*Organometallics* **2006,** *25,* 3541−3543 3541

# Construction of a Stable N-Heterocyclic Phosphenium Cation with an Electron-Rich Framework and Its Complexation to Rhodium

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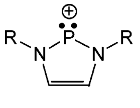
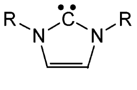
*Received May 28, 2006*

*Summary: The synthesis and characterization of a new N-heterocyclic phosphenium cation captured in a six-membered, electron-rich framework is presented. The cation reacts quantitatively with 1 equiv of Wilkinson's catalyst, Rh(PPh$_3$)$_3$Cl, to form a cationic rhodium−phosphenium complex, the first to be characterized in the solid state. Computational and X-ray diffraction studies support the existence of a strong dπ−pπ bond between rhodium and phosphorus.*

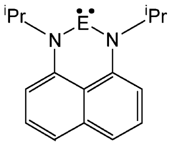
The heteroatom-stabilized, cyclic phosphenium cations **1** are isoelectronic analogues of the N-heterocyclic carbenes (NHCs) **2**. The strong $\sigma$-donor properties of NHCs have led to their now prominent role as ligands for catalytically relevant transition-metal complexes.[1] The fundamental electronic differences between **1** and **2** lead to reciprocal coordination behavior between NHCs and N-heterocyclic phosphenium cations, with their excellent $\pi$-acceptor and poor $\sigma$-donor properties.[2] These features suggest that coordinated phosphenium cations may enhance the electrophilicity of a metal center during catalysis.[3,4] While a number of N-heterocyclic phosphenium cations have been reported, these are dominated by five-membered 1,3,2-diazaphospholenium species (**1**).[2−8] Recently, we reported the successful synthesis of a stable N-heterocyclic carbene possessing a 1,8-bis(alkylamido)naphthalene ($^i$Pr$_2$DAN) framework (**3**).[9] This molecule possesses a novel topology and electronic framework in which a divalent carbon sits in a formally seven-$\pi$-electron, six-membered heterocyclic ring.[10] The utilization of this scaffold to support group 15 compounds, and phosphenium cations in particular, promises to yield novel compounds with applications in coordination chemistry and catalysis.



**1**

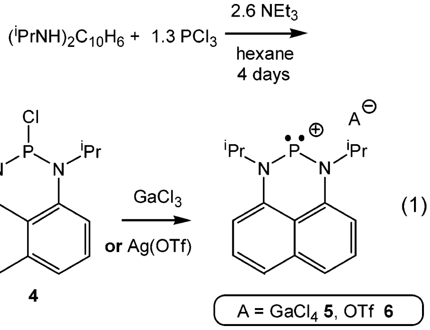


**2**



**3** E = C, Ge, Sn

The diaminochlorophosphine **4** provides a precursor for phosphenium synthesis and was prepared via the reaction of 1,8-bis(isopropylamino)naphthalene with an excess of phosphorus trichloride and triethylamine in hexane at room temperature (eq 1). Compound **4** was obtained as a colorless crystalline solid in excellent yield and exhibited a $^{31}$P NMR chemical shift of 102 ppm, typical of diaminochlorophosphines.[11] The identity of **4** was confirmed through spectroscopic, microanalytical, and single-crystal X-ray analyses.[12] Reaction of **4** with chloride abstraction agents provided ready access to the phosphenium salts [P($^i$PrN)$_2$C$_{10}$H$_6$][GaCl$_4$] (**5**) and [P($^i$PrN)$_2$C$_{10}$H$_6$][OTf] (**6**; OTf = OSO$_2$CF$_3$ (triflate)). For example, addition of GaCl$_3$ to a toluene solution of **4** resulted in immediate precipitation of the dark purple solid **5**, which exhibited a $^{31}$P NMR chemical shift of 239 ppm in CD$_2$Cl$_2$. This value is consistent with the localization of a positive charge at phosphorus and is similar to $^{31}$P NMR chemical shift values obtained for other N-heterocyclic phosphenium cations.[8] Dark red **6** is soluble in arene solvents and has a $^{31}$P NMR chemical shift of 142 ppm



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(12) Characterization and structural details for compound **4** are provided in the Supporting Information.

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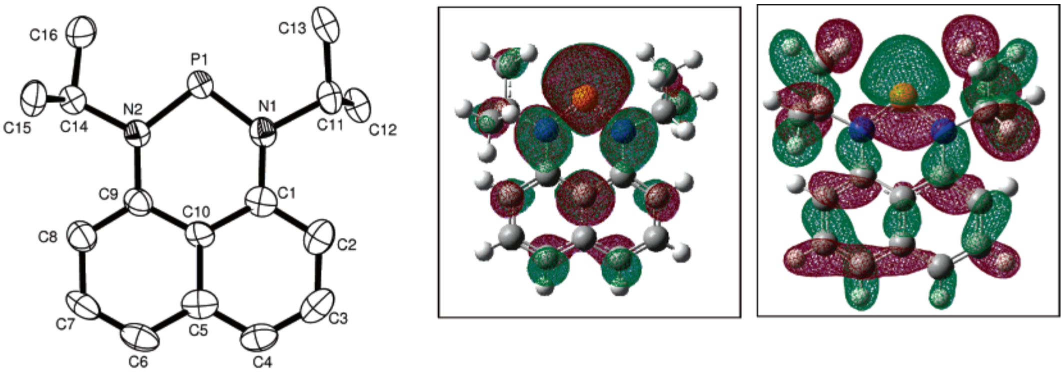
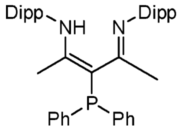


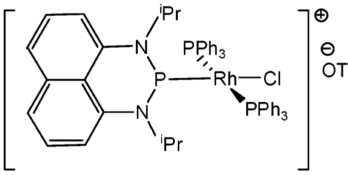
**Figure 1.** Thermal ellipsoid plot showing the molecular structure and atom-numbering scheme for the phosphenium cation in **5**. Hydrogen atoms and the $GaCl_4^-$ anion have been omitted for clarity. The insets show the LUMO (left) and P-centered lone pair HOMO-4 (right) obtained from DFT calculations.

in $C_6D_6$ and 179 ppm in $CD_2Cl_2$, suggesting significant cation/anion contacts in less polar solvents.

The structure of the phosphenium salt $[P(^iPrN)_2C_{10}H_6][GaCl_4]$ (**5**) (Figure 1) displays a well-separated cation−anion pair (closest P···Cl > 4 Å), demonstrating that the $^iPr_2DAN$ ligand is effective at stabilizing the electron-deficient phosphenium center. Associated with the formation of the cation are a contraction of the P−N bonds in **5** (P−N(1) = 1.609(8) Å; P−N(2) = 1.629(7) Å; N(1)−P−N(2) = 105.4(3)°) relative to those in phosphine **4** (P−N(1) = P−N(2) = 1.670(2) Å; N(2)−P(1)−N(1) = 99.7(1)°) and formation of a more planar heterocyclic ring, indicating increased P−N $\pi$-bonding in the cations. The cations in salts **5** and **6** represents a unique example of a six-membered N-heterocyclic phosphenium cation possessing a $\pi$-conjugated carbon backbone.[13] Furthermore, attempts by Burford and co-workers to prepare related $\beta$-diketiminate-supported phosphorus compounds resulted in the isolation of a product in which the phosphorus center added to the backbone of the ligand (**7**).[14] Our use of a 1,8-bis(alkylamido)naphthalene framework prevents this possible reaction pathway.



**7**



**8**

The results of density functional theory calculations[15] on **5** indicate that the nitrogen lone-pairs are delocalized into the P $p_z$-orbital, forming strong $\pi$-bonding interactions in the heterocyclic ring. The lone-pair of electrons localized on P resides in a low-energy (HOMO-4) orbital that is composed of substantial s character, is oriented in the molecular plane, and points away from the ring (Figure 1).

The ability of the $^iPr_2DAN$ phosphenium cation to stabilize catalytically relevant metal complexes is demonstrated by the reaction of the triflate salt $[P(^iPrN)_2C_{10}H_6][OTf]$ (**6**) with Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, in $CH_2Cl_2$ at room temperature to yield the orange metal−phosphenium complex **8**. The reaction was monitored by $^{31}P$ NMR spectroscopy, which showed liberation of free triphenylphosphine along with formation of complex **8** and a small amount of the diaminochlorophosphine **4**. Complex **8** appears as an $AX_2$ spin system consisting of an upfield doublet of doublets for Rh-bonded $PPh_3$ (31 ppm, $^1J_{Rh-P} = 104$ Hz, $^2J_{PP} = 51$ Hz) and a downfield doublet of triplets for the phosphenium (240 ppm, $^1J_{Rh-P} = 326$ Hz, $^2J_{PP} = 51$ Hz). The $^{31}P$ NMR spectrum is consistent with the topology for **8** shown above and is reminiscent of spectra previously reported for phosphenium−rhodium complexes by Baker and co-workers.[3b] A nearly identical $AX_2$ pattern in the $^{31}P$ NMR spectrum is observed when $Rh(PPh_3)_3Cl$ is reacted with the phosphenium gallate salt **5**. A further notable observation upon coordination of the phosphenium cations is a dramatic upfield shift in the $^1H$ NMR resonance for the methine septets of the $NCH(CH_3)_2$ groups from 3.8 ppm in free **6** to 6.0 ppm for **8**. We attribute this to the proximity of the NC*H* protons to the electron-rich metal center.[9]

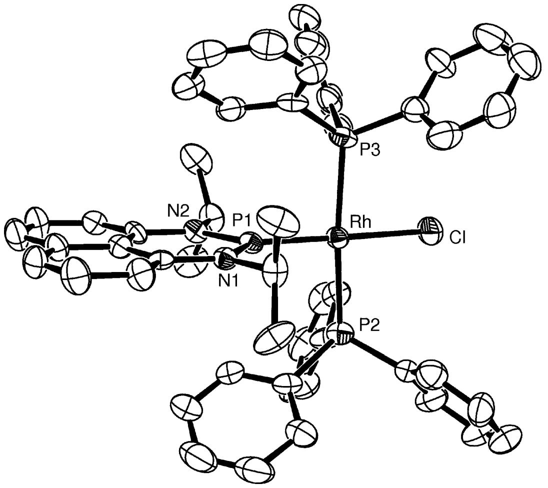


**Figure 2.** Thermal ellipsoid plot showing the molecular structure and partial atom-numbering scheme for the phosphenium−rhodium complex **8**. Hydrogen atoms, the disordered triflate anion, and a disordered solvent molecule have been omitted for clarity.

Red-orange crystals of the phosphenium−rhodium complex **8** were isolated, and single-crystal X-ray analysis produced a structure consistent with the spectroscopic data (Figure 2). This structure, the first solid-state characterization of a phosphenium cation bound to rhodium, displays the shortest reported phosphorus−rhodium(I) bond (Rh−P(1) = 2.089(2) Å).[16] The bound phosphenium exhibits a planar ($\sum$(P angles) = 360.0°), three-coordinate phosphorus center, militating against a stereochemically active lone pair of electrons on the phosphorus atom and consistent with a $\pi$-accepting phosphenium ligand. Visualization

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(13) Six-membered cations derived from 2-phospha-l,3-diazacyclohexanes are reported in: Maryanoff, B. E.; Hutchins, R. T. *J. Org. Chem.* **1972**, *37*, 3475.

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(15) Results of our calculations are presented in the Supporting Information.

of the orbitals of **8** confirmed that there are both $\sigma$- and $\pi$-bonding interactions between Rh and the P center of the phosphenium.[15]

Interestingly, there are only minor changes in the structural features of the coordinated phosphenium cation in **8** (P(1)−N(1) = 1.629(4) Å; P(1)−N(2) = 1.631(5) Å; N(1)−P(1)−N(2) = 106.8(2)°) in comparison to those of the free phosphenium cation in **5**. The planar phosphenium ligand is perpendicular to the square plane of the Rh center (∑(Rh angles) = 359.9°), which positions the N$^i$Pr groups on either side of this plane. Consistent with the $^1$H NMR observations, the $^i$Pr substituents are oriented to position the methine protons to point directly above and below the rhodium center. The Rh−Cl and Rh−PPh$_3$ bond lengths (Rh−P(2) = 2.354(2) Å; Rh−P(3) = 2.363(1) Å; Rh−Cl = 2.351(2) Å) are similar to those observed in the solid-state structure of the red form of Wilkinson's catalyst.[17] The P(2)−Rh−P(3) (172.81(6)°) and P(1)−Rh−Cl (177.20(6)°) angles in **8** deviate slightly from linearity, most likely as a consequence of steric crowding around the rhodium center.

In conclusion, the 1,8-bis(alkylamido)naphthalene framework has been shown to be effective at stabilizing a low-coordinate, electrophilic phosphorus center, despite the low steric bulk of the substituents at nitrogen. The novel topology and electronic framework of the resultant phosphenium cation make it an ideal ligand for use in transition-metal coordination chemistry, as illustrated by the successful isolation of a rhodium−phosphenium complex. Both computational and structural features support combined $\sigma$- and $\pi$-bonding interactions that produce a remarkably short Rh−P bond. Studies are currently underway to assess the catalytic potential of the complex **8** and related phosphenium complexes of other late-metal centers.

**Acknowledgment.** This work was supported by NSERC. H.A.S. is the recipient of an NSERC Postdoctoral Fellowship. G.D. thanks the Centre of Excellence in Integrated Nanotools for access to computational resources.

**Supporting Information Available:** Text giving experimental procedures and characterization data for new compounds, the structural details for compounds **4**, **5**, and **8**, a figure for the structure of **4**, and text and tables giving details of the DFT calculations on **5** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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