Addition of a Phosphinidene Complex to C=N Bonds: P-Ylides, Azaphosphiridines, and 1,3-Dipolar Cycloadditions

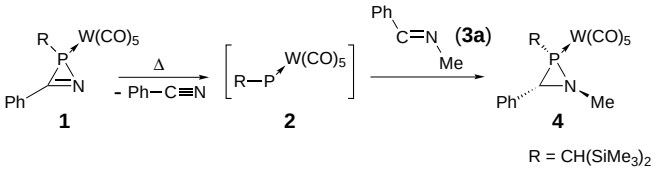
Mark J. M. Vlaar,[a] Pieter Valkier,[a] Frans J. J. de Kanter,[a] Marius Schakel,[a] Andreas W. Ehlers,[a] Anthony L. Spek,[b] Martin Lutz,[b] and Koop Lammertsma*[a]

Abstract: The terminal phosphinidene complex $PhPW(CO)_5$ adds to the imine bond of PhHC=N–Ph to give 3-membered ring azaphosphiridines, which undergo ring-expansion with an additional imine to yield a set of four isomeric five-membered ring diazaphospholanes. Treatment with the diimines $PhHC=N-(CH_2)_n-N=CHPh$ ($n = 2,3,4$) results instead—in all three cases—in only a single isomer of the $(CH_2)_n$ bridged diazaphospholane. For $n = 2$ or 3, this aminal group is easily hydrolyzed to afford new 6- and 7-membered ring heterocycles. No intermediate azaphosphiridine complex is observed during the addition reaction to the diimines. B3LYP/6–31G* calculations on an unsubstituted, uncomplexed system suggest that the initially formed P,N-ylide of the $H_2C=N-(CH_2)_2-N=CH_2$ diimine both kinetically and thermodynamically favors an intramolecular 1,3-dipolar cycloaddition over an imine insertion into the CPN ring of an intermediate azaphosphiridine. Single-crystal X-ray structures for the $(CH_2)_2$-bridged azaphospholane complex and the HCl adduct of the 7-membered hydrolysis product are presented.

Keywords: complexed phosphinidene · cycloaddition · density functional calculations · heterocycles · ylides

Introduction

A plethora of strained organophosphorus compounds has been synthesized by the addition of transition metal-complexed phosphinidenes to unsaturated carbon-carbon bonds.[1] R-P=M(CO)$_n$, generated in situ, has electrophilic, carbene-like reactivity; this illustrates the similarity in chemistry between low-coordinate phosphorus and carbon compounds. Relatively little is known about the reactivity of these phosphinidenes toward heteroolefins. Recently, we demonstrated for the first time that Ph-P=W(CO)$_5$ adds to the C=Si bond of a silene generated in situ to form a stable silaphosphirane (CSiP) ring.[2] A few studies on addition to C=N bonds have appeared. Mathey and co-workers[3] reported as early as 1986 that a methoxy-substituted phosphinidene adds to 1-azadienes to give 1,4-adducts, that is, 1,2-azaphospholenes. They did not observe intermediates during the formation of the five-membered ring structure. In 1994, Streubel et al.[4] reported the first, and so far only, 1,2-addition to a C=N bond. Azaphosphiridine complex **4** was obtained from thermal decomposition of the 2*H*-azaphosphirene complex **1** in the presence of imine **3a** (Scheme 1).



Scheme 1.

Recently, Mathey and co-workers[5] showed that phosphinidene complexes **6a–c**, generated from the corresponding 7-phosphanorbornadienes **5a–c**, react with an excess of imine **3a**. Only the five-membered 1,4,2-diazaphospholanes **7a–c** were formed (Scheme 2), but with MePW(CO)$_5$ (**6c**) they also obtained the four-membered 1,2,3-azadiphosphetidine complex **8**. It was suggested that the formation of these products results from the insertion of a second imine and phosphinidene, respectively, into the presumably weak P–N bond of the undetected azaphosphiridine intermediates. A CPN ring had also been proposed earlier as an intermediate in the reaction between phosphenium ions and imines[6] to afford five-membered ring compounds.[7]

[a] Prof. Dr. K. Lammertsma, M. J. M. Vlaar, P. Valkier, Dr. F. J. J. de Kanter, Dr. M. Schakel, Dr. A. W. Ehlers
Department of Organic and Inorganic Chemistry
Faculty of Sciences, Vrije Universiteit, De Boelelaan 1083
1081 HV, Amsterdam (The Netherlands)
Fax: (+31) 20-4447488
E-mail: lammert@chem.vu.nl

[b] Prof. Dr. A. L. Spek, Dr. M. Lutz
Bijvoet Center for Biomolecular Research
Crystal and Structural Chemistry, Utrecht University
Padualaan 8, 3584 CH, Utrecht (The Netherlands)

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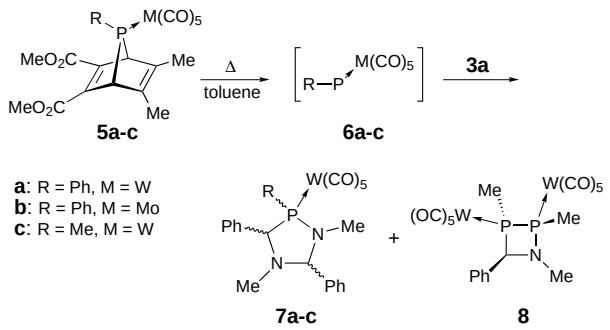
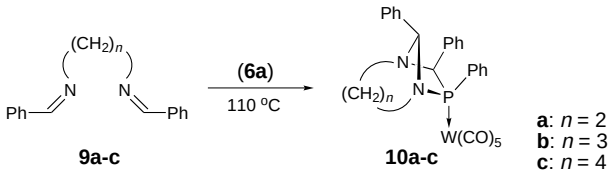


Scheme 2.

In pursuing applications of $PhPW(CO)_5$ (**6a**), we became interested in its reactivity toward imines and diimines. Here we report on the synthesis and properties of azaphosphiridine and bridged diazaphospholane complexes. We also address the mechanism through which the formal [1+2+2] adducts are formed.

Results and Discussion

Synthesis and characterization of bicyclic structures: Treatment of $PhPW(CO)_5$ (**6a**) with diimines (**9a–c**) at 110 °C in toluene gave the novel bicyclic compounds **10a–c** in good yields (54–74%) (Scheme 3). The reactions are remarkably



Scheme 3.

diastereoselective considering the high reactivity of the transient complexed phosphinidene; with only one of eight possible diastereomers being formed in each case. This is evident from the single ^{31}P NMR resonances for **10a**, **10b**, and **10c** at $\delta = 95.6$, 85.6, and 92.7, respectively. The configuration of **10b** was firmly established by a single-crystal X-ray structure determination (Figure 1). The structure has an endo P(1)–$W(CO)_5$ substituent, *cis* P(1)–Ph and C(4)–Ph groups in the *exo* position, and a bridgehead C(5)–Ph group directed toward the $(CH_2)_2$ methylene chain. It is not surprising that the rather congested five-membered C_2N_2P ring is slightly distorted. This is evident not only from the 1.937(5) Å P(1)–C(4) bond, which is rather long relative to the more usual 1.85 Å,[8] but also from the N(2)–C(5) bond of 1.496(5) Å, longer than the more typical 1.471(6) Å distance found for the N(1)–C(5) bond. The 1.730(4) Å P(1)–N(2) bond is of normal length. NOE experiments showed the configurations of the phenyl-substituted carbon centers in all three complexes, **10a**, **10b**, and **10c**, to be the same. They all show interactions of the $(CH_2)_n$ hydrogens with both the N-*C*5-N phenyl group and the P-*C*4-N hydrogen. The NOE interaction between the N-*C*5-N hydrogen and the P(1)-phenyl group confirms that **10c** has the same conformation at P(1) as **10b**, but the extent of this interaction is less evident for **10a**.

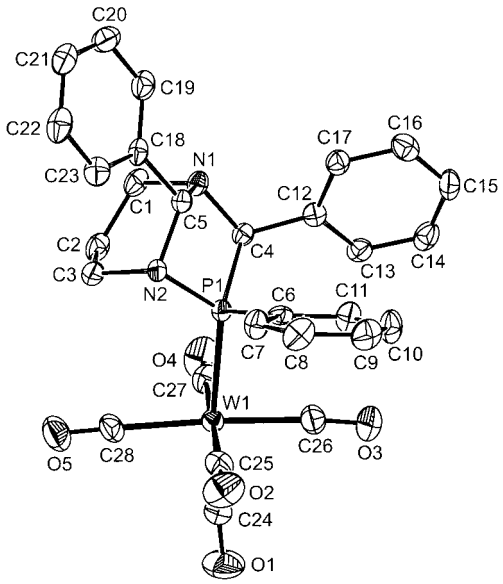
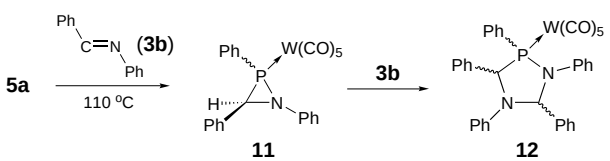


Figure 1. Displacement ellipsoid plot of **10b** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–W(1) 2.5164(11), P(1)–N(2) 1.730(4), P(1)–C(4) 1.937(5), P(1)–C(6) 1.833(4), N(1)–C(1) 1.485(5), N(1)–C(4) 1.465(5), N(1)–C(5) 1.471(6), N(2)–C(3) 1.489(5), N(2)–C(5) 1.496(5), C(1)–C(2) 1.524(7), C(2)–C(3) 1.520(7), C(4)–C(1)2 1.502(6), C(5)–C(1)8 1.522(6), W(1)–P(1)–N(2) 124.76(13), W(1)–P(1)–C(4) 118.37(14), W(1)–P(1)–C(6) 110.09(14), N(2)-P(1)-C(4) 92.53(18), P(1)-N(2)-C(5) 101.1(3), P(1)-N(2)-C(3) 114.6(3), N(1)-C(5)-N(2) 107.6(3), C(4)-N(1)-C(5) 105.7(3), P(1)-C(4)-N(1) 104.2(3), C(1)-N(1)-C(4) 111.1(3), C(3)-N(2)-C(5) 109.2(3), C(1)-N(1)-C(5) 109.4(4).

Treatment of **6a** with diimines containing larger methylene bridges ($n = 5$, 6) resulted in complex product mixtures, as monitored by ^{31}P NMR spectroscopy. These reactions were not further investigated. We speculate that the greater separation of the two imine groups causes loss of selectivity, due to competition between intra- and intermolecular cycloadditions.

Reaction mechanism: How are **10a–c** formed? Is their formation governed by an as yet unclear stepwise process or can both C=N groups be incorporated into a five-membered heterocycle simultaneously by a unique, but unlikely, carbene-like [1+2+2] cyclization?

Azaphosphiridines: To answer this question, we started by identifying possible intermediates. No azaphosphiridine could be identified in the reactions between the complexed phosphinidene and the diimines **9a–c**, but it was possible to observe such an intermediate during the addition of **6a** (at 110 °C) to the phenyl-substituted imine **3b**, by monitoring the reaction by ^{31}P NMR spectroscopy (Scheme 4). Interruption of this



Scheme 4.

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reaction, which eventually results in a set of four isomeric (0.5:0.7:1.0:1.0) diazaphospholanes (**12**), enabled the two azaphosphiridine complexes **11** to be isolated, purified, and spectroscopically characterized. These were obtained in 29% yield, after low-temperature chromatography, in a 7:1 isomeric ratio as determined by integration of their ^{31}P NMR resonances at $\delta = -37.0$ and -44.3. The configuration of the major isomer could not be established with certainty, but we assume that the *trans* orientation of the imine substituents is maintained in the three-membered ring. Heating the isolated isomeric mixture of **11** with excess imine **3b** in toluene at 110 °C produced the diazaphospholane complexes **12** in about the same isomeric ratio as obtained from the reaction between **6a** and **3b**. These data thus provide evidence that azaphosphiridines can be formed in reactions between complexed phosphinidenes and imines.

The next question is whether azaphosphiridines are intermediates in the formation of the bridged diazaphospholanes **10a–c**. In other words, is a CPN ring indeed formed first, after which the second C=N group is inserted intramolecularly, or is there a direct single-step pathway that leads to the diazaphospholanes? We ask this question because only one isomer of the bicyclic products **10a–c** is formed at 110 °C, which is a temperature at which P-epimerization is known to occur in complexed phosphiranes,[9, 10] while isomeric mixtures of **7a–c** and **12** are obtained for the intermolecular reaction (Scheme 2 and Scheme 4).

Energy profile: We resorted to DFT calculations at the B3LYP/6–31G* level to map the energy profile for ring-closure that results in the smallest bicyclic diazaphospholane that resembles **10a**. A simplified approach was used, eliminating the complexating $W(CO)_5$ group and replacing all substituents for hydrogens. Three minima were located—ylide **13**, azaphosphiridine **14**, and diazaphospholane **15**—and two transition structures—**16** and **17**—connecting these minima. These structures, with their main geometrical parameters, are displayed in Figure 2, while their absolute and relative energies are summarized in Table 1.

Geometries: We assume that ylide structure **13** ($d_{NP} = 1.779$ Å) represents the initial product that results from the interaction of a phosphinidene complex with the nitrogen atom of a C=N group of the diimine. The *gauche* conformation between the imine ($d_{CN} = 1.269$ Å) and iminium ($d_{CN} = 1.310$ Å) groups required for ring-closure to diazaphospholane **15** is more stable than the *anti* form, albeit by a modest 1.7 kcal mol^{-1}. In azaphosphiridine **14**, the energetic preference for the *gauche* conformation is only 0.6 kcal mol^{-1}. Its CPN ring has a rather long P–N (1.809 Å) bond and a slightly elongated P–C (1.855 Å) bond relative to those in the reported crystal structure for **4**. We attribute these differences to the absence of substituents in the computed structure. It is well recognized that the P–C bonds of phosphiranes shorten on P-substitution and on complexation by transition metal groups.[9]

The geometrical parameters of diazaphospholane **15** resemble those of the crystal structure of **10b**, taking into account that the calculated P–N and P–C bonds are longer, due to the absence of P-substituents and that thermal motion is absent in the calculated structure. However, the deviation in the P-N-C ($\Delta = 3.1°$) and N-C-N ($\Delta = 4.8°$) angles indicates the presence of steric strain in the highly substituted experimental structure.

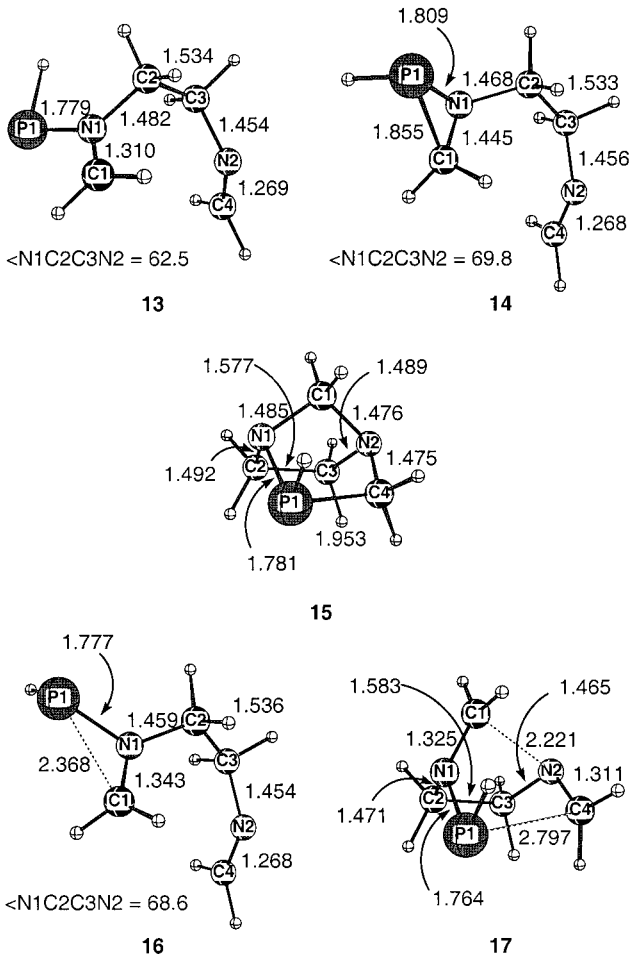


Figure 2. B3LYP/6–31G* Geometries of **13–17**.

Table 1. B3LYP/6–31G* Energies of **13–17**.

Structures	Energies	
	Absolute [a.u.]	Relative [kcal mol^{-1}]
13, gauche	608.60755	0.0
13, anti	608.60487	1.7
14, gauche	608.62267	– 9.5
14, anti	608.62177	– 8.9
15	608.65498	– 29.8
16, gauche	608.58192	16.1
16, anti	608.58059	16.9
17	608.59041	10.8

Energies: The energy profile is depicted in Figure 3. Azaphosphiridine **14** is 9.5 kcal mol^{-1} more stable than ylide **13**, while its energy difference relative to the global minimum, diazaphospholane **15**, is a significant 20.3 kcal mol^{-1}. In the ylide, a nitrogen atom of one of the imine groups interacts with singlet ^{1}PH, while the triplet form is 34.8 kcal mol^{-1} more stable.[11] This approach is justified because $PhPW(CO)_5$ has a

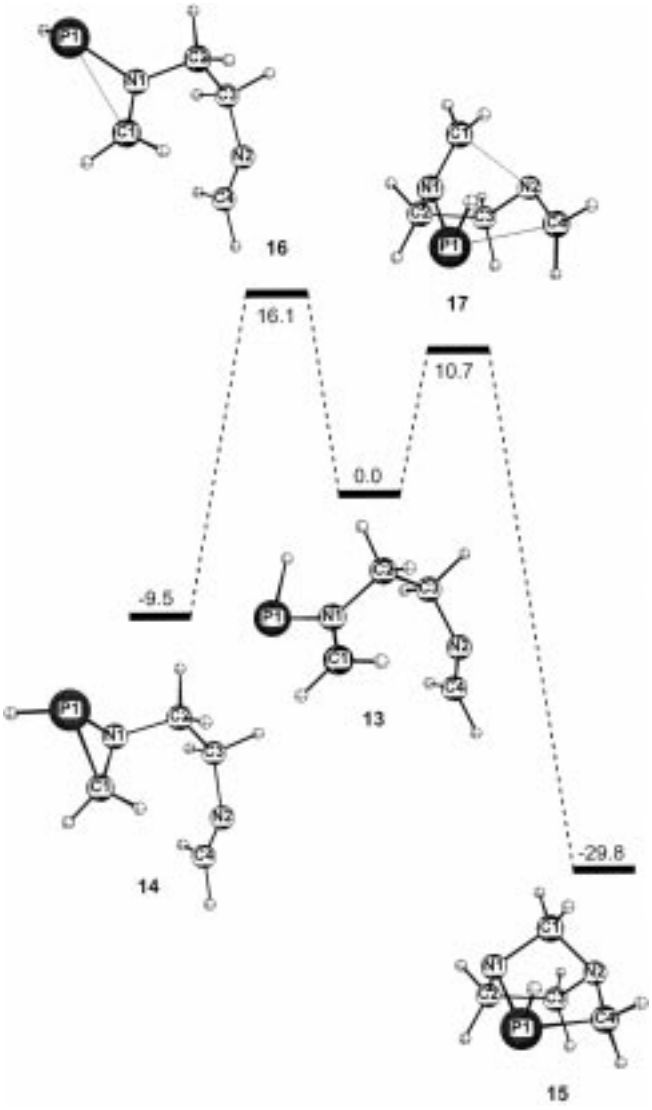
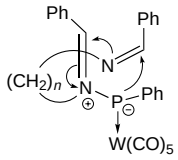


Figure 3. B3LYP/6–31G* Energy Profile.

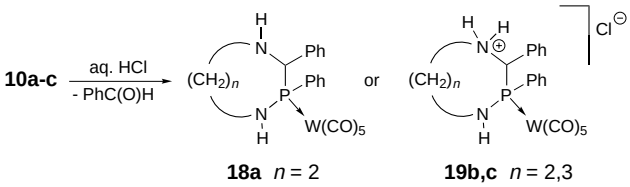
singlet ground state.[11] Inclusion of the $W(CO)_5$ group, however, was beyond our means.

Transition structure **17** represents a pericyclic ring-closure to the thermodynamically favored product (**15**). This pathway, which was confirmed by an IRC calculation, shows that the negatively charged phosphorus of **17** connects with the more electropositive carbon of the nearby C=N group with concurrent bond formation between the electronegative C=N nitrogen and the iminium group. This pericyclic ring-closure has an early transition state, as may be deduced from the long P(1)–C(4) and C(1)–N(2) distances of 2.797 and 2.221 Å, respectively, in structure **17**. The process represents a formal 6e [3+2] cycloaddition between the CNP and CN groups; this is in line with the observed high diastereoselectivity for formation of **10a**, in which the bulky $W(CO)_5$ group is located in the sterically least demanding position. The 10.7 kcal mol^{-1} barrier to this conversion to **15** is 4.4 kcal mol^{-1} lower than to the ring-closure to **14**. Hence, these B3LYP/6–31G* calculations suggest that formation of **15** is also kinetically preferred. Consequently, it seems unlikely that an azaphosphiridine complex is formed as an intermediate product in the reaction between phosphinidene complex **6a** and diimine **9a**. Instead, the computational data indicate that compounds **10a–c** are formed by intramolecular 1,3-dipolar cycloadditions of intermediate P,N-ylide complexes.



Analogies: While P,N-ylide complexes have not been observed directly, there is ample precedent for their formation.[4, 12] Crystal structures have been reported for the related P=P ylide complexes formed from addition of R-P=$W(CO)_5$ to phosphines, phospholes, and phospholenes.[13] Carbenes also react with imines to give azomethine C=N ylides, which undergo 1,3-dipolar cycloadditions with dipolarophiles such as olefins, aldehydes, and imines.[14] In this context, we again stress the close relationship between carbenes and R-P=$W(CO)_5$. Finally, the related N-3- and N-4-alkenyl nitrones undergo intramolecular 1,3-dipolar cycloadditions to give bicyclic compounds.[15]

Hydrolysis of bicyclic structures: Compounds **10a–c** contain aminal functionalities. These usually hydrolyze under acidic conditions, and this is indeed what is observed. In fact, **10a** eliminates benzaldehyde merely on being dissolved in chloroform,[16] to give a 92% yield of the novel, six-membered-ring complex **18a** (Scheme 5); this has a characteristic ^{31}P NMR



Scheme 5.

resonance at $\delta = 53.7$. The larger complex **10b** is stable in chloroform, but hydrolyzes on addition of one equivalent of aqueous HCl. The resulting monocyclic compound has a more deshielded ^{31}P NMR resonance at $\delta = 67.8$ and displays unexpectedly low solubility in ether. However, the presence of three N–H hydrogens in the ^{1}H NMR spectrum supports the presence of the novel seven-membered-ring compound **19b** as an HCl adduct. This was confirmed by a single-crystal X-ray structure determination (Figure 4), which indeed shows the presence of a chlorine anion. The quality of the data set and slight disorder in the flexible saturated ring did not allow us to determine the hydrogen positions; they were therefore, calculated. We assume N(1) to be the protonated nitrogen because its separation from Cl (3.047(8) Å) is less than that of N(2) (3.402(8) Å). For N(2), we assume a hydrogen position that enables hydrogen bonding to the chlorine, as the alternative position would result in an intermolecular H-bond to a carbonyl oxygen of a neighboring molecule. The seven-membered ring has a nearly ideal chair conformation with the Cl^- anion located above it on the same side as the equatorial

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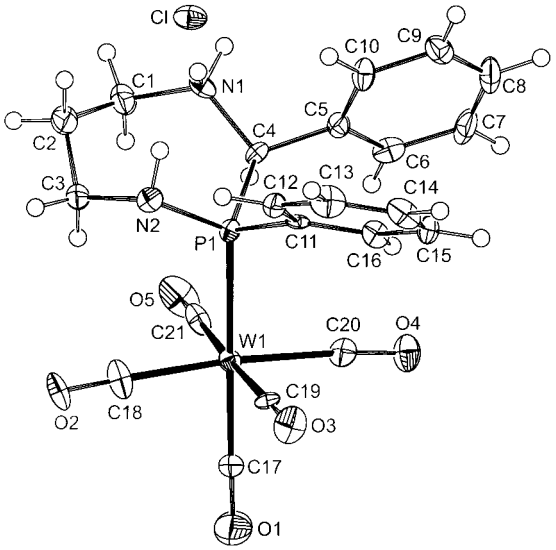


Figure 4. Displacement ellipsoid plot of **19b** drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P(1)–W(1) 2.503(2), P(1)–N(2) 1.674(7), P(1)–C(4) 1.907(9), P(1)–C(1)1 1.820(8), N(1)–C(1) 1.509(10), N(1)–C(4) 1.521(10), N(2)–C(3) 1.466(10), C(1)–C(2) 1.526(13), C(2)–C(3) 1.532(13), C(4)–C(5) 1.513(11), W(1)-P(1)-N(2) 118.5(3), W(1)-P(1)-C(4) 112.2(3), W(1)-P(1)-C(11) 112.6(2), N(2)-P(1)-C(4) 105.3(4), P(1)-N(2)-C(3) 120.9(6), P(1)-C(4)-N(1) 111.6(6), C(1)-N(1)-C(4) 116.5(7).

cis phenyl groups. These two phenyl groups are in parallel planes. The H-bond geometries of the axial N(1)- and N(2)-hydrogens have nearly linear N–H ··· Cl angles. Structure **19b** is less strained than the bicyclic **10b**. This can be inferred from its slightly shorter P(1)–N(2) and P(1)–C(4) bond lengths of 1.674(7) and 1.907(9) Å, respectively, and its 12.8° more relaxed N(2)-P(1)-C(4) angle of 105.3(4)°.

Compound **10c** is much less reactive than **10b**. Hydrolysis with one equivalent of HCl proceeds very slowly and does not go to completion. The formation of the monocyclic eight-membered ring compound **19c**, as an HCl adduct, is inferred from its ^{31}P NMR resonance at $\delta = 71.2$. Attempts to isolate **19c** were unsuccessful. Hydrolysis with excess HCl, formic acid, and p-toluenesulfonic acid gave no improvements.

Conclusion

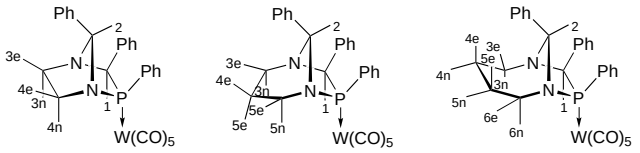
In this paper we have described the reaction of the transient electrophilic phosphinidene complex $PhPW(CO)_5$ (**6a**) with the diimines PhHC=N-$(CH_2)_n$-N=CHPh ($n = 2,3,4$). Each of the diimines gives a single diazaphospholane isomer, of which the smaller ones readily hydrolyze to monocyclic rings. No intermediates could be detected by monitoring the formation of the diazaphospholanes by ^{31}P NMR spectroscopy. Theoretical calculations at the B3LYP/6–31G* level suggest that the products result from an intramolecular 1,3-dipolar cycloaddition. The 1,3-dipole (or ylide) is the result of the phosphinidene complexing with an imine nitrogen. In agreement with the experimental observations, the calculations indicate that the barrier to ring closure to an azaphosphiridine is higher than that to the 1,3-dipolar cyclization.

In contrast, it was possible to isolate intermediate azaphosphiridine complexes from the reaction between $PhPW(CO)_5$ and PhN=C(H)Ph. This reaction ultimately affords a mixture of four isomeric diazaphospholanes, through incorporation of an additional imine.

Experimental Section

Computation: All electronic structure calculations were carried out by using the GAUSSIAN 98 suite of programs (G98).[17] For the density functional theory (DFT) calculations we used Becke's three-parameter hybrid exchange functional[18] combined with the Lee–Yang–Parr correlation functional,[19] denoted as B3LYP. The 6–31G* basis set was employed throughout for the geometry optimizations. First- and second-order energy derivatives were computed to confirm the nature of the minima and transition structures. Intrinsic reaction coordinate calculations (IRC) were performed to establish connections between transition structures and minima.

General: All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. Reagents were used as purchased. [5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (**5a**),[20] imine **3b**,[21] and the diimines **11a–e**[22] were synthesized according to literature procedures. NMR spectra were recorded on Bruker AC200 (^{1}H and ^{13}C), WM250 (^{31}P), and MSL400 (NOE and two-dimensional COSY) spectrometers with $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards. Melting points were determined on a Reichert melting-point apparatus and are uncorrected. High-resolution mass spectra were recorded on a Finnigan MAT90 spectrometer. Elemental analyses were obtained from Mikroanalytisches Labor Pascher, in Remagen-Bandorf (Germany). Structures of **10a–c** are shown with numbered and labeled hydrogen positions (e for *exo* and n for *endo*) to ease their NMR assignments.



Pentacarbonyl[2,3,7-triphenyl-1,4-diaza-3-phosphabicyclo[2:2:1]heptane-κ*P*] tungsten (10a): A solution of the 7-phosphanorbornadiene complex **5a** (400 mg, 0.61 mmol) and *N*,*N*′-dibenzylideneethane-1,2-diamine (**9a**) (145 mg, 0.61 mmol) in dry toluene (3.5 mL) was heated at 110 °C for 9 hours. Evaporation of the solvent, and purification of the residue by chromatography over silica gel 60 (0.2–0.5 mm) with Et_2O/pentane (1:9) as eluent gave 340 mg of a light yellow solid. Recrystallization by slow evaporation of a solution of **10a** in Et_2O/pentane (1:1) afforded colorless crystals. Yield: 302 mg, 74%; m.p. 174–175 °C; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 2.13–2.20$ (m, 1H; H_{3n}), 2.63–2.71 (m, 1H; H_{3e}), 2.85–2.92 (m, 1H; H_{4e}), 3.07–3.18 (m, 1H; H_{4n}), 4.37 (d, $^2J(P,H_1) = 11.4$ Hz, 1H; H_1), 5.38 (d, $^3J(P,H_2) = 4.2$ Hz, 1H; H_2), 6.72–7.22 (m, 13H; Ph), 7.70–7.74 (m, 2H; NC(*o*-Ph)N); ^{13}C NMR (50 MHz, C_6D_6, 25 °C): δ = 45.8 (s, PNC*C*N), 53.9 (s, PN*C*CN), 82.8 (d, $^1J(P,C) = 6.3$ Hz, PCN), 92.0 (s, NCN), 128.9–129.6 (m, Ph), 136.0 (d, $^2J(P,C) = 5.9$ Hz, PC-*ipso*-Ph), 136.5 (d, $^3J(P,C) = 2.4$ Hz, PNC-*ipso*-Ph), 138.2 (d, $^1J(P,C) = 36.0$ Hz, P-*ipso*-Ph), 196.6 (dd, $^2J(P,C) = 6.9$ Hz, $^1J(W,C) = 125.5$ Hz, CO *cis*) 198.7 (d, $^2J(P,C) = 26.5$ Hz, CO *trans*); ^{31}P NMR (101 MHz, C_6D_6, 25 °C): $\delta = 95.6$ ($^1J(W,P) = 259.1$ Hz); HR-MS: calcd for $C_{27}H_{21}N_2O_5PW$: 668.06800, found 668.06955 (δ = 5.7 × 10^{-4}).

Pentacarbonyl[6,7,8-triphenyl-1,5-diaza-6-phosphabicyclo[3:2:1]octane-κ*P*]tungsten (10b): The reaction was performed as for **10a**, but by using *N*,*N*′-dibenzylidene-propane-1,3-diamine (**9b**), to give colorless crystals of **10b**. Yield: 290 mg, 70%; m.p. 176–177 °C; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 0.61$ (dt, $^3J(H_{1e},H_{2e}) = 4.5$ Hz, $^2J(H_{2n},H_{2e}) = 14.1$ Hz, $^3J(H_2,H_{3e}) = 4.5$ Hz, 1H; H_{2e}), 2.01 (dtt, $^3J(H_{1n},H_{2n}) = 6.1$ Hz, $^3J(H_{1e},H_{2n}) = 13.5$ Hz, $^2J(H_{2n},H_{2e}) = 14.1$ Hz, $^3J(H_{3e},H_{2n}) = 13.5$ Hz,

$^3J(H_{3n},H_{2n}) = 6.6$ Hz, 1H; H_{2n}), 2.2 (dd, $^2J(H_{1n},H_{1e})$, $^3J(H_{2n},H_{1n}) = 6.1$ Hz, 1H; H_{1n}), 3.22 (dd, $^2J(H_3,H_3) = 14.8$ Hz, $^3J(H_{2n},H_{3n}) = 6.6$ Hz, 1H; H_{3n}), 3.3 (ddd, $^4J(P,H_{1e}) = 4.0$ Hz, $^2J(H_{1n},H_{1e}) = 13.9$ Hz, $^3J(H_{2e},H_{1e}) = 4.5$ Hz, $^3J(H_{2n},H_{1e}) = 13.5$ Hz, 1H; H_{1e}), 3.60 (dddd, $^3J(P,H_{3e}) = 35.8$ Hz, $^3J(H_{2e},H_{3e}) = 4.5$ Hz, $^3J(H_{2n},H_{3e}) = 13.5$ Hz, $^2J(H_3,H_3) = 14.8$ Hz, 1H; H_{3e}), 5.15 (d, $^3J(P,H_e) = 3.9$ Hz, 1H; NCH_eN), 5.2 (d, $^2J(P,H_n) = 7.2$ Hz, 1H; PCH_n), 6.68–7.28 (m, 13H; Ph), 7.61–7.65 (m, 2H; NC(*o*-Ph)N); ^{13}C NMR (50 MHz, C_6D_6, 25 °C): $\delta = 22.4$ (d, $^3J(P,C) = 3.3$ Hz, PNC*C*), 43.2 (d, $^2J(P,C) = 4.6$ Hz, PNC_2C), 46.0 (s, PN*C*C), 79.7 (d, $^1J(P,C) = 3.7$ Hz, PC), 85.9 (d, $^2J(PC) = 1.6$ Hz, NCN), 128.9–129.5 (m, Ph), 136.3 (d, $^2J(P,C) = 5.9$ Hz, PC-*ipso*-Ph), 137.7 (d, $^3J(P,C) = 1.6$ Hz, NC(*ipso*-Ph)N), 138.5 (d, $^1J(P,C) = 8.4$ Hz, P-*ipso*-Ph), 197.3 (dd, $^2J(P,C) = 6.6$ Hz, $^1J(W,C) = 125.6$ Hz, CO *cis*), 198.6 (d, $^2J(P,C) = 25.2$ Hz, CO *trans*); ^{31}P NMR (101 MHz, C_6D_6, 25 °C): $\delta = 85.6$ ($^1J(W,P) = 253.0$ Hz); HR-MS: calcd for $C_{28}H_{23}N_2O_5PW$ (in the X-ray section: Fw = 682.30) 682.08545, found: 682.08539 ($\delta = 3.4 \times 10^{-4}$); elemental analysis calcd for $C_{28}H_{23}N_2O_5PW$: C 49.29%, H 3.40%, N 4.15%; found C 49.19%, H 3.31%, N 4.25%.

Pentacarbonyl[7,8,9-triphenyl-1,6-diaza-7-phosphabicyclo[4:2:1]nonane-κP]tungsten (10c): The reaction was performed as for **10a**, but with *N,N'*-dibenzylidene-butane-1,4-diamine (**9c**), to give colorless crystals of **10c**. Yield: 231 mg, 54%; m.p. 194–195 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.16$–1.33 (m, 1H; H_{3e}), 1.63–1.76 (m, 2H; H_{2e} and H_{2n}), 1.82 (dt, $^2J(H_{3n},H_{3e}) = 14.8$ Hz, $^3J(H,H)$, 6.3 Hz, 1H; H_{3n}), 2.94 (dt, $^3J(H,H) = 3.2$ Hz, $^2J(H_{1n},H_{1e}) = 15$ Hz, 1H; H_{1n}), 3.43–3.54 (m, 1H; H_{1e}), 3.68 (ddt, $^3J(H,H) = 11.6$ Hz, $^3J(H,H) = 6.3$ Hz, $^3J(H,H) = 15.3$ Hz, 1H; H_{4n}), 3.95 (ddd, $^2J(H_{4n},H_{4e}) = 14.8$ Hz, $^3J(H,H) = 7.0$ Hz, $^3J(P,H_{4e}) = 28.6$ Hz, 1H; H_{4e}), 4.94 (d, $^2J(P,H_n) = 4.0$ Hz, 1H; PCH_n), 5.24 (s, 1H; NCH_eN), 6.80–7.19 (m, 5H; P-Ph), 7.24 (s, 5H; PC–Ph), 7.31–7.78 (m, 5H; NC(Ph)N); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 26.1$ (s, PNC_2C), 28.9 (s, PN*C*C), 47.5 (d, $^3J(P,C) = 10.1$ Hz, PNC_3C), 50.7 (s, PNC), 77.7 (d, $^2J(P,C) = 4.3$ Hz, PC), 83.2 (d, $^2J(P,C) = 5.2$ Hz, NCN), 126.7–129.7 (m, Ph), 135.9 (d, $^1J(P,C) = 6.3$ Hz, P-*ipso*-Ph), 137.8 (d, $^2J(P,C) = 1.5$ Hz, PC-*ipso*-Ph), 138.7 (s, NCC–*ipso*-Ph), 196.7 (dd, $^2J(P,C) = 6.7$ Hz, $^1J(W,C) = 126.1$ Hz, CO *cis*), 198.4 (d, $^2J(P,C) = 25.4$ Hz, CO *trans*); ^{31}P NMR (101 MHz, Et_2O, 25 °C): $\delta = 92.7$ ($^1J(W,P) = 258.4$ Hz); HR-MS: calcd for $C_{29}H_{25}N_2O_5$: 696.10110, found 696.101314 ($\delta = 5.8 \times 10^{-4}$); MS *m/z* (%): 696 (4) $[M]^+$, 668 (6) $[M - CO]^+$, 640 (2) $[M - 2CO]^+$, 612 (32) $[M - 3CO]^+$, 584 (16) $[M - 4CO]^+$, 556 (100) $[M - 5CO]^+$.

Pentacarbonyl[1,2-diphenyl-2*H*-azaphosphiridine-κP]tungsten (11): A solution of 7-phosphanorbornadiene complex **5a** (650 mg, 1.0 mmol) and **3b** (180 mg, 1.0 mmol) in dry toluene (10 mL) was heated at 110 °C for 5 hours. At that point some **5a** was still present in the reaction mixture, but the reaction was stopped for an optimal yield of **11**. Evaporation of the solvent followed by low temperature (−10 °C) chromatography of the residue over alumina with pentane/toluene (3:1) as eluent afforded **11** as a mixture of isomers in a 7:1 ratio and as a yellow solid; yield 180 mg, 29%. *Major Isomer*: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 4.05$ (d, $^2J(P,C) = 2.52$ Hz, 1H; PCH), 6.89–7.45 (m, 15H; Ph); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 53.3$ (d, $^1J(P,C) = 4.8$ Hz, P*C*(H)Ph), 117.8–147.4 (m, Ph), 194.4 (d, $^1J(P,C) = 8.0$ Hz, CO *cis*), 196.6 (d, $^1J(P,C) = 33.5$ Hz, CO *trans*); ^{31}P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = -37.0$ ($^1J(W,P) = 281.8$ Hz); HR-MS: calcd for $C_{24}H_{16}NO_5PW$: 613.027580, found 613.027576 ($\delta = 1.38 \times 10^{-4}$). *Minor Isomer*: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 4.23$ (d, 1H, $^2J(P,C) = 5.4$ Hz, PCH), 6.89–7.45 (m, 15H; Ph); ^{31}P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = -44.3$.

Pentacarbonyl[1,2,3,4,5-pentaphenyl-1,4,2-diazaphospholane]tungsten (12): A solution of the 7-phosphanorbornadiene complex **5a** (795 mg, 1.2 mmol) and **3b** (1.1 g, 6.0 mmol) in dry toluene (6 mL) was heated at 110 °C for 25 hours. Evaporation of the solvent, followed by chromatography of the residue over silica with Et_2O/pentane (2:8) as eluent afforded **12** (yield 591.4 mg, 68%) as a mixture of four diastereomers in a ratio of ca. 0.5:0.7:1:1 as determined by integration of their respective ^{31}P NMR resonances ($CHCl_3$) at $\delta = 92.9$, 91.2, 85.9 and 82.4 ppm. Preparative thin layer chromatography of this mixture with Et_2O/pentane (5:95) resulted in a partial separation of two diastereomers. One of these crystallized selectively from an Et_2O/pentane solution as light yellow crystals. m.p. 195–197 °C decomp.; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 5.75$ (d, $^2J(P,H) = 6.2$ Hz, 1H; CHPh), 5.82 (s, 1H; CHPh), 6.74–7.43 (m, 25H; Ph); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 76.0$ (d, $^1J(P,C) = 30.5$ Hz, P*C*(H)Ph), 86.2 (d, $^2J(P,C) = 0.8$ Hz, PN*C*), 122.8–144.8 (m, Ph), 196.4 (d, $^2J(P,C) = 7.3$ Hz, CO *cis*), 197.8 (d, $^2J(P,C) = 27.4$ Hz, CO *trans*); ^{31}P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 85.9$ ($^1J(W,P) = 276.8$ Hz); HR-MS: calcd for $C_{37}H_{27}N_2O_5PW$: 794.116750, found 794.117486 ($\delta = 2.75 \times 10^{-3}$). The NMR spectroscopic data did not allow for assignment of the conformation of the isolated isomer.

Pentacarbonyl[2,3-diphenyl-1,4-diaza-2-phosphacyclohexane-κP]tungsten (18a): A solution of **10a** (100 mg, 0.15 mmol) in $CHCl_3$ (3 mL) was stirred for 80 hours at room temperature. Filtration followed by evaporation under reduced pressure to remove the solvent and the benzaldehyde formed in the reaction gave **18a** as a white solid. Yield: 78 mg, 92%; m.p. 141–142 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.08$ (s, 1H; PCNH), 2.71–2.79 (m, 1H; PNCCH), 2.95–3.30 (m, 3H; PN*H-H-CH*), 3.44–3.70 (m, 1H; PNCH), 4.68 (d, $^2J(PH) = 4.1$ Hz, PCH), 6.98–7.31 (m, 10H; Ph); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 41.4$ (d, $^2J(P,C) = 5.7$ Hz, PNC), 49.7 (s, PCN*C*), 69.2 (d, $^1J(P,C) = 29.6$ Hz, PCN), 127.4–131.2 (m, Ph), 135.4 (d, $^1J(P,C) = 31.6$ Hz, P-*ipso*-Ph), 136.5 (s, PC-*ipso*-Ph), 196.8 (dd, $^2J(P,C) = 7.2$ Hz, $^1J(W,C) = 221.4$ Hz, CO *cis*), 199.0 (d, $^2J(P,C) = 23.2$ Hz, CO *trans*); ^{31}P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 53.7$ ($^1J(W,P) = 259.8$ Hz); HR-MS: calcd for $C_{20}H_{17}N_2O_5PW$: 580.038500, found 580.038554 ($\delta = 4.0 \times 10^{-4}$).

Pentacarbonyl[2,3-diphenyl-1,4-diaza-2-phosphacycloheptane-*N*-hydrochloride-κP]tungsten (19b): An aqueous HCl solution (0.29 mL, 0.29 mmol, 1N) was added to a solution of **10b** (200 mg, 0.29 mmol) in EtOH/$CHCl_3$ (4 mL, 1:4). The reaction mixture was stirred at room temperature for 5 minutes. Filtration followed by evaporation under reduced pressure to remove the solvent and the benzaldehyde formed in the reaction gave **19b** (153 mg, 92%) as a white solid, which could be recrystallized from either Et_2O or $CHCl_3$. M.p. 145–146 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 1.83$–1.91 (m, 1H; PNCCH), 2.40–2.70 (m, 1H; PNCCH), 2.90–3.13 (m, 1H; PNC_2CH), 3.40–3.58 (m, 2H; $PNCH_2$), 3.65–3.84 (m, 1H; PNC_2CH), 4.11–4.27 (m, 1H; PNH), 4.77–4.87 (m, 1H; PCH), 6.95–7.21 (m, 10H; Ph), 9.75 (s, 1H; PCN^+HCl), 10.15 (s, 1H; PCN^+HCl); ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): $\delta = 27.4$ (s, PNC*C*), 44.6 (d, $^2J(P,C) = 4.8$ Hz, PNC), 50.4 (s, PNC_2C), 78.4 (d, $^1J(P,C) = 6.1$ Hz, PCN), 127.6–131.1 (m, Ph), 131.6 (d, $^2J(P,C) = 3.6$ Hz, PC-*ipso*-Ph), 132.2 (d, $^1J(P,C) = 51.1$ Hz, P-*ipso*-Ph), 196.3 (dd, $^2J(P,C) = 7.3$ Hz, $^1J(W,C) = 125.9$ Hz, CO *cis*), 197.6(d, $^2J(P,C) = 26.7$ Hz, CO *trans*); ^{31}P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta = 67.8$ ($^1J(W,P) = 282.8$ Hz); HR-MS: calcd for $C_{21}H_{19}N_2O_5PW$: 594.05415 (free of HCl), found 594.05407 ($\delta = 4.9 \times 10^{-4}$).

Pentacarbonyl[2,3-diphenyl-1,4-diaza-2-phosphacyclooctane-*N*-hydrochloride-κP]tungsten (19c): The hydrolysis was carried out as described for **19b**, but the conversion was incomplete and isolation was unsuccessful. ^{31}P NMR (101 MHz, $CHCl_3$, 25 °C): $\delta = 71.2$ ($^1J(W,P) = 285.0$ Hz).

Crystal structure determination: X-ray intensities were measured on a Enraf–Nonius CAD4T diffractometer with rotating anode ($\lambda = 0.71073$ Å). The structures were solved with automated Patterson methods (DIRDIF97[23]) and refined with SHELXL-97[24] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. Molecular illustrations, structure checking, and calculations were performed with the PLATON package.[25] Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 155757 (compound **10b**) and 155758 (compound **19b**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK) (fax: (+44) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Compound 10b: $C_{28}H_{23}N_2O_5PW$, $Fw = 682.30$, colorless block, $0.38 \times 0.38 \times 0.25$ mm^3, monoclinic, *C*2/*c* (No. 15), $a = 24.8226(14)$, $b = 15.9257(13)$, $c = 14.2181(9)$ Å, $\beta = 111.557(5)°$, $V = 5227.5(6)$ Å^3, $Z = 8$, $\rho = 1.734$ g cm^{-3}. Temperature = 198 K. 12483 measured reflections up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}, of which 5998 were unique ($R_{int} = 0.066$). Absorption correction with the PLATON program [25] (DELABS routine, $\mu = 4.522$ mm^{-1}, 0.33–0.76 transmission). 334 refined parameters, 0 restraints. *R* values [$I > 2\sigma(I)$]: $R1 = 0.0365$, $wR2 = 0.0755$. *R* values [all refl.]: $R1 = 0.0525$, $wR2 = 0.0815$. $S = 0.994$. Rest electron density between −1.03 and 1.21 e Å^{-3}.

Compound 19b: $C_{21}H_{20}N_2O_5PW^+ \cdot Cl^-$, $Fw = 630.66$, yellow plate, $0.13 \times 0.13 \times 0.05$ mm^3, triclinic, $P\bar{1}$ (No. 2), $a = 8.8937(14)$, $b = 11.654(2)$, $c = 1.820(3)$ Å, $\alpha = 95.302(19)$, $\beta = 110.150(18)$, $\gamma = 95.757(13)°$, $V =$

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1133.7(4) Å^3, $Z = 2$, $\rho = 1.847$ g cm^{-3}. Temperature = 150 K. 8558 measured reflections up to a resolution of $(\sin\delta/\lambda)_{max} = 0.59$ Å^{-1}, of which 3996 were unique ($R_{int} = 0.095$). Absorption correction with the PLATON program[25] based on psi-scans ($\mu = 5.318$ mm^{-1}, 0.67–0.98 transmission). 280 refined parameters, 51 restraints. R values [$I > 2\sigma(I)$]: $R1 = 0.0450$, $wR2 = 0.0794$. R values [all refl.]: $R1 = 0.0724$, $wR2 = 0.0874$. $S = 0.988$. Rest electron density between −1.83 and 1.36 e Å^{-3}.

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