Intra- and Intermolecular [3+2] Cycloaddition Reactions of *P*-Cp*-Substituted Nitrilium Phosphane-Ylide Tungsten Complexes

Rainer Streubel,*,† Udo Schiemann,† Nils Hoffmann,† Yvonne Schiemann,† Peter G. Jones,† and Dietrich Gudat‡

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms Universität Bonn, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany

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Thermal ring opening of {pentacarbonyl[2-pentamethylcyclopentadienyl-3-phenyl-2*H*-azaphosphirene-κP]tungsten(0)} (**1**) in toluene in the presence of either 1-piperidinonitrile or ethyl cyanoformate yields predominantly tricyclic P-heterocycle complexes **4a**,**b** via intramolecular trapping reactions of transiently formed nitrilium phosphane-ylide complexes **3a**,**b**; complex **4a** was isolated and fully characterized. On prolonged heating, complexes **4a**,**b** transformed into 2*H*-1,3,2-diazaphosphole complexes **5a**,**b**, which were also characterized by NMR spectroscopy. In the case of 1-piperidinonitrile, acyclic dinuclear complex **6** was formed as byproduct via a 2-fold 1,3-addition reaction of complex **3a** with water. Furthermore, preliminary studies on ring opening of complex **4a** showed retro-[2+1] and retro-[3+2] cycloaddition reactions, depending on the substrate. If dimethyl acetylenedicarboxylate was employed, the tetracyclic phosphorus−carbon cage complex **10** was obtained, and if 1-piperidinonitrile was used, the 2*H*-1,3,2-diazaphosphole complex **5a** was formed selectively. The structures of 2*H*-1,3,2-diazaphosphole complex **5a**, the acyclic dinuclear complex **6**, and the tetracyclic P-heterocycle complex **10** were determined by single-crystal X-ray diffraction.

Introduction

There is much current interest in the development of sophisticated ligands including either sp^2- and/or sp^3-hybridized phosphorus atoms in heterocyclic rings as bonding sites for transition metals. For example, diazaphospholes[1] of type **II** and **III** have been investigated in some detail, especially with regard to reactivity of the $\sigma^2\lambda^3$-phosphorus center and aromaticity, both of which were found to be similar to the parent N-heterocycle system **I**, the 1,2,3-triazole.[2] The finding with respect to aromaticity is in marked contrast to the situation in 1*H*-phospholes,[3] which are only weakly aromatic in most cases because of the inherent pyramidal preference of $\sigma^3\lambda^3$-phosphorus in its compounds.[4] A breakthrough in this area was the synthesis of the first phosphole having a planar coordination environment at phosphorus, 1-[bis(trimethylsilyl)methyl]-3,5-bis(trimethylsilyl)-1,2,4-triphosphole,[5] which was described very recently.

We became interested in such heterocyclic ligands, which also belong to the area of biomimetic P-heterocycles, when we synthesized the first 2*H*-1,3,2- and 2*H*-1,4,2-diazaphosphole tungsten complexes[6,7] having the novel diazaphospholes **IV** and **V** as ligand systems; meanwhile, a derivative of the 2*H*-1,3,2-diazaphospholes (**IV**) is also known in the noncoordinated form.[8] Furthermore, regarding the synthetic potential of η^1-phosphole[3a] (**VI**) and η^5-phospholide complexes[9] (**VII**), we decided to exploit our synthetic route to 2*H*-1,3,2-diazaphosphole complexes **VIII** and also, in the longer

* Corresponding author. Telefax: Int. +531/391-5387. E-mail: r.streubel@tu-bs.de.
† Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig.
‡ Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms Universität Bonn.

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(3) Review of phospholes: (a) Mathey, F. *Chem. Rev.* **1988**, *88*, 429. (b) Hughes, A. N. In *Handbook of Organophosphorus Chemistry*; Robert, E., Ed.; Marcel Dekker: New York, 1993. (c) Quin, L. D. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 3, p 757. (d) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; p 203.

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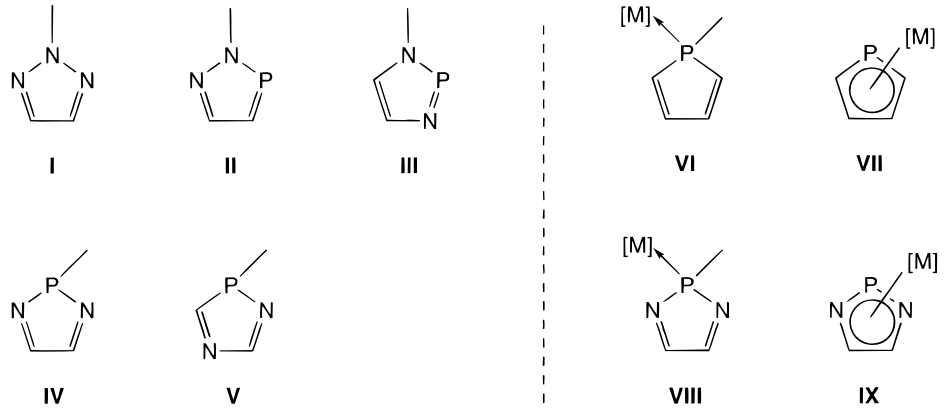
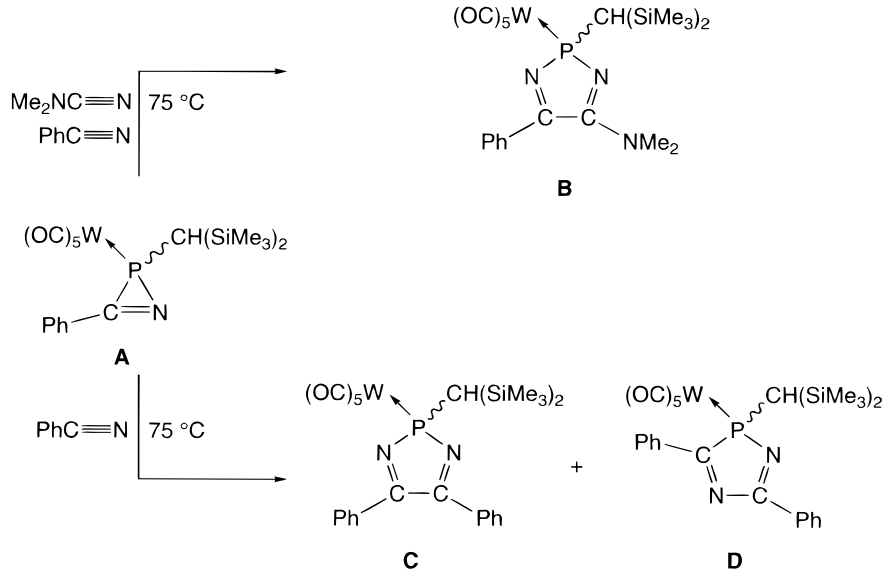
Scheme 1



Scheme 2



term, to η^5-1,3,2-diazaphospholide complexes of type **IX** (Scheme 1). Therefore, we first focused our interest on the investigation of [3+2] cycloaddition reactions of nitrilium phosphane-ylide complexes with nitriles. This reaction was first reported for the 2-bis(trimethylsilyl)-methyl-substituted 2*H*-azaphosphirene complex **A** and used for the synthesis of 2*H*-1,3,2- and 2*H*-1,4,2-diazaphosphole complexes, thus giving either the 2*H*-1,3,2-diazaphosphole complex **B**,[6] if a mixture of benzonitrile and dimethyl cyanamide was employed, or a mixture of two regioisomers, the 2*H*-1,3,2-diazaphosphole complex **C** and the 2*H*-1,2,4-diazaphosphole complex **D**,[7] if benzonitrile was used as solvent (Scheme 2). The reaction courses were explained by assuming two different nitrilium phosphane-ylide complexes as reactive intermediates, displaying different regioselectivities toward benzonitrile.[6,7]

Our investigations of thermolysis of 2*H*-azaphosphirene tungsten complex **1**[10] in toluene had shown previously that, depending on the reaction conditions,[11,12] with dimethyl acetylenedicarboxylate (DMAD) a 2*H*-1,2-azaphosphole complex was obtained as [3+2] cycloaddition product. Because of the observed weakness[11] of the exocyclic P−C bond of this 2*H*-1,2-azaphosphole complex derivative, we became especially interested in the same aspect of the related 2*H*-1,3,2-diazaphosphole ligand system. Furthermore, pentamethylcyclopentadienyl-substituted 2*H*-1,3,2-diazaphospholes (the pentamethylcyclopentadienyl substituent will be denoted hereafter as Cp*) are also promising precursors for providing access to the corresponding 1,3,2-diazaphospholides via reductive cleavage of the exocyclic P−C bond; the 1,3,2-diazaphospholide system was synthesized previously using a 1*H*-1,3,2-diazaphosphole precursor.[13] Because of all these aspects, we were interested in investigating the thermolysis of the 2*H*-azaphosphirene complex **1** in toluene in the presence of electronically different nitriles.

Here we report on studies of (1) intra- and intermolecular [3+2] cycloaddition reactions of transiently formed *P*-pentamethylcyclopentadienyl-substituted nitrilium phosphane-ylide complexes, generated by thermal ring opening of the corresponding 2*H*-azaphosphirene complex, with nitrile derivatives and (2) a dual ring opening behavior of a tricyclic phosphorus−carbon

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Scheme 3

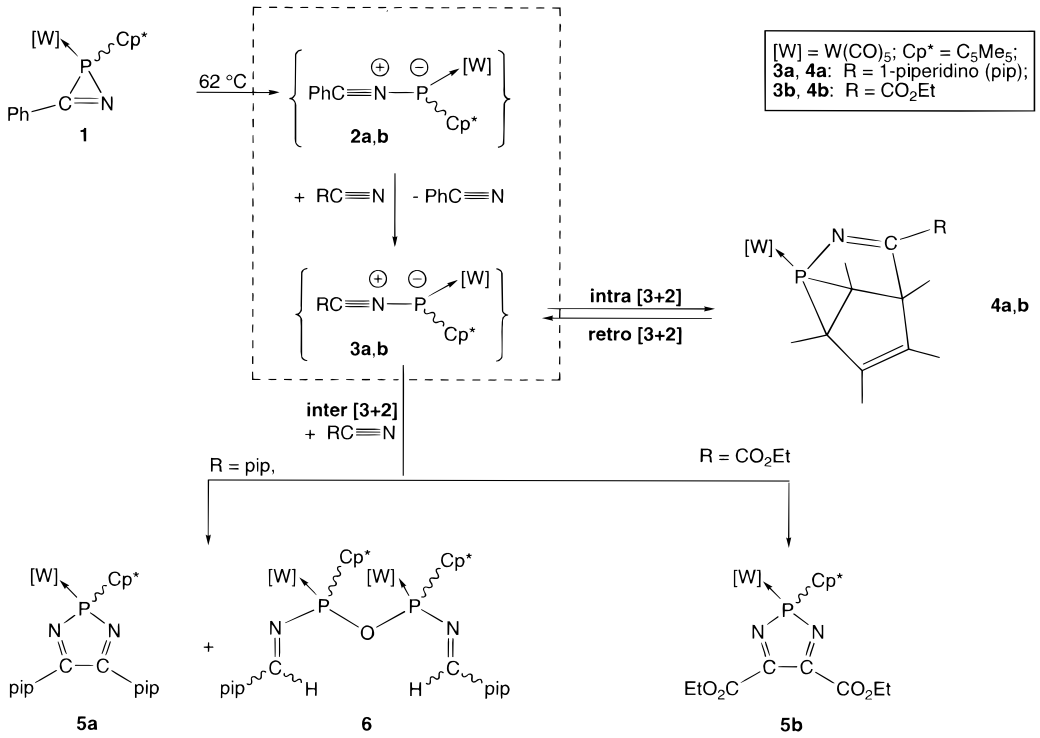
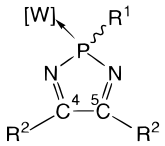


Table 1. Selected NMR Spectroscopic Data[a] of 4,5-Substituted 2*H*-1,3,2-Diazaphosphole Complexes 5a,b and 11a,b[6]



compd	R^1	R^2	R^3	δ ^{31}P	$\lvert^1J(P,W)\rvert$	δ $^{13}C^{4,5}$	$\lvert J(P,C^{4,5})\rvert$	δ $^{13}C^{P}$	$\lvert J(P,C^{P})\rvert$
5a	Cp*	pip[b]	pip	137.7	278	161.6	2.5	62.2	8.4
11a[6]	$CH(SiMe_3)_2$	pip	pip	133.2	264	160.7	6.4	25.5	3.2
5b	Cp*	CO_2Et	CO_2Et	186.6	273	158.2	3.6	62.7	4.8
11b[6]	$CH(SiMe_3)_2$	CO_2Et	CO_2Et	184.4	253	157.1	1.5	21.4	*c*

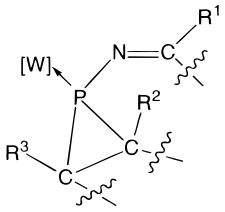
[a] $CDCl_3$, δ [ppm], J [Hz]. [b] pip = 1-piperidino. [c] Not resolved.

cage complex, thus revealing unprecedented substrate-dependent retro-[2+1] and/or retro-[3+2] cycloaddition reactivities. We further report the single-crystal X-ray structure analyses of 2*H*-1,3,2-diazaphosphole complex **5a**, the acyclic dinuclear complex **6**, and the polycyclic phosphorus−carbon cage complex **10**.

Results and Discussion

Thermolysis of 2*H*-azaphosphirene complex **1** in toluene with 2 equiv of 1-piperidinonitrile or ethyl cyanoformate yielded the 2*H*-1,3,2-diazaphosphole complexes **5a**,**b** in moderate to good yields (Scheme 3). In the case of 1-piperidinonitrile, the acyclic dinuclear complex **6** was formed as byproduct; the amounts of **6** strongly depended on the dryness of the employed nitrile. Selected NMR data of **5a**,**b** and **6** are collected in Table 1 and will be discussed below together with those of further products. ^{31}P NMR spectroscopy revealed that the complexes **5a**,**b** were formed together with the complexes **4a**,**b**, having resonance values at higher field, and on prolonged heating, their intensities decayed in favor of those of the five-membered heterocycle complexes **5a**,**b**. Complex **4a** could be isolated by low-temperature column chromatography, whereas complex **4b** decomposed during chromatography. The reaction course is explained by assuming the transient formation of nitrilium phosphane-ylide complexes **3a**,**b**, which undergo predominantly intramolecular [3+2] cycloaddition reactions with a π-bond of the Cp*-ring furnishing the tricyclic P-heterocycle complexes **4a**,**b** and/or show intermolecular [3+2] cycloaddition reactions with the respective nitrile derivatives giving 2*H*-1,3,2-diazaphosphole complexes **5a**,**b**. It is notable that, under these conditions, complexes **4a**,**b** subsequently underwent retro-[3+2] cycloaddition reactions, thus yielding again the nitrilium phosphane-ylide complexes **3a**,**b**. Further strong evidence for the intermediacy of nitrilium phosphane-ylide complex **3a** is provided by the formation of byproduct **6** via a 2-fold 1,3-addition of the O−H groups of water to the 1,3-dipole system of complex **3a**. Furthermore, the determined configuration and orientation of this 1,3-addition is in accord with the hitherto observed regioselectivity of such *C*-dialkyl-

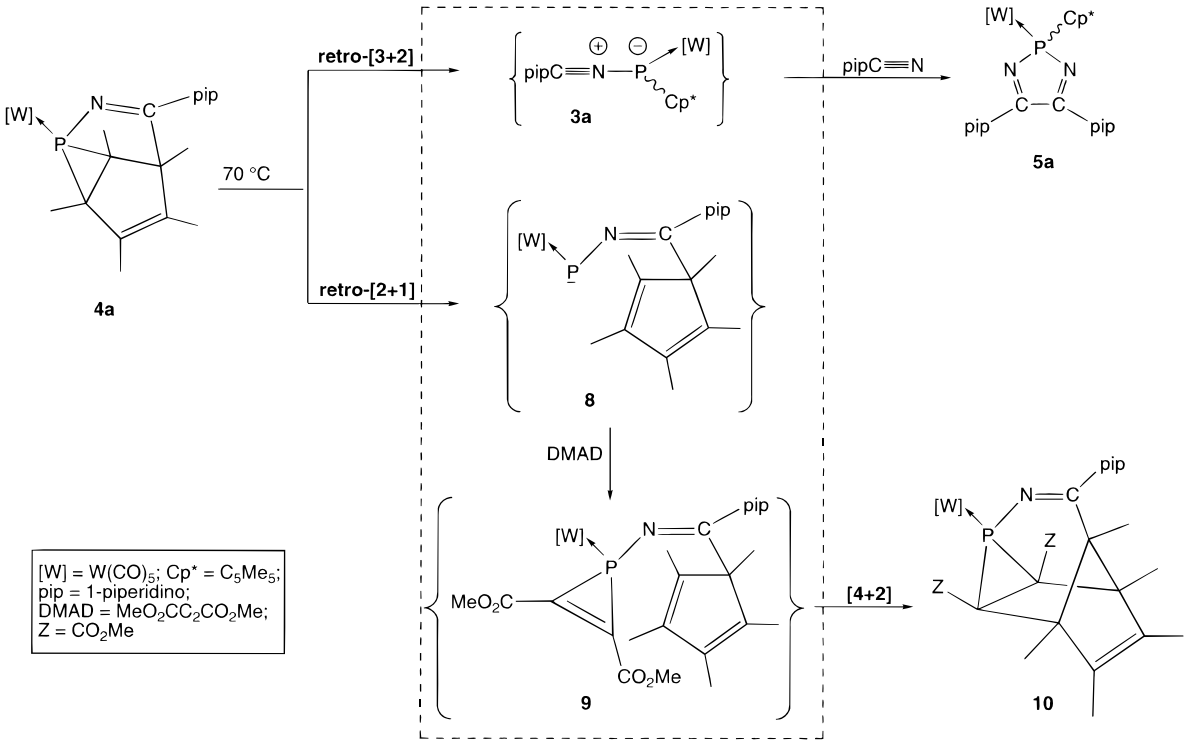
Table 2. NMR Spectroscopic Data[a] of the Most Significant Structural Unit (shown) of the Polycyclic P-Heterocycle Complexes 4a,b and 10



compd	R^1	R^2	R^3	δ ^{31}P	$\lvert^1J(P,W)\rvert$	δ $^{13}C^{R1}$	$\lvert J(P,C^{R1})\rvert$	δ $^{13}C^{R2}$	$\lvert J(P,C^{R2})\rvert$	δ $^{13}C^{R2}$	$\lvert J(P,C^{R2})\rvert$
4a	pip[b]	Me	Me	−45.0	275	179.0	5.7	60.5	34.3	56.0	9.2
4b	CO_2Et	Me	Me	−34.4	251	*c*	*c*	*c*	*c*	*c*	*c*
10	pip	CO_2Me	CO_2Me	−34.3	300	179.2	15.1	74.5	*d*	74.5	*d*

[a] $CDCl_3$, δ [ppm], J [Hz]. [b] pip = piperidino. [c] Not isolated. [d] Not resolved.

Scheme 4



amino-substituted nitrilium phosphane-ylide complexes (cf. ref 14).

To study more thoroughly the observed retro-[3+2] cycloaddition reaction, we thermolyzed a pure sample of the tricyclic P-heterocycle complex **4a** under the same reaction conditions in toluene with 2 equiv of either 1-piperidinonitrile (i) or DMAD (ii). Surprisingly, we obtained two significantly different types of products: in the first case (i), the 2*H*-1,3,2-diazaphosphole complex **5a**, but in the other (ii) selectively the novel phosphorus−carbon cage complex **10**. Taking the already reported (cf. ref 11) reactivity of the transient terminal phosphanediyl complex [$(OC)_5$WPCp*] (**7**) toward DMAD into account, which yielded, after a [2+1] and an intramolecular [4+2] cycloaddition reaction, a homoethylene phosphaprismane complex as final product, a reasonable explanation for the formation of complex **10** is the following: retro-[2+1] cycloadddition of complex **4a** furnishes the *P*-imino-substituted terminal phosphanediyl complex **8** transiently, which by [2+1] cycloaddition with DMAD forms the phosphirane ring of complex **9** and via a rapid subsequent intramolecular [4+2] cycloaddition the final product **10** (Scheme 4). All findings together represent a unprecedented case of a dual ring opening behavior of a P-heterocycle, a retro-[3+2] and a retro-[2+1] cycloaddition reaction, furnishing a nitrilium phosphane-ylide complex in the former and an electrophilic terminal phosphanediyl complex in the latter as reactive intermediates.

Discussion of Selected NMR Spectroscopic Data. The analytical data including elemental analyses, MS spectrometric data, and IR and NMR spectroscopic data readily confirm the molecular structures of all compounds reported here, which had in most cases been separated and purified by column chromatography at low temperature and subsequent crystallization. NMR data will be discussed hereafter; for further analytical data see the Experimental Section. Comparison of the NMR spectroscopic data of the 2*H*-1,3,2-diazaphosphole complexes **5a**,**b** with their 2-bis(trimethylsilyl)methyl-substituted analogues **11a**,**b**[6] reveals some noteworthy details (Table 1). The phosphorus resonances of com-

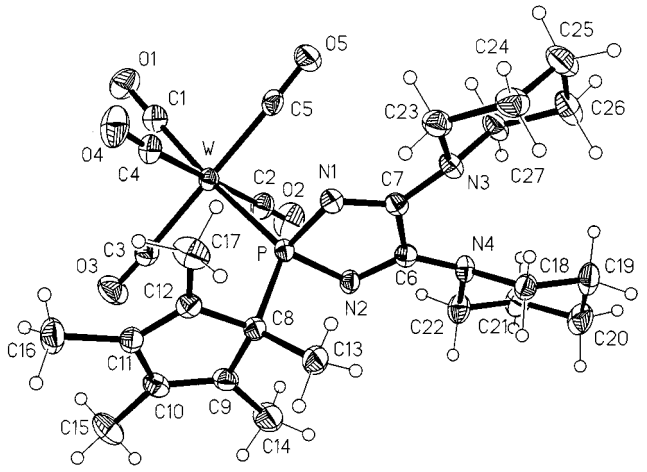


Figure 1. Molecular structure of complex **5a** (ellipsoids represent 50% probability level). Selected bond lengths (Å) and angles (deg): W−C(1) 2.003(3), C(1)−O(1) 1.146(3), P−W 2.4967(7), P−N(1) 1.704(2), P−N(2) 1.706(2), N(1)−C(7) 1.295(3), N(2)−C(6) 1.300(3), N(3)−C(7) 1.367(3), N(4)−C(6) 1.370(3), C(6)−C(7) 1.536(3), P−C(8) 1.877(2); W−P−C(8) 123.68(8), N(1)−P−N(2) 97.62(10), P−N(1)−C(7) 107.59(17), P−N(2)−C(6) 107.65(17).

plexes **5a**,**b** and **11a**,**b** display no significant dependence on the *P*-substituent $\Delta|^1J(P,W)| = 14-20$ between Cp* and $CH(SiMe_3)_2$) but the carbon resonances on the substituents at the C^4 and C^5 atoms of the 2*H*-1,3,2-diazaphosphole ring. The C^4/C^5 resonances are much less affected by the ring substitution pattern, generally appearing at about 157−160 ppm with small carbon−phosphorus coupling constants.

The phosphorus resonances of the complexed polycycles **4a**,**b** and **10** are shifted to higher field as expected due to the incorporation of the phosphorus into a three-membered heterocycle. The molecular constitution of **4a** was deduced unambiguously from the ^1H and ^{13}C NMR data and the HR mass spectrum. The key for the assignment of the polycyclic ring system was provided by a characteristic doublet at δ 179.0 (J(P,C) 5.7 Hz), indicative of the presence of an amidine unit, and the occurrence of altogether two olefinic and three aliphatic resonances for the quaternary carbon atoms of the former Cp* substituent. The attachment of a methyl group at each quaternary carbon and the atom connectivities within the polycyclic skeleton were determined on the basis of a complete set of one- and three-bond correlation signals obtained from 2D ^1H, ^{13}C HMQC, and HMBC spectra, and final assignment of all ^{13}C resonances was helped by taking into account the splittings due to coupling to the phosphorus atom. Compound **4b** was not isolated, but a structural similarity to that for **4a** was assumed on the basis of the similar values of δ ^{31}P and J(W,P).

Discussion of Selected X-ray Structural Data. The molecular structures of 2*H*-1,3,2-diazaphosphole complex **5a**, the acyclic dinuclear complex **6**, and the polycyclic phosphorus−carbon cage complex **10** were confirmed for the solid state by X-ray crystallography (Figures 1−3).

Complex **5a** has an almost planar five-membered ring with a mean deviation of 0.03 Å and localized endocyclic

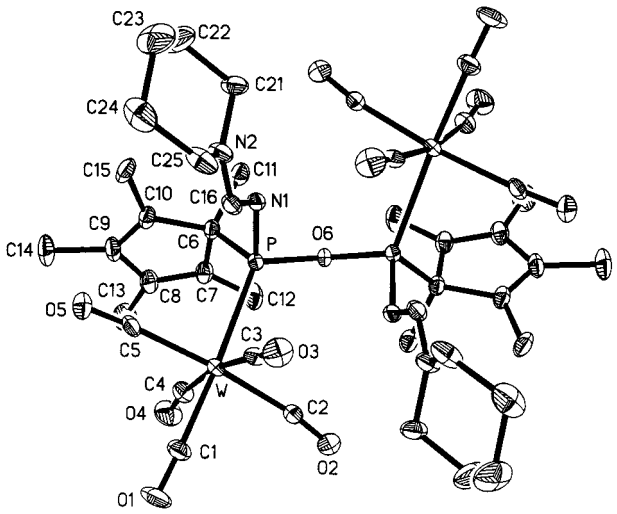


Figure 2. Molecular structure of complex **6** (ellipsoids represent 30% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): W−C(1) 2.003(7), C(1)−O(1) 1.135(7), P−W 2.5561(15), P−O(6) 165.5(2), P−N(1) 1.671(5), P−C(6) 1.881(6), N(1)−C(16) 1.308(7), N(2)−C(16) 1.320(7); W−P−C(6) 114.88(19), O(6)−P−C(6) 100.1(2), N(1)−P−C(6) 100.7(3), O(6)−P−N(1) 100.7(2), P−O(6)−P#1 131.2(3), P−N(1)−C(16) 121.6(4), N(1)−C(16)−N(2) 125.2(6).

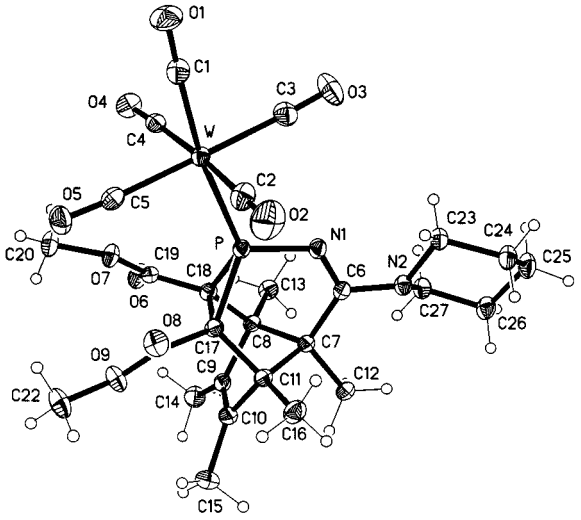


Figure 3. Molecular structure of complex **10** (ellipsoids represent 50% probability level). Selected bond lengths (Å) and angles (deg): W−C(1) 1.9972(19), C(1)−O(1) 1.151(2), P−W 2.4774(5), P−N(1) 1.6550(15), P−C(17) 1.8150(18), P−C(18) 1.8896(17), C(17)−C(18) 1.543(2), N(1)−C(6) 1.301(2), N(2)−C(6) 1.375(2); W−P−N(1) 114.29(6), N(1)−P−C(17) 108.12(8), N(1)−P−C(18) 105.83(7), C(17)−P−C(18) 49.19(7), N(1)−C(6)−N(2) 116.88(16).

nitrogen−carbon double-bond distances[15] (N(1)−C(7) 1.295(3) and N(2)−C(6) 1.300(3) Å) (Figure 1). The planes of the 1-piperidino groups defined by the atoms C(23)−N(3)−C(27) and C(18)−N(4)−C(22) subtend interplanar angles to the five-membered ring of 31° and 32°. Although the ring has also substantially shortened exocyclic nitrogen−carbon bond distances and angle sums at the N(3) and N(4) nitrogen atoms of 347.5° and

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346.3°, this provides only weak evidence for a $p_\pi-p_\pi$ electron interaction of the nitrogen lone pair and the C−N π-bond. The W−P distance in complex **5a** is 2.4967(7) Å and the $\Sigma°(P_{PR3})$ value 304°; all parameters of complex **5a** are very similar to those of related 2-bis(trimethylsilyl)methyl-substituted 2*H*-1,3,2-diazaphosphole complexes (cf. ref 6).

The molecular structure of the acyclic dinuclear complex **6** (Figure 2), which displays crystallographically 2-fold symmetry, shows rather unexceptional structural features except for a slightly widened P−O(6)−P#1 angle of 131.2(3)° and a surprising long phosphorus−tungsten distance of 2.5561(15) Å, both of which might be due to steric reasons.

A comparison of some of the key findings for the polycyclic structure of complex **10** (Figure 3) to those for the closely related {pentacarbonyl[3,4,5,6,8-pentamethyl-1-phosphatetracyclo[4.1.1.1^{3,6}0^{2,7}]-2,7-bis(methoxycarbonyl)-oct-4-ene-κP]tungsten(0)}[12] (**12**) reveals for complex **12** a smaller $\Sigma°(P_{PR3})$ value (195° versus 263° in **10**) and a shorter W−P distance (2.4569(8) versus 2.4774(5) Å in **10**). It is notable that the carbon−tungsten distance of the *trans*-CO group in complex **12** is slightly shortened (1.980(3) versus 1.9972(19) Å in **10**). These results provide initial evidence for a better σ-donor *and* π-acceptor ability of complex **12** compared to **10**. Because of the current increasing interest in the catalytic use of complexes with polycyclic phosphane ligands having a phosphirane subunit,[16] this special aspect deserves further intensive studies.

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. NMR spectra were recorded on Bruker AC200 (^{1}H 200.1 MHz, ^{13}C 50.3 MHz, ^{31}P 81.0 MHz) and Bruker AMX300 (^{1}H 300.1 MHz, ^{13}C 75.4 MHz) spectrometers using [D]-chloroform and [D_6]benzene as solvents if not stated otherwise. Chemical shifts are given relative to external TMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P). The signs for ^1J(W,P) and ^3J(W,P) of **6** were determined from simulation of the observed higher order multiplet of the ^{183}W satellites in the ^{31}P{^{1}H} NMR spectrum and are based on the assumption of a positive sign for ^1J(W,P). Mass spectra were recorded on a Finigan Mat 8430 (70 eV); apart from *m*/*z* values of the molecule ions, only *m*/*z* values are given having intensities of more than 20%. Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed using a Carlo Erba analytical gas chromatograph. The κP notation in the used nomenclature shall serve for differentiation between P- and N-coordination of the appropriate heterocycle to the metal.

{Pentacarbonyl[2-pentamethylcyclopentadienyl-3-phenyl-2*H*-azaphosphirene-κP)tungsten(0)} (**1**)[10] was synthesized according to the quoted reference.

Procedure for the Preparation of the Complexes 4a,b, 5a,b, and 6. Solutions of 1.09 g (1.8 mmol) of 2*H*-azaphosphirene tungsten complex **1** and 0.2 mL of 1-piperidinonitrile or ethyl cyanoformate in 6 mL of toluene are stirred for 90 min at 62 °C (**4a**,**b**) or with 0.6 mL of 1-piperidinonitrile or ethyl cyanoformate in 8 mL of toluene for 3 h at 62 °C (**5a**,**b**). The solutions are then concentrated to dryness in vacuo (ca. 0.01 mbar), and the residues are subjected to low-temperature column chromatography (SiO_2, −11 °C, *n*-hexane/diethyl ether, 99:1 to 95:5). The eluates are concentrated to dryness in vacuo and the residues crystallized from *n*-pentane at −20 °C (**5a**).

{**Pentacarbonyl[1,4,5,6,7-pentamethyl-3-(1-piperidino)-2-aza-8-phosphatricyclo-[2.2.1^{1,4}.1^{4,7}.0^{1,7}]-oct-2,5-diene-κP]-tungsten(0)**} **(4a):** pale yellow oil, yield 0.60 g (55%); ^{1}H NMR ($CDCl_3$) δ 1.14 (d, ^3J(P,H) = 13.9 Hz, 3H, CH_3), 1.33 (d, ^3J(H,H) = 16.9 Hz, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.34 (m_c, 6H, NCH$_2$CH_2), 3.71 (m_c, 4H, NCH_2); ^{13}C{H} NMR ($CDCl_3$) δ 11.2 (s, C^2-*C*H$_3$), 11.7 (d, ^2J(P,C) = 1.9 Hz, C^7-*C*H$_3$), 12.7 (d, ^3J(P,C) = 2.7 Hz, C^6-*C*H$_3$), 14.2 (d, ^2J(P,C) = 9.9 Hz, C^1-*C*H$_3$), 16.7 (d, ^3J(P,HC = 4.6 Hz, C^4-*C*H$_3$), 24.5 (s, NCH$_2$CH$_2$*C*H$_2$) 26.2 (s, NCH$_2$*C*H$_2$), 49.1 (s, N*C*H$_2$), 56.0 (d, ^1J(P,C) = 9.5 Hz, C^7), 60.5 (d, ^2J(P,C) = 34.3 Hz, C^1), 71.4 (d, J(P,C) = 4.2 Hz, C^4), 132.0 (d, ^3J(P,C) = 5.7 Hz, C^5), 133.5 (d, ^2J(P,C) = 9.5 Hz, C^6), 179.0 (d, ^2J(P,C) = 5.7 Hz, PN=*C*), 196.3 (d, ^2J(P,C) = 9.4 Hz, *cis*-CO), 199.3 (d, ^2J(P,C) = 31.6 Hz, *trans*-CO); ^{31}P{H} NMR ($CDCl_3$) δ −45.8 (d, ^1J(P,W) = 275 Hz); MS (70 eV, EI) (^{184}W); *m*/*z* (%) 600 (44) [M$^{\bullet+}$], 572 (8) [(M − CO)$^+$], 544 (11) [(M − 2 CO)$^+$], 516 (14) [(M − 3 CO)$^+$], 460 (48) [(M − 5 CO)$^+$], 490 (76) [(M − $C_6H_{10}N$)$^+$], 406 (100) [($C_{12}H_{15}O_2$-PW)$^+$]; HR-MS (70 eV, EI for $C_{21}H_{25}N_2O_5P^{182}W$) *m*/*z* theor 598.1013, found 598.0983; IR (KBr) $\tilde{\nu}$ 2072 (m), 1984 (m), 1940 (vs) (CO, cm^{-1}); 1605 (m) (C=N, cm^{-1}). Anal. Calcd for $C_{21}H_{25}N_2O_5PW$ (600.25): C 42.02, H 4.20, N 4.67. Found: C 42.45, H 4.39, N 4.51.

{**Pentacarbonyl[1,4,5,6,7-pentamethyl-3-(ethyloxycarbonyl)-2-aza-8-phosphatricyclo[2.2.1^{1,4}.1^{4,7}.0^{1,7}]oct-2,5-diene-κP]tungsten(0)**} **(4b):** ^{31}P{H} NMR ($CDCl_3$) δ −34.4 (d, ^1J(P,W) = 251 Hz).

{**Pentacarbonyl[2-pentamethylcyclopentadienyl-4,5-bis(1-piperidino)-2*H*-1,3,2-diazaphosphole-κP]tungsten-(0)**} **(5a):** yellow powder, mp 162 °C dec; 0.46 g (33%); ^{1}H NMR ($CDCl_3$) δ 0.62 (d, ^3J(P,H) = 11.8 Hz, 3H, Cp*-C^1-CH_3), 1.67 (m_c, 8H, CH_2), 1.85 (d, ^4J(P,H) = 4.6 Hz, 6H, Cp*-C$^{2/2}$−CH_3), 1.99 (s, 6H, Cp*-C$^{3/3}$−CH_3), 3.50 (m_c, 6H, NCH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 10.7 (d, ^2J(P,C) = 5.6 Hz, Cp*-C^1-*C*H$_3$), 11.70/11.71/11,75 (s, Cp*-CH$_3$), 24.4 (s, CH$_2$*C*H$_2$), 25.3 (s, NCH$_2$*C*H$_2$), 49.7 (s, N*C*H$_2$), 62.2 (d, ^1J(P,C) = 8.4 Hz, *C*p*-C^1), 136.9 (d, ^2J(P,C) = 4.6 Hz, *C*p*-C^2), 140.8 (d, ^3J(P,C) = 6.8 Hz, *C*p*-C^3), 161.6 (d, $^{(2+3)}J$(P,C) = 2.5 Hz, PN=*C*), 196.4 (d, ^1J(P,C) = 8.3 Hz, ^1J(W,C) = 118.0 Hz, *cis*-CO), 200.1 (d, ^2J(P,C) = 27.6 Hz, *trans*-CO); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 137.7 (s, ^1J(P,W) = 278 Hz); MS (70 eV, EI) (184W); *m*/*z* (%) 710 (20) [M$^{\bullet+}$], 575 (100) [(M − $C_{10}H_{15}$)$^+$], 547 (39) [(M − $C_{10}H_{15}$ − CO)$^+$], 519 (48) [(M − $C_{10}H_{15}$ − 2 CO)$^+$], 491 (12) [(M − $C_{10}H_{15}$ − 3 CO)$^+$], 463 (52) [(M − $C_{10}H_{15}$ − 4 CO)$^+$], 435 (27) [(M − $C_{10}H_{15}$ − 5 CO)$^+$], 135 (18) [($C_{10}H_{15}$)$^+$], 84 (29) [(NC_5H_{10})$^+$]; IR (KBr) $\tilde{\nu}$ 2068 (m), 1976 (m), 1932 (vs), 1914 (vs) (CO, cm^{-1}); 1535 (s) (C=N, cm^{-1}). Anal. Calcd for $C_{27}H_{35}N_4O_5PW$ (710.40): C 45.65, H 4.97, N 7.89. Found: C 44.85, H 5.02, N 7.41.

{**Pentacarbonyl[2-pentamethylcyclopentadienyl-4,5-bis(ethoxycarbonyl)-2*H*-1,3,2-diazaphosphole-κP]tungsten(0)**} **(5b):** yellow oil, yield 0.45 g (36%); ^{1}H NMR ($CDCl_3$) δ 0.68 (d, ^3J(P,H) = 13.7 Hz, 3H, Cp*-C^1-CH_3), 1.61 (t, ^3J(H,H) = 6.3 Hz, 6H, OCH$_2$CH_3), 1.91 (d, ^4J(P,H) = 4.9 Hz, 6H, Cp*-C$^{2/2}$−CH_3), 2.02 (s br, 6H, Cp*-C$^{3/3}$−CH_3), 4.51 (q, ^3J(H,H) = 6.3 Hz, 4H, OCH_2CH$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 10.6−11.8 (s, CH$_3$), 13.8 (s, CO$_2$CH$_2$*C*H$_3$), 63.1 (s, CO$_2$*C*H$_2$CH$_3$), 62.7 (d, J(P,C) = 4.8 Hz, Cp*-C^1), 135.2 (s, Cp*-C^{2,2}), 143.6 (d, J(P,C) = 8.0 Hz, Cp*-C^{3,3}), 158.2 (d, ^2J(P,C) = 3.6 Hz, PN=*C*), 161.4 (d, ^2J(P,C) = 15.7 Hz, *C*O$_2$CH$_2$), 193.7 (d, ^2J(P,C) = 7.0 Hz, *cis*-*C*O); ^{31}P NMR ($CDCl_3$) δ 186.6 (q, ^3J(P,H) = 13.7 Hz, ^1J(P,W) = 273 Hz).

{***P*,*P*′-Oxybis[pentacarbonyl{[*N*-(*C*-(1-piperidino)imino)](pentamethyl-2,4-cyclopentadien-1-yl)phosphane}-tungsten(0)]**} **(6).** Crystallization from pentane at −20 °C afforded **6** as pale yellow crystals, mp 178 °C dec: ^{1}H NMR δ 0.87 (m_c), 1.41 (m_c), 1.49 (m_c), 1.52 (m_c), 1.57 (m_c), 1.73 (m_c),

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2.22 (m_c), 3.42 (m_c), 4.25 (m_c), 3.72 (m_c), 7.91 (m_c, 2H, N=C*H*); $^{13}C\{^1H\}$ NMR δ 11.7/11.9/13.5/14.3 (s, Cp*-*C*H$_3$), 15.7 (m_c, Cp*-*C*H$_3$), 24.4 (m_c, *C*H$_2$), 25.4 (m_c, *C*H$_2$), 26.3 (m_c, *C*H$_2$), 26.9 (m_c, *C*H$_2$), 44.2 (m_c, N*C*H$_2$), 51.2 (m_c, N*C*H$_2$), 69.1 (m_c, Cp*-C1), 130.7 (m_c, Cp*), 140.2 (m_c, Cp*), 140.4 (m_c, Cp*), 142.7 (m_c, Cp*); 168.0 (m_c, *C*O$_2$Me), 161.8 (m_c, PN*C*H), 198.5 (m_c, *cis*-*C*O), 198.8 (m_c, *trans*-*C*O); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 156.0 (s, $^1J(P^1,W) = +302$ Hz, $^3J(P^2,W) = -1$ Hz, $^2J(P,P) = 34.7$ Hz); IR (KBr) $\tilde{\nu}$ 2061 (s), 1984 (s), 1972 (s), 1942 (vs), 1926 (vs), 1907 (vs), 1899 (vs) (CO, cm^{-1}); 1610 (s) (C=N, cm^{-1}). Anal. Calcd for $C_{42}H_{52}N_4O_{11}P_2W_2$ (1218.51): C 41.40, H 4.30, N 4.54. Found: C 41.58, H 4.39, N 4.48.

Procedure for the Preparation of {Pentacarbonyl-[2,10-bis(methoxycarbonyl)-3,4,5,6,7-pentamethyl-8-(1-piperidino)-9-aza-1-phosphatetracyclo-[4.3.1^{1,6}.6.1^{3,7}.0^{2,10}]-dec-4,8-diene-κP]tungsten(0)} (10). A solution of 1.09 g (1.8 mmol) of 2*H*-azaphosphirene tungsten complex **1** and 0.2 mL of 1-piperidinonitrile in 6 mL of toluene was stirred at 62 °C for 90 min. Then the reaction mixture was cooled to ambient temperature, 0.6 mL of dimethyl acetylenedicarboxylate was added, and the mixture was heated at 75 °C for 15 min with slow stirring. The solvent was removed in vacuo and the product separated by low-temperature column chromatography (SiO_2, −25 °C, *n*-hexane/diethyl ether, 90:10). Evaporation of the second fraction yielded **10:** pale yellow crystals, mp 137 °C dec; yield 0.35 g (46%); ^1H NMR ([D$_8$]toluene) δ 0.83 (s, 3H, C*H*$_3$), 0.89 (s, 6H, C*H*$_3$), 1.16 (m_c, 6H, NCH$_2$C*H*$_2$), 1.60 (d, J(P,H) = 1.2 Hz, 6H, C*H*$_3$), 2.71 (m_c, 4H, NC*H*$_2$), 3.41 (s, 6H, OC*H*$_3$); $^{13}C\{^1H\}$ NMR ([D$_8$]toluene) δ 11.0 (s, CH$_3$), 12.1(s, CH$_3$), 15.0 (d, ^4J(P,C) = 3.7 Hz, C^7-CH$_3$), 24.4 (s, NCH$_2$-CH$_2$*C*H$_2$), 25.8 (s, NCH$_2$*C*H$_2$), 50.4 (s, N*C*H$_2$), 51.5 (s, CO$_2$*C*H$_3$), 57.0 (d, ^3J(P,C) = 29.6 Hz, PN=C*C*^{7}), 61.9 (d, ^2J(P,C) = 3.8 Hz, *C*$^{3/6}$), (67.3 (d, J(P,C) = 11.2 Hz, *C*$^{2/10}$), 143.3 (d, ^3J(P,C) = 2.8 Hz, *C*$^{4/5}$), 168.1 (d, ^4J(P,C) = 4.3 Hz, *C*O$_2$Me), 179.2 (d, ^2J(P,C) = 14.7 Hz, PN=*C*), 196.5 (d, ^2J(P,C) = 9.5 Hz, *cis*-*C*O), 199.8 (d, ^2J(P,C) = 38.4 Hz, *trans*-*C*O); ^{31}P NMR ([D$_8$]-toluene): δ −34.5 (s, ^1J(P,W) = 310 Hz); MS (70 eV, EI, ^{184}W); *m*/*z* (%) 742 (2) [M$^{\bullet+}$], 714 (31) [(M − CO)$^+$], 686 (28) [(M$^+$ - 2 CO)$^+$], 658 (15) [(M - 3 CO)$^+$], 630 (100) [(M − 4 CO)$^+$], 602 (33) [(M − 5 CO)$^+$]; IR (KBr) $\tilde{\nu}$ 2075 (m), 1998 (m), 1936 (vs), 1918 (vs) (CO, cm^{-1}); 1713 (m br) (CO$_2$Me, cm^{-1}); 1653 (m) (C=N, cm^{-1}); HR-MS (70 eV, EI; for $C_{27}H_{31}N_2O_9P^{184}W$) *m*/*z* theor 742.1270, found 742.1270 ± 2. Anal. Calcd for $C_{27}H_{31}N_2O_9PW$, (742.1): C 45.65, H 4.97, N 7.89. Found: C 44.85, H 5.02, N 7.41.

X-ray Crystallographic Analyses. Structure Determination of 5a. Crystal data: $C_{27}H_{35}N_4O_5PW$, $M = 710.41$, $P2_1/c$, $a = 18.3849(14)$ Å, $b = 9.7930(8)$ Å, $c = 18.3388(14)$ Å, $\beta = 118.082(3)°$, $V = 2913.1(4)$ Å^3, $Z = 4$, $d_{calc} = 1.620$ Mg/m^3, $\mu = 4.062$ mm^{-1}, $T = 143$ K. A pale yellow tablet (0.33 × 0.23 × 0.12 mm) was mounted in inert oil. A total of 23 687 intensities were measured (2θ 4.86−60°) using monochromated Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer. After absorption correction (multiple scans) 8491 were unique ($R_{int} = 0.0495$) and used for all calculations (program SHELXL-97[17]). Hydrogen atoms were refined as rigid methyl groups or with a riding model. The final *wR(F^2)* was 0.0422 with conventional *R(F)* 0.0254, for 348 parameters and 64 restraints; highest peak 0.823, hole −1.327 e/Å^3.

Structure Determination of 6. Crystal data: $C_{49}H_{60}N_4O_{11}P_2W_2$, $M = 1310.65$, *C*2/*c*, $a = 22.199(3)$ Å, $b = 23.215(3)$ Å, $c = 11.5504(11)$ Å, $\beta = 102.607(12)°$, $V = 5808.9(14)$ Å^3, $Z = 4$, $d_{calc} = 1.499$ Mg/m^3, $\mu = 4.067$ mm^{-1}, $T = 173$ K. A pale yellow prism (0.60 × 0.20 × 0.20 mm) was mounted in inert oil. A total of 7798 intensities were measured (2θ 6.26−50°) using monochromated Mo Kα radiation on a Siemens P4 diffractometer. After absorption correction (ψ-scans) 5111 were unique ($R_{int} = 0.0193$) and used for all calculations. Hydrogens were refined as above. The structure contains a toluene molecule severely disordered about an inversion center, for which only an idealized hexagon could be refined. The final *wR(F^2)* was 0.0832 with conventional *R(F)* 0.0295, for 293 parameters; highest peak 0.986, hole −0.466 e/Å^3.

Structure Determination of 10. Crystal data: $C_{27}H_{31}N_2O_9PW$, $M = 742.36$, $P\bar{1}$, $a = 11.6400(10)$ Å, $b = 12.3360(12)$ Å, $c = 12.5783(12)$ Å, $\alpha = 77.975(3)°$, $\beta = 64.102(3)°$, $\gamma = 63.118(3)°$, $V = 1449.0(2)$ Å^3, $Z = 2$, $d_{calc} = 1.701$ Mg/m^3, $\mu = 4.095$ mm^{-1}, $T = 143$ K. A colorless crystal (0.25 × 0.20 × 0.17 mm) was mounted in inert oil. A total of 17 209 intensities were measured (2θ 3.6−60°) using monochromated Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer. After absorption correction (multiple scans) 8369 were unique ($R_{int} = 0.0195$) and used for all calculations. Hydrogens were refined as above. The final *wR(F^2)* was 0.0449, with conventional *R*(*F*) 0.0181, for 368 parameters and 300 restraints; highest peak 1.356, hole −1.277 e/Å^3.

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Supporting Information Available: For **5a**, **6**, and **10**, tables of crystal data and structure refinement details, atomic coordinates, displacement parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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