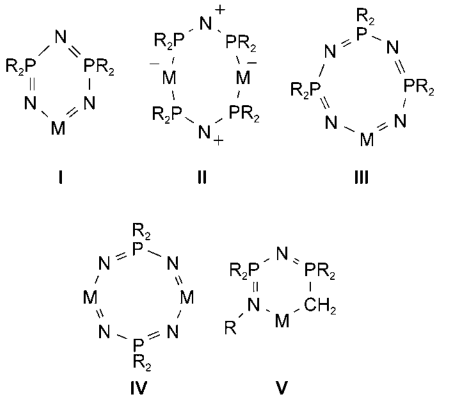
Metallacycles

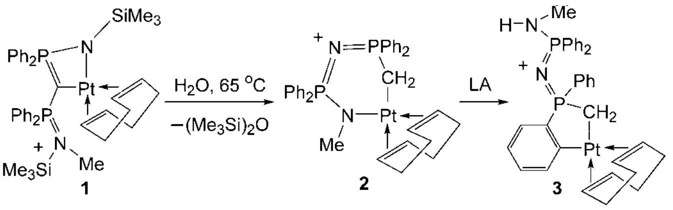
Water-Induced Rearrangement of a Platinacyclic Carbene Produces a Platinacyclic Carbaphosphazene with an Intraannular Pt–C Bond in a Pt–N–P–N–P–C Ring**

*Min Fang, Nathan D. Jones, Michael J. Ferguson, Robert McDonald, and Ronald G. Cavell**

The cyclophosphazenes are a key family of inorganic heterocycles. These rings, which contain alternating four-coordinate P^V and two-coordinate N^{III} atoms $(R_2P{=}N)_n$ ($n \geq 3$), have attracted considerable attention, principally because they are precursors to polyphosphazenes of high molecular weight.[1] These polyphosphazenes constitute the largest and one of the most important classes of inorganic polymers. A large body of synthetic phosphazine chemistry has furnished a wide array of organocyclophosphazenes with exocyclic P–E bonds (E = O, S, N, and C).[2] More recently, the cyclophosphazenes have served as ligands for transition metals,[3,4] and their complexes have found application in catalysis,[5] dendrimers,[6] and cancer therapeutics.[7] Cyclophosphazenes containing metal centers that are covalently bonded in the ring (e.g., **I**–**IV**; Scheme 1) are also well established,[8] but have a shorter history: the first example was reported by Roesky et al. in 1986 (**I**, $M = WCl_3$, R = Ph).[9] Although a variety of these compounds are now known, to the best of our knowledge, there have been no previous reports of M-N-P-N-P-C ring systems (**V**). Herein, we present an unusual synthetic route to the first example of such a metallacycle, which involves a water-induced rearrangement of our previously reported Pt-N-P-C-P-N carbene [**1**][OTf] ($OTf = CF_3SO_3^-$) into the unique Pt-N-P-N-P-C platinacyclophosphazene [**2**][OTf] (Scheme 2). In the presence of Lewis acids (LA), [**2**][OTf] converts quantitatively to its orthometalated isomer, [**3**][OTf] (Scheme 2; LA = MeOTf, AgOTf). Both metallacarbaphosphazenes **2** and **3**, which contain the $[P{=}N{=}P]^+$ fragment, have been fully characterized spectroscopically and by X-ray crystallography.

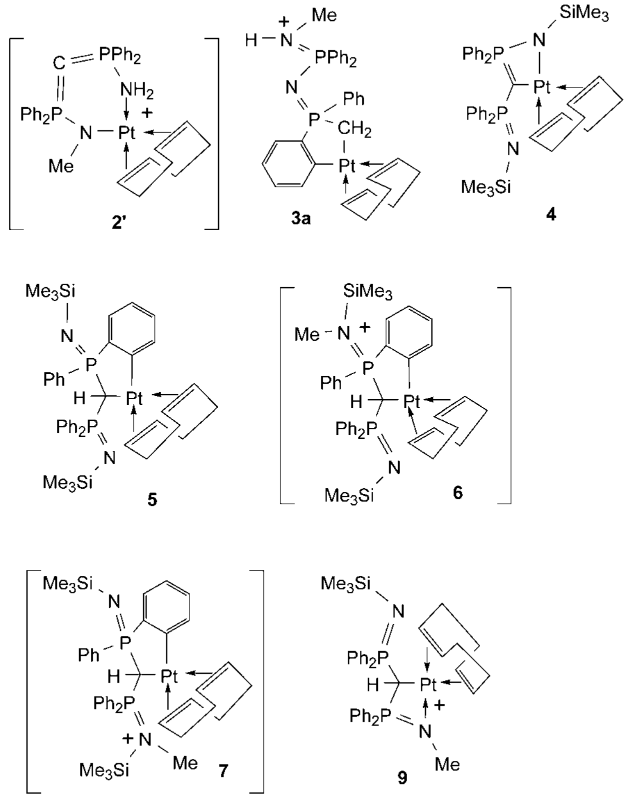


Scheme 1. Known cyclic metallaphosphazene structures (**I**–**IV**) and the metallacarbaphosphazene ring obtained in this work (**V**).



Scheme 2. The syntheses of **2** and **3** (LA = AgOTf and MeOTf, all anions = OTf).

Recently, we reported the synthesis, characterization, and reactivity of the phosphoranimine-stabilized carbene complex **4** (Scheme 3),[10,11] which, when heated to 65 °C in the presence of H_2O, gave the orthometalated methanide **5** quantitatively within minutes. No orthometalation occurred



Scheme 3. Structures discussed in the text. The structure **2′** is the unrearranged isomer of the title compound with a carbodiphosphorane structure. The bracketed structures are unobserved species.

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[**] We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the American Chemical Society Petroleum Research Fund (ACS-PRF) for financial support. N.D.J. acknowledges the Killam Trust for a post-doctoral fellowship.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200461525

over a period of several hours in the absence of H_2O. Methyl triflate (MeOTf) reacted with **4** to give [**1**][OTf]. However, when this complex was heated in the presence of H_2O (1 equiv), neither of the anticipated *N*-methyl analogues of **5** ([**6**][OTf] and [**7**][OTf]—which are shown in brackets to indicate that they are not observed) were formed, but instead the unusual platinacyclophosphazene [**2**][OTf] resulted (Scheme 2). In the absence of H_2O, [**1**][OTf] was stable. To ensure a high yield of [**2**][OTf], a solution of H_2O (1 equiv) in THF was added dropwise to a solution of [**1**][OTf] in THF; when neat H_2O was added, unidentified side products resulted and yields were low.[12] The reaction was complete within 24 h. Typical conversions of [**2**][OTf], as determined in situ by $^{31}P\{^1H\}$ NMR spectroscopy, were 60–70%, with the best conversion being about 90%; yields were approximately 60%. The platinacyclic carbaphosphazene [**2**][OTf] is insensitive to and insoluble in H_2O; heating a THF solution that contained [**2**][OTf] and H_2O to 65 °C for several days had no effect. In the solid state, [**2**][OTf] was also stable in air.

The structures of [**2**][OTf] (monoclinic or triclinic polymorph depending on crystal growing methods)[13] were deduced by using a combination of X-ray crystallography and NMR spectroscopy. Although the crystallographic data for the monoclinic form of [**2**][OTf] gave a good fit ($R_1 =$ 2.3%) when it was assumed that there was no rearrangement of the backbone (as the structure of the unrearranged isomer of **2**, **2'**), this structure was not compatible with NMR data. Heteronuclear correlation through multiple quantum coherence (HMQC) NMR studies (see Supporting Information) revealed no NH_2 protons. In addition to the cross signals arising from the CH_2 protons in 1,5-cyclooctanediene (cod) ligand, one additional CH_2 signal was found. Moreover, the putative "P=C=P" group in **2'** would be expected to show a nucleophilic character that is conspicuously absent in the reactivity of **2** (see below). Refinement of the X-ray crystallographic data by assuming [**2**][OTf] gave a slightly better fit ($R_1 = 2.2\%$).[13] A similar result was obtained for the refinement of the triclinic polymorph of [**2**][OTf]. Similarly, the identity of [**3**][OTf] was confirmed by using a combination of X-ray crystallography and NMR spectroscopy.

Bond lengths and angles for **2** in the two determinations of [**2**][OTf] (monoclinic or triclinic polymorph) are very similar. A labeled ORTEP representation of the molecular structure of the monoclinic isomorph of [**2**][OTf][13] is shown in Figure 1 (the structure of **2** in triclinic [**2**][OTf] is included in the Supporting Information). The $CF_3SO_3^-$ ion is not coordinated to the metal center and has only a few close contacts with hydrogen atoms (the separations which are less than the sum of van der Waals radii are for Ph–H: F(2)-H(13) 2.518(2), F(2)-H(14) 2.631(2), O(1)-H(25) 2.683(3), O(2)-H(22) 2.491(3), O(2)-H(43) 2.633(3), and O(3)-H(34) 2.483(3) Å; for the methylene bridge hydrogen atom: O(2)-H(1B) 2.360(3) Å). Within the six-membered ring, C(1), P(1), N(1), and P(2) are essentially coplanar (dihedral angle φ(P(2)-N(1)-P(1)-C(1)) = 2.6(2)°). N–P bond lengths of the P(1)-N(1)-P(2) fragment are virtually identical (1.593(2) and 1.599(2) Å, respectively) and are consistent with the P–N bond lengths determined for other compounds that contain a $[P{=}N{=}P]^+$ fragment,[14–16] for example, 1.57(1) Å in $[Ph_3P{=}N{=}PPh_3]^+$ and 1.572(3) Å in $[Ph_2(NH_2)P{=}N{=}P(CH_3)Ph_2]^+$.[16] Therefore, it can be concluded that **2** contains a $\{P{=}N{=}P\}^+$ fragment. Atoms P(2), N(2), Pt, and C(2) are also nearly coplanar (φ = (P(2)-N(2)-Pt-C(2)) = 177.1(3)°, and the sum of angles around N(2) is 360.0(5)°). The P(2)–N(2) bond length of 1.627(2) Å is between that of a P–N single and double bond, thus indicating that there is electronic delocalization over P(1), N(1), P(2), and N(2), even though N(2) is not coplanar with the P(2)-N(1)-P(1) plane ($\varphi = -45.5(2)°$). The Pt–C(1) bond length (2.072(3) Å) is within the typical range for a Pt–C single bond (2.039–2.085 Å).[17] The Pt–N(2) bond length (2.051(2) Å) is close to those found for Pt–N dative bonds, such as 2.049 Å found in Pt^{II}–NH_3 complexes.[17]

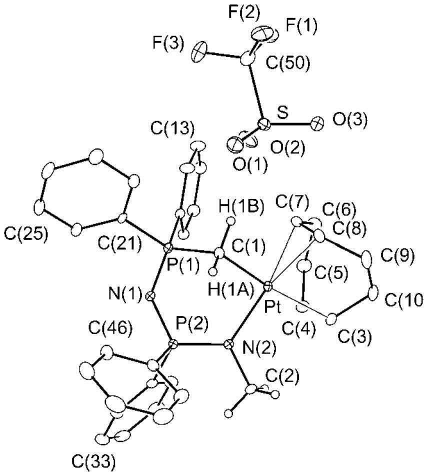

Figure 1. ORTEP diagram of the structure of [**2**][OTf] (monoclinic polymorph). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms on methylene [C(1)] and methyl [C(2)] centers are shown with arbitrarily small thermal parameters, those on the cod and phenyl rings are not shown. Selected bond lengths [Å] and angles [°]: Pt–N(2) 2.051(2), Pt–C(1) 2.072(3), P(1)–N(1) 1.593(2), P(1)–C(1) 1.777(3), P(1)–C(11) 1.807(3), P(1)–C(21) 1.800(3), P(2)–N(1) 1.599(2), P(2)–N(2) 1.627(2), N(2)–C(2) 1.482(4); angles: N(2)-Pt-C(1) 90.92(10), Pt-C(1)-P(1) 108.5(1), C(1)-P(1)-N(1) 112.2(1), P(1)-N(1)-P(2) 123.2(2), N(1)-P(2)-N(2) 114.7(1), P(2)-N(2)-Pt 123.2(1); P(2)-N(2)-C(2) 117.4(2), Pt-N(2)-C(2) 119.4(2); dihedral angles: P(2)-N(1)-P(1)-C(1) 2.6(2), P(2)-N(2)-Pt-C(2) 177.1(3), N(2)-P(2)-N(1)-P(1) −45.5(2), Pt-C(1)-P(1)-N(1) 57.6(2).

The N-P-C-P-N to N-P-N-P-C rearrangement reported herein is unique in that it gives a cyclic product but is not without precedence in giving acyclic compounds. Two previous examples have been reported. $(Me_3SiN{=}PPh_2)_2CH_2$, **8**, was converted to the acyclic cation $[Ph_2(NH_2)PNP(CH_3)Ph_2]^+$ by treatment with aqueous HCl solution[18] or by treatment with Ph_3GeCl or Ph_3SnCl in wet solvents.[16] Possible intermediates for these rearrangements are shown in the Supporting Information. In these systems and in the conversion of **1** into **2** (Scheme 2), hydrolysis of the N–Si bonds is promoted by the formation of an iminium group, which presumably renders the silicon much more electrophilic and susceptible to attack by H_2O. In contrast, complex **4**, which bears no iminium groups, does not undergo N-P-C-P-N to N-P-N-P-C rearrangement in the presence of H_2O. The key rearrangement step is the attack of the basic phosphoranimine nitrogen atom on an electrophilic phosphorus atom, which leads to P–C bond cleavage.

We were able to identify an intermediate, **9** (Scheme 3), by means of in situ NMR spectroscopic studies (^{31}P NMR at 25 °C: $\delta = 73.8$ (br s, ^{1}J(P,Pt) = 393 Hz), −7.2 ppm (br s, ^{1}J(P,Pt) = 95 Hz)). The formation was further confirmed by electrospray mass spectrometry (m/z calcd (observed) 802.24697 (802.24722) [M^{+}] with an isotope-match score of 0.9482). The intermediate **9** was the major product formed (calculated by in situ ^{31}P NMR spectroscopy: 80 % of P atoms) when only about 0.5 equivalent H_2O was added to [**1**][OTf]. The ^{1}H NMR data for Pt–CH in **9** ($\delta = 4.11$ ppm, dd, J(H,Pt) = 73 Hz, ^{2}J(H,P) = 7.5 Hz, ^{2}J(H,P) = 8.4 Hz) is similar to data for the same feature in **5** ($\delta = 4.00$ ppm, dd, ^{2}J(H,Pt) = 96, ^{2}J(H,P) = 13, ^{2}J(H,P) = 16 Hz).[10] Other characterization data for **9** are given in the Supporting Information. We surmise that the initial step is hydrolysis of the N–Si bond of the iminium moiety in **1**, which then undergoes N-to-C proton transfer. Coordination of the methylated N to Pt displaces the other P=N imine center to form **9**. The resultant Me_3SiOH by-product of this reaction condenses to $(Me_3Si)_2O$ (as determined by ^{1}H and ^{29}Si NMR spectroscopies) and H_2O. The liberated silylated phosphimine moiety in **9** further reacts with H_2O to again form Me_3SiOH (which condenses as above) and a P=NH group. Subsequent P–C bond cleavage and proton transfer from the N atom to the C atom completes the rearrangement into **2**.

In the presence of substoichiometric quantities of the electrophiles (AgOTf and MeOTf, about 0.5 equivalent), **2** was quantitatively converted into **3** (Scheme 2); there was no incorporation of the electrophile into the product.[19] Analysis by NMR spectroscopy and mass spectrometry showed that the products of the reactions mediated by either of these Lewis acid catalysts were identical. Without catalyst, the conversion of **2** into **3** occurred but was extremely slow; heating a C_6D_6 solution of **2** to 65 °C for two weeks gave less than 33 % conversion. No intermediate was observed by in situ ^{31}P NMR spectroscopy for either the catalyzed or uncatalyzed reactions. The precise role of the catalytic electrophile in this reaction remains poorly understood. It is possible that reversible association between electrophile and the amido N atom in **2** (all the possible resonance forms **2a–d** are given in the Supporting Information) gives rise to a coordinatively unsaturated Pt center, which then undergoes orthometallation.[20]

The $\overline{\text{Pt-C-C-P-C}}$ metallacyclic structure of [**3**][OTf] is shown in Figure 2.[13] As in [**2**][OTf], the $CF_3SO_3^-$ ion does not coordinate to the metal center. The close O–H contact (2.145(2) Å) between $CF_3SO_3^-$ and the HNMe fragment suggests that the NH proton bears a significant positive charge and that the resonance form **3a** is an important contributor to the structure of **3** (see the Supporting Information for the remaining resonance forms).

Related crystal structures of complexes with similar rings have been reported.[10,21,22,23] The C(1), P(1), N(1), and P(2) atoms in **3** are coplanar as they are in **2**. The P–N bond lengths in the {P=N=P}$^{+}$ fragment (1.607(2) and 1.583(2) Å) and P-N-P angle (128.4(1)°) are similar to those in **2** (1.593(2) and 1.599(2) Å, and 123.2(2)°).

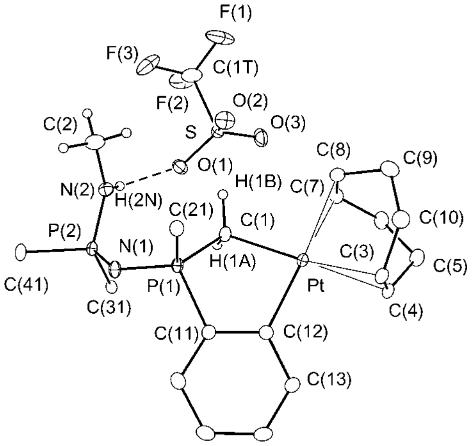

Figure 2. ORTEP diagram of the structure of [**3**][OTf]. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50 % probability level. Hydrogen atoms on methyl, methylene, and N(2) centers are shown with arbitrarily small thermal parameters, those on the cod and phenyl rings are not shown. For all phenyl rings, except that forming the orthometalated center, only the *ipso* carbon atom is shown. The dotted line indicates the interaction of the triflate oxygen atom with the hydrogen atom on N(2). Selected bond lengths [Å] and angles [°]: Pt–C(1) 2.072(2), Pt–C(12) 2.040(2), P(1)–N(1) 1.607(2), P(1)–C(1) 1.775(3), P(1)–C(11) 1.786(3), P(2)–N(1) 1.583(2), P(2)–N(2) 1.635(2), N(2)–C(2) 1.465(4), C(11)–C(12) 1.411(3); angles: P(1)-N(1)-P(2) 128.4(1), C(1)-Pt-C(12) 85.5(1); dihedral angles: C(1)-P(1)-N(1)-P(2) 0.9(2), N(2)-P(2)-N(1)-P(1) 48.1(2), P(1)-C(11)-C(12)-Pt −1.5(3), C(1)-P(1)-C(11)-C(12) −23.0(2).

In summary, the first example of a $\overline{\text{M-C-P-N-P-N}}$ metallaheterocycle, the platinacyclic carbaphosphazene [**2**][OTf] has been synthesized in high yield through a unique four- to six-membered ring expansion and rearrangement induced by water. The synthetic method described herein for [**2**][OTf] may provide routes for synthesizing new metal-containing cyclophosphazenes. The mechanisms through which **2** and **3** were formed are currently under investigation.

Received: August 3, 2004
Revised: November 25, 2004

Keywords: carbenes · metallacycles · phosphorus · platinum · rearrangement

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[12] Synthesis of [**2**][OTf]: A THF solution containing H_2O (4.94 mL, 0.0245 M, 0.121 mmol) was added dropwise to a stirred solution of [**1**][OTf] (130 mg, 0.127 mmol) in THF (10 mL). The mixture was heated to 65 °C for 24 h. Removal of the solvent and recrystallization from THF gave [**2**][OTf] (73 mg, 65 %). $^{31}P\{^1H\}$ NMR (161.9 MHz, [D_8]THF): $\delta = 33.5$ (d, $^2J(P,P) = 6.1$, $^2J(P,Pt) = 122$ Hz), 25.0 ppm (d, $^2J(P,P) = 6.0$, $^2J(P,Pt) = 124$ Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, [D_8]THF) for CH_2Pt: $\delta = 15.3$ ppm (dd, $^1J(P,C) = 46$, $^3J(P,C) = 8.4$ Hz, $^1J(C,Pt)$ not observed). Complete synthetic and characterization data are given in the Supporting Information.

[13] CCDC-242499 ([**2**][OTf], monoclinic form), CCDC-2425001 ([**2**][OTf], triclinic form), and CCDC-242451 ([**3**][OTf]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The full crystal data and their completely labeled diagrams are included in the Supporting Information.

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[19] Synthesis of [**3**][OTf]: A mixture of MeOTf (5.3 µL, 47 µmol), [**2**][OTf] (82 mg, 93 µmol) and C_6H_6 (4 mL) was stirred for 1 day at room temperature and then heated to 68–70 °C for 7 h. Removal of the solvent gave spectroscopically pure [**3**][OTf] quantitatively. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): $\delta = 21.7$ (s), 37.7 ppm (s, $^2J(P,Pt) = 217$ Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, [D_8]THF) for CH_2Pt: $\delta = 26.1$ ppm (dd, $^1J(P,C) = 50$, $^3J(P,C) = 1.2$ Hz, $^1J(C,Pt)$ not observed); Microscope IR: $\tilde{\nu} = 3246\ cm^{-1}$ (m, ν_{NH}). Complete synthetic and characterization data are given in the Supporting Information.

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