Donor-Stabilized Silyl Cations. 10. Pentacoordinate Siliconium-Ion Salts with a Triphenylphosphinimino-*N* Ligand Group: Two-Bond P−N−Si Coupling as a Measure for Coordination Strength[1]

Akella Sivaramakrishna,[†] Inna Kalikhman,*,[†] Evgenia Kertsnus,[†]
Alexander A. Korlyukov,[‡] and Daniel Kost*,[†]

*Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel, and
A. N. Nesmeyanov Institute of Organoelement Compounds, Vavilov Street 28, 119991 Moscow, Russia*

A new donor group, triphenylphosphinimino, is described as a ligand in pentacoordinate siliconium halide dichelates, $[XSiL_2]^+hal^-$, where L is the bidentate ligand $-OC(CH_2Ph)=NN(=PPh_3)-$, X = Me, C_6H_{11}, i-Bu, CH_2Cl, $CHCl_2$, Cl, Br, and hal = Cl, Br. The complex **16** (X = Me, hal = Cl) was characterized by crystal structure analysis, and the others were characterized by NMR spectroscopy and elemental analysis. The phosphinimino ligand is a stronger donor than previously studied dimethylamino and isopropylidenimino ligands, causing all of the complexes to be pentacoordinate siliconium-halide salts in the crystal as well as in solution. Two-bond $^{31}P-N-^{29}Si$ coupling constants across the N→Si dative bond increase with increasing monodentate-ligand electron-withdrawing power and may serve as a criterion for coordination strength.

Introduction

Hexacoordinate silicon compounds have recently been shown to interconvert with pentacoordinate complexes. Sometimes this is due to reversible cleavage of the N→Si dative bond,[1,2] and in other cases an irreversible transformation was observed.[3,4] We have reported on the ionization of neutral hexacoordinate silicon dichelates (**1**) in solution, to the corresponding pentacoordinate siliconium-ion salts (**2**), under suitable conditions (eq 1).[5,6]

1 ⇌ **2**   (1)

X, R = Me, Ph, PhCH$_2$

3, R, X = Me, Ph, PhCH$_2$ **4**, X = Me, Ph, PhCH$_2$
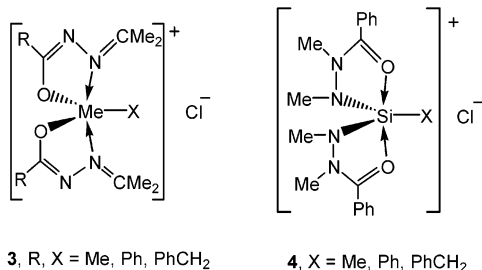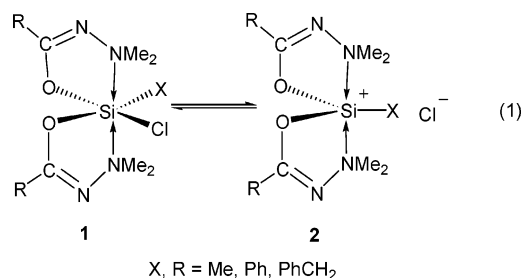
The extent of ionization depends on a variety of parameters: the nature of the solvent, temperature, counterion, and ligand strength. We have recently shown that the isopropylideneimino

group in **3** acts as a stronger donor than dimethylamino in **1** and **2**, by observing that ionization is complete in CDCl$_3$ solutions of **3** at room temperature, while equally substituted **1** and **2** are hexacoordinate (**1**) and do not ionize.[7,8] This is also evident from the significantly shorter N→Si distances in **3**, relative to analogous **2**, in the solid state.[7] Likewise, the oxygen donor in **4** was found to cause complete ionization in solution and in the solid state.[9] Investigation of the effect of ligands upon the ionization process led to the preparation and study of a new class of silicon complexes: those with a triphenylphosphinimino-*N* ligand group, which are the subject of the present report.[10] The new ligand was expected, and indeed was found, to be superior in terms of donor strength, in comparison with the other nitrogen-donor ligands (in **2** and **3**), due to its ylide

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(9) Kalikhman, I.; Krivonos, S.; Lameyer, L.; Stalke, D.; Kost, D. *Organometallics* **2001**, *20*, 1053.

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* To whom correspondence should be addressed. E-mail: kostd@bgumail.bgu.ac.il.

† Ben-Gurion University of the Negev.

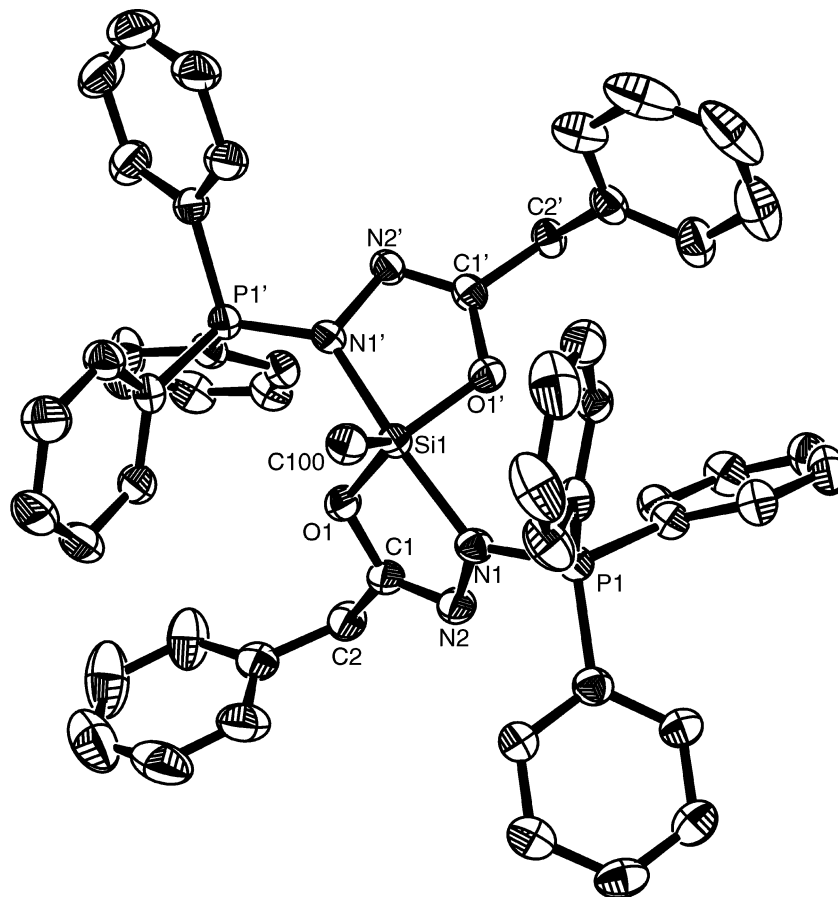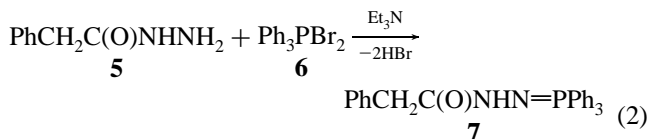‡ A. N. Nesmeyanov Institute of Organoelement Compounds.

Figure 1. Molecular structure of **16** in the solid state, depicted at the 50% probability level. Hydrogens, chloride anion, and disordered solvent molecules have been omitted.

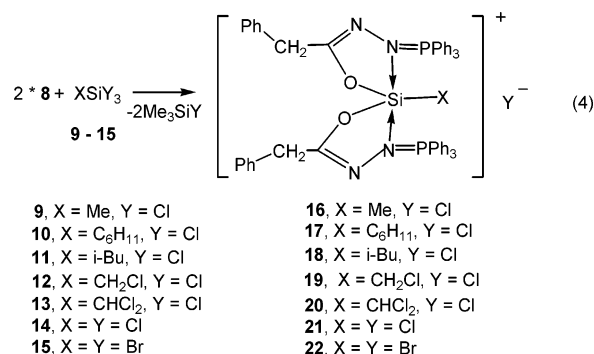character[11,12] and the resulting excess electron density on nitrogen.

Results and Discussion

N-Phenylacetamidotriphenylphosphinimine (**7**) was prepared from phenylacethydrazide (**5**) and triphenylphosphine dibromide (**6**) as described previously for the benzhydrazide analogue (eq 2).[11–13] It was then converted to the *O*-trimethylsilyl derivative (*E,Z* isomer mixture of **8**) by reaction with trimethylsilyl chloride in the presence of Et$_3$N (eq 3).

$$\text{PhCH}_2\text{C(O)NHNH}_2 + \text{Ph}_3\text{PBr}_2 \xrightarrow[-2\text{HBr}]{\text{Et}_3\text{N}}$$
$$\textbf{5} \qquad\qquad\qquad \textbf{6}$$
$$\text{PhCH}_2\text{C(O)NH}{=}\text{PPh}_3 \quad (2)$$
$$\textbf{7}$$

$$\textbf{7} + \text{Me}_3\text{SiCl} \xrightarrow[-\text{HCl}]{\text{Et}_3\text{N}} \text{PhCH}_2\text{C(OSiMe}_3){=}\text{NN}{=}\text{PPh}_3 \quad (3)$$
$$\textit{E,Z}\text{-}\textbf{8}$$

A transsilylation reaction of **8** with excess alkyl trichlorosilanes (**9–13**) or tetrahalosilanes (**14**, **15**, eq 4) afforded exclusively ionic pentacoordinate silicon dichelate chloride (or bromide) salts (**16–22**) in high yield. Structural evidence for **16** comes from its single-crystal X-ray diffraction analysis and its ^{29}Si, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The structures of

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17–22 are likewise obtained from their NMR spectral analyses and from the obvious analogy with **16**.

$$2 * \textbf{8} + \text{XSiY}_3 \xrightarrow[-2\text{Me}_3\text{SiY}]{} \left[\begin{array}{c} \text{structure} \end{array} \right]^{+} Y^{-} \quad (4)$$
$$\textbf{9 - 15}$$

9, X = Me, Y = Cl	**16**, X = Me, Y = Cl
10, X = C$_6$H$_{11}$, Y = Cl	**17**, X = C$_6$H$_{11}$, Y = Cl
11, X = i-Bu, Y = Cl	**18**, X = i-Bu, Y = Cl
12, X = CH$_2$Cl, Y = Cl	**19**, X = CH$_2$Cl, Y = Cl
13, X = CHCl$_2$, Y = Cl	**20**, X = CHCl$_2$, Y = Cl
14, X = Y = Cl	**21**, X = Y = Cl
15, X = Y = Br	**22**, X = Y = Br

The molecular structure of **16** within the crystal is depicted in Figure 1, and selected bond lengths and angles are listed in Table 1, along with those of equally substituted compounds with other donor groups, namely, N=CMe$_2$ (**3**, R = Ph, X = Me, with triflate counterion)[7] and NMe$_2$ (**2**, R = Ph, X = Me, with triflate counterion),[6a] for comparison. It is evident that the geometry of **16** corresponds to a slightly distorted trigonal bipyramid (TBP), with nitrogen atoms occupying the axial positions.

The crystal data in Table 1 provide evidence for the stronger donor ability of the triphenylphosphinimino donor group in the present compounds, relative to the dimethylamino and isopropylideneimino donors in **2** and **3**, respectively. The dative N→Si bonds in **16** are substantially shorter than those in its analogues **2** and **3**, direct evidence for the stronger coordination (Table

Table 1. Selected Bond Lengths (Å) and Angles (deg) from the Crystal Structure of 16, Compared with Those from Analogous Complexes 2[6] and 3[7] (R = Ph, X = Me) with Different *N*-Donor Groups

	compound (donor group) [anion]		
	16 (N=PPh$_3$) [Cl$^-$]	**3**[7] (N=CMe$_2$) [OTf$^-$]	**2**[6] (NMe$_2$) [OTf$^-$]
	Bond Lengths		
Si−N	1.902(3), 1.916(3)	1.9337(17), 1.9659(17)	1.9665(17), 1.9681(19)
Si−O	1.696(3), 1.699(2)	1.6747(14), 1.6811(14)	1.6844(15), 1.6964(14)
Si−C	1.8623(13)	1.834(2)	1.835(2)
	Angles		
NSiN	164.84(13)	176.44 (7)	154.78(8)
OSiO	122.44(12)	120.85(8)	136.27(8)
OSiC	118.59(12)	117.82(9)	113.54(10)
	118.96(11)	121.26(9)	110.17(10)
OSiN	89.32(12)	90.42(7)	83.94(7)
	83.04(11)	83.58(7)	87.18(7)
CSiN	98.51(10)	98.62(9)	101.05(10)
	96.66(10)	94.93(9)	104.14(9)

1). As a result, the other bonds to silicon are weaker in **16** relative to **2** and **3**, as evident from the relatively longer Si−O and Si−C bonds.

Examination of the bond angles in Table 1 reveals a significant difference only in the structures of **16** and **3** in comparison with **2**. The former have bond angles quite close to the angles required by a TBP geometry, while **2** is significantly more distorted from the ideal TBP.[6] This is best seen in Table 1 by comparison of the equatorial bond angles: the O−Si−O and O−Si−C angles in **16** and **3** are near the required 120°, whereas in **2** they are very different and correspond to a geometry about midway between TBP and square pyramid.[6b]

Table 2 lists selected multinuclear NMR data from the various spectra of the triphenylphosphinimino complexes. The ^{29}Si chemical shifts for the alkyl-substituted compounds (**16**−**18**) are all near −78 ppm, and they shift gradually to higher field as the ligands become more electron-withdrawing. All of these ^{29}Si chemical shifts are well within the range characteristic of pentacoordination and, hence, support the proposed ionic structures (eq 4).

The fact that all of the new triphenylphosphinimino complexes are pentacoordinate in solution indicates that the donor ability of the new ligand is greater than those of the previously reported complexes **2**[6a] and **3**.[7,8] In the latter, the difluoro and dichloro complexes were completely hexacoordinate in solution (no observable dissociation), and in **3**, with X = Br (and bromide counterion), a temperature-dependent equilibrium dissociation was found. In contrast, **21** and **22** are found to be completely dissociated in CDCl$_3$ solution at ambient temperature. The ionic nature of **16**−**22** is further supported by the fact that they are insoluble in toluene, whereas essentially all of the neutral hexacoordinate silicon compounds studied to date are soluble in this solvent, as long as they do not ionize.[14]

Of particular interest in Table 2 are the coupling constants observed through the N→Si dative bond,[15] between ^{31}P and ^{29}Si. For each of the triphenylphosphinimino complexes listed in Table 2 the ^{29}Si{^{1}H} resonance is split into a triplet, due to coupling to the two homotopic ^{31}P nuclei.[16] For the alkyl-substituted compounds **16**−**18**, the two-bond coupling constants

are essentially equal, at a relatively small value: 5.1−5.7 Hz. This interaction increases gradually in the compounds with the more electron-withdrawing ligands, **19**−**22**. It appears that in the presence of the electron-withdrawing ligands coordination is stronger than in the alkyl complexes **16**−**18**, causing significantly greater two-bond coupling constants. The effect of the X-ligands on the P−N−Si coupling constants has been correlated with the coordinative shift ΔSi, the difference between δ^{29}Si of the complex and the corresponding tetracoordinate analogue.[17] In the present case the chemical shift for XSiCl$_3$ was taken as reference.[18] ΔSi represents the change in the ^{29}Si chemical shift of the complex caused by coordination, in the presence of the X ligand. Indeed, the coupling constants across the N→Si bond correlate smoothly with the corresponding ΔSi shifts, as shown in Figure 2. The monotonic change of ^2J(^{31}P−N−^{29}Si) as a function of ΔSi (Figure 2) suggests that, like the ^{29}Si shifts, which are known to move to higher field with increasing coordination intensity,[19] also the two-bond coupling constants respond to coordination strength by an increase in spin−spin interaction.[20] The halogeno ligands attached directly to silicon (**21**, **22**) generate greater spin−spin interactions than the chloro- and dichloro-methyl ligands (in **19** and **20**, respectively), in which carbon, and not halogen, is attached to silicon. It may be concluded that the magnitude of the two-bond coupling constant across the N→Si dative bond can serve as a criterion for the strength of coordination.

It is interesting to note that the two-bond spin−spin inter actions discussed above are of the same order of magnitude as those reported for similar interactions through *covalent* P−N−Si bonds.[21]

In the alkyl- and chloroalkyl-substituted **16**−**20**, the diastereotopic CH$_2$ protons give rise, as expected, to coupled AB spin systems (Table 2). Surprisingly, however, these AB systems are absent in the dihalo complexes (**21**, **22**) at room temperature. When the temperature of a CD$_2$Cl$_2$ solution of **21** or **22** is lowered, the CH$_2$ resonance broadens and eventually splits into an AB quartet (at 180 K, **21**: 2.82, 3.02 ppm, $^2J_{HaHb}$ = 16.0 Hz, coalescence temperature: 203 K; **22**: 2.66, 2.72 ppm, $^2J_{HaHb}$ = 16.5 Hz, coalescence temperature: 205 K), evidence of a rapid exchange process that is slowed at low temperature. To render the diastereotopic methylene protons equivalent, this exchange must involve inversion of configuration at silicon. Inversion could possibly result either from an intramolecular ligand reorganization at silicon, such as the Berry or Turnstile pseudorotations, or from an intermolecular exchange of halide

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(16) For two-bond ^{31}P−O→^{29}Si coupling constants in pentacoordinate silicon complexes see: (a) Peveling, K.; Schürmann, M.; Ludwig, R.; Jurkschat, K. *Organometallics* **2001**, *20*, 4654. (b) Dannappel, K.; Schürmann, M.; Costisella, B.; Jurkschat, K. *Organometallics* **2005**, *24*, 1031.

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(19) For relevant reviews see: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99−189. (b) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K, 1998; Vol. 2, Part 2, pp 1339−1445. (c) Bassindale, A. R.; Glynn, S. J.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K, 1998; Vol. 2, Part 1, pp 495−511. (d) Chuit, C.; Corriu, R. J. P.; Reyé, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (e) Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221−273.

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Table 2. Selected NMR Data for Phosphinimino Complexes, CDCl₃ Solution at 300 K

compd	^{29}Si{^{1}H}, ppm	$^2J(^{29}$Si^{31}P), Hz	ΔSi,[a] ppm	^{31}P, ppm	H_2C, ppm ($^2J_{HaHb}$, Hz)	^{13}C=N, ppm ($^3J_{PSi}$, Hz)
16	−78.1 t	5.1	−90.4	36.4	2.86, 2.94 (14.8)	156.5 d(22.3)
17	−77.9 t	5.2	−90.4	39.0	2.64, 2.86 (15.0)	157.3 d(21.5)
18	−78.3 t	5.7	−90.0	38.8	2.71, 2.85 (15.0)	157.3 d(21.7)
19	−86.8 t	7.2	−88.2	38.2	2.86, 2.92 (15.0)	156.7 d(22.0)
20	−91.8 t	10.2	−85.0	42.2	2.57, 2.61 (14.8)	158.5 d(21.0)
21	−95.8 t	13.6	−76.9	41.6	2.75 (s)[b]	157.3 d(20.2)
22	−103.5 t	14.0	−69.2	41.7	2.79 (s)[c]	157.7 d(20.0)

[a] Difference between ^{29}Si chemical shift of complex and corresponding XSiCl₃. Data for XSiCl₃ taken from ref 18. [b] At 180 K in CD₂Cl₂ solution (2.82, 3.02 ppm, AB quartet $^2J_{HaHb}$ = 15.0 Hz). [c] At 180 K in CD₂Cl₂ solution (2.66, 2.72, ppm, AB quartet $^2J_{HaHb}$ = 15.5 Hz).
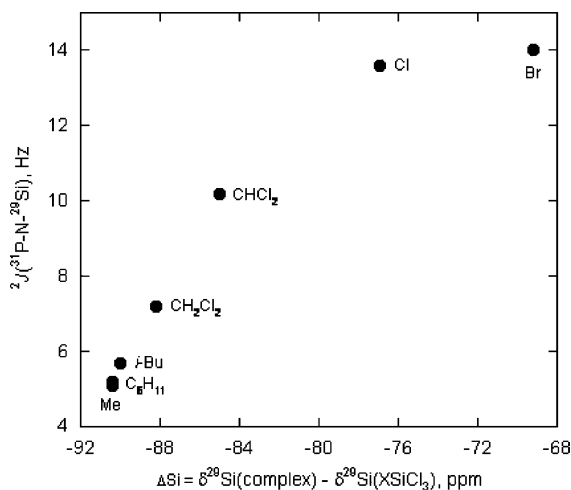

Figure 2. Plot of the two-bond coupling constants ($^2J(^{31}$P−N−^{29}Si)) of **16**−**22** as a function of ΔSi [δ(complex) − δ(XSiCl₃)] in CDCl₃ solution at 300 K. Labels in plot refer to X-ligands.

counterions by a rapid S$_N$2-type nucleophilic displacement.[22] Either one of these processes would cause time-averaging of the CH₂ proton signals, as found experimentally. However, the results strongly suggest that halide displacement is the process responsible for the observed spectral changes, since exchange phenomena are observed only in the dihalo complexes **21** and **22**, and pseudorotation would be expected to occur equally likely in the alkyl complexes, **16**−**20**.

^{31}P NMR chemical shifts for the phosphinimino complexes, given in Table 2, do not change substantially among the various complexes, nor do the three-bond coupling constants observed between phosphorus and the imino carbon.

Conclusion

Novel hypercoordinate silicon bis-chelate complexes with the phosphinimino-*N* ligand group have been prepared and characterized by X-ray crystallography and multinuclear NMR spectroscopy. The new ligand is found superior, in terms of strength of coordination to silicon, relative to previously reported dimethylamino- and isopropylideneimino-coordinated analogous complexes. All of the new complexes are pentacoordinate ionic siliconium halide salts. In the chloro-siliconium chloride (**21**) and bromo-siliconium bromide (**22**) complexes, rapid displacement of the halogeno ligand by external halide is found, resulting in rapid inversion of the configuration at silicon.

Two-bond ^{31}P−N−^{29}Si coupling constants were measured across the N→Si dative bond; their magnitudes increase with increasing electron withdrawal by the monodentate ligands, reflecting the increase in the strength of coordination.

(22) Schley, M.; Wagler, J.; Roewer, G. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2914.

Experimental Section

The reactions were carried out under dry argon using Schlenk techniques. Solvents were dried and purified by standard methods. Reagents (including polyhalosilanes) were purchased from Sigma-Aldrich. Halosilanes were distilled and kept in sealed ampules prior to use. NMR spectra were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.13, 202.46, 125.76, and 99.36 MHz, respectively, for ^{1}H, ^{31}P, ^{13}C, and ^{29}Si spectra. Unless noted, ^{29}Si spectra were measured with broad-band ^{1}H decoupling, to enable measurement of ^{31}P−^{29}Si coupling constants. Spectra are reported in δ (ppm) relative to TMS, as determined from standard residual solvent-proton (or carbon) signals for ^{1}H and ^{13}C, relative to external (capillary) H₃PO₄ for ^{31}P, and directly from TMS for ^{29}Si. Melting points were measured in sealed capillaries using a Büchi melting point instrument and are uncorrected. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Germany.

Single-crystal X-ray diffraction measurements for **16** were performed on a Bruker Smart 1000 CCD diffractometer at 120(2) K. The crystals of C$_{58.5}$H$_{55.5}$Cl$_{11.5}$N₄O$_{2.5}$P₂Si are triclinic, space group $P\bar{1}$; a = 14.167(4) Å, b = 16.592(3) Å, c = 17.193(4) Å; α = 61.488(4)°, β = 68.668(4)°, γ = 83.820(6)°. Z = 2, V = 3297(1) Å³. A total of 26 714 reflections were collected, and 14 364 independent reflections were used in further refinement. The structure of **16** was solved by direct methods and refined by full-matrix technique against F^2 in the anisotropic approximation.[23] The refinement converged to wR_2 = 0.1238 and R_1 = 0.0637 for 7030 reflections with $I > 2\sigma(I)$. Several solvate molecules of ether and CHCl₃ are strongly disordered. The contribution of unidentified solvent was removed from overall scattering using the SQUEEZE program within PLATON.[24] The empirical formula represents the following calculated molecular formula: C$_{53}$H$_{47}$N₄O₂P₂Si$^+$, Cl$^-$, and 3.5CHCl₃ and 0.5(C₂H₅)₂O. Despite the uncertainty in solvate ordering in the crystal, the molecular structure is well defined. Complete details of the structure are given in the Supporting Information. The hydrogen atoms for these molecules were not localized. Crystallographic data for **16** have been deposited with the Cambridge Crystallographic Data Centre and assigned the number CCDC 297487. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

***N*-(Phenylacetamido)triphenylphosphinimine (7).** To a solution of 6.26 g (23.8 mmol) of Ph₃P in 60 mL of CCl₄ was added dropwise 3.74 g (23.4 mmol) of Br₂ in 20 mL of CCl₄ at ice-cold temperature. The mixture was kept at reflux temperature for 2 h and then cooled to room temperature. A pale yellow precipitate (Ph₃PBr₂) was obtained and used without isolation. To the reaction mixture was added 3.55 g (23.6 mmol) of phenylacetic acid hydrazide, followed by dropwise addition of 5.00 g (49.4 mmol) of triethylamine in 50 mL of CCl₄. The mixture was refluxed for 12 h and then cooled to room temperature. The precipitate that

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(24) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2005.

had formed was filtered off and dissolved in CHCl$_3$, and Et$_3$N·HBr was washed out with water in a separating funnel. The product was recrystallized from CHCl$_3$ and dried under reduced pressure, to yield 7.53 g (77%) of **7**, mp 178−180 °C. ^{1}H NMR (CDCl$_3$, 300 K): δ 3.35 (s, 2H, CH$_2$), 7.03−7.89 (m, 20H, Ph), 8.82 (d, 1H, NH). ^{13}C NMR (CDCl$_3$, 300 K): δ 40.5 (CH$_2$), 119.2, 120.1, 126.3, 128.1, 129.3, 129.4 134.3, 134.4, 134.5, 134.8 (Ph), 172.1 (NC=O). Anal. Calcd for C$_{26}$H$_{23}$N$_2$OP: C, 76.08; H, 5.65; N, 6.82. Found: C, 76.35; H, 5.89; N, 6.54.

***O*-Trimethylsilyl-*N*-(triphenylphosphinimino)phenylacetimidate (8).** Me$_3$SiCl (1.71 g, 15.7 mmol) in 10 mL of diethyl ether was added dropwise to a mixture of 4.80 g (11.7 mmol) of **7** and 1.45 g (14.4 mmol) of triethylamine in 100 mL of ether. The mixture was refluxed for 14 h. After cooling, Et$_3$N·HCl was filtered off and volatiles were removed at low pressure. The oily residue was washed with 10 mL of *n*-hexane and filtered, yielding 3.21 g (60%) of an oily product, **8**, consisting of a 2:1 mixture of *E,Z* isomers. ^{1}H NMR (CDCl$_3$, 300 K) major isomer: δ 0.06 (s, 9H, SiCH$_3$), 4.19 (s, 2H, CH$_2$), 7.24−7.80 (m, Ph); minor isomer: δ 0.16 (s, 9H, SiCH$_3$), 3.55 (s, 2H, CH$_2$), 7.24−7.80 (m, Ph). ^{13}C NMR (CDCl$_3$, 300 K) major isomer: δ 0.1 (SiCH$_3$), 34.0 (CH$_2$), 125.3−138.3 (Ph), 157.7 (d, $^3J_{PC}$ = 41.5 Hz, N=C−O); minor isomer: δ 1.9 (SiCH$_3$), 41.9 (CH$_2$), 125.3−138.3 (Ph), 149.9 (d, $^3J_{PC}$ = 39.0 Hz, N=C−O). ^{31}P NMR (CDCl$_3$, 300 K) major isomer: δ 17.0; minor isomer: 19.9. ^{29}Si NMR (CDCl$_3$, 300 K) major isomer: δ 16.4; minor isomer: δ 15.0. Anal. Calcd for C$_{29}$H$_{31}$N$_2$OPSi: C, 72.17; H, 6.47; N, 5.80. Found: C, 72.35; H, 6.53; N, 6.02.

Bis[*N*-(triphenylphosphinimino)phenylacetimidato-*N′,O*]methylsiliconium Chloride (16). MeSiCl$_3$ (0.27 g, 1.8 mmol) was added to a solution of 0.37 g (0.8 mmol) of **8** in 5 mL of chloroform. The mixture was allowed to stir at room temperature for 10 min, after which the volatiles were removed under reduced pressure, leaving an oily residue. The residue crystallized out of 10 mL of *n*-hexane and was recrystallized from a CHCl$_3$−Et$_2$O mixture. The yield was 0.34 g (98%) of a white powder, mp 70−73 °C. A single crystal for X-ray analysis was grown from a CHCl$_3$−Et$_2$O mixture. ^{1}H NMR (CDCl$_3$, 300 K): δ 0.44 (s, 3H, SiCH$_3$), 2.86, 2.94 (ABq, $^2J_{AB}$ = 14.8 Hz, 4H, CH$_2$), 6.67−7.64 (m, 40H, Ph). ^{13}C NMR (CDCl$_3$, 300 K): δ 7.33 (SiCH$_3$), 36.4 (CH$_2$), 122.6−135.2 (Ph), 156.5 (d, $^3J_{PC}$ = 22.3 Hz, N=C−O). ^{31}P NMR (CDCl$_3$, 300 K): δ 36.4. ^{29}Si{^{1}H} NMR (CDCl$_3$, 300 K): δ −78.1 (t, $^2J_{SiP}$ = 5.1 Hz). Anal. Calcd for C$_{53}$H$_{47}$ClN$_4$O$_2$P$_2$Si·CHCl$_3$: C, 63.78; H, 4.76; N, 5.51. Found: C, 62.86; H, 5.20; N, 5.45.

Bis[*N*-(triphenylphosphinimino)phenylacetimidato-*N′,O*]cyclohexylsiliconium Chloride (17). 17 was prepared as described for **16**, from 0.35 g (0.7 mmol) of **8** and 0.22 g (1.0 mmol) of cyclohexyltrichlorosilane. Yield: 0.34 g (97%) of **17**, mp 84−86 °C. ^{1}H NMR (CDCl$_3$, 300 K): δ 0.09−1.38 (m, 11H, cyclohexyl), 2.64, 2.86 (ABq, $^2J_{AB}$ = 15.0 Hz, 4H, CH$_2$), 6.63−7.64 (m, 40H, Ph). ^{13}C NMR (CDCl$_3$, 300 K): δ 36.1 (Ph*C*H$_2$), 122.8−134.8 (Ph), 157.3 (d, $^3J_{PC}$ = 21.5 Hz, N=C−O). ^{31}P NMR (CDCl$_3$, 300 K): δ 39.0. ^{29}Si{^{1}H} NMR (CDCl$_3$, 300 K): δ −77.9 (t, $^2J_{SiP}$ = 5.2 Hz). Anal. Calcd for C$_{58}$H$_{55}$ClN$_4$O$_2$P$_2$Si·CHCl$_3$: C, 65.32; H, 5.20; N, 5.16. Found: C, 65.73, H 4.83, N, 5.54.

Bis[*N*-(triphenylphosphinimino)phenylacetimidato-*N′,O*]isobutylsiliconium Chloride (18). 18 was prepared as described for **16** from 0.22 g (1.2 mmol) of isobutyltrichlorosilane and 0.37 g (0.8 mmol) of **8**. Yield: 0.34 g (94%) of **18**, mp 80 °C (dec). ^{1}H NMR (CDCl$_3$, 300 K): δ 0.21, 0.28 (2d, $^3J_{HH}$ = 6.5 Hz, 6H, CH$_3$), 0.35 (m, 2H, SiCH$_2$), 1.0 (m, 1H, CH), 2.71, 2.85 (ABq, $^2J_{AB}$ = 15.0 Hz, 4H, Ph*C*H$_2$), 6.40−7.40 (m, 40H, Ph). ^{13}C NMR (CDCl$_3$, 300 K): δ 35.6 (Ph*C*H$_2$), 31.5 (CH), 23.8, 24.1, 24.7 (CH$_2$, CH$_3$), 122.1−134.2 (Ph), 157.3 (d, $^3J_{PC}$ = 21.7 Hz, N=C−O). ^{31}P NMR

(CDCl$_3$, 300 K): δ 38.8. ^{29}Si{^{1}H} NMR (CDCl$_3$, 300 K): δ −78.3 (t, $^2J_{SiP}$ = 5.7 Hz). Anal. Calcd for C$_{56}$H$_{53}$ClN$_4$O$_2$P$_2$Si·CHCl$_3$: C, 64.65; H, 5.14; N, 5.29. Found: C, 64.25; H, 5.45; N, 5.36.

Bis[*N*-(triphenylphosphinimino)phenylacetimidato-*N′,O*](chloromethyl)siliconium Chloride (19). 19 was prepared as described above for **16** from 0.42 g (0.9 mmol) of **8** and 0.28 g (1.5 mmol) **12**. **19** was obtained in 97% yield (0.40 g) as a solid, mp 66 °C (dec), which after melting turned to a white foam. ^{1}H NMR (CDCl$_3$, 300 K): δ 2.11, 2.38 (ABq, $^2J_{AB}$ = 14.4 Hz, 2H, CH$_2$Cl), 2.86, 2.92 (ABq, $^2J_{AB}$ = 15.0 Hz, 4H, Ph*C*H$_2$), 6.27−7.61 (m, 40H, Ph). ^{13}C NMR (CDCl$_3$, 300 K): δ 33.3 (CH$_2$Cl), 35.7 (Ph*C*H$_2$), 122.1−134.2 (Ph), 156.7 (d, $^3J_{PC}$ = 22.0 Hz, N=C−O). ^{31}P NMR (CDCl$_3$, 300 K): δ 42.2. ^{29}Si{^{1}H} NMR (CDCl$_3$, 300 K): δ −86.8 (t, $^2J_{SiP}$ = 7.2 Hz). Anal. Calcd for C$_{53}$H$_{46}$Cl$_2$N$_4$O$_2$P$_2$Si·CHCl$_3$: C, 61.70; H, 4.51; N, 5.33. Found: C, 61.12; H, 4.76; N, 5.30.

Bis[*N*-(triphenylphosphinimino)phenylacetimidato-*N′,O*](dichloromethyl)siliconium Chloride (20). 20 was prepared as described above for **16** from 0.27 g (0.6 mmol) of **8** and 0.24 g (1.1 mmol) of **13**. **20** was obtained in 92% yield (0.25 g), mp 90 °C (dec). ^{1}H NMR (CDCl$_3$, 300 K): δ 2.57, 2.61 (ABq, $^2J_{AB}$ = 14.8 Hz, 4H, Ph*C*H$_2$), 5.53 (s, 1H, CHCl$_2$), 6.27−7.61 (m, 40H, Ph). ^{13}C NMR (CDCl$_3$, 300 K): δ 35.1 (Ph*C*H$_2$), 57.8 (CHCl$_2$), 121.3−133.5 (Ph), 158.5 (d, $^3J_{PC}$ = 21.0 Hz, N=C−O). ^{31}P NMR (CDCl$_3$, 300 K): δ 38.2. ^{29}Si{^{1}H} NMR (CDCl$_3$, 300 K): δ −86.8 (t, $^2J_{SiP}$ = 10.2 Hz). Anal. Calcd for C$_{53}$H$_{45}$Cl$_3$N$_4$O$_2$P$_2$Si·CHCl$_3$: C, 59.74; H, 4.27; N, 5.16. Found: C, 59.37; H, 4.36; N, 4.87.

Bis[*N*-(triphenylphosphinimino)phenylacetimidato-*N′,O*]chlorosiliconium Chloride (21). To a stirred solution of 0.40 g (0.8 mmol) of **8** in 5 mL of chloroform was added by condensation 0.18 g (1.1 mmol) of SiCl$_4$ (**14**). The color of the solution turned intense red at room temperature and, after stirring for 5−10 min, faded to yellow. The solution was stirred for 10 min at room temperature followed by removal of the volatiles under reduced pressure. The solid residue was recrystallized from a CHCl$_3$−Et$_2$O mixture and dried under vacuum. The yield was 0.36 g (94%), mp 86 °C (dec). ^{1}H NMR (CDCl$_3$, 300 K): δ 2.75 (s, 4H, Ph*C*H$_2$), 6.55−7.56 (m, 40H, Ph). ^{13}C NMR (CDCl$_3$, 300 K): δ 35.4 (CH$_2$), 121.4−134.1 (Ph), 157.3 (d, $^3J_{PC}$ = 20.2 Hz, N=C−O). ^{31}P NMR (CDCl$_3$, 300 K): δ 41.6. ^{29}Si NMR (CDCl$_3$, 300 K): δ −95.8 (t, $^2J_{SiP}$ = 13.6 Hz). Anal. Calcd for C$_{52}$H$_{44}$Cl$_2$N$_4$O$_2$P$_2$Si·CHCl$_3$: C, 61.37; H, 4.37; N, 5.40. Found: C, 62.20; H, 4.73; N, 5.54.

Bis[*N*-(triphenylphosphinimino)phenylacetimidato-*N′,O*]bromosiliconium Bromide (22). To a solution of 0.49 g (1.0 mmol) of **8** in 5 mL of dry CHCl$_3$ was added 0.40 g (1.1 mmol) of SiBr$_4$ (**15**). The solution was stirred for 10 min at ambient temperature, followed by removal of volatiles under reduced pressure. The semisolid residue was washed with 10 mL of *n*-hexane to form a solid, 0.44 g (88% yield), mp 62 °C (dec). ^{1}H NMR (CDCl$_3$, 300 K): δ 2.79 (s, 4H, Ph*C*H$_2$), 6.55−7.56 (m, 40H, Ph). ^{13}C NMR (CDCl$_3$, 300 K): δ 35.6 (CH$_2$), 121.4−134.1 (Ph), 157.7 (d, $^3J_{PC}$ = 20.0 Hz, N=C−O). ^{31}P NMR (CDCl$_3$, 300 K): δ 41.7. ^{29}Si NMR (CDCl$_3$, 300 K): δ −103.5 (t, $^2J_{SiP}$ = 14.0 Hz). Anal. Calcd for C$_{52}$H$_{44}$Br$_2$N$_4$O$_2$P$_2$Si·CHCl$_3$: C, 56.53; H, 4.03; N, 4.98. Found: C, 56.29; H, 4.34; N, 4.55.

Supporting Information Available: Figure of the crystal structure of **16** including chloride and disordered solvate molecules. Tables of crystallographic data for **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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