Cyclic Heteroallenes

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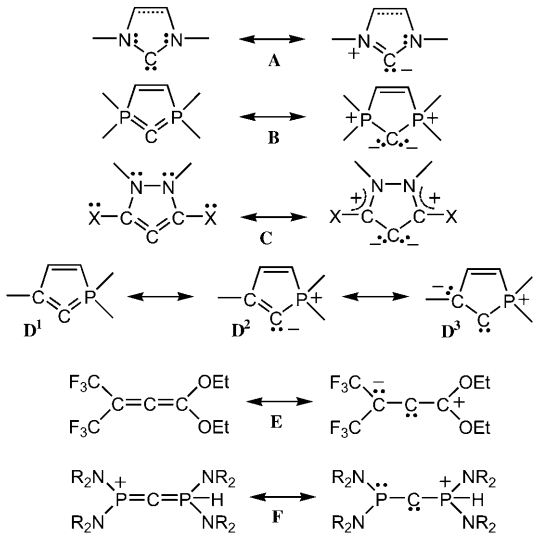
Synthesis and Ligand Properties of a Stable Five-Membered-Ring Vinylidenephosphorane**

Matthew Asay, Tsuyoshi Kato, Nathalie Saffon-Merceron, Fernando P. Cossío, Antoine Baceiredo, and Guy Bertrand**

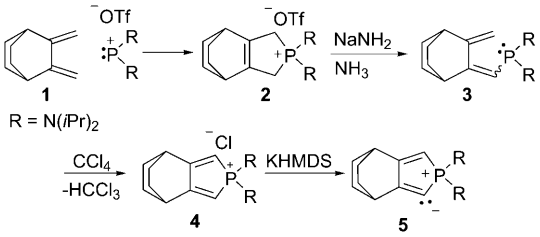
Dedicated to Professor Edgar Niecke on the occasion of his 70th birthday

Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of the various systems. Recently, N-heterocyclic carbenes (NHCs) **A** (Scheme 1) have emerged as powerful ligands, largely because of their strong donor properties, which are due to the presence of a lone pair and a partially filled vacant orbital.[1] In our search for even stronger donor ligands, we became interested in carbodiphosphoranes,[2] especially their cyclic versions **B**,[3] because, as we have learned from carbene chemistry, they lead to more robust transition-metal complexes than their acyclic congeners.[4] We have demonstrated using the $\nu_{av}(CO)$ infrared frequency of $[(L)Rh(CO)_2Cl]$ complexes[3] that these species, which feature a carbon formally bearing two lone pairs,[5] were indeed stronger donors than NHCs **A**. Along this line, we have also reported the synthesis of acyclic and cyclic push–push bent allenes (carbodicarbenes) **C**,[6] which are electronically similar to carbodiphosphoranes.[7,8] These results led us to consider a mixed system **D** with a phosphorus–carbon ylidic bond and a carbon–carbon double bond. Interestingly, such heteroallenes have a resonance form **D³** directly related to the previously reported push–pull allenes **E**[9] and push–pull carbenes **F**,[10] as shown by their resonance forms. In contrast to the numerous examples of acyclic derivatives,[2] only one cyclic vinylidenephosphorane, stable at low temperature for a short period of time, has been described, and no crystallographic data or coordination behavior has been reported.[11] Herein we present the synthesis, single crystal X-ray diffraction study, and ligand properties of a cyclic vinylidenephosphorane **5** that is stable at room temperature both in solution and in the solid state.



Scheme 1. Similarities and differences between NHCs **A**, carbodiphosphoranes **B**, push–push allenes **C**, vinylidenephosphoranes **D**, push–pull allenes **E**, and push–pull carbenes **F**.

The cyclic phospholium salt **4**, without undesired acidic protons, was chosen as the precursor for the target vinylidenephosphorane **5**. Starting from the readily available diene **1**,[12] a formal [4+1] cycloaddition with bis(diisopropyl)aminophosphenium triflate gives rise to the phospholenium salt **2** (Scheme 2).[13] Deprotonation of **2** with $NaNH_2$ in ammonia



Scheme 2. Synthesis of cyclic phosphaallene **5**. KHMDS = potassium hexamethyldisilazide, OTf = triflate = CF_3SO_3.

[*] M. Asay, Dr. T. Kato, Dr. N. Saffon-Merceron, Dr. A. Baceiredo
Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069), Université Paul Sabatier
Narbonne, 31062 Toulouse Cedex 9 (France)
Fax: (+33) 5-6155-8204
E-mail: baceired@chimie.ups-tlse.fr
Homepage: http://hfa.ups-tlse.fr
M. Asay, Prof. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California, Riverside
Riverside, CA 92521-0403 (USA)
Fax: (+1) 951-827-2725
E-mail: gbertran@mail.ucr.edu
Prof. F. P. Cossío
Departamento de Química Orgánica I
Universidad del País Vasco-Euskal Herriko Unibertsitatea
Facultad de Química
P. K. 1072, San Sebastián—Donostia (Spain)

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affords the ring-opened phosphine **3** (*Z* or *E*).[14] Subsequent treatment with one equivalent of CCl_4 at room temperature leads directly to the desired phospholium chloride **4**.[15] The structure of **4** was unambiguously established by NMR spectroscopy and X-ray crystallography[16] (Figure 1, left). Heterocycle **4** has a planar five-membered ring with significant C=C−C=C diene character.

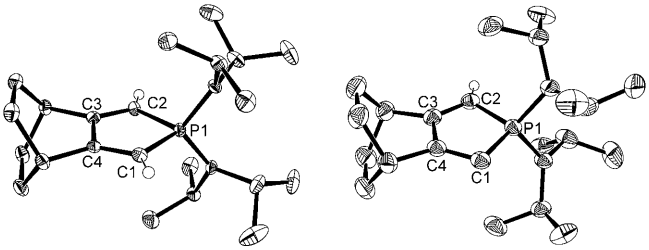

Figure 1. X-ray crystal structures of **4** (left) and **5** (right). Triflate anion (for **4**) and H atoms (for **4** and **5**) are omitted for clarity. Selected bond lengths [Å] and angles [°]: **4**: P1–C1 1.782(3), C1–C4 1.329(4), P1–C2 1.791(2), C2–C3 1.342(3), C3–C4 1.497(4); P1-C1-C4 107.99(19), P1-C2-C3 107.17(19), C1-P1-C2 94.65 (12); **5**: P1–C1 1.783(15), C1–C4 1.358(2), P1–C2 1.789(16), C2–C3 1.342(2), C3–C4 1.510(2); P1-C1-C4 99.94(11), P1-C2-C3 101.97(12), C1-P1-C2 102.04 (8).

Deprotonation of salt **4** in THF using KHMDS leads to the desired vinylidenephosphorane **5** as the major product, as indicated by ^{31}P NMR spectroscopy ($\delta = +86$ ppm). Compound **5** is indefinitely stable in solution and in the solid state. As expected, the ^{1}H and ^{13}C NMR spectra show that the product is no longer symmetrical. The ^{13}C NMR signal of the central carbon atom was observed at $\delta = 184.2$ ppm, which is significantly downfield-shifted relative to the starting material ($\delta = 108.7$ ppm). Interestingly, a similar downfield signal was observed for the push–pull allene **E** ($\delta = 199$ ppm),[9] which highlights, at least to some extent, the similarities between **D** and **E**. Compound **5** was isolated in crystalline form from a concentrated diethyl ether solution at −30 °C (32 % yield of isolated product, m.p. = 81–82 °C) and subjected to a single crystal X-ray analysis (Figure 1, right).[16]

The most striking feature of **5** is the P1−C1 bond length of 1.783 Å, which is essentially the same as that of the phosphonium precursor **4** (1.782 Å). This bond is exceptionally long compared to those observed for a nonstabilized phosphorus ylide (1.66 Å),[17a] the previously reported five-membered cyclic carbodiphosphorane of type **B** (1.64–1.66 Å),[3] and, even more strikingly, an acyclic vinylidenephosphorane (1.68 Å).[17b] The only significant change in geometry between **4** and **5** is the P1-C1-C4 bond angle, which decreased significantly from 108° to 100°. Interestingly, the same phenomenon is always observed for carbenes and bent allenes when compared with their conjugate-acid precursors.[1,6]

To better understand the electronic properties of **5**, DFT calculations were performed at the B3LYP/6-31G* level of theory.[18] The calculated geometric parameters show an excellent agreement with those obtained experimentally (P1−C1(calcd) 1.789 Å).[19] As expected, the highest occupied molecular orbital (HOMO) is localized primarily on C1 in the molecular plane. However, the lowest unoccupied MO (LUMO) is not the antibonding (σ*) orbital of the phosphonio moiety, as is generally observed in other ylides,[20] but corresponds mainly to the π system, which demonstrates that the phosphorane acts as a π acceptor (Figure 2).

The Wiberg bond orders[21] were also calculated, and it was found that the organic part of the heterocycle has significant diene character (C1−C4 1.817, C4−C3 1.018, C3−C2 1.769). The C−P bond orders (C1−P1 1.027, C2−P1 0.848) indicate a weak interaction of the phosphonio group with the conjugated π electrons and C1 lone pair, which is in agreement with the observed long P−C bonds. These calculations, along with the X-ray crystallographic data, indicate that the predominant resonance form of **5** is **D²**.

The singlet–triplet energy gap of **5** was calculated to be 32.4 kcal mol^{-1}, which is smaller than in NHCs (68.1–84.8 kcal mol^{-1}),[1] but in the range of those calculated for alkylaminocarbenes (23–46 kcal mol^{-1}).[22] This finding, in addition to the acute P1-C1-C4 bond angle, indicates that **5** is an excellent candidate to be a strong electron-donating ligand, which should lead to robust transition-metal complexes. Indeed, mixing **5** with [{RhCl(cod)}$_2$] leads to the corresponding complex **6** as a thermally very stable orange solid (m.p. 197–198 °C; Figure 3, cod = cycloocta-l,5-diene). The formation of **6** can clearly be ascertained by ^{13}C NMR spectroscopy, in which the central carbon peak moves upfield

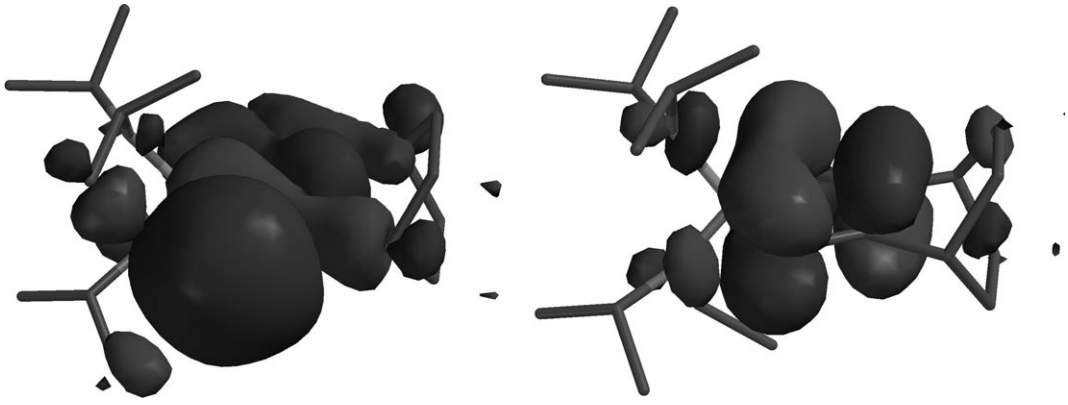

Figure 2. Calculated HOMO (left) and LUMO (right) of **5**.

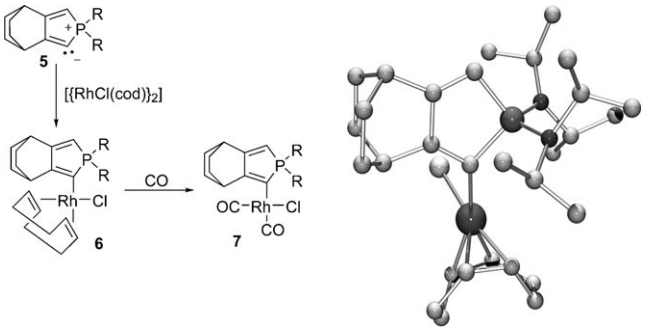

Figure 3. Synthesis of cyclic vinylidenephosphorane rhodium(I) complexes **6** and **7** and X-ray structure of **6**. cod = cycloocta-l,5-diene.

(as is typical for metal complexes of NHCs **A**, carbodiphosphoranes **B**, and bent allenes **C**) to $\delta = 148.0$ ppm (dd, $^1J_{CP} = 41.5$ Hz, $^1J_{CRh} = 13.7$ Hz). As expected, the X-ray crystal structure[16] confirmed the η^1 ligation, although a disorder precludes discussion of structural details.

The corresponding dicarbonyl complex **7** can easily be synthesized by bubbling carbon monoxide through a dichloromethane solution of **6**. The infrared spectrum shows the characteristic CO stretching frequencies with an average value of 2017 cm^{-1}. This value clearly shows that the cyclic vinylidenephosphorane **5** is a much stronger donor than five-membered NHCs **A** (2036–2060 cm^{-1}),[23] comparable to bent allenes **C** (2018 cm^{-1}),[6] but weaker than carbodiphosphoranes **B** (2001 cm^{-1}).[3] However, it is important to note that complexes **6** and **7** appear to be much more robust than the corresponding carbodiphosphorane complexes.

In conclusion, a cyclic vinylidenephosphorane stable at room temperature has been synthesized. It features a very long phosphorus–carbon bond, much longer that in the acyclic version, leaving the carbon lone pair fully available for coordination to metals. Accordingly, this species behaves as a strong electron-donating ligand for transition metals.

Experimental Section

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. The synthesis of **4** and detailed computational data are given in the Supporting Information.

5: THF was added (5 mL) to a mixture of **4** (173 mg, 0.337 mmol) and KHMDS (74 mg, 0.371 mmol) at −78 °C. The solution was stirred at −78 °C for 10 min and then allowed to warm to room temperature. After 1 h, all volatiles were removed under vacuum, and **5** was extracted in diethyl ether. The ether solution was concentrated, and brownish-red crystals formed at −30 °C; 32 % yield (22 mg); m.p. 81–82 °C; $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 243 MHz): $\delta = 86.4$ ppm; ^{13}C NMR (C_6D_6, 25 °C, 151 MHz): $\delta = 22.9$ (s, CH_3), 26.2 (s, CH_2), 27.1 (s, CH_2), 34.5 (broad, CH), 37.7 (broad, CH), 46.9 (s, *i*Pr), 113.7 (d, $^1J_{CP} = 121$ Hz, PCH), 163.1 (broad, C), 164.8 (broad, C), 184.5 ppm (broad, PC).

6: Freshly generated **5** (prepared from **4** (308 mg, 0.601 mmol) and KHMDS (132 mg, 0.662 mmol) in THF (5 mL)) was added to a THF (3 mL) solution of [{RhCl(cod)}$_2$] (148 mg, 0.3 mmol) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 4 h. All volatiles were removed under vacuum, and the resultant solid was washed with diethyl ether and then extracted with chloroform. Orange single crystals were grown from a concentrated chloroform/ether solution (3:1); 42 % yield (154 mg); m.p. 197–198 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 243 MHz): $\delta = 73.9$ ppm (d, $^2J_{PRh} = 11.6$ Hz); ^{13}C NMR ($CDCl_3$, 25 °C, 151 MHz): $\delta = 24.1$ (broad, CH_3), 24.5 (broad, CH_3), 25.0 (CH_2), 26.6 (CH_2), 29.1 (CH_2), 33.2 (d, $^3J_{CP} = 22.3$ Hz, CH_2), 33.6 (CH_2), 36.9 (d, $^3J_{CP} = 35.5$ Hz, CH), 48.0 (d, $^2J_{CP} = 5.1$ Hz, NCH), 64.3 (CH), 92.9 (CH), 108.6 (d, $^1J_{CP} = 89.5$ Hz, PCH), 148.0 (dd, $^1J_{CP} = 41.5$ Hz, $^1J_{CRh} = 13.7$ Hz, PC), 163.6 (d, $^2J_{CP} = 22.8$ Hz, C), 163.9 ppm (d, $^2J_{CP} = 42.6$ Hz, C).

7: CO was bubbled into a CH_2Cl_2 (3 mL) solution of complex **6** (154 g, 0.252 mmol). The volatiles were removed under vacuum to give **7** as a yellow-orange solid; 99 % yield (139 mg); m.p. 138–140 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 243 MHz): $\delta = 73.9$ (d, $^2J_{PRh} = 8.5$ Hz); ^{13}C NMR ($CDCl_3$, 25 °C, 151 MHz): $\delta = 23.9$ (d, $^3J_{CP} = 1.7$ Hz, CH_3), 24.0 (d, $^3J_{CP} = 3.0$ Hz, CH_3), 24.9 (CH_2), 25.5 (CH_2), 33.1 (d, $^3J_{CP} = 21.6$ Hz, CH), 37.1 (d, $^3J_{CP} = 32.9$ Hz, CH), 48.3 (d, $^2J_{CP} = 5.1$ Hz, NCH), 110.0 (d, $^1J_{CP} = 94.8$ Hz, PCH), 140.6 (dd, $^1J_{CP} = 35.9$ Hz, $^1J_{CRh} = 30.7$ Hz, PC), 163.8 (dd, $^2J_{CP} = 39.7$ Hz, $^2J_{CRh} = 2.0$ Hz, C), 165.4 (d, $^2J_{CP} = 22.3$ Hz, C), 185.6 (d, $^1J_{CRh} = 78.6$ Hz, CO), 185.6 ppm (dd, $^1J_{CRh} = 53.4$ Hz, $^3J_{CP} = 11.8$ Hz, CO); IR (CH_2Cl_2): $\tilde{\nu}_{CO} = 2058$, 1976 cm^{-1}.

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