DOI: 10.1002/zaac.201200542

On the Synthesis and Coordination Properties of *N*-Aryl-substituted 1,3,2-Diazaphospholidine-4,5-diimines

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Keywords: Phosphorus heterocycles; Nitrogen heterocycles; N-ligands; Coordination modes; Amidines

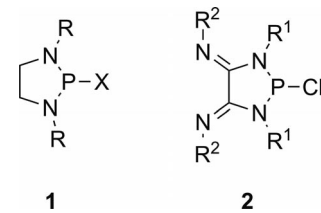
Abstract. New 1,3,2-diazaphospholidine-4,5-diimines were synthesized by condensation of lithiated oxalamidines with PCl_3 or $PhPCl_2$, and characterized by spectral and analytic data. The products react selectively with [(nbd)W(CO)$_4$], [Mo(CO)$_6$], or [(PhCN)$_2$PdCl$_2$] to give stable complexes, in which the heterocycle binds as chelating, bidentate ligand through the nitrogen atoms of the diimine unit. Formation of *P*-bound or dinuclear complexes was not observed. Reaction with PCl_3 or $AsCl_3$ in the presence of $SnCl_2$ as reducing agent was unspecific. Evidence for the formation of bicyclic products arising from formal [4+1] cycloaddition between the diimine unit and a transient pnictogen(I) species was not obtained, and only a diimine complex of $SnCl_4$ was isolated in moderate yield. Single-crystal X-ray diffraction studies reveal that coordination of the diimine unit induces a substantial structural distortion of the ligand framework, which allows to explain the occurrence of substantial ^{31}P coordination shifts despite the absence of a direct metal-phosphorus bond.

Introduction

1,3,2-Diazaphospholidines (**1**) are N-heterocyclic phosphanes that make not only viable precursors for reactive phosphenium ions (in case of *X* = halide),[1] but attract currently growing attention as ligands for catalytically active transition metal complexes. *P*-Chloro- and *P*-phenyl-substituted diazaphospholidines have thus been applied in Suzuki-Miyaura[2] or Mizoroki-Heck cross-coupling reactions.[3] Chiral diazaphospholidines are useful ligands in enantioselective addition or substitution reactions.[4] Bis-diazaphospholidines featuring two rings connected via a suitable spacer unit have excellent chelating properties[4,5] and chiral derivatives thereof were used in asymmetric hydroformylation[6] or allylic alkylation reactions.[7]

The diazaphospholidine ligands used to date lack any functional modification of their C_2N_2 backbone, and the phosphorus atom remains thus the only metal binding site in the ring. We have recently prepared a 1,3,2-diazaphospholidine-4,5-diimine (**2**),[8] which combines the P-donor function with two exocyclic imine functionalities that make up an oxalamidine unit.[9] Oxalamidines are, like diimines in general,[10] well known to form stable chelate complexes with various transition metals.[11] Consequently, **2** can be regarded as potential ditopic ligand, whose rigid molecular skeleton orientates both donor sites into opposite directions in space. Specimens of this type have been denoted as Janus-head ligands[12] and are attracting interest due to their ability to accommodate two different metal atoms in close spatial proximity.[13]

Herein we report on the synthesis of further derivatives of **2** featuring both P–Cl and P–Ph substituents, and on first studies of the coordination properties of these species. Furthermore, we have also explored the feasibility of a [1+4] cycloaddition between the 1,2-diimine unit and a transient P(I) species[14] for the construction of a fused heterocyclic ring system (Scheme 1).



1 **2**

Scheme 1. *R* = Alkyl, Aryl; *X* = Cl, F, NMe_2, Ph, OPh; R^1 = 2,6-$iPr_2C_6H_3$ (Dipp), R^2 = 2,6-$Me_2C_6H_3$ (Dmp).

Results and Discussion

The 1,3,2-diazaphospholidine-4,5-diimines (**5**, **6**) were prepared using the same procedure that had previously been reported for **2**.[8] Oxalamidine precursors **3** and **4** were synthesized as described by Beckert et al..[15] In order to avoid problems arising from the formation of mixtures of constitutional isomers, we choose specimen with identical substituents on all

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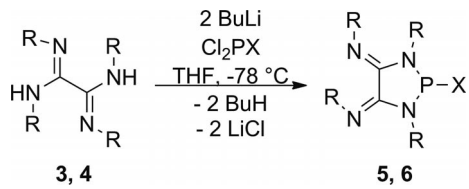
nitrogen atoms. Conversion into the target heterocycles **5** and **6** was accomplished by metalation with two equivalents of butyllithium at –78 °C, followed by slow addition of the appropriate dichlorophosphane (Scheme 2). The products were isolated as moisture and air sensitive, pale yellow powders, and characterized by analytical and spectroscopic data. The *P*-chloro derivative **6** displays sharp signals in the ^{1}H NMR spectrum, whereas the signals of the *P*-phenyl derivative **5** are significantly broadened, presumably as a consequence of hindered rotation of the *N*-aryl moieties.[8] The ^{31}P chemical shifts of **5** (δ^{31}P = 90.1) and **6** (δ^{31}P = 134.6, cf. δ^{31}P = 134 for **2**[8]) are smaller than those of other known 1,3-diarylated 2-phenyl- (δ^{31}P around 110[16]) or 2-chloro-1,3,2-diazaphospholidines (δ^{31}P = 137–155[17]), respectively; this common trend suggests that the shielding is presumably a characteristic signature of the imine substitution.



Scheme 2. Synthesis of 1,3,2-diazaphospholidin-4,5-diimines **5**, **6** (**3**, **5**: *R* = Dmp, *X* = Ph; **4**, **6**: *R* = Mes, *X* = Cl).

Single crystals of **5** were obtained from toluene at –20 °C and characterized by a single-crystal X-ray diffraction study (Figure 1). The crystal contains isolated molecules whose most obvious attribute is the different configuration of the two imine double bonds. This structural motif had already been noted for **2**,[8] and serves presumably to minimize steric strain between the bulky N-aryl moieties. The coordination around the endocyclic nitrogen atoms has to be described as essentially planar [sum of bond angles 354.0(2)° for N2 and 359.1(2)° for N5]. The phosphorus atom exhibits the same pyramidal coordination [sum of bond angles 296.7(2)°] as in other diazaphospholidines.[8,17] The C3–C4 distance [1.510(2) Å] represents a typical single bond value. The P1–N2 and P1–N5 distances [1.727(1)–1.737(1) Å] are slightly longer than in **2**, whereas the difference in the formal carbon–nitrogen single [C4–N5/C3–N2 1.383(2)–1.404(2) Å] and double bond lengths [C3–N3/C4–N4 1.268(2) Å] is somewhat less pronounced. These features suggest that π conjugation in the amidine units has increased at the expense of the n(N)–σ*(P*X*) hyperconjugative interaction in the NPN unit.

In order to explore the coordination properties of compounds **5** and **6** we chose to study reactions with low valent metal carbonyls {[(nbd)W(CO)$_4$], [Mo(CO)$_6$]; nbd = norbornadiene} and [(PhCN)$_2$PdCl$_2$], whose central metal atoms [Mo(0), W(0), Pd^{II}] are known to form stable complexes with both phosphane and diimine donors. Complex **7** (Scheme 3) was obtained after refluxing **5** with [(nbd)W(CO)$_4$] in toluene for 2 h. The product was isolated after work-up as red, crystalline solid and characterized by analytical and spectroscopic data. Prominent spectral features include the observation of (i) a ^{31}P NMR signal with a coordination shifts $\Delta\delta^{31}$P(coord) = δ^{31}P(complex) – δ^{31}P(ligand) of approx.

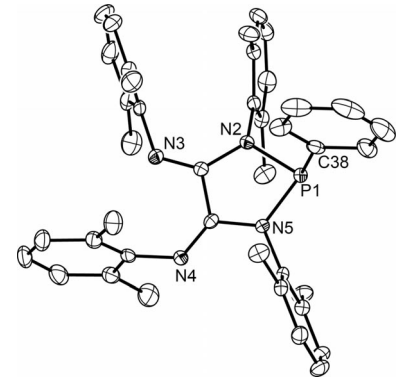
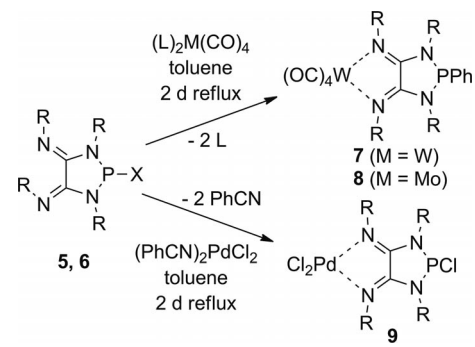


Figure 1. Molecular structure of **5**. Thermal ellipsoids are drawn at 50 % probability level, hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: P1–C38 1.824(2), P1–N5 1.727(1), P1–N2 1.737(1), C3–C4 1.510(2), C3–N2 1.404(2), C4–N5 1.383(2), C3–N3 1.268(2), C4–N4 1.268(2), N2–P1–C38 104.34(7), N5–P1–C38 102.67(8), N2–P1–N5 89.66(7).

+30 ppm but no sign of coupling to a magnetically active ^{183}W nucleus, (ii) two equally intense ^{13}C NMR signals attributable to the carbon atoms of carbonyl ligands at δ^{13}C = 213, 191, (iii) a shift of the ν(C=N) band in the IR spectrum from 1651 cm^{-1} to 1565 cm^{-1} in **5**, and (iv) a characteristic pattern of ν(CO) vibrational modes between 1830–1985 cm^{-1}[18] indicative of a *cis*-W(CO)$_4$ unit. These findings led to the hypothesis that the metal atom binds via the diimine unit rather than the phosphorus lone-pair, which was corroborated by the independent synthesis of **7** via base-induced condensation of a preformed amidine complex [(**3**)W(CO)$_4$] with PhPCl$_2$. Formation of an analogous molybdenum complex **8** was also observed in the reaction of **5** with [Mo(CO)$_6$] but required longer reaction times.



Scheme 3. Synthesis of 1,3,2-diazaphospholidine-4,5-diimine complexes **7**–**9** (**5**, **7**, **8**: *R* = Dmp, *X* = Ph; **6**, **9**: *R* = Mes, *X* = Cl; (L)$_2$*M*(CO)$_4$ = (norbornadiene)W(CO)$_4$, Mo(CO)$_6$).

The molecular structures of complexes **7** and **8** were confirmed by single-crystal X-ray diffraction studies on samples obtained by crystallization from toluene at –20 °C. The molecular structure of **7** is displayed in Figure 2; the structure of **8** is essentially identical and is not shown. The octahedral coordination environment at the metal atom is distinguished by a strong deflection of the two mutually *trans*-positioned carbonyls from an ideal linear arrangement [C1C–W–C1D 164.9(2)° for **7**, 164.6(2)° for **8**]. This distortion exceeds that

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in other [(diimine)M(CO)$_4$] complexes, where C–M–C angles range between 170 and 172°,[11,19] and is presumably attributable to repulsive interactions between the carbonyls and the *N*-aryl groups. The M–N distances and the flat envelope conformation of the chelate ring are similar as in other known diimine complexes (M–N 2.21–2.28 Å[11,19]). The metal coordination induces lengthening of P–N distances [1.748(4)–1.757(3) Å] and further levelling of formal carbon–nitrogen single [1.375(6)–1.386(7) Å] and double bonds [1.282(7)–1.302(8) Å] as compared to **5** [P–N 1.727(1)–1.737(1) Å; C–N 1.383(2)–1.404(2) Å, C=N 1.268(2) Å]. In combination with the pronounced red shift of the ν(C=N) mode in the IR spectrum, these features suggest that the metal coordination further enhances the π electron conjugation in the amidine moieties, but diminishes the hyperconjugation in the NPN unit of the ligand. As these changes must be considered to exert a perceptible change in the local electron distribution around the phosphorus atom, it is easily understood how even the remote binding of a metal atom can induce a substantial ^{31}P coordination shift.

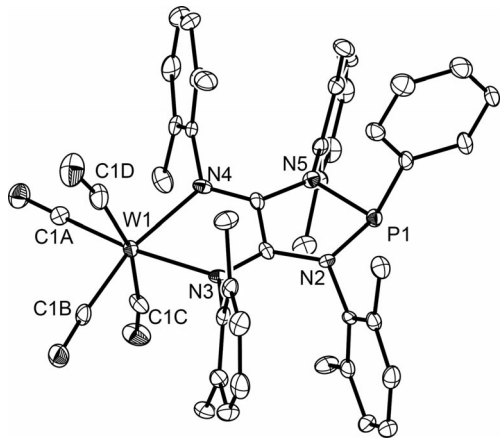


Figure 2. Molecular structure of **7** (M =W). Thermal ellipsoids are drawn at 50 % probability level, hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /° (values in brackets denote appropriate data for **8**, M = Mo): P1–C6 1.824(4) [1.832(6)], P1–N5 1.756(5) [1.750(5)], P1–N2 1.748(4) [1.757(5)], C3–N2 1.384(7) [1.378(8)], C4–N5 1.375(6) [1.386(7)], C3–C4 1.484(8) [1.480(8)], C3–N3 1.302(6) [1.292(7)], C4–N4 1.282(7) [1.297(7)], N4–M1 2.254(4) [2.297(5)], N3–M1 2.247(4) [2.282(5)], M1-C1A 1.973(6) [1.957(7)], M1-C1B 1.964(6) [1.970(7)], M1-C1C 2.042(5) [2.038(6)], M1-C1D 2.026(6) [2.032(7)], N5–P1–C6 100.9(2) [101.2(2)], N2–P1–C6 105.0(2) [105.2(2)], N5–P1–N2 90.1(2) [90.0(2)].

Knowing that 2-chloro-1,3,2-diazaphospholidines can bind central Pd^{II} atoms via the free electron pair at phosphorus,[2] we also examined the appropriate reaction of the *P*-chloro derivative **6**. Reaction with [(PhCN)$_2$PdCl$_2$] in refluxing toluene and evaporation of the solvent gave an orange, moisture and air sensitive solid, which was characterized by analytical and spectroscopic data. Observation of a ^{31}P NMR signal with a similar positive coordination shift [$\Delta\delta^{31}$P(coord) = 26] as **7** and **8** suggested that the product might likewise be described as a diimine complex **9** (Scheme 3). This hypothesis was finally confirmed by a single-crystal X-ray diffraction study (Figure 3).

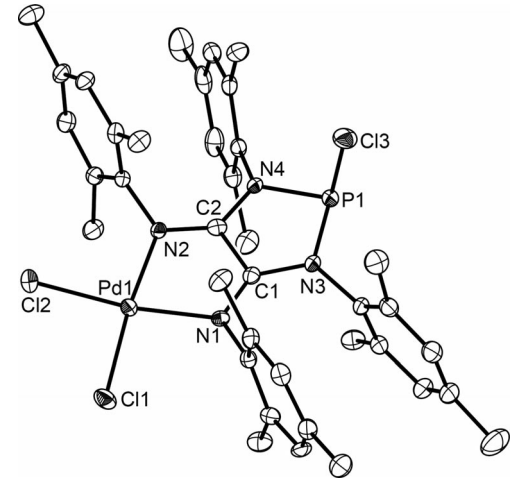


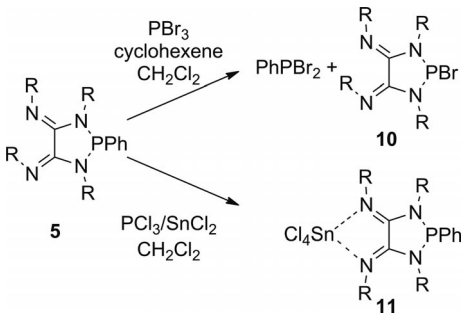
Figure 3. Molecular structure of **9**. Thermal ellipsoids are drawn at 50 % probability level, hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: P1–Cl3 2.075(1), P1–N4 1.721(1), P1–N3 1.718(1), C1–N3 1.376(1), C2–N4 1.378(1), C1–C2 1.498(1), C1–N1 1.289(1), C2–N2 1.282(1), N2–Pd1 2.046(1), N1–Pd1 2.052(1), Pd1–Cl2 2.278(1), Pd1–Cl1 2.280(1), N4–P1–Cl3 101.55(2), N3–P1–Cl3 101.01(2), N4–P1–N3 91.40(2), N2–Pd1–N1 80.96(2), Cl1–Pd1–N1 93.92(2), Cl2–Pd1–N2 93.43(1), Cl2–Pd1–Cl1 92.08(2).

As expected, the palladium atom is coordinated by two chlorides and the nitrogen atoms of the diimine unit, and exhibits the typical square-planar coordination expected for a central Pd^{II}(d^8) atom. The structural features of the diimine-palladium moiety match those of related diimine complexes like [bis(2,6-diisopropyl-phenyl)-1,4-diazabutadiene]-PdCl$_2$[20] or 2,6-*i*Pr-BIAN-PdCl$_2$ (BIAN = bis-iminoacenaphthen).[21] The structural features of the ligand are closely similar to those of compounds **7** and **8**. As there, the coordination environment at the endocyclic nitrogen and phosphorus atoms can be described as planar [sum of bond angles 356.5(1)° at N4 and 358.3(6)° at N3] and pyramidal [sum of bond angles 294.0(6)° at P1], respectively. A further shortening of the P–Cl bond [P1–Cl3 2.075(1) Å] with respect to **2** [P–Cl 2.127(2) Å[8]] is offset by a lengthening of the adjacent P–N bonds [P1–N4 1.721(1) Å, P1–N3 1.718(1) Å vs. 1.700(4) Å and 1.708(5) Å in **2**[8]] and a similar bond length equalization in the amidine as for **7** and **8**.

^{31}P NMR spectroscopic monitoring revealed that all studied reactions of **5** and **6** with metal complexes proceeded quite selectively and (apart from minor and varying amounts of hydrolysis products) quantitatively; in particular, we were unable to observe any signals attributable to complexes with P-coordinated ligands or, when an excess of metal complex was employed, dinuclear complexes with μ-bridging coordination of diazaphospholidine-diimines.

The high affinity of Lewis-acidic metal fragments towards the diimine moiety prompted us to investigate also the prospect of using **5** to trap transient phosphorus(I) electrophiles in a [4+1] cycloaddition. This approach allowed to convert open diimines in a single step into appropriate phosphorus heterocycles[14,22] and may in the presented case give direct access to elusive bicyclic heteropentalenes. In contrast to our expecta-

tions, **5** did not react with PI_3, and reaction with excess PBr_3 in the presence of cyclohexene proceeded via metathesis to give a mixture of unreacted PBr_3 ($\delta^{31}P$ = 227), $PhPBr_2$ ($\delta^{31}P$ = 150[23]), and a product, which we assign as *P*-bromo-1,3, 2-diazaphospholidine-4,5-diimine (**10**) ($\delta^{31}P$ = 145, Scheme 4). Even if this species could not be isolated, the assignment is backed by the independent synthesis of the same product by reaction of **3** with BuLi and PBr_3.



Scheme 4. (*R* = Dmp).

Reaction of **5** with PCl_3 in the presence of $SnCl_2$ as reducing agent[14,24] produced a red solution. A ^{31}P NMR survey showed a signal attributable to $PhPCl_2$ ($\delta^{31}P$ = 161) along with further signals around 130–135 and 99–106 ppm, respectively. Work-up produced a moderate yield (37 %) of an orange, crystalline product, which was identified by means of a single-crystal X-ray diffraction study as the tin(IV) complex **11** (Scheme 4). Complex **11** was also obtained as the only isolable product from the analogous reaction of **5** with $AsCl_3$ and $SnCl_2$ (Figure 4).

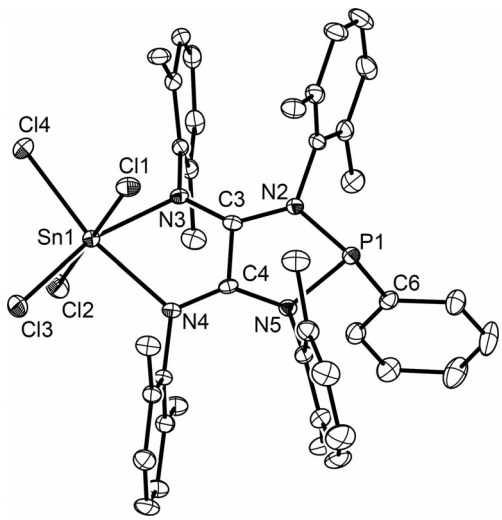


Figure 4. Molecular structure of **11**. Thermal ellipsoids are drawn at 50 % probability level, hydrogen atoms are omitted for clarity. Selected bond lengths /Å and angles /°: P1–C6 1.798(3), P1–N2 1.754(1), P1–N5 1.752(1), C4–N5 1.350(1), C3–N2 1.350(1), C4–C3 1.516(1), C3–N3 1.294(1), C4–N4 1.291(1), Sn1–N4 2.540(2), Sn1–N3 2.564(2), Sn-Cl1 2.421(3), Sn1–Cl2 2.385(2), Sn1–Cl3 2.382(2), Sn1–Cl4 2.375(2), N2–P1–C6 103.48(4), N5–P1–C6 101.84(5), N2–P1–N5 89.03(4), N4–Sn1–N3 74.43(2).

The molecular structure of **11** bears some similarity with those of other structurally characterized Sn^{IV}-diimine complexes.[25] The values of Sn–Cl distances [2.376(1)–2.422(1) Å] and N–Sn–N angles [74.43(6)°] match the analogous features of [(dipp-BIAN)$SnCl_4$] (**12**) (Sn–Cl 2.353–2.406 Å, N–Sn–N 74.3°[25]) or [(bipy)$SnCl_4$] (Sn–Cl 2.359–2.409 Å[26]). On the contrary, the Sn–N distances of some 2.54–2.56 Å are substantially larger than those of typical N→Sn^{IV} donor-acceptor bonds (2.18–2.30 Å in **12** or related octahedral tin tetrahalide complexes[25,26]). We consider this finding quite remarkable given that a similar difference between the $M(CO)_4$ complexes **7** and **8** and [(dipp-BIAN)$M(CO)_4$] is absent, and attribute this deviation tentatively to the different properties of the central metal atoms in both types of complexes: the zerovalent metal atoms in **7**, **8** may engage in both N→M σ dative and M→N π retrodative interactions, whereas the central Sn^{IV} atom in **11** is essentially a Lewis acceptor, and the N→M σ-bonding contribution dominates. Under these circumstances, the electron withdrawing effect of the endocyclic nitrogen atoms next to the diimine unit can be considered to make an oxalamidine like **5** a weaker donor than alkyl- or aryl-substituted diimines. Inspection of the metric parameters in the ligand of **11** reveals further that the equalization of the single and double bonds in the amidine units and the lengthening of P–N bonds are even more pronounced than in **7**–**9**. As a compensation, the P1–C6 bond 1.798(2) Å] is shorter than a normal single bond of 1.836 ± 0.010 Å.[27]

The outcome of the spectroscopic studies reveals that the reaction between **5** and $PCl_3/SnCl_2$ is rather unspecific and follows (in view of the detection of both $PhPCl_2$ and **11** among the products) in part a metathesis and in part a redox pathway. Even if it must be assumed that some PCl_3 is thus reduced, the imine moiety of **5** does not trap the suspected low valent phosphorus fragment but rather the $SnCl_4$ formed as oxidation product. The reason for this deviation from the reported reactivity of other diimines[14,22] is not totally clear. However, we assume that the need to isomerize one of the C=N bonds in **5** prior to formation of a chelate adduct and a lower σ-donor strength of the imino-nitrogen atoms are obstacles that do not completely prevent the formation of chelate complexes with strong and persistent Lewis acids, but may severely interfere with the stabilization and capture of a fragile and transient phosphorus(I) species.

Conclusions

1,3,2-Diazaphospholidine-4,5-diimines were prepared by condensation of lithiated oxalamidines with PCl_3 or phenyl dichlorophosphane, respectively. The heterocycles form stable metal complexes by acting as chelating bidentate *N*-donor ligands through their diimine unit, but showed no activity as P-donors. Complex formation induces a structural distortion of the ligand framework, which indicates that π delocalization in the amidine units is enhanced at the expense of hyperconjugative interactions in the NPN moiety. These effects allow explaining the large ^{31}P coordination shifts upon metal binding at the remote nitrogen atoms, and may also be assumed to

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reduce the nucleophilic character of the phosphorus atom, which offers a viable explanation for the one-sided coordination behavior. Reaction of a diazaphospholidine-4,5-diimine with $AsCl_3$ or PCl_3 in the presence of $SnCl_2$ did not proceed via formal [1+4] cycloaddition of the diimine unit with a transient pnictogen(I) species to give a heteropentalene, but rather via formation of a low yield of a diimine-$SnCl_4$ complex. It remains to be established if this deviation from a common reaction pattern for diimines is due to the unfavorable steric or electronic predisposition of the starting material or the destabilization of the expected bicyclic product by increased ring strain.

Experimental Section

All manipulations were carried out in an atmosphere of dry argon using standard vacuum line techniques. Solvents were dried by standard procedures. Oxalamidines **3** and **4** were prepared as described in reference[15]. All other chemicals were commercially available and used as received. NMR spectra were recorded with a Bruker Avance 250 (^{1}H, 250.1 MHz; ^{13}C, 62.8 MHz; ^{31}P, 101.2 MHz) spectrometer at 303 K; chemical shifts are referenced to external $SiMe_4$ (^{1}H, ^{13}C) or 85 % H_3PO_4 (^{31}P). Coupling constants are given in absolute values. Elemental analyses were determined with a Perkin-Elmer 2400 CHN/O Analyzer; large deviations between found and calculated values are presumably due to incomplete combustion and formation of metal carbide (**8**) or hydrolysis during sample preparation (**9**). Melting points were determined in sealed capillaries with a Büchi Melting Point B-545 apparatus. IR spectra were recorded with a Nicolet 6700 FTIR spectrometer equipped with a Smart orbit unit with a diamond crystal and a MCTA-detector.

General Procedure for the Preparation of Compounds 5 and 6: Oxalamidine **3** (502 mg, 1.0 mmol) or **4** (558 mg, 1.0 mmol) were dissolved in THF (10 mL) and the solution cooled to –78 °C. Butyllithium (1.5 mL of a 1.6 M solution, 2.4 mmol) were subsequently added. The solution was stirred for 30 min. $PhPCl_2$ (215 mg, 1.2 mmol) or PCl_3 (165 mg, 1.2 mmol) was added, and the mixture was stirred for further 12 h. Solvents were removed in vacuo, the residue taken up in toluene or Et_2O (10 mL), and filtered through Celite. The products were obtained after removal of the solvent under reduced pressure as air and moisture sensitive, pale yellow powders that could be purified by recrystallization.

2-Phenyl-tetrakis-(2,6-dimethylphenyl)-1,3,2-diazaphospholidine-4,5-diimine (5): Yield 505 mg (83 %); m.p. 134.5 °C. $C_{40}H_{41}N_4P$ (608.75): calcd. C 78.92, H 6.88, N 9.20 %; found: C 78.73, H 6.82, N 9.19 %. **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ = 90.1 (s). **^{1}H NMR** ($CDCl_3$, 300 K): δ = 1.66 (broad s, 6 H, CH_3), 1.84 (broad s, 6 H, CH_3), 2.26 (s, 6 H, CH_3), 2.66 (s, 6 H, CH_3), 6.38–7.07 (m, 12 H, CH), 7.37–7.58 (m, 3 H, *m*/*p*-C_6H_5), 7.78–7.92 (m, 2 H,, *o*-C_6H_5) ppm. (+)-**EI-MS** (70 eV): *m*/*z* (%) = 608.3 (65) [M^+], 593.3 (100) [M^+-CH_3], 531.3(7) [M^+-Ph]. **IR** (KBr): $\tilde{\nu}$ = 1651 (s, br) (C=N) cm^{-1}.

2-Chloro-tetramesityl-1,3,2-diazaphospholidine-4,5-diimine (6): Yield 390 mg (63 %); m.p. 178 °C. $C_{38}H_{44}ClN_4P{\cdot}CH_3CN$ (664.23): calcd. C 72.33, H 7.13, N 10.54 %; found C 71.90, H 6.99, N 9.63 %. **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ = 134.6 (s). **^{1}H NMR** ($CDCl_3$, 300 K): δ = 1.73 (s, 6 H, *p*-CH_3), 2.04 (s, 6 H, *o*-CH_3), 2.09 (s, 6 H, *p*-CH_3), 2.20 (s, 6 H, *p*-CH_3), 2.34 (s, 6 H, *o*-CH_3), 2.41 (s, 6 H, *o*-CH_3), 6.23 (s, 2 H, CH), 6.54 (s, 2 H, CH), 6.70 (s, 2 H, CH), 6.85 (s, 2 H, CH) ppm (+)-**EI-MS** (70 eV): *m*/*z* (%) = 622.3 (40) [M^+], 607.3 (100) [M^+-CH_3]. **IR** (KBr): $\tilde{\nu}$ = 1666 (s, br) (C=N) cm^{-1}.

General Procedure for the Preparation of Compounds 7 and 8: Ligand **5** (3.05 g, 5 mmol) was dissolved in toluene (20 mL) and [(nbd)$W(CO)_4$] (2.7 g, 7 mmol) or [$Mo(CO)_6$] (1.85 g, 7 mmol) were added in one portion. The reaction mixture was refluxed for 2 d and turned eventually dark red to violet. The solution was cooled to room temperature and filtered through Celite. The filtrate was evaporated to dryness and the residue recrystallized from toluene at –20 °C.

2-Phenyl-tetra-(2,6-dimethylphenyl)-1,3,2-diazaphospholidine-4,5-diimine-tetracarbonyltungsten (7): Yield: 2.56 g, (57 %); m.p. 175 °C. $C_{44}H_{41}N_4O_4PW$ (904.63): calcd. C 58.42, H 4.57, N 6.19 %, found C 57.97, H 4.22, N 5.88 %. **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ = 120.9 (s). **^{1}H NMR** ($CDCl_3$, 300 K): δ = 1.92 (s, 6 H, CH_3), 2.24 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 2.68 (s, 6 H, CH_3), 6.38 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, CH), 6.48 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, CH), 6.65 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, CH), 6.79–6.91 (m, 4 H, CH), 6.99 (d, 2 H, $^3J_{HH}$ = 7.10 Hz, CH), 7.48 (m, 2 H, *m*-Ph), 7.61 (m, 1 H, *p*-Ph), 7.84 (m, 2 H, *o*-Ph) ppm. **IR** (KBr): $\tilde{\nu}$ = 1985 (s), 1909 (m), 1867 (m), 1830 (s) (CO), 1565 (m) (C=N) cm^{-1}.

2-Phenyl-tetra-(2,6-dimethylphenyl)-1,3,2-diazaphospholidine-4,5-diimine-tetracarbonylmolybdenum (8): Yield 2.20 g (54 %), m.p. 183 °C. $C_{44}H_{41}MoN_4O_4P$ (816.73): calcd. C 64.71, H 5.06, N 6.86 %, found C 64.12, H 4.97, N 6.83 %. **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ = 118.2 (s). **^{1}H NMR** ($CDCl_3$, 300 K): δ = 1.28 (s, 6 H, CH_3), 2.23 (s, 6 H, CH_3), 2.66 (s, 6 H, CH_3), 2.69 (s, 6 H, CH_3), 6.37 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, CH), 6.46 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, CH), 6.63 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, CH), 6.77–6.89 (m, 4 H, CH), 6.98 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, CH), 7.46 (m, 2 H, *m*-Ph), 7.60 (m, 1 H, *p*-Ph), 7.84 (m, 2 H, *o*-Ph) ppm.

2-Chloro-tetramesityl-1,3,2-diazaphospholidine-4,5-diimine-palladium(II)chloride (9): Ligand **5** (3.1 g, 5 mmol) was dissolved in toluene (20 mL) and [$(PhCN)_2PdCl_2$] (2.68g, 7 mmol) was added in one portion. The reaction mixture was refluxed for 2 d. The solution was cooled to room temperature, filtered through Celite, and the filtrate was evaporated to dryness. Recrystallization of the residue in toluene at –20 °C gave **9** as orange solid. Yield 2.56 g (57 %), m.p. 288 °C. $C_{38}H_{44}Cl_3N_4PPd$ (800.54): calcd. C 57.01, H 5.54, N 7.00 %, found C 56.04, H 5.64, N 6.38 %. **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ = 160.0 (s). **^{1}H NMR** ($CDCl_3$, 300 K): δ = 2.06 (s, 18 H, CH_3), 2.17 (s, 6 H, CH_3), 2.44 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 6.22 (s, 2 H, CH), 6.47 (s, 2 H, CH), 6.64 (s, 2 H, CH), 6.80 (s, 2 H, CH) ppm. **IR** (KBr): $\tilde{\nu}$ = 1620 (s), 1601 (s) (C=N) cm^{-1}.

2-Phenyl-tetra-(2,6-dimethylphenyl)-1,3,2-diazaphospholidine-4,5-diimine-tetrachlorotin (11): PCl_3 (1 mmol, 72 mg, 47 µL) was added drop wise to a stirred solution of anhydrous $SnCl_2$ (190 mg, 1 mmol) in THF (15 mL). This mixture was added to a solution of **5** (608 mg, 1 mmol) in THF (15 mL). The yellow solution turned orange. The reaction mixture was stirred overnight and evaporated to dryness. The remaining, light orange residue was extracted with acetonitrile and filtered through Celite. The filtrate was concentrated to a volume of 10 mL and stored at 4 °C. The product precipitated as orange, crystalline solid, which was collected by filtration. Yield 320 mg (37 %), m.p. 167 °C. $C_{42}H_{44}Cl_4N_4PSn{\cdot}CH_3CN$ (910.33): calcd. C 55.41, H 4.87, N 7.69 %, found: C 55.03, H 4.61, N 7.18 %. **^{31}P{^{1}H} NMR** ($CDCl_3$, 300 K): δ = 99.5 (s). **^{1}H NMR** ($CDCl_3$ 300 K): δ = 1.21 (s, 6 H, CH_3), 2.32 (s, 6 H, CH_3), 2.77 (s, 6 H, CH_3), 2.79 (s, 6 H, CH_3), 6.39 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, CH), 6.51 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, CH), 6.73–6.91 (m, 4 H, CH), 6.96 (d, 2 H, $^3J_{HH}$ = 7.5 Hz, CH), 7.04 (d, 2 H, $^3J_{HH}$ =

7.0 Hz, CH), 7.53 (m, 2 H, *m*-Ph), 7.68 (m, 1 H, *p*-Ph), 7.85 (m, 2 H, *o*-Ph). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$): δ = 19.8, 21.9, 22.0, 22.1, 22.7 (CH_3), 126.9, 128.5, 128.8, 129.3, 129.35, 129.41, 129.45, 129.51, 131.1, 131.5, 135.6, 136.47, 136.52, 136.55, 136.99, 137.0 (C_{Aryl}), 151.6 (C=N) ppm. (+)-**ESI-MS**: *m/z* = 833.11 $[M - Cl]^+$, 609.32 $[M\text{-}SnCl_3]^+$.

X-ray Crystallography: Crystallographic data were collected with a Bruker-Nonius KappaCCD diffractometer at T = 123(2) (**5**, **7**, **8**, and **11**) or 100(2) K using Mo-K_α radiation (λ = 0.71073 Å). Direct methods (Patterson methods for **7**) (SHELX-97[28]) were used for structure solution, and non-hydrogen atoms were refined anisotropically (SHELX-97[28], full-matrix, least-square on F^2). Hydrogen atoms were refined with a riding model. A semi-empirical absorption correction was applied for **7**, **8**, and **11**.

5: $C_{40}H_{41}N_4P$; M = 608.74; crystal size 0.50 × 0.30 × 0.10 mm; monoclinic, space group $P2_1/n$, a = 12.754(1), b = 17.673(2), c = 15.083(2) Å, β = 97.52(1)°, V = 3370.5(6) Å^3, Z = 4, ρ = 1.200 Mg·m^{-3}, μ = 0.116 mm^{-1}, θ_{max} = 27.48°; 24618 reflections, 7527 independent reflections (R_{int} = 0.040), 414 parameters, R_1 = 0.048 [$I > 2\sigma(I)$], wR_2 = 0.112 (all data), S = 1.03, largest diff. peak/hole 0.331/–0.323 e·Å^{-3}.

7: $C_{44}H_{41}N_4O_4PW$·0.5toluene; M = 950.69; crystal size 0.25 × 0.10 × 0.05 mm; monoclinic, space group $P2_1/c$, a = 11.303(2), b = 21.281(4), c = 17.298(3) Å, β = 101.79(2)°, V = 4073.1(13) Å^3, Z = 4, ρ = 1.550 Mg·m^{-3}, μ = 2.926 mm^{-1}, θ_{max} = 27.48°; 35093 reflections, 9382 independent reflections (R_{int} = 0.088), 511 parameters, 14 restrains, R_1 = 0.048 [$I > 2\sigma(I)$], wR_2 = 0.095 (all data), S = 1.03, largest diff. peak/hole 1.467/–1.503 e Å^3.

8: $C_{44}H_{41}MoN_4O_4P$·0.5toluene; M = 862.78; crystal size 0.32 × 0.08 × 0.04 mm; monoclinic, space group $P2_1/c$, a = 11.352(1), b = 21.305), c = 17.312(2) Å, β = 101.79(2)°, V = 4098.6(8) Å^3, Z = 4, ρ = 1.398 Mg·m^{-3}, μ = 0.409 mm^{-1}, θ_{max} = 25.00°; 22936 reflections, 7193 independent reflections (R_{int} = 0.112), 512 parameters, 14 restrains, R_1 = 0.067 [$I > 2\sigma(I)$], wR_2 = 0.161 (all data), S = 1.03, largest diff. peak/hole 1.029/–0.918 e Å^3.

9: $C_{38}H_{44}Cl_3N_4PPd$; M = 800.49; crystal size 0.15 × 0.15 × 0.16 mm; monoclinic, space group $P2_1/c$, a = 13.4754(6), b = 20.1664(11), c = 15.0554(8) Å, β = 105.715(3)°, V = 3938.4(3) Å^3, Z = 4, ρ = 1.350 Mg·m^{-3}, μ = 0.745 mm^{-1}, θ_{max} = 28.34°, 9778 reflections/7193 independent reflections (R_{int} = 0.0969), 436 parameters, 0 restrains, R_1 = 0.0674 [$I > 2\sigma(I)$], wR_2 = 0.0974 (all data), S = 1.211, largest diff. peak/hole 0.457/–0.364 e·Å^{-3}. A highly disordered solvent molecule (toluene) was removed with the SQUEEZE routine of Platon[29].

11: $C_{40}H_{41}Cl_4N_4PSn$·acetonitrile; M = 910.28; crystal size 0.30 × 0.15 × 0.10 mm; monoclinic, space group $P2_1/n$, a = 12.482(1), b = 26.391(3), c = 12.623(1) Å, β = 104.99(1)°, V = 4016.7(6) Å^3, Z = 4, ρ = 1.505 Mg·m^{-3}, μ = 0.980 mm^{-1}, θ_{max} = 27.48°; 41753 reflections, 9150 independent reflections (R_{int} = 0.033), 487 parameters, R_1 = 0.028 [$I > 2\sigma(I)$], wR_2 = 0.061 (all data), S = 1.10, largest diff. peak/hole 0.658/–0.490 e Å^3.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-914696 (**5**), -914697 (**7**), -914713 (**8**), -914555 (**9**), and -914698 (**11**), (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft, the Academy of Finland (*M. N.*), and the COST action CM802 (phoscinet) is gratefully acknowledged. We thank *J. Trinkner* and *K. Wohlbold* (Institut für Organische Chemie, University of Stuttgart) for recording the mass spectra.

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Received: December 11, 2012
Published Online: February 7, 2013

