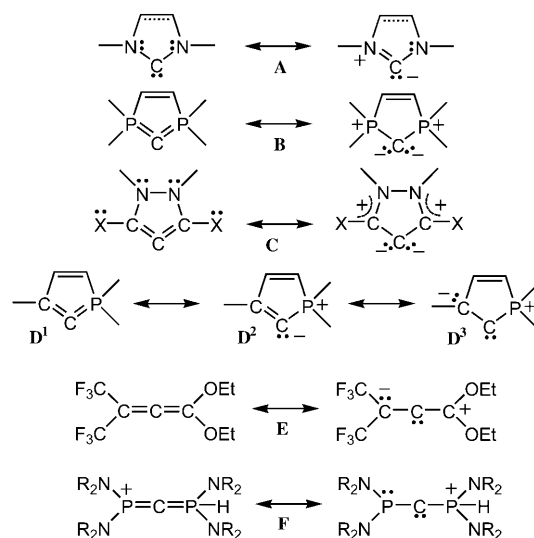


Synthesis and Ligand Properties of a Stable Five-Membered-Ring Vinylidenephosphorane**

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

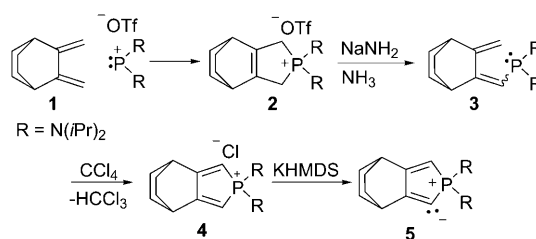
Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of the various systems. Recently, N-heterocyclic carbenes (NHCs) **A** (Scheme 1) have emerged as powerful ligands, largely 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 $\nu_{\text{av}}(\text{CO})$ infrared frequency of $[(\text{L})\text{Rh}(\text{CO})_2\text{Cl}]$ 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 **D**³ 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 vinylidene-



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**.

phosphorane, 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.

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)aminophosphonium triflate gives rise to the phospholenium salt **2** (Scheme 2).^[13] Deprotonation of **2** with NaNH_2 in ammonia



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

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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 $\text{C}=\text{C}-\text{C}=\text{C}$ diene character.

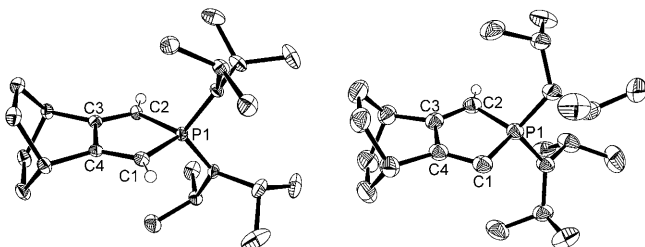


Figure 1. X-ray crystal structures of **4** (left) and **5** (right). Triflate anion (for **4**) and H atoms (for **4** and **5**) are omitted for clarity. Selected bond lengths [Å] and angles [°]: **4**: P1–C1 1.782(3), C1–C4 1.329(4), P1–C2 1.791(2), C2–C3 1.342(3), C3–C4 1.497(4); P1–C1–C4 107.99(19), 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 ^1H 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. = $81\text{--}82^\circ\text{C}$) 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 vinylidene-phosphorane (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 **D**².

The singlet–triplet energy gap of **5** was calculated to be $32.4\text{ kcal mol}^{-1}$, which is smaller than in NHCs ($68.1\text{--}84.8\text{ kcal mol}^{-1}$),^[1] but in the range of those calculated for alkylaminocarbenes ($23\text{--}46\text{ kcal mol}^{-1}$).^[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 $[\text{RhCl}(\text{cod})_2]$ leads to the corresponding complex **6** as a thermally very stable orange solid (m.p. $197\text{--}198^\circ\text{C}$; Figure 3, cod = cycloocta-1,5-diene). The formation of **6** can clearly be ascertained by ^{13}C NMR spectroscopy, in which the central carbon peak moves upfield

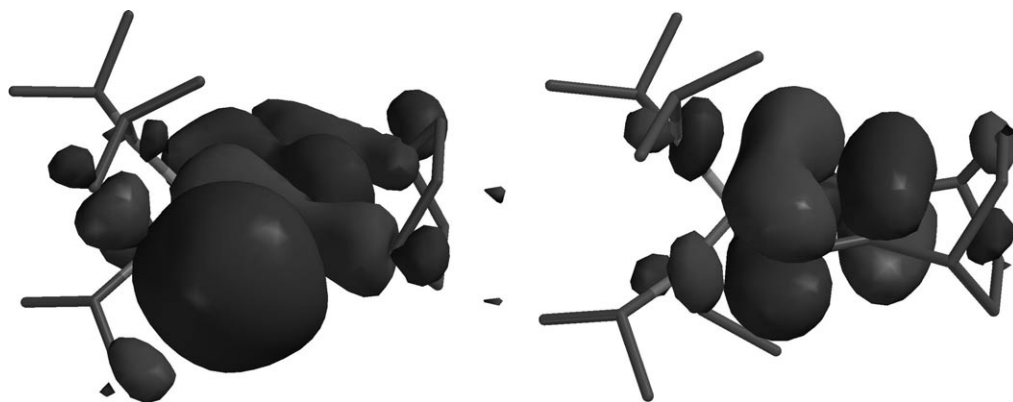


Figure 2. Calculated HOMO (left) and LUMO (right) of **5**.

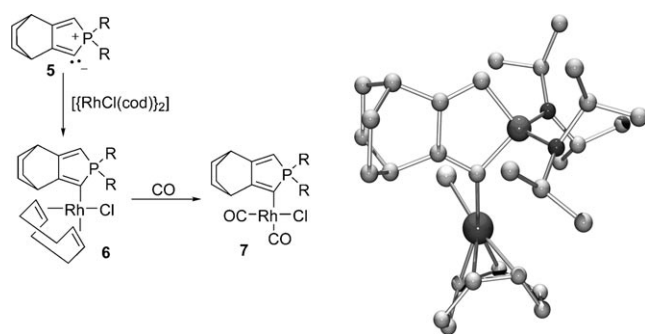


Figure 3. Synthesis of cyclic vinylidenephosphorane rhodium(I) complexes **6** and **7** and X-ray structure of **6**. cod = cycloocta-1,5-diene.

(as is typical for metal complexes of NHCs **A**, carbodiphosphoranes **B**, and bent allenes **C**) to $\delta = 148.0$ ppm (dd, $^1J_{\text{CP}} = 41.5$ Hz, $^1J_{\text{CRh}} = 13.7$ 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** ($2036\text{--}2060\text{ cm}^{-1}$),^[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 than 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. $81\text{--}82^\circ\text{C}$; $^{31}\text{P}\{^1\text{H}\}$ 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, $i\text{Pr}$), 113.7 (d, $^1J_{\text{CP}} = 121$ 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 $[\text{RhCl}(\text{cod})_2]$ (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. $197\text{--}198^\circ\text{C}$; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 25°C , 243 MHz): $\delta = 73.9$ ppm (d, $^2J_{\text{PRh}} = 11.6$ 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, $^3J_{\text{CP}} = 22.3$ Hz, CH_2), 33.6 (CH_2), 36.9 (d, $^3J_{\text{CP}} = 35.5$ Hz, CH), 48.0 (d, $^2J_{\text{CP}} = 5.1$ Hz, NCH), 64.3 (CH), 92.9 (CH), 108.6 (d, $^1J_{\text{CP}} = 89.5$ Hz, PCH), 148.0 (dd, $^1J_{\text{CP}} = 41.5$ Hz, $^1J_{\text{CRh}} = 13.7$ Hz, PC), 163.6 (d, $^2J_{\text{CP}} = 22.8$ Hz, C), 163.9 ppm (d, $^2J_{\text{CP}} = 42.6$ 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. $138\text{--}140^\circ\text{C}$; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 25°C , 243 MHz): $\delta = 73.9$ (d, $^2J_{\text{PRh}} = 8.5$ Hz); ^{13}C NMR (CDCl_3 , 25°C , 151 MHz): $\delta = 23.9$ (d, $^3J_{\text{CP}} = 1.7$ Hz, CH_3), 24.0 (d, $^3J_{\text{CP}} = 3.0$ Hz, CH_3), 24.9 (CH_2), 25.5 (CH_2), 33.1 (d, $^3J_{\text{CP}} = 21.6$ Hz, CH), 37.1 (d, $^3J_{\text{CP}} = 32.9$ Hz, CH), 48.3 (d, $^2J_{\text{CP}} = 5.1$ Hz, NCH), 110.0 (d, $^1J_{\text{CP}} = 94.8$ Hz, PCH), 140.6 (dd, $^1J_{\text{CP}} = 35.9$ Hz, $^1J_{\text{CRh}} = 30.7$ Hz, PC), 163.8 (dd, $^2J_{\text{CP}} = 39.7$ Hz, $^2J_{\text{CRh}} = 2.0$ Hz, C), 165.4 (d, $^2J_{\text{CP}} = 22.3$ Hz, C), 185.6 (d, $^1J_{\text{CRh}} = 78.6$ Hz, CO), 185.6 ppm (dd, $^1J_{\text{CRh}} = 53.4$ Hz, $^3J_{\text{CP}} = 11.8$ Hz, CO); IR (CH_2Cl_2): $\tilde{\nu}_{\text{CO}} = 2058$, 1976 cm^{-1} .

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