Ligand Behavior of a (*Z*)-Phosphazide (a 1,2,3,4λ^5-Triazaphosphinine) and of the Corresponding Phosphazene (a 1,2λ^5-Azaphosphete)

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Received September 12, 1995[⊗]

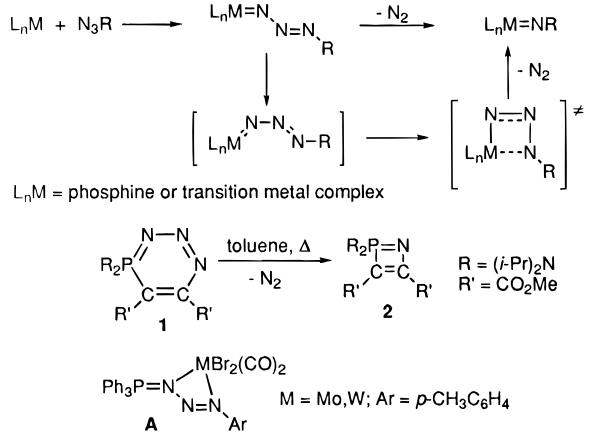
Abstract: 1,2,3,4λ^5-Triazaphosphinine **1** reacts with $PdCl_2(PhCN)_2$ and $W(CO)_5(THF)$ at room temperature, affording, according to ^{31}P NMR spectroscopy, η^1-triazaphosphinine complexes **3** and **5**, which after elimination of dinitrogen give the bis(η^1-azaphosphete)palladium(II) complex **4** and (η^1-azaphosphete)$W(CO)_5$ complex **6**, in 65% and 88% yield, respectively. Complex **4** can also be obtained in 90% yield by addition of $PdCl_2(PhCN)_2$ to 1,2λ^5-azaphosphete **2**. Addition of *cis*-$Mo(CO)_4(pip)_2$ to **1** leads to (η^1-triazaphosphinine)$Mo(CO)_4$(pip) complex **7**, which was isolated in 70% yield. In solution, at room temperature for 2 days, **7** transforms into to η^1-(five-membered cyclophosphazene)-$Mo(CO)_5$ complex **9** in 45% yield. When 2 equiv of $W(CO)_5$(pip) is added to **1**, complex **10** featuring a five-membered cyclophosphazene bonded to $W(CO)_5$(pip) *via* a hydrogen bond is isolated in 80% yield. 1,2λ^5-Azaphosphete **2** reacts with piperidine, affording five-membered phosphazene ring **11** in 95% yield, which by subsequent treatment with $Mo(CO)_5$(pip) and $W(CO)_5$(pip) gives complexes **9** (75% yield) and **10** (83% yield), respectively. Schwartz's reagent reacts with **1**, affording five-membered zirconacyclophosphazene **12** in 45% yield. Complexes **4**, **7**, **10**, and **12** are characterized by single-crystal X-ray analyses. These results as a whole demonstrate that in contrast with (*E*)-phosphazides which behave as four-electron donors *via* the α- and γ-nitrogen atoms and which are stabilized by complexation, (*Z*)-phosphazides, such as the 1,2,3,4λ^5-triazaphosphinine **1**, act as two-electron donors *via* the β-nitrogen atom, and are destabilized by the metal with respect to nitrogen elimination.

Introduction

It is well known that organic azides react with phosphines and transition metals, with extrusion of dinitrogen, giving phosphazenes[1] and terminal imido complexes,[2] respectively. The mechanism of the so-called Staudinger reaction has been investigated in detail. A few examples of the initial phosphazides have been characterized,[1b] while the first terminal metal azides have only recently been isolated independently by Bergman[3] and Cummins.[4] So far, all these three-nitrogen atom-containing species appeared to have an (*E*)-configuration; the geometry of the (*Z*)-isomers is close to that of the supposed transition state leading to the final products[5] (Scheme 1).

However, we have recently reported the synthesis of 1,2,3,4λ^5-triazaphosphinine **1**,[6] which features a phosphazide skeleton in a (*Z*)-configuration. Due to its six-membered ring structure, extrusion of dinitrogen giving four-membered cyclophosphazene **2** only occurs in refluxing toluene. The unusual stability of **1** gave us the opportunity to gain more of an insight into the reactivity of (*Z*)-phosphazides, especially toward transition metal fragments. Note that so far even the chemical reactivity of (*E*)-phosphazides has been poorly studied and only two transition

Scheme 1



metal complexes **A** are known[7] (Scheme 1). On the other hand, although the coordination chemistry of phosphazenes has been widely studied,[8] the ligand behavior of four-π-electron four-membered cyclophosphazenes[9] is still a virgin area.

Results and Discussion

Slow evolution of dinitrogen was observed when palladium dichloride was added at room temperature to a toluene solution of 1,2,3,4λ^5-triazaphosphinine **1**, affording 1,2λ^5-azaphosphete **2** in 95% yield. Since even a catalytic amount of $PdCl_2$ induces the ring contraction, this reaction is an interesting alternative to the thermal route (refluxing toluene) for the preparation of

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) (a) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635. (b) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353. (c) Johnson, A. W. *Ylides and Imines of Phosphorus;* Wiley: New York, 1993.

(2) (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239. (b) Cummins, C. C.; Schrock, R. R.; Davies, W. M. *Inorg. Chem.* **1994**, *33*, 1449.

(3) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 6382.

(4) Fickes, M. G.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 6384.

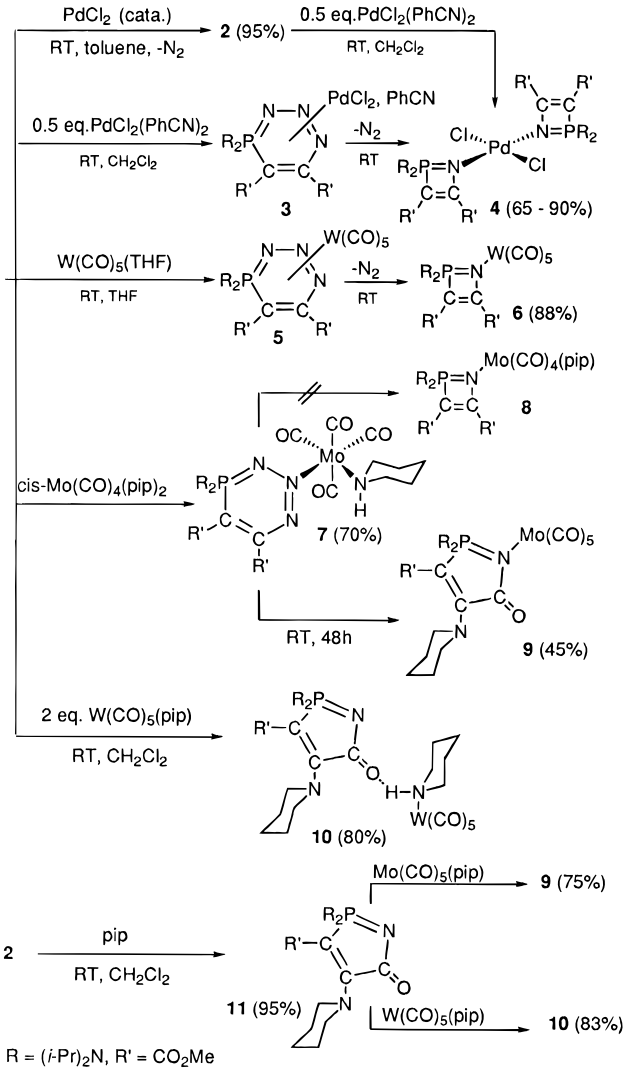
(5) Bock, H.; Schnöller, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *87*, 636.

(6) (a) Tejeda, J.; Réau, R.; Dahan, F.; Bertrand, G. *J. Am. Chem. Soc.* **1993**, *115*, 7880. (b) Bieger, K.; Tejeda, J.; Réau, R.; Dahan, F.; Bertrand, G. *J. Am. Chem. Soc.* **1994**, *116*, 8087.

(7) (a) Hillhouse, G. L.; Haymore, B. L. *J. Organomet. Chem.* **1978**, *162*, C23. (b) Hillhouse, G. L.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1982**, *21*, 2064.

0002-7863/96/1518-1038$12.00/0

Scheme 2



2. More interestingly, an evanescent signal at +11.6 ppm was detected by ^{31}P NMR spectroscopy during the course of the reaction of a dichloromethane solution of **1** with1/2 equiv of $PdCl_2(PhCN)_2$ at room temperature. Since this chemical shift is close to that of **1** (+6.2), it is quite likely that it is due to a (1,2,3,4λ^5-triazaphosphinine)palladium(II) complex of type **3**. However, evolution of dinitrogen also occurred, leading to complex **4**, which was isolated in 65% yield (Scheme 2). The same complex **4** can also be obtained in 90% yield by adding $PdCl_2(PhCN)_2$ to 2 equiv of the azaphosphete **2**. The NMR data for **4** are very similar to those for the free ligand **2** (Table 1), suggesting that the four-π-electron system is not pertubated by the metal. A single-crystal X-ray diffraction study revealed that **4** is a bis(η^1-azaphosphete)palladium(II) complex (Figure 1, Table 2). The geometric data for the free and the coordinated ring are compared in Table 3. In both cases, the four-membered ring is almost planar [maximum deviation from planarity: **2**, 0.003(4) Å; **4**, −0.013(3) Å], and the diagonal P···C2 distance is short [**2**, 2.109(4) Å; **4**, 2.156(4) Å]. The only discrepancy lies in the values of the N1−P−N2 and N1−P−N3 angles which are notably different in the free heterocycle [111.1(2)°, 116.8(2)°] and nearly equal in the coordinated ring [112.8(1)°, 114.1(1)°].[10] The palladium center is out of the plane of the four-membered ring as indicated by the torsion angles Pd−N1−P−C1 [157.6(3)°] and Pd−N1−C2−C1 [−159.9(2)°].

Table 1. Comparison of Selected Spectroscopic Data for Compounds **1**−**7** and **9**−**11**

		δ (^{13}C)(J_{PC})[a]			
	δ (^{31}P)	PC	PC*C*	CO	CO
2	+52.46	91.88 (81.6)	182.37 (28.0)	158.30 (0.0)	164.05 (64.3)
4	+52.74	96.40 (95.2)	180.48 (13.0)	158.42 (5.7)	162.21 (52.6)
6	+52.55	95.76 (94.8)	183.63 (19.1)	157.91 (5.3)	162.93 (54.0)
9	+51.60	90.54 (120.1)	163.47 (7.8)	169.45 (14.8)[b]	163.27 (35.4)
10	+54.29	90.88 (118.2)	163.82 (7.8)	169.95 (14.7)[b]	164.07 (42.9)
11	+54.08	90.57 (118.5)	163.31 (2.0)	169.52 (14.6)[b]	163.77(29.7)
1	+5.74	81.77 (113.2)	150.44 (2.4)	166.23 (11.6)	166.81 (2.7)
3	+11.61				
5	+9.70				
7	+6.49	83.49 (115.5)	151.57 (3.6)	165.08 (13.1)	165.80 (4.3)

[a] Chemical shifts in parts per million and coupling constants in hertz. [b] Endocyclic carbonyl group.

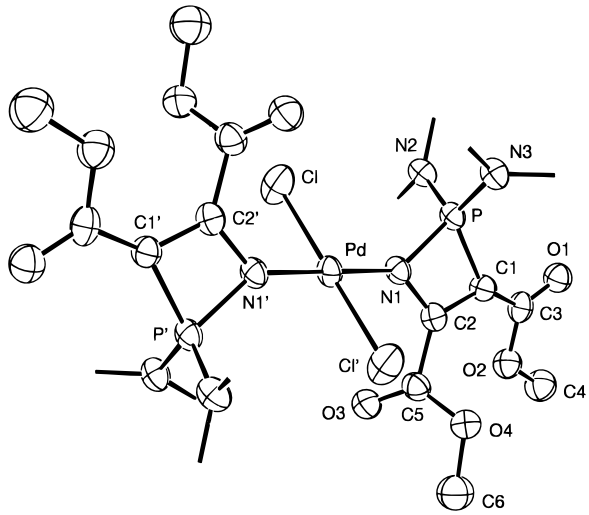


Figure 1. ORTEP drawing of **4** (apostrophe denotes centrosymmetric operation $1-x, 1-y, 1-z$) showing the numbering used. The methyl groups of the isopropyl moieties are not shown for clarity.

Table 2. Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **4**[a]

Pd−Cl	2.291(1)	Pd−N1−C2	131.2(2)
Pd−N1	2.013(2)	N1−P−N2	114.1(1)
P−N2	1.620(3)	N1−P−N3	112.8(1)
P−N3	1.618(3)	C1−P−N2	116.8(2)
C3−O1	1.196(4)	C1−P−N3	117.8(2)
C3−O2	1.346(5)	Pd−N1−P−C1	157.6(3)
C5−O3	1.191(5)	N1−P−C1−C2	−1.1(2)
C5−O4	1.327(5)	P−C1−C2−N1	1.4(3)
Cl−Pd−N1	90.59(8)	C1−C2−N1−Pd	−159.9(2)
Pd−N1−P	136.3(2)		

[a] PdClCl′N1N1′ plane perfect due to crystallographic symmetry.

According to ^{31}P NMR spectroscopy, compound **1** also reacts with $W(CO)_5$(THF) at −10 °C, affording complex **5** (^{31}P NMR δ +9.7), but once again slow evolution of dinitrogen occurred. The final product of the reaction was the (η^1-azaphosphete)-tungsten pentacarbonyl complex **6** which was isolated in 88% yield (Table 1 and Scheme 2).

(8) See, for examples: (a) Balakrishna, M.; Klein, R.; Uhlenbrock, S.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 5676. (b) Katti, K. V.; Santarsiero, B. D.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 5919. (c) Chandrasekaran, A.; Krishnamurthy, S. S.; Nethaji, M. *Inorg. Chem.* **1994**, *33*, 3085. (d) Balakrishna, M.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1993**, *32*, 3079.

(9) Apart from derivative **2**, only two other types of four-π-electron four-membered cyclophosphazenes are known, namely, the 1,3,2λ^5,4λ^5-diazadiphosphetes (cyclodiphosphazenes) (Baceiredo, A.; Bertrand, G.; Majoral, J.-P.; Sicard, G.; Jaud, J.; Galy, J. *J. Am. Chem. Soc.* **1984**, *106*, 6088) and the 1,3,2λ^5-diazaphosphetes (Alcaraz, G.; Baceiredo, A.; Nieger, M.; Bertrand, G. *J. Am. Chem. Soc.* **1994**, *116*, 2159).

Table 3. Comparison of Selected Bond Lengths (Å) and Angles (deg) for Compounds **2**[6a] and **4**

	2	**4**
P−N1	1.702(3)	1.725(3)
N1−C2	1.352(5)	1.354(4)
C2−C1	1.406(6)	1.391(4)
P−C1	1.764(4)	1.755(4)
C1−C3	1.419(6)	1.432(5)
C2−C5	1.497(6)	1.500(5)
N1−C2−C1	109.7(3)	107.4(3)
C2−C1−P	82.6(3)	85.7(2)
C1−P−N1	81.2(2)	78.9(1)
P−N1−C2	86.5(2)	88.0(2)

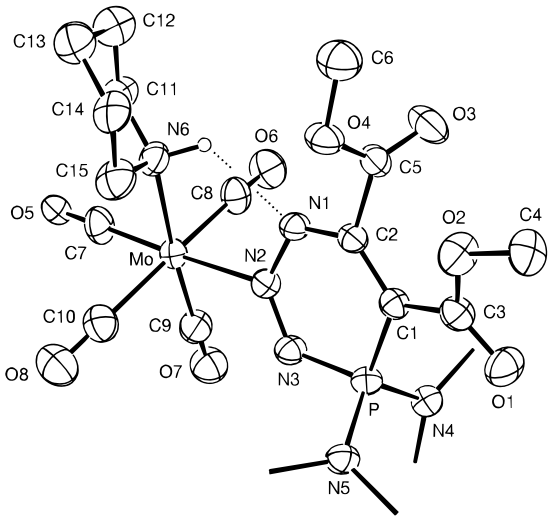


Figure 2. ORTEP drawing of **7** showing the numbering used. The methyl groups of the isopropyl moieties are not shown for clarity. The only H atom shown is that involved in the hydrogen bond illustrated by dotted lines.

Finally, by reacting **1** with *cis*-$Mo(CO)_4(pip)_2$ (pip = piperidine),[11] we were able to isolate 1,2,3,4λ^5-triazaphosphinine complex **7** in 70% yield (mp 115 °C dec) (Scheme 2). The spectroscopic data for the free and the coordinated six-membered ring are similar (Table 1), but do not indicate which nitrogen atom is coordinated to the metal. The structure of **7** was clearly established by an X-ray diffraction study (Figure 2, Table 4). Here also, the geometric parameters for the ring are not significantly modified by the coordination to the metal (Table 5). The less sterically hindered nitrogen atom N_β is the coordinated center, and the stability of the complex is probably increased by an intramolecular hydrogen-bonding interaction between the coordinated piperidine and the N_γ atom of the phosphazide moiety [N6···N1, 2.884(4) Å; H(N6)···N1, 2.23 Å; N6−H(N6)···N1, 124°]. Note that the complex **7** reveals a new type of coordination mode of a phosphazide moiety. So far, due to their (*E*)-configuration, phosphazides are known[7] to coordinate the metal in a chelating mode through the N_α and N_γ atoms, forming a four-membered metallacycle, **A** (Scheme 1).

Even though **7** demonstrated a remarkable stability in the solid state, it slowly decomposed in solution (2 days at room temperature), yielding **9** in 45% yield. At first glance, the NMR data for **9** (Table 1) were consistent with the expected four-π-electron four-membered ring molybdenum complex **8**. However, according to ^{13}C and ^1H NMR only one methoxy group was present. A careful comparison of the ^{13}C NMR data for **9**, with those for complexes **4** and **6**, shows that the signals of the PC*C* and of one of the CO carbon atoms were shielded ($\Delta\delta$ > 20 ppm) and deshielded ($\Delta\delta$ > 10 ppm), respectively, while the $^1J_{PC}$ coupling constant was notably larger (ΔJ > 25 Hz). Lastly, although a piperidine fragment was apparent by NMR, the absorption bands characteristic of a $Mo(CO)_5$ fragment[12] were present in the infrared spectrum, showing that the piperidine is part of the organic fragment. All attempts to obtain crystals of **9** suitable for an X-ray diffraction study failed.

Since nothing surprising occurred with $W(CO)_5(THF)$, we suspected that the piperidine ligand could play a role, and thus we investigated the reaction of **1** with $W(CO)_5(pip)$. Two equivalents of $W(CO)_5(pip)$ was necessary to obtain a clean reaction, and complex **10** was isolated after workup in 80% yield (Scheme 2). The spectroscopic data for the organic part of **10** were similar to those observed for **9** (Table 1), clearly demonstrating the similar nature of both phosphazene rings. The only difference was the presence for compound **10** of a second set of signals characteristic of a piperidine group bonded to the metal.[11] The exact structure of **10** was established by an X-ray diffraction study (Figure 3, Table 6).

The organometallic complex $W(CO)_5(pip)$ is linked by a hydrogen bond [N5···O1, 2.882(7) Å; H(N5)−O1, 1.94 Å; N5−H(N5)···O1, 163°] to an almost planar five-membered cyclo-

Table 4. Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **7**

Mo−N2	2.258(2)	N6−Mo−C8	93.2(1)
Mo−N6	2.324(3)	N6−Mo−C9	175.8(2)
Mo−C7	1.934(4)	N6−Mo−C10	95.4(2)
Mo−C8	1.997(4)	C7−Mo−C8	86.8(2)
Mo−C9	1.945(4)	C7−Mo−C9	88.4(2)
Mo−C10	2.043(5)	C7−Mo−C10	86.6(2)
P−N4	1.623(3)	C8−Mo−C9	84.2(2)
P−N5	1.628(3)	C8−Mo−C10	169.6(2)
C3−O1	1.196(5)	C9−Mo−C10	87.5(2)
C5−O3	1.181(5)	N3−P−N4	109.7(1)
Mo−N2−N1	115.0(2)	N3−P−N5	105.5(1)
Mo−N2−N3	120.8(2)	C1−P−N4	113.3(2)
N2−Mo−N6	83.4(1)	C1−P−N5	116.1(1)
N2−Mo−C7	177.6(1)	P−C1−C2−N1	2.0(5)
N2−Mo−C8	91.8(1)	C1−C2−N1−N2	4.5(6)
N2−Mo−C9	93.4(1)	C2−N1−N2−N3	−3.5(5)
N2−Mo−C10	95.0(1)	N1−N2−N3−P	−4.5(5)
N6−Mo−C7	94.7(1)	N2−N3−P−C1	9.3(3)
		N3−P−C1−C2	−7.6(3)
N6···N1	2.884(4)		
H(N6)···N1	2.23	N6−H(N6)···N1	124

Table 5. Comparison of Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**[6b] and **7**

	1	**7**
P−N3	1.666(2)	1.664(3)
N3−N2	1.296(4)	1.292(4)
N2−N1	1.335(3)	1.355(4)
N1−C2	1.356(4)	1.339(4)
C1−C2	1.375(4)	1.370(5)
C1−P	1.744(3)	1.760(3)
C1−C3	1.478(4)	1.469(4)
C2−C5	1.508(4)	1.524(4)
P−N3−N2	126.4(2)	126.0(2)
N3−N2−N1	124.0(2)	124.2(2)
N2−N1−C2	120.2(2)	120.1(2)
N1−C2−C1	129.9(3)	130.6(3)
C2−C1−P	115.4(2)	115.1(2)
C1−P−N3	103.1(1)	103.2(2)

(10) For a discussion on this weak Jahn−Teller distortion, see: (a) Trinquier, G. *J. Am. Chem. Soc.* **1986**, 108, 568. (b) Alcaraz, G.; Baceiredo, A.; Nieger, M.; Schoeller, W. W.; Bertrand, G. submitted for publication.

(11) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680.

(12) Kirtley S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; p 1110.

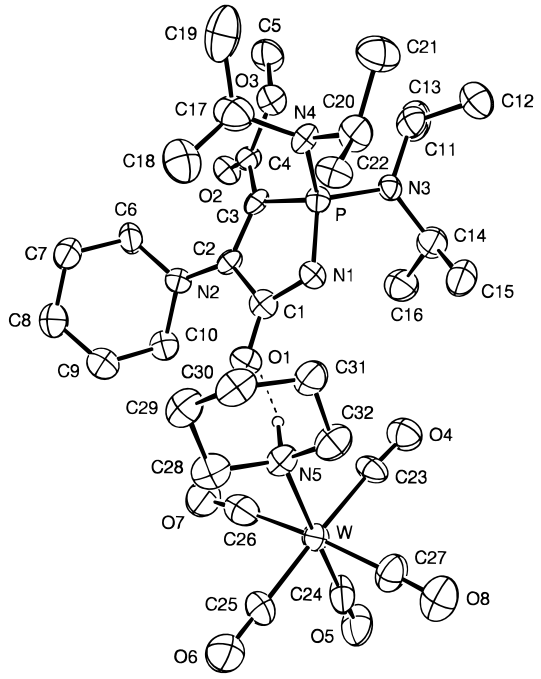


Figure 3. ORTEP drawing of **10** showing the numbering used. The methyl groups of the isopropyl moieties are not shown for clarity. The only H atom shown is that involved in the hydrogen bond illustrated by dotted lines.

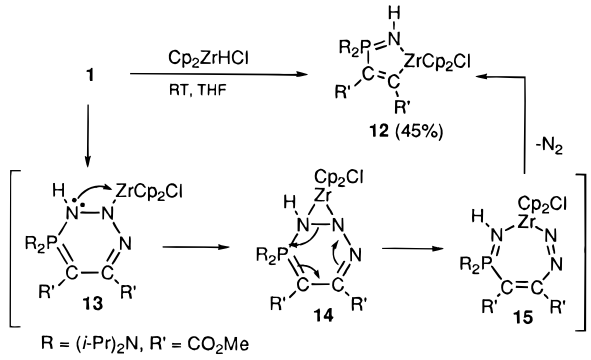
Table 6. Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **10**

P−N1	1.613(4)	N1−C1−O1	124.4(6)
N1−C1	1.327(7)	C2−C1−O1	121.4(5)
C1−C2	1.523(8)	C1−C2−N2	121.3(5)
C2−C3	1.387(7)	C3−C2−N2	127.2(5)
C3−P	1.761(6)	C2−C3−C4	126.0(5)
P−N3	1.635(5)	P−C3−C4	126.6(4)
P−N4	1.645(4)	C23−W−N5	88.6(2)
C1−O1	1.243(7)	C23−W−C24	89.6(3)
C2−N2	1.335(7)	C23−W−C25	178.0(3)
C3−C4	1.465(8)	C23−W−C26	91.8(3)
C4−O2	1.190(8)	C23−W−C27	89.8(3)
W−N5	2.293(5)	C24−W−N5	178.0(3)
W−C23	2.033(7)	C24−W−C25	89.2(4)
W−C24	1.935(8)	C24−W−C26	90.1(3)
W−C25	1.974(10)	C24−W−C27	84.6(3)
W−C26	2.040(9)	C25−W−N5	92.6(3)
W−C27	1.980(8)	C25−W−C26	89.8(4)
C3−P−N1	98.9(2)	C25−W−C27	88.4(4)
P−N1−C1	110.4(4)	C26−W−N5	89.2(2)
N1−C1−C2	114.2(5)	C26−W−C27	174.4(3)
C1−C2−C3	110.9(5)	C27−W−N5	96.2(3)
C2−C3−P	105.5(4)	P−N1−C1−C2	2.0(6)
N1−P−N3	108.6(2)	N1−C1−C2−C3	0.5(7)
N1−P−N4	115.1(2)	C1−C2−C3−P	−2.6(5)
C3−P−N3	117.4(3)	C2−C3−P−N1	3.4(4)
C3−P−N4	111.1(2)	C3−P−N1−C1	−3.2(4)
N5···O1	2.882(7)	N6−H(N6)···N1	163
H(N5)−O1	1.94		

phosphazene [maximum deviation 0.021(5) Å] featuring a piperidinyl substituent and an endocyclic carbonyl group. The role of the excess $W(CO)_5$(pip) is to provide the second piperidine required for the formation of **10.** At this stage, it was unclear whether the skeletal reorganization involved the metal.

In the absence of any transition metal complexes, no reaction occurred by addition of piperidine to six-membered ring **1**. In marked contrast, under the same experimental conditions the four-membered ring **2** was rapidly converted into the five-membered heterocycle **11** (95% yield). Its spectroscopic data compared well with those of the phosphazene ring in complexes **9** and **10** (Table 1).

Scheme 3



We checked that treatment of compound **11** by $Mo(CO)_5$(pip) and $W(CO)_5$(pip) gave rise again to complexes **9** (75% yield) and **10** (83% yield), respectively (Scheme 2). The dramatic difference in the mode of complexation of **11** with these two d^6-transition metal complexes could be due to the stronger acidity of the NH group in the case of tungsten.

At that point, we can conclude that the complexation of **1** has a destabilizing effect with respect to dinitrogen elimination. The chemistry observed so far for **1**, free[6] or as a ligand, is similar to that of transient (*Z*)-phosphazides, which means restricted to elimination of dinitrogen; further rearrangements observed belong to the chemistry of the phosphazene **2**.

We believed that to block the elimination of dinitrogen, one possibility would be to modify the phosphazide moiety by a 1,2-addition reaction. Hydrozirconation, which is known to take place with a large range of multiple bonds, was chosen.[13]

Derivative **1** reacted in THF at room temperature with Schwartz's reagent, affording complex **12** in 45% yield (Scheme 3). Mass spectroscopy and elemental analysis revealed that again dinitrogen was lost during the process. However, under the same reaction conditions, **12** was not obtained by reacting **2** with Cp_2ZrHCl. Therefore, the formation of **12** involves the six-membered ring **1**. In the ^{13}C NMR spectrum, besides the expected signals for the carbomethoxy, the cyclopentadienyl, and the diisopropylamino groups, two doublets of doublets were observed [+225.63 (J_{CP} = 51.9 Hz, J_{CH} = 4.4 Hz); 125.79 (J_{CP} = 164.8 Hz, J_{CH} = 7.9 Hz)]. These data strongly suggested the presence of a P−C═C−Zr sequence and of a hydrogen atom (+2.78, d, J_{PH} = 2.2 Hz) bonded either to the nitrogen or to the metal atom. The structure of **12** was clearly established by a single-crystal X-ray diffraction study (Figure 4 and Table 7). Derivative **12** consists of a five-membered ring, the Cp_2ZrCl fragment is σ-bound to one carbon, and the coordination sphere of the metal is completed by ligation of the phosphazene moiety. Note that compound **12** is one of the very rare examples of a five-membered heterocycle containing both a metal and a phosphazene.[14]

Formally, an insertion of the metal into the carbon-nitrogen bond occurred during this reaction. The most reasonable mechanism is to invoke the hydrozirconation of the NN bond α to phosphorus, the zirconium atom reacting at the less hindered nitrogen[13] (N_β), giving **13**. The lone pair of the amine nitrogen (N_α) can then complete the coordination sphere of the

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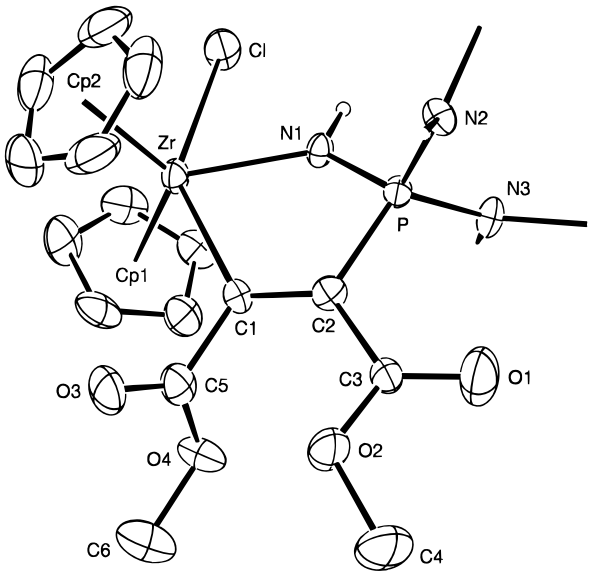

Figure 4. ORTEP drawing of **12** showing the numbering used. The methyl groups of the isopropyl moieties are not shown for clarity.

Table 7. Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **12**

P−N1	1.603(3)	N2−P−N3	106.3(1)
N1−Zr	2.205(3)	C2−P−N2	109.4(2)
Zr−C1	2.446(4)	C2−P−N3	117.1(2)
C1−C2	1.346(5)	P−C2−C3	117.4(3)
C2−P	1.804(4)	C1−C2−C3	126.4(4)
P−N2	1.655(3)	C2−C1−C5	117.2(4)
P−N3	1.656(3)	C5−C1−Zr	120.4(3)
C2−C3	1.489(6)	Cl−Zr−C1	142.01(8)
C3−O1	1.191(5)	Cl−Zr−Cp1	97.6(2)
C1−C5	1.495(6)	Cl−Zr−Cp2	99.6(2)
C5−O3	1.208(5)	Cl−Zr−N1	72.22(8)
Zr−Cl	2.647(1)	Cp1−Zr−Cp2	125.8(2)
Zr−Cp1[a]	2.254(5)	C1−Zr−Cp1	98.3(2)
Zr−Cp2[a]	2.250(5)	C1−Zr−Cp2	98.6(2)
N1−P−C2	99.2(2)	N1−Zr−Cp1	121.1(1)
P−C2−C1	115.8(3)	N1−Zr−Cp2	113.1(2)
C2−C1−Zr	122.4(3)	Zr−C1−C2−P	−3.3(4)
Cl−Zr−N1	70.0(1)	C1−C2−P−N1	−4.9(3)
Zr−N1−P	131.0(2)	C2−P−N1−Zr	13.8(2)
N1−P−N2	116.4(2)	P−N1−Zr−C1	−12.8(2)
N1−P−N3	108.9(1)	N1−Zr−C1−C2	7.8(3)

[a] Cp1 and Cp2 are the centroids of cyclopentadienyl rings C7C8C9C10C11 and C12C13C14C15C16, respectively.

metal, leading to the bicyclic derivative **14**. A ring expansion reaction[15] then occurs, giving the seven-membered ring **15** possessing an azo group, which eliminates dinitrogen, affording the observed product.

Conclusion

From these results as a whole, it appears that triazaphosphinine **1** acts with transition metals as an η^1 two-electron donor *via* the β-nitrogen atom, in contrast to (*E*)-phosphazides which behave as η^2 four-electron donors *via* the α- and γ-nitrogen atoms. Coordination of phosphazides to a metal center results in a stabilization in the case of (*E*)-phosphazides, and a destabilization with respect to dinitrogen extrusion in the case of 1,2,3,4λ^5-triazaphosphinine **1**. The results observed with Schwartz's reagent demonstrate that the chemistry of (*Z*)-phosphazides is not restricted to dinitrogen elimination, giving the corresponding phosphazenes. It can also be noted that, not surprisingly, in contrast to its organic analogues, especially the azetes,[16] 1,2λ^5-azaphosphete **2** acts as an η^1-ligand, giving stable complexes.

Experimental Section

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC80, AC200, WM250, and AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in parts per million relative to Me_4Si as an external standard, and ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

Bis(η^1-azaphosphete)palladium(II) Complex 4. A toluene solution (15 mL) of **1** (1.00 g, 2.41 mmol) was added dropwise, at −80 °C, to a toluene solution (8 mL) of bis(benzonitrile)palladium dichloride (0.47 g, 1.22 mmol). The solution was allowed to warm to room temperature, the mixture was filtered, and the solvent was removed *in vacuo*. **4** was obtained as yellow crystals from an ether solution (5 mL) at −20 °C (1.49 g, 65% yield): mp 170 °C dec; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.33 (d, J_{HH} = 6.9 Hz, 24 H, C*H*$_3$CHN), 1.54 (d, J_{HH} = 6.9 Hz, 24 H, C*H*$_3$CHN), 3.55 (s, 6 H, CH_3O), 3.81 (s, 6 H, CH_3O), 4.18 (sept d, J_{PH} = 15.6 Hz, J_{HH} = 6.9 Hz, 8 H, CH_3C*H*N); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 23.02 (d, J_{PC} = 3.8 Hz, *C*H$_3$CHN), 23.87 (d, J_{PC} = 1.7 Hz, *C*H$_3$CHN), 49.35 (d, J_{PC} = 5.3 Hz, CH_3*C*HN), 50.38 (s, CH_3O), 52.19 (s, CH_3O), 96.40 (d, J_{PC} = 95.2 Hz, PC), 158.42 (d, J_{PC} = 5.7 Hz, CO), 162.21 (d, J_{PC} = 52.6 Hz, CO), 180.48 (d, J_{PC} = 13.0 Hz, PC*C*); ^{31}P NMR ($CDCl_3$, 32.438 MHz) δ +52.74; IR (CH_2Cl_2) 1742, 1673 (CO) cm^{-1}. Anal. Calcd for $C_{36}H_{68}N_6O_8P_2PdCl_2$: C, 45.41; H, 7.20; N, 8.82. Found: C, 45.46; H, 7.24; N, 8.79.

(η^1-Azaphosphete)pentacarbonyltungsten Complex 6. A THF solution (15 mL) of **1** (1.00 g, 2.41 mmol) was added dropwise, at −80 °C, to a THF solution (8 mL) of $W(CO)_5$(THF) (0.99 g, 2.50 mmol). The solution was allowed to warm to room temperature, and the solvent was removed *in vacuo*. **6** was obtained as a very viscous oil from a toluene/ether solution (10/5 mL) at −20 °C (1.51 g, 88% yield): ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 22.90 (d, J_{PC} = 3.6 Hz, *C*H$_3$CHN), 23.72 (d, J_{PC} = 2.3 Hz, *C*H$_3$CHN), 49.49 (d, J_{PC} = 4.7 Hz, CH_3*C*HN), 50.83 (s, CH_3O), 52.78 (s, CH_3O), 95.76 (d, J_{PC} = 94.8 Hz, PC), 157.91 (d, J_{PC} = 5.3 Hz, CO), 162.93 (d, J_{PC} = 54.0 Hz, CO), 183.63 (d, J_{PC} = 19.1 Hz, PC*C*), 197.24 (d, J_{PC} = 1.9 Hz, J_{WC} = 130.5 Hz, CO_e), 199.88 (d, J_{PC} = 1.5 Hz, CO_a); ^{31}P NMR ($CDCl_3$, 32.438 MHz) δ +52.55. Anal. Calcd for $C_{23}H_{34}N_3O_9PW$: C, 38.83; H, 4.82; N, 5.91. Found: C, 38.89; H, 4.86; N, 5.97.

***cis*-(η^1-1,2,3,4λ^5-Triazaphosphinine)(piperidine)-tetracarbonylmolybdenum Complex 7.** A CH_2Cl_2 solution (10 mL) of **1** (1.00 g, 2.41 mmol) was added dropwise, at room temperature, to a CH_2Cl_2 solution (10 mL) of *cis*-bis(piperidine)tetracarbonylmolybdenum (0.91 g, 2.41 mmol). After 30 min, the mixture was filtered and the solvent was removed *in vacuo*. The residue was washed three times with ether (3 × 2 mL) and three times with pentane (3 × 5 mL). **7** was obtained as violet crystals from a THF solution at −20 °C (1.20 g, 70% yield): mp 115 °C dec; ^{1}H NMR (C_6D_6, 200 MHz) δ 0.86 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 1.15−1.20 (m, 6 H, $NCH_2CH_2CH_2$), 1.25 (d, J_{HH} = 6.8 Hz, 12 H, C*H*$_3$CHN), 2.79 (m, 4 H, NCH_2), 3.29 (s, 3 H, CH_3O), 3.53 (m, 4 H, CH_3C*H*N), 3.55 (s, 3 H, CH_3O), 4.05 (br t, J_{HH} = 12.0 Hz, NH); ^{13}C NMR (C_6D_6, 50.323 MHz) δ 22.52 (s, *C*H$_3$CHN), 23.10 (s, $NCH_2CH_2CH_2$), 23.15 (s, *C*H$_3$CHN), 28.22 (s, NCH_2CH_2), 47.81 (d, J_{PC} = 4.6 Hz, CH_3*C*HN), 50.97 (s, CH_3O), 52.13 (s, CH_3O), 55.45 (s, NCH_2), 83.49 (d, J_{PC} = 115.5 Hz, PC), 151.57 (d, J_{PC} = 3.6 Hz, PC*C*), 165.08 (d, J_{PC} = 13.1 Hz, CO), 165.80 (d, J_{PC} = 4.3 Hz, CO), 208.34 (s, MoCO), 220.1 (s, MoCO); ^{31}P NMR (C_6D_6, 32.438 MHz) δ +6.49; IR (CH_2Cl_2) 2009, 1900, 1890, 1830 (MoCO), 1746, 1712 [CO(OCH_3)] cm^{-1}. Anal. Calcd for $C_{27}H_{45}N_6O_8PMo$: C, 45.76; H, 6.40; N, 11.86. Found: C, 45.81; H, 6.44; N, 11.88.

(η^1-Five-membered cyclophosphazene)pentacarbonylmolybdenum Complex 9. A benzene solution (10 mL) of **7** (0.50 g, 0.70 mmol)

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(16) Ledermann, M.; Regitz, M.; Angermund, K.; Binger, P.; Krüger, C.; Mynott, R.; Gleiter, R.; Hyla-Kryspin, I. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1559.

Table 8. Crystallographic Data[a] for Complexes **4**, **7**, **10**, and **12**

	4	**7**	**10**	**12**
chem formula	$C_{36}H_{68}Cl_2N_6O_8P_2Pd$	$C_{27}H_{45}N_6O_8PMo$	$C_{32}H_{52}N_5O_8PW$	$C_{28}H_{45}ClN_3O_4PZr$
fw	952.22	708.6	849.6	645.33
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a, Å	10.087(1)	24.156(2)	15.747(2)	17.427(2)
b, Å	17.256(2)	17.592(2)	15.214(2)	19.899(2)
c, Å	13.839(2)	17.569(2)	16.999(2)	9.264(1)
β, deg	99.59(1)	110.30(2)	103.74(1)	105.09(1)
V, Å^3	2375.2(4)	7002(1)	3956(1)	3101.8(7)
F(000)	1000	2960	1728	1352
Z	2	8	4	4
D_{calc}, g cm^{-3}	1.331	1.344	1.426	1.382
μ (Mo Kα), mm^{-1}	0.59	0.46	2.89	0.49
$T_{min}-T_{max}$[b]	0.964−1.000	0.880−0.999	0.455−0.853	0.976−0.999
2θ range, deg	3−50	3−48	3−50	3−48
no. of data collected	4169	5669	7200	5181
no. of unique data	4169	5476	6940	4849
R_{av} (on I)		0.014	0.023	0.025
no. of observed data[c]	2780	4049	4119	2826
no. of params varied	250	388	424	343
S	1.100	1.149	1.132	1.011
w	unit	unit	$[\sigma^2(F_o) + 0.0015F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.0001F_o^2]^{-1}$
$(\Delta/\sigma)_{max}$	0.020	0.010	0.024	0.010
R[d]	0.028	0.028	0.036	0.029
R_w[e]	0.030	0.029	0.046	0.028
$(\Delta/\rho)_{max}$, $(\Delta/\rho)_{min}$, eÅ^{-3}	0.38,-0.36	0.28, −0.27	0.80, −0.50	0.28, −0.21

[a] All data collected at $T = 293$ K on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å) using ω-2θ scans. [b] From empirical absorption corrections for **4**, **7**, and **12**: North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A21*, 351. From Gaussian absorption corrections for **10**: Coppens, P.; Leiserowitz, L.; Rabinovitch, D. *Acta Crystallogr.* **1965**, *18*, 1035. [c] $F_o^2 > 3\sigma(F_o^2)$ for **4** and **10**. $F_o^2 > 2\sigma(F_o^2)$ for **7** and **12**. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_w = [\sum(w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

was allowed to stand for 2 days at room temperature. The solvent was removed *in vacuo*, and the residue was washed three times with ether (3 × 2 mL). **9** was obtained as a viscous pale yellow oil (0.21 g, 45% yield); ^{1}H NMR (C_6D_6, 200 MHz) δ 1.10 (d, $J_{HH} = 6.8$ Hz, 12 H, CH_3CHN), 1.23 (d, $J_{HH} = 6.8$ Hz, 24 H, CH_3CHN), 1.41 (br m, 2 H, NCH$_2$CH$_2$CH_2), 1.62 (br m, 4 H, NCH$_2$CH_2), 3.61 (s, 3 H, CH$_3$O), 3.62−3.81 (br m, 8 H, CH$_3$CHN and NCH$_2$); ^{13}C NMR (C_6D_6, 50.323 MHz) δ 22.86 (s, *C*H$_3$CHN), 22.97 (s, *C*H$_3$CHN), 23.58 (s, NCH$_2$-CH$_2$*C*H$_2$), 26.78 (s, NCH$_2$*C*H$_2$), 47.21 (d, $J_{PC} = 5.4$ Hz, CH$_3$*C*HN), 50.42 (s, CH$_3$O), 53.20 (s, N*C*H$_2$), 90.54 (d, $J_{PC} = 120.1$ Hz, PC), 163.27 (d, $J_{PC} = 35.4$ Hz, CO(OMe)), 163.47 (d, $J_{PC} = 7.8$ Hz, PC*C*), 169.45 (d, $J_{PC} = 14.8$ Hz, PCC*C*), 198.95 (s, MoCO), 200.73 (s, MoCO); ^{31}P NMR (C_6D_6, 32.438 MHz) δ +51.60; IR (CH_2Cl_2) 2013, 1983, 1858 (MoCO), 1678, 1654 [CO(OCH$_3$)] cm^{-1}. Anal. Calcd for $C_{27}H_{41}N_4O_8PMo$: C, 47.93; H, 6.10; N, 8.28. Found: C, 47.96; H, 6.12; N, 8.32.

(Five-membered cyclophosphazene)tungsten Complex 10. A CH_2Cl_2 solution (10 mL) of **1** (0.50 g, 1.20 mmol) was added dropwise, at room temperature, to a CH_2Cl_2 solution (10 mL) of (piperidine)-pentacarbonyltungsten (0.98 g, 2.40 mmol). After 3 h, ether (10 mL) was added and the mixture was filtered. **10** was obtained as yellow crystals from this solution at room temperature (0.82 g, 80% yield): mp 112 °C dec; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.14 (d, $J_{HH} = 6.8$ Hz, 12 H, CH_3CHN), 1.26 (d, $J_{HH} = 6.8$ Hz, 12 H, CH_3CHN), 1.46 (br m, 2H, NCH$_2$CH$_2$CH_2), 1.62 (br m, 10 H, NCH$_2$CH_2CH_2 and NCH$_2$CH_2), 2.82 (br m, 4H, NCH$_2$), 3.65 (s, 3 H, CH$_3$O), 3.67−3.82 (br m, $J_{HH} =$ 6.8 Hz, 8 H, CH$_3$CHN and NCH$_2$), the NH is not observed; ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 22.56 (s, NCH$_2$CH$_2$*C*H$_2$), 23.05 (d, $J_{PC} = 1.9$ Hz, *C*H$_3$CHN), 23.24 (d, $J_{PC} = 2.4$ Hz, *C*H$_3$CHN), 23.84 (s, NCH$_2$-CH$_2$*C*H$_2$), 27.01 (s, NCH$_2$*C*H$_2$), 28.55 (s, NCH$_2$*C*H$_2$), 47.33 (d, $J_{PC} =$ 5.7 Hz, CH$_3$*C*HN), 50.53 (s, CH$_3$O), 53.35 (s, NCH$_2$), 59.78 (s, NCH$_2$), 90.88 (d, $J_{PC} = 118.2$ Hz, PC), 163.82 (d, $J_{PC} = 7.8$ Hz, PC*C*), 164.07 (d, $J_{PC} = 42.9$ Hz, CO(OMe)), 169.95 (d, $J_{PC} = 14.7$ Hz, PCC*C*), 198.74 (s, $J_{WC} = 131.2$ Hz, CO$_e$), 201.80 (s, CO$_a$); ^{31}P NMR ($CDCl_3$, 32.438 MHz) δ +54.29; IR (CH_2Cl_2) 1971, 1926 (WCO), 1676, 1636 (CO) cm^{-1}. Anal. Calcd for $C_{32}H_{52}N_5O_8PW$: C, 45.25; H, 6.17; N, 8.24. Found: C, 45.22; H, 6.21; N, 8.26.

Five-Membered Cyclophosphazene 11. Neat piperidine (0.5 mL, 5.0 mmol) was added dropwise, at room temperature, to a THF solution (10 mL) of **2** (0.93 g, 2.40 mmol). After 2 h, the solvent and excess of piperidine were removed *in vacuo*. **11** was obtained as colorless crystals from an ether/pentane solution at room temperature (1.0 g, 95% yield): mp 129 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.08 (d, $J_{HH} = 6.8$ Hz, 12 H, CH_3CHN), 1.21 (d, $J_{HH} = 6.8$ Hz, 12 H, CH_3CHN), 1.55 (br m, 6 H, NCH$_2$CH_2CH_2), 3.61 (s, 3 H, CH$_3$O), 3.64−3.73 (br m, 8 H, CH$_3$CHN and NCH$_2$); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 22.69 (d, $J_{PC} = 2.0$ Hz, *C*H$_3$CHN), 22.85 (d, $J_{PC} = 1.7$ Hz, *C*H$_3$CHN), 23.47 (s, NCH$_2$CH$_2$*C*H$_2$), 26.61 (s, NCH$_2$*C*H$_2$), 46.83 (d, $J_{PC} = 5.4$ Hz, CH$_3$*C*HN), 50.17 (s, CH$_3$O), 52.93 (s, NCH$_2$), 90.57 (d, $J_{PC} = 118.5$ Hz, PC), 163.31 (d, $J_{PC} = 2.0$ Hz, PC*C*), 163.77 (d, $J_{PC} = 29.7$ Hz, *C*O(OMe)), 169.52 (d, $J_{PC} = 14.6$ Hz, PCC*C*); ^{31}P NMR ($CDCl_3$, 32.438 MHz) δ +54.08; IR (CH_2Cl_2) 1681, 1639 (CO) cm^{-1}. Anal. Calcd for $C_{22}H_{41}N_4O_3P$: C, 59.98; H, 9.38; N, 12.72. Found: C, 60.00; H, 9.41; N, 12.77.

Five-Membered Zirconacyclophosphazene 12. A THF solution (10 mL) of **1** (0.50 g, 1.20 mmol) was added dropwise, at room temperature, to a THF solution (10 mL) of dicyclopentadienylzirconium hydrochloride (0.31 g, 1.20 mmol). After 20 h, the solution was filtered on Fluorisil and the solvent was removed in *vacuo*. **12** was obtained as an air stable pale yellow solid from a THF solution (5 mL) at room temperature (0.35 g, 45% yield): mp 170 °C dec; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.19 (d, $J_{HH} = 6.7$ Hz, 24 H, CH_3CHN), 2.78 (d, $J_{PH} =$ 2.2 Hz, 1 H, PNH), 3.62 (s, 3 H, CH$_3$O), 3.64−3.70 (br m, 4 H, CH$_3$CHN), 3.74 (s, 3 H, CH$_3$O), 5.95 (s, 10 H, Cp); ^{13}C NMR ($CDCl_3$, 50.323 MHz) δ 22.97 (d, $J_{PC} = 3.5$ Hz, *C*H$_3$CHN), 47.81 (d, $J_{PC} = 5.8$ Hz, CH$_3$*C*HN), 50.69 (s, CH$_3$O), 51.65 (s, CH$_3$O), 111.22 (s, Cp), 125.79 (d, $J_{PC} = 164.8$ Hz, PC), 161.97 (d, $J_{PC} = 27.8$ Hz, CO), 176.82 (d, $J_{PC} = 39.1$ Hz, CO), 225.63 (d, $J_{PC} = 51.9$ Hz, PC*C*Zr); ^{31}P NMR ($CDCl_3$, 32.438 MHz) δ +56.38; IR (CH_2Cl_2) 3364 (NH), 1713 (CO) cm^{-1}. Anal. Calcd for $C_{28}H_{45}N_3O_4PZrCl$: C, 52.11; H, 7.03; N, 6.51. Found: C, 52.13; H, 7.08; N, 6.56.

Solution and Refinement of Structures 4, 7, 10, and 12. Atomic scattering factors (f', f'') were taken from a standard source.[17] The initial structural solutions were obtained by the Patterson analysis. Atoms not located from the initial structure solution were found by successive difference Fourier maps with intervening cycles of least-

(17) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

squares refinement (SHELX-76). Crystallographic data are provided in Table 8. All non-hydrogen atoms were treated anisotropically. Full-matrix least-squares refinements were used in all cases. All hydrogen atoms were located by difference Fourier maps, and their positions were idealized in the subsequent cycles of refinement. Final *R* values are provided in Table 8.

Acknowledgment. Thanks are due to the Deutsche Forschungsgemeinschaft and the Centre Culturel Hariri for grants to K. Bieger and G. Bouhadir, respectively, and to the CNRS for financial support of this work.

Supporting Information Available: Tables of crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles, torsion angles, and least-squares planes equations for **4**, **7**, **10**, and **12** (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded form the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9531440