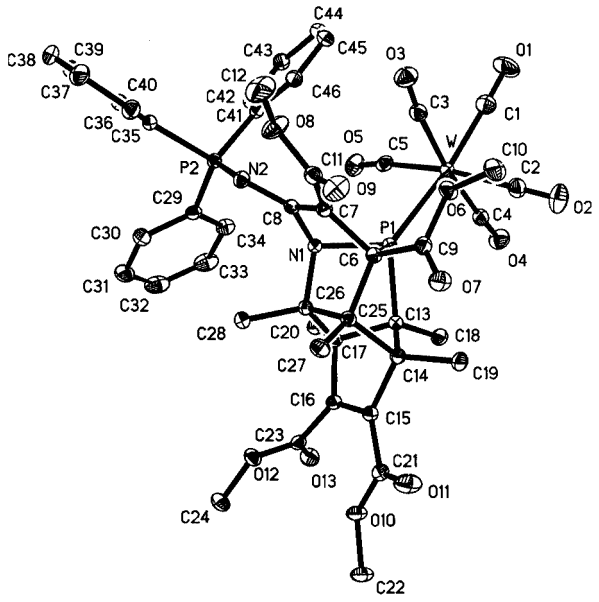


Figure 3. Molecular structure of **13** from the crystal (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity); selected bond lengths [A] and angles [°] (values for both molecules are given): W−P1−C6 125.82(5), N1−P1−C13 92.77(6), P1−N1−C8 106.15(9), N1−C8−C7 110.37(13), C6−C7−C8 110.90(13), C7−C6−P1 99.88(10). Specified hydrogen bonds (with esds except fixed and riding H): D−HH···AD···A<(DHD) 0.952.553.393(2)147.3C(32)−H(32)···O(11), 0.952.493.403(2)161.9C(37)−H(37)···O(13)

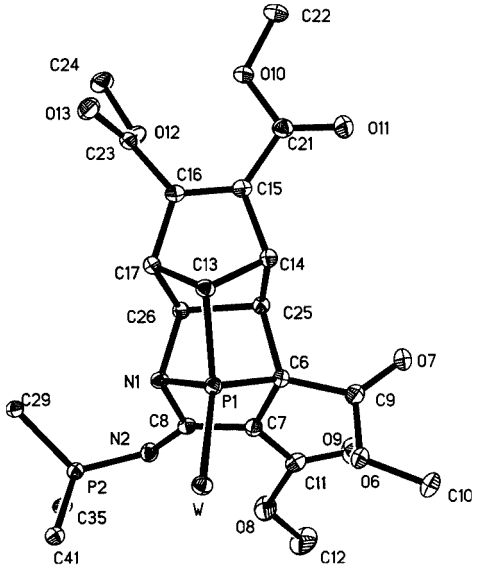


Figure 4. Reduced molecular structure of **13** (top-view)

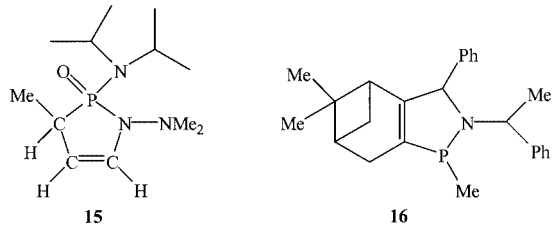


Figure 5. Azaphospholenes **15**[30] and **16**.[31]

Conclusions

We have shown that the stability of *P*-Cp*-substituted 2*H*-1,2-azaphosphole complexes can be significantly enhanced by choosing the right substituent and that they are now available for further investigations − two new reactions were presented here. Furthermore, this example can be regarded as a blueprint for the synthesis of other phosphorus-carbon and phosphorus-nitrogen-carbon cage compounds thus underlining once more the usefulness of *P*-Cp*-substituted 2*H*-azaphosphirene complexes in the construction of new and unusual polycyclic phosphane ligands.

Experimental Section

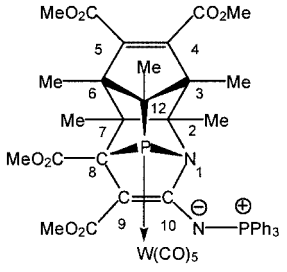
General Procedures: All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware, and solvents were dried according to standard procedures. The NMR spectra were obtained on the Bruker spectrometers Avance DRX400 and Avance DPX200 at operation frequencies of 400 MHz (^{1}H), 101 MHz (^{13}C), 161 MHz (^{31}P) and of 200 MHz (^{1}H), 50 MHz (^{13}C), 81 MHz (^{31}P), respectively. Chemical shifts were referenced to internal tetramethylsilane (^{1}H, δ = 0.00 ppm), $CDCl_3$ (^{13}C, δ = 77.0 ppm) and to the frequency of virtual external 85% orthophosphoric acid (^{31}P, δ = 0.0 ppm). The latter frequency was determined independently from a concentric capillary of H_3PO_4 in neat $CDCl_3$. DEPT-135 spectra were carried out to determine the degree of substitution of the carbon atoms. The spectrometer software used was XWin NMR version 2.6. The manufacturer's pulse programs 'invigstp' (gradient-selected phase-sensitive HSQC) and 'inv4gslplrnd' (gradient-selected HMBC) controlled the two-dimensional NMR spectroscopic experiments[33]. The 2D experiments were optimized for coupling constants of 145 Hz [$^1J_{C,H}$] and 7.7 Hz [$^{2,3}J_{C,H}$]. Digital resolutions were chosen to be small enough in both dimensions to permit the resolution of closely lying chemical shifts. All coupling constants reported involve ^{31}P unless otherwise specified. Electron impact (EI) (70 eV), chemical ionization (CI) (ammonia), and fast atom bombardment (FAB) (Xenon, NBA) mass spectra were recorded on a double focusing mass spectrometer Finnigan MAT-8430; Exact mass resolution R = 10000 (10%-valley-definition). Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). UV/vis spectra were recorded on a Hewlett Packard HP 8452. Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed by using a Carlo Erba analytical gas chromatograph. The κP-notation in the nomenclature is intended to differentiate between *P*- and *N*-coordination of the appropriate heterocycle to the metal.

[Pentacarbonyl{3,4-bis(methoxycarbonyl)-2-pentamethylcyclopentadienyl-5-(*N*-triphenylphosphonioimidoyl)-2*H*-1,2-azaphosphole-κP}tungsten(0)] (11): Carbonitrile **10** (0.9 mmol) and DMAD (0.85 mmol) were added to a solution of 2*H*-azaphosphirene complex **9** (0.51 g, 0.86 mmol), dissolved in toluene (5 mL). The solution was heated at 75 °C for 25 min while stirring slowly and was controlled by ^{31}P NMR spectroscopy. All volatile components were then removed in vacuo (ca. 0.01 mbar) and the products separated by low-temperature column chromatography (SiO_2, −10 °C, 10 × 2 cm, *n*-pentane/diethyl ether, 50:50). Evaporation of the third fraction yielded complex **11** as a yellow solid.

Yield: 620 mg, 77%; m.p. 87 °C (decomp.). ^{1}H NMR: δ = 0.83 (d, *J* = 15.0 Hz, 3 H, cp*-1-Me), 1.25 (br. s, 3 H, cp*-5-Me), 1.52 (br. s, 3 H, cp*-2-Me), 1.660 (dd, *J* = 4.2, 1.2 Hz, 3 H, cp*-4-Me), 1.673 (dd, *J* = 4.3, 1.2 Hz, 3 H, cp*-3-Me), 3.74 (s, 3 H, 4- or 3-azaphosphole(azap)-COO*Me*), 3.94 (s, 3 H, 3- or 4-azap-*COOMe*), 7.44 (m_c, 6 H, H-*meta* of PPh_3), 7.55 (m_c, 3 H, H-*para* of PPh_3), 7.80 (m, 6 H, H-*ortho* of PPh_3) ppm. ^{13}C NMR: δ = 11.16 (d, *J* = 1.5 Hz, cp*-4-Me), 11.22 (d, *J* = 0.7 Hz, cp*-5-Me), 11.4 (d, *J* = 1.5 Hz, cp*-3-Me), 12.2 (d, *J* = 1.6 Hz, cp*-2-Me), 13.7 (d, *J* = 0.9 Hz, cp*-1-Me), 52.1 (s, azap-4- or 3-COO*Me*), 52.5 (s, azap-3- or 4-COO*Me*), 62.6 (dd, *J* = 6.1, 0.5 Hz, cp*-C-1), 127.3 (d, *J* = 100.7 Hz, C-*ipso* of PPh_3), 128.7 (d, *J* = 12.5 Hz, C-*meta* of PPh_3), 132.5 (d, *J* = 2.9 Hz, C-*para* of PPh_3), 133.4 (d, *J* = 10.1 Hz, C-*ortho* of PPh_3), 137.1 (s, cp*-C-5), 137.2 (d, *J* = 3.0 Hz, cp*-C-2), 139.4 (d, *J* = 6.7 Hz, cp*-C-3), 140.0 (d, *J* = 5.9 Hz, cp*-C-4), 149.4 (dd, *J* = 26.1, 18.9 Hz, azap-C-4), 151.6 (dd, *J* = 4.4, 2.7 Hz, azap-C-3), 163.8 (dd, *J* = 10.7, 2.3 Hz, azap-4- or 3-*C*OOMe), 165.4 (dd, *J* = 14.5, 1.0 Hz, azap-3- or 4-*C*OOMe), 166.5 (dd, *J* = 11.7, 5.5 Hz, azap-C-5), 196.5 (d, *J* = 7.4, *J*(^{183}W,C) = 126.5 Hz, WCO-*cis*), 199.5 (d, *J* = 25.4 Hz, WCO-*trans*) ppm. ^{31}P NMR: δ = 18.1 (d, *J* = 1.2 Hz, PPh_3), 105.0 [br. s, *J*(^{183}W,P) = 256.0 Hz, azap-P] ppm. UV/Vis (CH_3CN): λ (lg ε) = 228 (4.90), 248 (4.64), 274 (4.15), 300 (3.86), 324 (3.84), 360 (3.71), 380 (3.52) nm. IR (KBr): ṽ = 2069 (vs, CO), 1980 (vs, CO), 1931 (s, CO), 1741 (vs, CO_2), 1719 (vs, CO_2) cm^{-1}. MS (EI, ^{184}W): *m*/*z* = 934 (1) $[M]^{+\cdot}$, 903 (1) $[M - OCH_3]^+$, 799 (100) $[M - Cp^*]^{+\cdot}$, 771 (18) $[M - Cp^*\text{-}CO]^{+\cdot}$, 743 (45) $[M - Cp^*\text{-}2CO]^{+\cdot}$, 687 (40) $[M - Cp^*\text{-}4CO]^{+\cdot}$, 659 (90) $[M - Cp^*\text{-}5CO]^{+\cdot}$, 631 (35) $[M - Cp^*\text{-}6CO]^{+\cdot}$, 262 (20) $[PPh_3]^{+\cdot}$, 183 (30) $[PPh_2]^+$. $C_{40}H_{36}N_2O_9P_2W$ (934.5): calcd. C 51.41, H 3.88, N 3.00; found C 51.26, H 4.23, N 3.20.

{Pentacarbonyl[2,3-bis(methoxycarbonyl)-2-(1,4,5,6,7-pentamethylnorborna-2,5-dien-7-yl)-3,4-bis(methoxycarbonyl)-5-(*N*-triphenylphosphonioiminoyl)-2*H*-1,2-azaphosphole-κP]tungsten(0)} (12): Carbonitrile **10** (1 mmol) and DMAD (2 mmol) were added to a toluene (6 mL) solution of 2*H*-azaphosphirene complex **11** (0.6 g, 1 mmol). The solution was heated at 75 °C for 20 h while stirring slowly and was controlled by ^{31}P NMR spectroscopy. All volatile components were then removed in vacuo (ca. 0.01 mbar) and the products separated by low-temperature column chromatography (SiO_2, −10 °C, 10 × 2 cm, *n*-pentane/diethyl ether, 20:80). Evaporation of the third fraction yielded complex **12** as a yellow solid. Yield: 850 mg, 79%; m.p. 152 °C (decomp.). ^{1}H NMR: δ = 0.08 [s, 3 H, norbornadiene(nor)-4-Me], 1.37 (d, *J* = 15.7 Hz, 3 H, nor-7-Me), 1.45 (s, 3 H, nor-5-Me), 1.49 (s, 3 H, nor-6-Me), 1.59 (s, 3 H, nor-1-Me), 3.63 (s, 3 H, 3- or 2-nor-COO*Me*), 3.66 (s, 3 H, 2- or 3-nor-COO*Me*), 3.82 [s, 3 H, 4- or 3-azaphosphole(azap)-COO*Me*], 3.98 (s, 3 H, 3- or 4-azap-COO*Me*), 7.46 (m_c, 6 H, H-*meta* of PPh_3), 7.57 (m_c, 3 H, H-*para* of PPh_3), 7.80 (m_c, 6 H, H-*ortho* of PPh_3) ppm. ^{13}C NMR: δ = 9.0 (s, nor-4-Me) 11.36 (d, *J* = 4.0 Hz, nor-1-Me) 11.44 (s, nor-5-Me), 12.4 (s, nor-6-Me), 16.4 (d, *J* = 18.4 Hz, nor-7-Me), 51.6 (s, 3- or 2-nor-COO*Me*), 51.7 (s, 2- or 3-nor-COO*Me*), 52.3 (s, 4- or 3-azap-COO*Me*), 52.5 (s, 3- or 4-azap-COO*Me*), 66.0 (d, *J* = 8.6 Hz, nor-C-1), 68.3 (d, *J* = 4.6 Hz, nor-C-4), 90.5 (d, *J* = 5.5 Hz, nor-C-7), 126.8 (d, *J* = 100.3 Hz, C-*ipso* of PPh_3), 128.6 (d, *J* = 12.5 Hz, C-*meta* of PPh_3), 132.5 (d, *J* = 2.9 Hz, C-*para* of PPh_3), 133.4 (d, *J* = 10.1 Hz, C-*ortho* of PPh_3), 145.3 (dd, *J* = 26.1, 19.1 Hz, ap-C-4), 146.3 (s, nor-C-6), 147.7 (s, nor-C-5), 149.0 (d, *J* = 7.4 Hz, nor-C-2), 151.0 (dd, *J* = 3.7, 2.8 Hz, azap-C-3), 156.5 (d, *J* = 5.5 Hz, nor-C-3), 161.9 (dd, *J* = 11.9, 2.3 Hz, 4- or 3-azap-*C*OOMe), 165.1 (d, *J* = 1.2 Hz, 2- or 3-nor-*C*OOMe), 165.4 (dd, *J* = 14.8, 0.9 Hz, 3- or 4-azap-*C*OOMe), 165.8 (dd, *J* = 9.1, 5.7 Hz, azap-C-5), 166.0 (s, 3- or 2-nor-*C*OOMe), 197.2 [d, *J* = 6.8, *J*(^{183}W,C) = 127.3 Hz, WCO-*cis*], 199.8 (d, *J* = 23.6 Hz, WCO-*trans*) ppm. ^{31}P NMR: δ = 18.5 (d, *J* = 1.3 Hz, PPh_3), 97.0 [d, *J* = 1.3, *J*(^{183}W,P) = 242.6 Hz, PW] ppm. UV/Vis (CH_3CN): λ (lg ε) = 230 (4.89), 258 (4.48), 272 (4.30), 284 (4.17), 296 (4.10), 316 (3.89), 340 (3.65), 360 (3.39) nm. IR (KBr): ṽ = 2079 (vs, CO), 1988 (vs, CO), 1939 (s, CO), 1735 (vs, CO_2), 1724 (vs, CO_2) cm^{-1}. MS (EI, ^{184}W): *m*/*z* = 1076 (7) $[M]^{+\cdot}$, 752 (30) $[M - W(CO)_5]^{+\cdot}$, 277 (100) [Nor.]$^+$, 262 (78) $[PPh_3]^{+\cdot}$, 183 (55) $[PPh_2]^+$. $C_{46}H_{42}N_2O_{13}P_2W$ (1076.6): calcd. C 51.32, H 3.93, N 2.60; found C 49.77, H 4.04, N 2.54.

[Pentacarbonyl{4,5,8,9-tetrakis(methoxycarbonyl)-2,3,6,7,12-pentamethyl-10-triphenylphosphonioiminoyl-1-aza-11-phosphatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene-κP}tungsten(0)] (13): 12 (0.37 g, 0.00034 mol) was dissolved in *o*-xylene (1.8 mL) and heated at 120 °C for 100 min while stirring slowly. All volatile components were then removed in vacuo (ca. 0.01 mbar) and the products separated by low-temperature column chromatography (SiO_2, −10 °C, 10 × 2 cm, *n*-pentane/diethyl ether, 10:30). Evaporation of the second fraction and recrystallization from diethyl ether yielded complex **13** as pale a yellow solid.



Yield: 200 mg, 53%; m.p. 142 °C (decomp.). ^{1}H NMR: δ = 0.65 (s, 3 H, 3-Me), 0.74 (s, 3 H, 2-Me), 1.00 (d, *J* = 15.4 Hz, 3 H, 12-Me), 1.07 (s, 3 H, 6-Me), 1.35 (s, 3 H, 7-Me), 3.55 (s, 3 H, 8- or 9-COO*Me*), 3.68 (s, 3 H, 4- or 5-*COOMe*), 3.73 (s, 3 H, 5- or 4-*COOMe*), 3.74 (s, 3 H, 9- or 8-COO*Me*), 7.47 (m_c, 6 H, H-*meta* of PPh_3), 7.56 (m_c, 3 H, H-*para* of PPh_3), 7.82 (m, 6 H, H-*ortho* of PPh_3) ppm. ^{13}C NMR: δ = 9.2 (d, *J* = 14.8 Hz, 12-Me), 10.7 (s, 3-Me), 13.3 (v. br. s, 6-Me), 13.8 (br. d, *J* = 4.8 Hz, 7-Me), 15.5 (br. d, *J* = 4.1 Hz, 2-Me), 50.3 (s, 8- or 9-COO*Me*), 51.3 (d, *J* = 0.7 Hz, 9- or 8-COO*Me*), 51.96 (s, 4- or 5-COO*Me*), 52.02 (s, 5- or 4-*COOMe*), 61.4 (br. d, *J* = 13.6 Hz, C-7), 68.6 (d, *J* = 1.3 Hz, C-3), 68.9 (s, C-6), 73.7 (d, *J* = 13.6 Hz, C-12), 74.5 (dd, *J* = 11.0, 1.5 Hz, C-8), 85.6 (br. d, *J* ≈ 1.3 Hz, C-2), 98.6 (dd, *J* = 14.1, 7.5 Hz, C-9), 128.6 (d, *J* = 12.8 Hz, C-*meta* of PPh_3), 130.3 (d, *J* = 105.7 Hz, C-*ipso* of PPh_3), 132.1 (d, *J* = 3.0 Hz, C-*para* of PPh_3), 132.9 (d, *J* = 10.7 Hz, C-*ortho* of PPh_3), 141.7 (d, *J* = 4.2 Hz, C-4), 142.6 (br. d, *J* = 4.8 Hz, C-5), 159.8 (dd, *J* = 4.3, 1.2 Hz, C-10), 164.8 (d, *J* = 0.4 Hz, 5- or 4-*C*OOMe), 165.0 (s, 4- or 5-*C*O-OMe), 166.1 (dd, *J* = 5.3, 1.1 Hz, 8- or 9-*C*OOMe), 169.3 (br. s, 9- or 8-*C*OOMe), 195.5 [d, *J* = 7.8, *J*(^{183}W,C) = 125.4 Hz, WCO-*cis*], 197.8 (d, *J* = 29.9 Hz, WCO-*trans*) ppm. ^{31}P NMR: δ = 1.3 (s, $Ph_3P{=}N$), 158.4 [s, *J*(^{183}W,P) = 269.9 Hz, $C_2P{-}N$] ppm. UV/Vis (CH_3CN): λ (lg ε) = 232 (4.93), 252 (4.51), 264 (4.35), 276 (4.22), 300 (4.09), 318 (3.92), 332 (3.85), 356 (3.76) nm. IR (KBr): ṽ = 2074 (s, CO), 1990 (s, CO), 1939 (vs, CO), 1929 (vs, CO), 1742 (s, CO_2), 1732 (s, CO_2) cm^{-1}. MS (EI, ^{184}W): *m*/*z* = 1076 (10) $[M]^{+\cdot}$, 934 $[M - DMAD]^{+\cdot}$, 752 (15) $[M - W(CO)_5]^{+\cdot}$, 277 (30) $[HNPPh_3]^+$, 262 (48) $[PPh_3]^{+\cdot}$, 183 (46) $[PPh_2]^+$, 28 (100) [CO]. MS (*pos.*-DCI, ^{35}Cl, ^{184}W): *m*/*z* = 1077 (22) $[M + H]^+$. MS (*neg.*-DCI, ^{35}Cl, ^{184}W): = *m*/*z* = 1076 (12) $[M]^{-\cdot}$, 814 (38) $[M - PPh_3]^{-\cdot}$, 324 (62) $[W(CO)_5]^{-\cdot}$. $C_{46}H_{42}N_2O_{13}P_2W$ (1076.6) : calcd. 1074.1644; found 1074.1652 (δ = −0.7 ppm).

CCDC-193063 and -193064 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to the Fonds der Chemischen Industrie and the Deutsche Forschungs-gemeinschaft for financial support.

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Received November 27, 2002

