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Going for strain: synthesis of the first 3-imino-azaphosphiridine complexes and their surprising conversion into oxaphosphirane complex valence isomers

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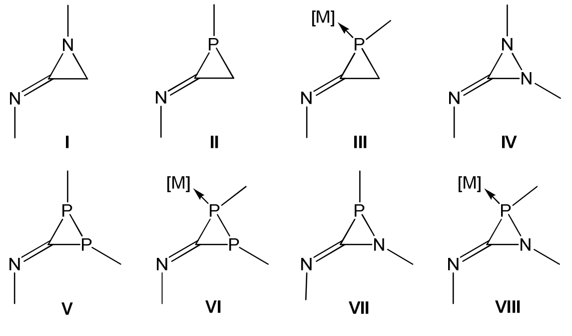
Reaction of a Li/Cl phosphinidenoid complex with *N,N'*-dialkyl carbodiimides yielded the novel 3-imino-azaphosphiridine complexes; reaction with water led selectively to the first stable valence isomer of an oxaphosphirane complex.

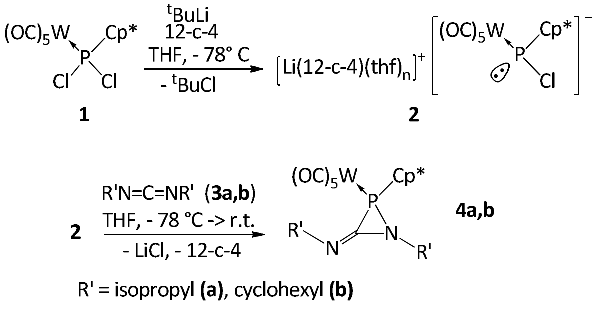
3-Imino-aziridines[1] (**I**) (Scheme 1) belong to the group of highly strained three-membered heterocycles and, hence, enable a wide range of interesting synthetic transformations. In contrast and to the best of our knowledge, 3-imino-phosphiranes **II** are unknown, but transition metal complexes **III**[2] were described. Including a second heteroatom such as a group 15 element leads to the series **IV** - **VII**, of which only the synthesis of **IV**,[3] **V**[4] and **VI**[5] was reported. Heterocycle **VII**[6] was proposed as reactive intermediate, only.



Scheme 1. 3-Imino-aziridines (**I**), and related heterocycles **II-VII** including some transition metal complexes (**III**, **VI**, **VIII**) (exocyclic lines denote organic substituents).

Due to our longstanding interest in the chemistry of complexes possessing strained heterocyclic ligands having polar ring bonds such as 2*H*-azaphosphirenes,[7] oxaphosphiranes[8] and azaphosphiridines,[9] we contemplated about reactions of Li/Cl phosphinidenoid complexes[10] and cumulenes. The first example of this is reported herein, together with theoretical calculations of the ring strain energy of the hitherto unknown complexes **VIII** and a proposed pathway for their conversion into the first stable valence isomers of oxaphosphirane complexes.

When Li/Cl phosphinidenoid complex **2**,[11] prepared from complex **1**,[12] was reacted in situ with diisopropyl- and dicyclohexyl carbodiimides **3a,b**, formation of the novel 3-iminoazaphosphiridine complexes **4a,b** was observed (Scheme 2); low temperature ^{31}P NMR monitoring didn't reveal any further evidence for intermediates. Compared to data of known azaphosphiridine complex derivatives,[9] the complexes **4a,b** possess significantly downfield-shifted $^{31}P\{^1H\}$ NMR resonances, observed at 4.0 ppm ($^1J_{WP}$ = 265.6 Hz) and at 1.5 ppm ($^1J_{WP}$ = 265.9 Hz). The imino carbon atoms of **4a,b** exhibit $^{13}C\{^1H\}$ NMR resonances at 139.7 ppm and 139.9 ppm, respectively, showing relatively small sum of scalar coupling constants (**4a**: $J_{C,P}$ = 5.5 Hz and **4b**: $J_{C,P}$ = 5.2 Hz).



Scheme 2. Synthesis of 3-imino-azaphosphiridine complexes **4a,b**.

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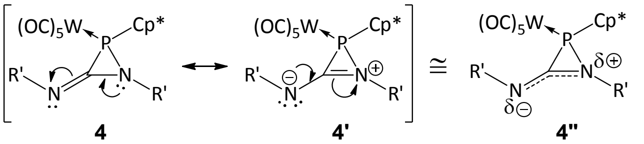
Electronic Supplementary Information (ESI) available: experimental protocols, ^{1}H NMR monitoring, X-ray crystallographic analyses and computational details. See DOI: 10.1039/c000000x/

The structure of 3-imino-azaphosphiridine complex **4a**, confirmed by X-ray diffraction analysis (Fig. 1),[12] shows a pyramidal geometry at the N1 atom (sum of bond angles: 342.7º). Interestingly, the N1–C1 bond length (1.366(8) Å) is shorter than 1.48-1.47 Å as reported for azaphosphiridine complexes not possessing the 3-imino group.[9a] The N2–C1 bond length (1.249(6) Å) is similar to the corresponding C–N bond length of the imino group in the *N*-phenyl-2-iminophosphirane iron complex (1.273(7) Å),[2a,2b] showing considerable C=N double bond character. Despite contribution of canonical structure **4'** which is less important than **4**, the compounds might be best depicted by resonance hybrid structures **4''** (Scheme 3).



Scheme 3. Resonance structures of 3-imino-azaphosphiridine complexes **4**.

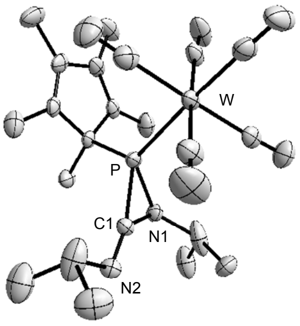
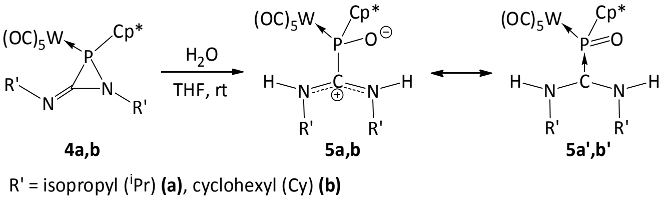


Figure 1. Molecular structure of 3-imino-azaphosphiridine complex **4a**. (50 % probability level, hydrogen atoms are omitted for clarity; only the main part of the disordered moiety is shown here (see ESI). Selected structural parameters (distances [Å] and angles [°]): P-W 2.4779(9), P-C(1) 1.840(6), C(1)-N(1) 1.366(8), C(1)-N(2) 1.249(6), P-N(1) 1.795(5), C(1)-P-N(1) 44.1(3), N(1)-C(1)-P 66.2(3), P-N(1)-C(1) 69.7(4), P-C(1)-N(2) 154.4(9), N1-C1-N2 138.9(9).

When THF solutions of complexes **4a,b** were treated with 1 eq. of water at ambient temperature, the formation of complexes **5a,b** occurred selectively (Scheme 4) which were obtained in pure form and good yields via crystallization from diethyl ether solutions (for details see ESI). Complexes **5a,b** possess $^{31}P\{^1H\}$ resonances at 84.3 ppm ($^1J_{WP}$ = 269.0 Hz) and 85.0 ppm ($^1J_{WP}$ = 269.8 Hz). The resonances of the carbon nuclei, directly bound to two nitrogens, appear as doublets in the $^{13}C\{^1H\}$ NMR spectra (**5a**: 171.9 ppm, $^1J_{P,C}$ = 14.4 Hz and **5b**: 170.8 ppm, $^1J_{P,C}$ = 14.1 Hz). Interestingly, the ^1H NMR spectra ($CDCl_3$) of **5a** showed a broad singlet at 6.7 ppm for the N-*H* protons at ambient temperature which, upon cooling to –70 °C, splits into two doublets at 5.1 and 8.0 ppm ($^4J_{PC}$ = 8.0 Hz) revealing that rotation around the P–C^N bond is hampered due to an PO–H–N hydrogen bonding. According to the Gutowsky–Holms equation ($K_c = \pi\nabla/\sqrt{2}$),[14a,b] and the Eyring equation $\{\Delta G^{\neq}_c = 4.58T_c[10.32 + \log (T_c/K_c)]\}$[14b,15] the free energy activation at coalescence temperature for this process was calculated to be between 10.9 and 11.4 kcal mol^{-1}.

Complexes **5a,b** were also structurally confirmed (Fig. 2, for **5b** see ESI)[16] revealing a unique bonding of a zwitterion ligand possessing a delocalized cationically charged moiety where the sum of the bond angles around C1 (**5a**) atom is 359.8°, almost identical C–N distances, a slightly elongated P–C (1.897(2) Å) and shortened P-O bond (1.5201(16) Å) as compared with those of **4a**.



Scheme 4. Synthesis of **5a,b**.

This situation bears also features of a carbene donor adduct to a terminal phosphinidene oxide complex as expressed by the formula **5'**. Albeit having a O1–C1 distance of 2.64 Å, which is shorter than the sum of van der Waals radii (3.22 Å),[17] it is clearly the first example of a valence isomer of an oxaphosphirane complex. Furthermore, there is a O1···H-N2 hydrogen bond (O1-H 2.06, O1-N2 2.639(2) Å), which reflects the situation in solution at low temperature.

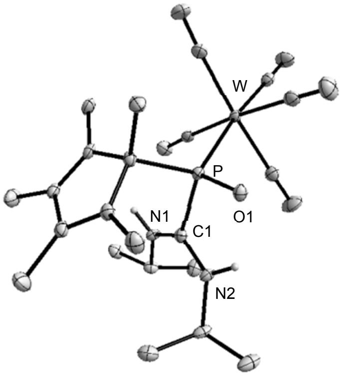


Figure 2. Molecular structures of complex **5a**. (50% probability levels, hydrogen atoms, except at N, are omitted for clarity). Selected X-ray crystal structure data (distances [Å] and angles [°]): P-W 2.5384(6), P-C(1) 1.897(2), C(1)-N(1) 1.319(3), C(1)-N(2) 1.311(3), P-O 1.5201(16), C(1)-P-O 100.61(10), N(1)-C(C1)-N(2) 127.1(2), N(1)-C(1)-P 122.71(17), N(2)-C(1)-P 110.03(16).

Complexes **4** and their reactivity were also studied computationally at the DFT level (see Computational Details in the ESI). First, the *E*/*Z* isomerism of the exocyclic C=N bond was inspected using model complexes bearing either H (**c**) or methyl groups (**d**) as P- and N-substituents. The *Z*-isomer is the most stable diastereomer by 1.57 and 2.97 kcal/mol for complexes **4c** and **4d**, respectively. A very important feature of these complexes is their remarkably large ring strain energy (RSE) of 50.58 and 52.26 kcal mol^{-1} computed for both diastereomers $\mathbf{4^Z c}$ and $\mathbf{4^E c}$, using homodesmotic reactions (see the ESI) like those employed previously for related systems,[18] which is almost twice as much as the value for parent azaphosphiridine complexes (23.9 kcal mol^{-1}).[18] Moreover, the Lagrange kinetic energy at the ring critical point (RCP), *G*(r), was recently shown to correlate with RSEs within related systems,[19] at much lower computational cost, and also successfully employed within a related oxaphosphirane series.[20] This computationally inexpensive *G*(r) quantity suggests that the ring strain slightly increases with trimethyl substitution on going from **4c** (0.1311 au) to **4d** (0.1362 au).

A small but significant contribution of resonance structures **4'** (Scheme 3) is supported by the inspection of typical bond-strength related parameters such as the Wiberg bond index (WBI)[21] and the electron density ρ(r) at bond critical points (BCP) within the atoms-in-molecules (AIM) framework.[22] The slightly larger than single bond order found for the endocyclic C-N bond in **4c,d** (WBI = 1.176 and 1.169; ρ(r) = 32.69×10^2 and 32.73×10^2 e/a_o^3) and smaller than double bond for the exocyclic one (WBI = 1.886 and 1.816; ρ(r) = 41.31×10^2 and 41.12×10^2 e/a_o^3). The weakest endocyclic bond in **4c,d** was found to be the P-N bond (WBI = 0.778 and 0.748; ρ(r) = 14.77×10^2 and 15.07×10^2 e/a_o^3), which is responsible for ring opening reactions (*vide infra*).

The basic character of the exocyclic N atom in model complex **4d** enables initial hydrogen bond (HB) formation leading to the van der Waals complex **4d**·H_2O, which promotes weakening of the exocyclic C=N bond (lower double bond character) thus allowing rotation of this bond to afford the slightly less stable isomer **4d**^{E}·H_2O (Figure 3).

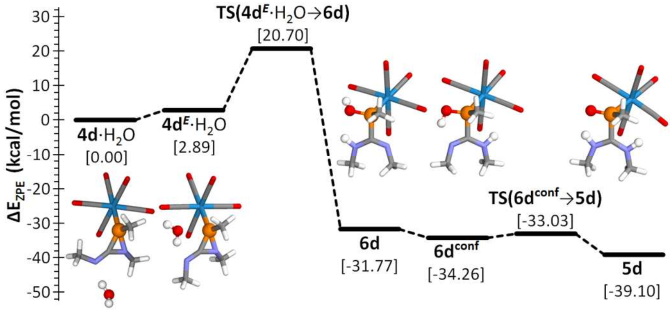


Figure 3. Calculated energy profile (COSMO$_{THF}$/LPNO-NCEPA1/def2-TZVPP//B3LYP-D3/def2-TZVP) for the hydrolysis of model complex **4d** (see text) to **5d**.

This *E*-configured van der Waals complex displays two-point anchoring of the water molecule to **4d**^{E} by means of a OH···N HB (d = 2.025 Å; WBI = 0.030) and a weak secondary O···P interaction (d = 3.1985 Å; WBI = 0.020), as visualized in a NCI (noncovalent interactions) plot[23] (Figure 4). This in turn entails an important change in **4d**^{E} as it remarkably increases the ring strain (*G*(r) = 0.1566 au) and weakens the P-N bond (WBI = 0.726; ρ(r) = 14.55×10^2 e/a_o^3), thus giving rise to a cascade set of reactions (Figure 3).

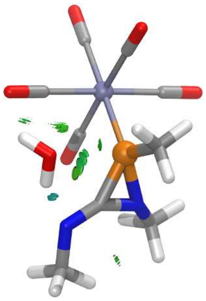


Figure 4. Computed (B3LYP-D3/def2-TZVP-f) structure for **4d**^{E}·H_2O with NCIplot highlighting key stabilizing NCIs. The RDG s = 0.25 au isosurface is coloured over the range $-0.07 < \mathrm{sign}(\lambda_2)\cdot\rho < 0.07$ au: blue denotes strong attraction, green stands for moderate interaction, and red indicates strong repulsion (see the ESI).

The proposed reaction sequence starts with a low barrier (20.7 kcal mol^{-1}), exergonic, unusual pericyclic [2σ+(2π+2σ)] process corresponding to the formal addition of water across the P-C=N termini and leading to the open-chain intermediate **6d** that displays intramolecular NH···O(H)P HB-stabilization. Rotation around the C-P bond affords conformer **6d**$^{\mathbf{conf}}$ that is stabilized by a different (and stronger) intramolecular HB of POH···N type and enables the final slightly exergonic and very low barrier O-to-N proton transfer leading to **5d**.

In order to inspect further the bonding in **5d**, the heterolytic P-C bond dissociation energy (BDE) was computed to 53.69 Kcal·mol^{-1}, which is rather low for a not heavily substituted system (as in **5a,b**) in comparison to the reported mean value of *ca.* 123 kcal/mol.[24] Furthermore, descriptors for bond strength points to a weak P-C bond in **5d** (WBI = 0.726; ρ(r) = 13.92×10^2 e/a_o^3) in comparison to the closely related precursor **6d**$^{\mathbf{conf}}$ (WBI = 0.828; ρ(r) = 15.99×10^2 e/a_o^3) and even the strained P-C bond in **4d** (WBI = 0.809; ρ(r) = 15.47×10^2 e/a_o^3), thus providing some additional support for the formulation as a diaminocarbene-stabilized phosphinidene oxide complex **5'** (Scheme 4). Rotation around the C-P bond in **5d** requires to surpass a transition state barrier of 7.62 kcal/mol ($CHCl_3$ solution), which is in quite good agreement with the experimental value obtained for **5a**, especially if taking the larger substituents at both N and P into account.

Conclusions

It was demonstrated that a Li/Cl phosphinidenoid complex can be used to gain easy access to the hitherto unknown 3-imino-azaphosphiridine complexes. Theoretical calculations reveal a largely increased ring strain energy of more than 50 kcal mol^{-1}. Furthermore, a pathway for their reaction with water to yield zwitterionic complexes is discussed. The latter represent the first stable valence isomers of oxaphosphirane complexes.

Notes and references

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