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ORGANOMETALLICS
Note

Template Synthesis of Donor-Functionalized NX-Carbenes (X = P, Si)

Insun Yu, Christopher J. Wallis, Brian O. Patrick, and Parisa Mehrkhodavandi*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada

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Summary: Donor-functionalized (*phosphino*)(*amino*)- *and* (*silyl*)(*amino*)*carbenes are generated via nucleophilic attack at the carbon atom of a coordinated isocyande on a piano-stool iron*(*II*) *complex. The template synthesis methodology involves the formation of ylidene complexes, which are reduced to yield the desired carbene complexes. The electronic properties of the resulting carbene complexes are similar and indicate that in the* (*phosphino*)(*amino*)*carbene the phosphine lone pair is not interacting with the carbene carbon and is available for further reactivity.*

Changing the carbon-bound substituents of stable singlet carbenes can have a profound effect on their steric and electronic properties as ligands.[1,2] A large collection of N-heterocyclic carbenes (NHCs) with varied N-bound substituents and their donor-functionalized analogues have been reported.[1] Whereas NHCs use two C-bound donors to stabilize the carbene (push−push carbenes), early work on acyclic carbenes[2] and recent expansion of the field to stable cyclic (alkyl)(amino)carbenes (CAACs)[3a] have demonstrated that "push−spectator" carbenes (NX-carbenes; X = C, P, Si) can be stronger donors than NHCs and, with a judicious choice of alkyl substituents, can lead to efficient catalysis.[3b]

P- or Si-functionalized carbenes remain largely unexplored as ligands,[2a,d,4] although rare examples were shown to be excellent ligands for rhodium.[5,6] Challenges in the synthesis of the free carbenes and in the formation of complexes via ligand substitution pathways have severely limited the utility of these species as ligands. Donor-functionalized analogues of these carbenes are hitherto unknown.

Herein we report donor-functionalized (phosphino)-(amino)- and (silyl)(amino)carbenes formed using template synthesis.[7,8] Recently, template synthesis via nucleophilic attack at the carbon atom of a coordinated isocyanide[9,10] has been used to form M-NHC complexes with an H substituent at the N-position. These complexes were further utilized to form the first NHC-containing macrocycles,[11] but to our knowledge this strategy has not been used for P- or Si-substituted carbenes. Our general methodology involves nucleophilic attack on a chelating isocyanide-triphenylphosphine ligand coordinated to a CpFe(CO) fragment, complex **1**, to form ylidene complexes followed by protonation of the resulting imine to yield the desired carbene complexes (Scheme 1).[12,13]

The reaction of the iron isocyanide complex **1**[12] with 1 equiv of $KPPh_2$ or $KSiPh_3$ in THF at −78 °C affords the corresponding iron ylidene complexes **2** and **3**, respectively.[14]

*Corresponding author. E-mail: mehr@chem.ubc.ca.

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(13) Liu et al. reported a diaminocarbene-phosphine complex via the well-known nucleophilic addition of *n*-propylamine to a coordinated isocyanide complex, **1** (ref 12a). We have found analogous reactions with the less nucleophilic $HPPh_2$ and $HSiPh_3$ to be impossible.

(14) Complex **3** was obtained in 28% isolated yield along with an unidentified byproduct (10% isolated yield).

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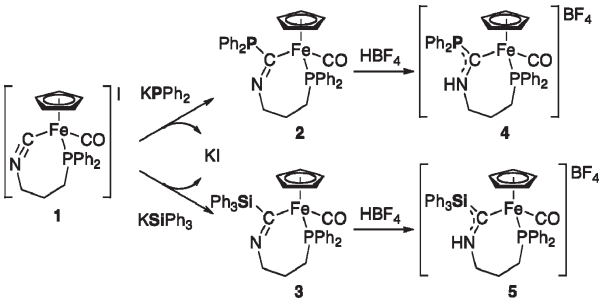
Scheme 1. Methodology for the Template Synthesis of Donor-Functionalized NX-Carbenes (X = P, Si)

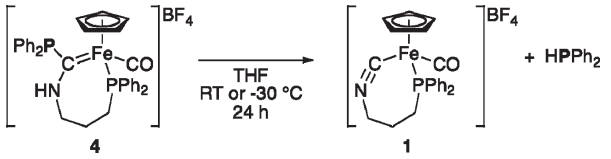


The molecular structures of **2** and **3** were determined by single-crystal X-ray crystallography and show octahedral piano-stool iron centers similar to that of the reported isocyanide complex **1**.[12] The metal-bound carbon atoms in **2** and **3** are planar. The Fe−$C_{ylidene}$ distances in **2** and **3** of 2.005(3) and 1.997(3) Å are significantly longer than the Fe−$C_{isocyanide}$ distance reported for **1** (1.77 Å), indicating that the latter has a greater bond order than the Fe−$C_{ylidene}$ bonds. In contrast to the sole reported Rh-NPC complex[6a,b] the ylidene-bound phosphorus atom in **2** is not coordinated to the metal. In this case η^2 coordination is not expected because complex **2** features a coordinatively saturated iron center.[15]

The reaction of the ylidene complexes **2** and **3** with an equimolar amount of HBF_4 in $CHCl_3$ at −35 °C forms the corresponding carbene complexes **4** and **5** (Scheme 1). The (silyl)(amino)carbene complex **5** was obtained in 97% isolated yield; however, although the analogous (phosphino)-(amino)carbene complex **4** is formed quantitatively, it decomposes in solution and more slowly in the solid state (see below). The characteristic downfield N-*H* ^{1}H NMR resonances at 9.64 and 10.62 ppm confirm the formation of the carbene complexes **4** and **5**, respectively; the resonance for the related diaminocarbene iron complex appears at 7.97 ppm.[12a,13] The $^{13}C\{^1H\}$ NMR spectra for **4** and **5** show significantly deshielded Fe-$C_{carbene}$ signals at 276.4 and 299.4 ppm. These downfield signals are indicative of push−spectator carbenes;[2a] the $^{13}C\{^1H\}$ NMR signals for reported complexes of push−push carbenes are significantly more upfield.[6a,b] The (silyl)(amino)carbene fragment does not behave as a push−pull carbene and instead is analogous to aryl- or alkylamino carbenes.[6c]

A THF solution of the (phosphino)(amino)carbene complex **4** reverts to the isocyanide complex **1** and diphenylphosphine in a few hours, although traces of **1** are evident after only a few minutes at room temperature (Scheme 2).[16] The $^{31}P\{^1H\}$ NMR spectrum of **4** shows two sets of doublets at 38.1 and 51.0 ppm for the Fe- and carbene-bound phosphines, respectively ($^3J_{P-P}$ = 12 Hz). Over time, these signals disappear and new signals for Fe-*P* in **1** (54.4 ppm) and diphenylphosphine (−40 ppm) appear. The reaction likely occurs via intramolecular deprotonation of the cyclic amine by the carbene-bound diphenylphosphine, followed by phosphine elimination.[6d] This indicates that, unlike the amino functionality, there is no π contribution from the phosphino moiety; it retains its lone pair and is able to deprotonate the amine. A similar reaction is not observed with the analogous diaminocarbene complex.[12a,13]

Scheme 2. Conversion of Carbene Complex 4 to 1 and $HPPh_2$



The carbonyl stretching frequencies of complexes **2**−**5** were used to gauge the electronic differences between the ligands. The ylidene complexes **2** and **3** had ν_{CO} stretches at 1912 and 1915 cm^{-1}, respectively, while the carbene complexes **4** and **5** had stretches at 1956 and 1959 cm^{-1}. Although the ylidene complexes **2** and **3** are neutral while the carbene complexes **4** and **5** are cationic and thus a direct comparison between them is not meaningful, the progressive increase in the stretching frequencies of the latter suggests a decreased electron density on the metal and corresponds to the decrease in π electron contribution to the carbene center as substituents are changed from N (ν_{CO} 1949 cm^{-1}) to P to Si.

In this work we have described the first examples of donor-functionalized NX-carbenes (X = P, Si), which were generated via a two-step template synthesis on a piano-stool iron(II) complex. Spectroscopic evaluation of these complexes indicates that although they are both "push−spectator" carbenes, they are nevertheless electronically distinct. This work opens up avenues for template synthesis of currently inaccessible acyclic and cyclic carbenes. We are conducting computational studies to elucidate the electronic properties of these systems and will expand this methodology to a series of acyclic and cyclic carbene complexes on Ru and Rh centers.

Experimental Section

General Methods. Unless otherwise specified all procedures were carried out using standard Schlenk techniques or in an MBraun glovebox. A Bruker Avance 300 MHz spectrometer and Bruker Avance 400dir MHz spectrometer were used to record the ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectra. ^{1}H NMR chemical shifts are given in ppm versus residual protons in deuterated solvents as follows: δ 5.32 for CD_2Cl_2 and δ 7.27 for $CDCl_3$. $^{13}C\{^1H\}$ NMR chemical shifts are given in ppm versus residual ^{13}C in solvents as follows: δ 54.00 for CD_2Cl_2 and δ 77.23 for $CDCl_3$. $^{31}P\{^1H\}$ NMR chemical shifts are given in ppm versus 85% H_3PO_4 set at 0.00 ppm. A Waters/Micromass LCT mass spectrometer equipped with an electrospray (ESI) ion source and a Kratos-50 mass spectrometer equipped with an electron impact ionization (EI) source were used to record low-resolution and high-resolution spectra. IR spectra were obtained on a Thermo Scientific FT-IR spectrometer (Nicolet 4700). Diffraction measurements for X-ray crystallography were made on a Bruker X8 APEX II diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software of Bruker-AXS. Unless specified, all non-hydrogens were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions but were not refined. CHN analysis was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of unknown samples was determined by using a

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(16) The decomposition occurs at room temperature as well as at −35 °C over several hours. The phosphine release from **6** and formation of **1** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (see SI). The direct reaction of isocyanide complex **1** with $HPPh_2$ does not result in the formation of carbene complex **7**.

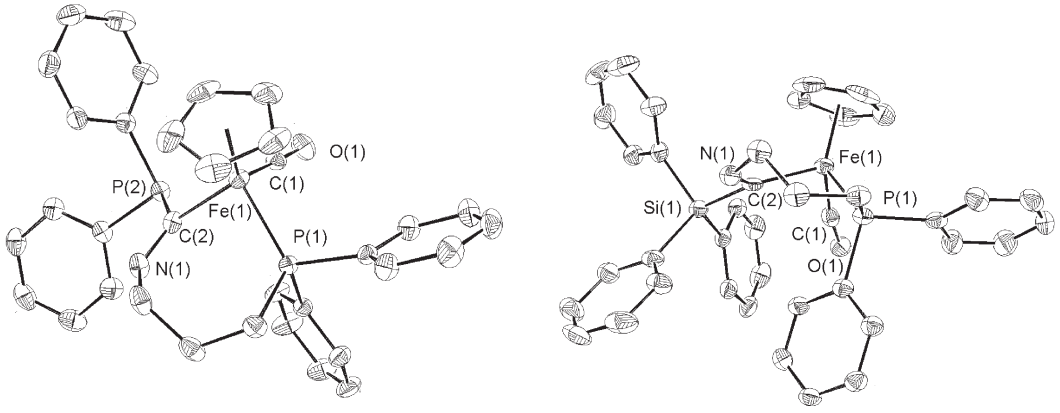

Figure 1. Molecular structures of **2** (left) and **3** (right) (thermal ellipsoids at 35% probability). Selected bond lengths (Å) and angles (deg): **2** C1−Fe1 1.732(5), C2−Fe1 1.997(3), P1−Fe1 2.173(5), C1−O1 1.158(2), C2−N1 1.262(2), C2−P2 1.885(2), P2−C2−Fe1 111.7(9). **3** C1−Fe1 1.741(3), C2−Fe1 2.005(3), P1−Fe1 2.186(9), C1−O1 1.163(3), C2−N1 1.289(4), C2−Si1 1.913(3), Si1−C2−Fe1 122.6(8).

calibration factor. The calibration factor was determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition.

All solvents were degassed and dried using 3 Å molecular sieves in an MBraun solvent purification system. THF, Et_2O, and C_6H_6 (C_6D_6) were further dried over Na/benzophenone and distilled under N_2. CH_3CN (CD_3CN), CH_2Cl_2 (CD_2Cl_2), and $CHCl_3$ ($CDCl_3$) were dried over CaH_2 and vacuum-transferred to a Strauss flask and then degassed through a series of freeze−pump−thaw cycles. Deuterium-labeled NMR solvents were purchased from Cambridge Isotope Laboratory. Other chemicals and solvents were purchased from Aldrich, Fisher, Alfa Aesar, or Strem and were used without further purification. 1-Azido-3-chloropropane, *N*-(3-chloroprophyl)triphenylphosphinimine, *N*-(3-(diphenylphosphino)propyl)triphenylphosphinimine, $CpFe(CO)_2I$, complex **1**,[1] $KPPh_2$,[2] and $KSiPh_3$[3] were prepared according to literature procedures.

Synthesis of Complex 2. A solution of $KPPh_2$ was prepared by adding a THF solution (10 mL) of diphenylphosphine (0.70 g, 3.78 mmol) to potassium metal (0.18 g, 4.62 mg/atom) in THF (10 mL) dropwise at −78 °C, and the resulting solution was stirred at −78 °C for 12 h. The solution of $KPPh_2$ was filtered at room temperature through Celite to remove the excess potassium metal. The filtered solution was added dropwise to a suspension of the iron(II) isocyanide-phosphine complex (**1**) (2.00 g, 3.78 mmol) in THF (30 mL) at −78 °C, and the reaction mixture was stirred at room temperature overnight. Half of the solvent (ca. 15 mL) was removed *in vacuo*. The resulting yellow suspension was filtered, and the collected precipitate was washed twice with a minimal amount of THF. The yellow precipitate was redissolved in benzene, and the solution was filtered through Celite to remove KI. The solvent was removed *in vacuo* to yield complex **2** as a yellow powder (1.78 g, 80%). X-ray quality yellow needles were grown in $CDCl_3$ at room temperature: IR ($CDCl_3$) 1912 cm^{-1} (ν_{CO}); ^1H NMR (300 MHz, $CDCl_3$) δ 1.52 (m, 1 H), 2.00−2.25 (m, 1 H), 2.73 (td, J = 12.97, 2.88 Hz, 1 H), 3.02−3.17 (m, 1 H), 3.63 (t, J = 10.51 Hz, 1 H), 3.91 (d, J = 1.37 Hz, 5 H), 4.57 (dd, J = 10.43, 7.96 Hz, 1 H), 7.10−7.23 (m, 5 H), 7.32−7.43 (m, 6 H), 7.44−7.54 (m, 5H) 7.79 (m, 2H), 7.86−7.98 (m, 2H); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ 23.04 (s, 1 C), 36.97 (d, J = 20.08 Hz, 1 C), 56.05 (d, J = 19.64, 1 C), 84.00 (s, 5C), 126.64−143.15 (m, 24 C), 214.30 (dd, J = 70.57, 23.96 Hz, −C=N−), 221.04 (dd, J = 16.91, 20.42 Hz, −CO); $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$) δ 31.51 (d, J = 23.76 Hz, −C-PPh_2), 57.28 (d, J = 23.76 Hz, Fe-PPh_2−); MS (ESI, m/z) calcd mass 588.1309, obsd mass 588.1319 (M+). (This compound slowly decomposes in the solid state at −35 °C; EA was not possible.)

Synthesis of Complex 3. Triphenylsilylpotassium ($KSiPh_3$) was obtained as a yellow precipitate by reacting a solution of hexaphenyldisilane (0.40 g, 0.76 mmol) in Et_2O (10 mL) with potassium metal (0.12 g, 3.04 mg/atom) at 35 °C under static vacuum for 48 h. The solvent was removed *in vacuo*, and the yellow residue was dissolved in THF (20 mL). This solution was filtered and added dropwise to a suspension of the iron(II) isocyanide-phosphine complex (**1**) (0.79 g, 1.52 mmol) in THF (50 mL) at −78 °C, and the reaction mixture was warmed to room temperature with stirring overnight. The solvent was removed *in vacuo*, the residue redissolved in benzene, and the solution filtered through Celite to remove KI. The solvent was again removed *in vacuo* to collect a dark yellow precipitate. In order to purify the product, the precipitate was left as a suspension in Et_2O (20 mL) at room temperature overnight and then filtered. The filtrate, containing a major amount of byproduct and a small amount of complex **3**, was removed as a brown solution. These steps were repeated four times until complex **3** was isolated as a yellow solid (0.282 g, 28%). X-ray quality orange prisms of complex **3** were grown in $CDCl_3$ at −35 °C: IR ($CDCl_3$) 1915.17 cm^{-1} (ν_{CO}); ^1H NMR (400 Hz, $CDCl_3$) δ 1.75−2.09 (m, 2 H), 2.57−2.80 (m, 2 H), 4.03 (t, J = 10.28 Hz, 1 H), 4.22 (s, 5H), 5.02−5.14 (m, 1 H), 7.11−7.23 (m, 4 H), 7.29−7.40 (m, 13 H), 7.41−7.55 (m, 2 H), 7.67−7.79 (m, 5H); $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$) δ 22.64 (s, 1C), 34.52 (d, J = 20.99 Hz, 1C), 59.57 (d, J = 5.65 Hz, 1C), 83.40 (s, 5C), 127.22−140.44 (m, 30C), 219.49 (d, J = 36.33 Hz, −CO), 234.38 (d, J = 16.15 Hz, −C=N−); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 58.37 (s, 1P); MS (ESI, m/z) calc mass 662.1731, obsd mass 662.1736 (M+). Anal. Calcd for **3** ($[C_{40}H_{36}FeNOPSi]\cdot 1/2[CHCl_3]$): N, 1.94; C, 67.44; H, 5.10. Found: N, 2.54; C, 67.34; H, 5.29.

Synthesis of Complex 4. A solution of complex **2** (0.61 g, 1.03 mmol) in $CHCl_3$ (10 mL) was cooled to −35 °C, and an equimolar solution of 6.2 M HBF_4 (0.17 mL) in diethyl ether was added dropwise using a microsyringe. The solution was warmed to room temperature for 5 min, the solvent was removed *in vacuo*, and complex **4** was collected as a yellow solid. To separate complex **4** from decompostion products iron(II) isocyanide-phosphine (**1**) and diphenylphosphine, the product was suspended in THF overnight at room temperature. The suspension was filtered through a frit to collect the product **4** (0.208 g, 30%): IR ($CDCl_3$) 1955.87 cm^{-1} (ν_{CO}); ^1H NMR ($CDCl_3$) δ 1.37 (br s., 1 H), 2.20−2.48 (m, 1 H), 3.10−3.41 (m, 2 H), 4.17 (s, 6 H), 4.29 (br s, 1 H), 7.22 (br s., 2 H), 7.31−7.39 (m, 4 H), 7.43−7.55 (m, 6 H), 7.60 (d, J = 6.04 Hz, 3 H), 7.70 (d, J = 9.06 Hz, 2 H), 7.87 (t, J = 7.00 Hz, 2 H), 9.64 (br s, 1 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 23.68 (br s, 1 C), 34.94

(d, J = 24.48 Hz, 1 C), 51.47 (br s, 1 C), 85.93 (s, 5C), 128.62−139.56 (m, 24 C), 217.17 (dd, J = 19.58, 8.97 Hz, −CO), 276.39 (dd, J = 61.20, 23.66 Hz, =C-NH−); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 38.05 (d, J = 11.88 Hz, −C-PPh_2), 50.98 (d, J = 11.88 Hz, Fe-PPh_2−); MS (ESI, m/z) calcd mass 588.1309, obsd mass 588.1298 (M+). (This compound slowly decomposes in the solid state at −35 °C and in solution; EA was not possible.)

Synthesis of Complex 5. A solution of HBF_4 (6.2 M, 0.012 mL, 0.074 mmol) in Et_2O was added to a solution of complex **3** (0.05 g, 0.08 mmol) in $CHCl_3$ (5 mL) at −35 °C. The reaction mixture was stirred at room temperature for 1 h. The solvent was then removed *in vacuo*. Et_2O was added to the residue to precipitate complex **5** as a yellow solid (0.058 g, 97%): IR ($CDCl_3$) 1958.83 cm^{-1} (ν_{CO}); ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (br s, 1 H), 2.23−2.53 (m, 1 H), 2.90 (t, J = 12.91, 1 H), 3.25−3.45 (m, 1 H), 4.40 (br s, 6 H), 4.50 (br s, 1 H), 6.95−7.14 (m, 3 H), 7.26−7.77 (m, 22 H), 10.62 (br s, 1 H); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ 23.09 (s, 1C), 34.99 (d, J = 22.61 Hz, 1C), 54.28 (br s, 1C), 85.80 (s, 5C), 127.86−138.89 (m, 30C), 216.45 (d, J = 32.29 Hz, −CO), 299.38 (br s, =C-NH−); $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$) δ 55.42; MS (ESI, m/z) calcd mass 662.1732, obsd mass 662.1747 (M+). Anal. Calcd for **5** ($C_{40}H_{37}BF_4FeNOPSi$): N, 1.87; C, 64.11; H, 4.98. Found: N, 2.17; C, 64.24; H, 5.21.

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Supporting Information Available: Experimental and crystallographic details as well as observation of the decomposition of **7** to **1** and $HPPh_2$. This material is available free of charge via the Internet at http://pubs.acs.org.