CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200701466

Neutral and Cationic Phosphoramide Adducts of Silicon Tetrachloride: Synthesis and Characterization of Their Solution and Solid-State Structures

Scott E. Denmark* and Brian M. Eklov[a]

Abstract: The solution and solid-state structures of hexamethylphosphoramide (HMPA) adducts of tetrachlorosilane ($SiCl_4$) are discussed. In solution, the *meridional* and *facial* isomers of the hexa-coordinate cationic complex $3\,HMPA{\cdot}SiCl_3^+$ Cl^- (**2**) predominate at all HMPA concentrations, and are in equilibrium with the hexa-coordinate neutral *trans*- and *cis*-$2\,HMPA{\cdot}SiCl_4$ complexes (**1**), as well as the penta-coordinate cationic *cis*-$2\,HMPA{\cdot}SiCl_3^+\,Cl^-$ (**3**). Single crystal X-ray analyses are reported for the ionized *mer*-$3\,HMPA{\cdot}SiCl_3^+\,HCl_2^-$ and the neutral *trans*-$2\,HMPA{\cdot}SiCl_4$ complexes.

Keywords: asymmetric catalysis • donor–acceptor systems • Lewis acids • Lewis bases • silicon

Introduction

Hypervalent silicon species play important roles as reagents and intermediates in modern organic chemistry, in particular as powerful Lewis acid catalysts.[1] Recent studies in these laboratories have described various carbonyl addition reactions that rely upon the addition of a chiral Lewis base to the weakly Lewis acidic $SiCl_4$.[2] This Lewis acid–Lewis base interaction leads to the formation of a silyl cation that expresses increased Lewis acidity that leads to significant rate enhancements as well as exquisite stereoselectivities.[2d] A detailed understanding of the structure of these Lewis acid–Lewis base complexes is fundamental to the continued development of this class of reactions, as well as other reactions of main-group elements. To this end, we have chosen to study the solution and solid-state structures of HMPA–$SiCl_4$ complexes.

The structures of five- and six-coordinate silicon species have been studied extensively for many years, and interesting observations of dative silicon–heteroatom interactions have been reported recently.[3] However, the great majority of these studies rely upon a covalently attached Lewis base. Our current study focuses on intermolecular Lewis acid–Lewis base interactions and the resulting hypervalent complexes.

Results and Discussion

Solution structures

^{29}Si and ^{31}P NMR studies:[4] Initial NMR spectroscopic studies demonstrated that mixtures of HMPA and $SiCl_4$ produce species that are fluxional at room temperature. The ^{31}P NMR spectra showed a single broad resonance, and ^{29}Si NMR spectra were entirely featureless. Consequently, all of the spectral data discussed below were recorded between −60 and −100 °C, where the signals were well resolved.[5]

Stoichiometric constraints: The ^{31}P NMR spectra of mixtures containing 0.2, 0.5, 1.0, 2.0, 3.0, and 5.5 equiv of HMPA per $SiCl_4$ (in CD_2Cl_2 at 0.3 M in silicon) are shown in Figure 1, and the corresponding ^{29}Si spectra are shown in Figures 2 and 3. It is important to note that the ^{31}P spectra do not display any free phosphoramide (free HMPA appears at $\delta=$ 26 ppm) until more than 3.0 equiv of HMPA have been added. Conversely, the ^{29}Si NMR spectra display free $SiCl_4$ until 3.0 equiv of HMPA have been added. This applies an important stoichiometric constraint upon the species in solution, namely all of the phosphoramide is coordinated to a silicon atom until more than 3.0 equiv of HMPA have been added. At this point, no free $SiCl_4$ remains in solution, leaving a complex with a 3:1 HMPA/$SiCl_4$ ratio.

---

[a] Prof. Dr. S. E. Denmark, Dr. B. M. Eklov
Department of Chemistry, University of Illinois
Urbana, Illinois 61801 (USA)
Fax: (+1) 217-333-3984
E-mail: denmark@scs.uiuc.edu

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

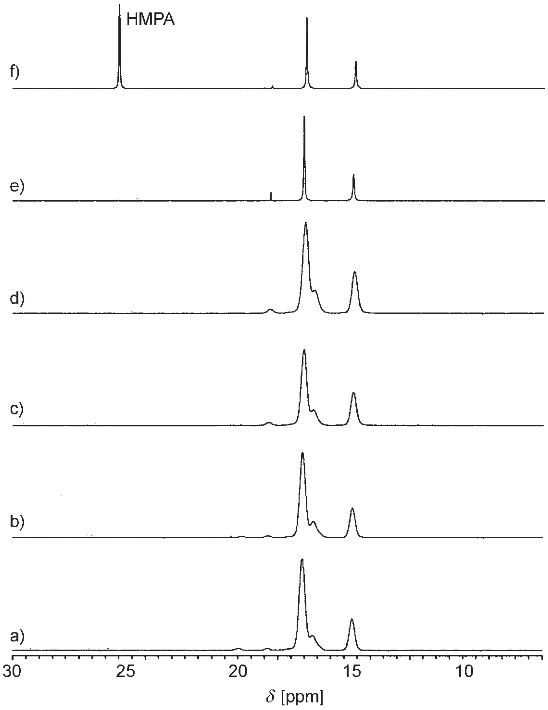

Figure 1. ^{31}P NMR spectra at −70 °C (CD_2Cl_2, 0.3 M) with different HMPA/$SiCl_4$ ratios. a) 0.2 equiv HMPA, b) 0.5 equiv HMPA, c) 1.0 equiv HMPA, d) 2.0 equiv HMPA, e) 3.0 equiv HMPA, and f) 5.5 equiv HMPA.

Also, with the exception of the ^{31}P resonance at 18.7 ppm, the relative ratio of the ^{31}P resonances is surprisingly static over the entire HMPA concentration range. The resonance at 18.7 ppm increases as more HMPA is added, until 2.0 equiv has been added. This resonance then decreases in intensity between 2.0 and 3.0 equiv of HMPA, at which point it is no longer observed.

^{29}Si NMR structural assignments: Simple inspection of the ^{29}Si spectra (chemical shift and multiplicity) allowed straightforward structural assignments for some of the resonances. The resonance at −120.5 ppm (Figure 2, triplet, J = 15 Hz) is attributed to the bisphosphoramide ligated five-coordinate complex, $2\,HMPA{\cdot}SiCl_3{}^+\,Cl^-$ (**3**).[6] This resonance was observed if any phosphoramide was present in solution, and grew in intensity as the amount of HMPA was increased to 2.0 equiv[7] However, this resonance disappears if 3.0 equiv (or more) of HMPA are present in solution.

The remaining resonances fall within a rather small chemical shift region, all of which are in the six-coordinate regime.[8] The triplet (J = 9.7 Hz) that appears at −205.5 ppm (Figure 3e) is assigned to the neutral di-ligated complex *cis*-$2\,HMPA{\cdot}SiCl_4$ (*cis*-**1**). The *trans*-$2\,HMPA{\cdot}SiCl_4$ complex (*trans*-**1**) is assigned to the singlet at −207.8 ppm, and will be discussed in detail below.

The quartet splitting (J = 5 Hz) of the resonance at δ = −210 ppm requires a six-coordinate silicon species bound to

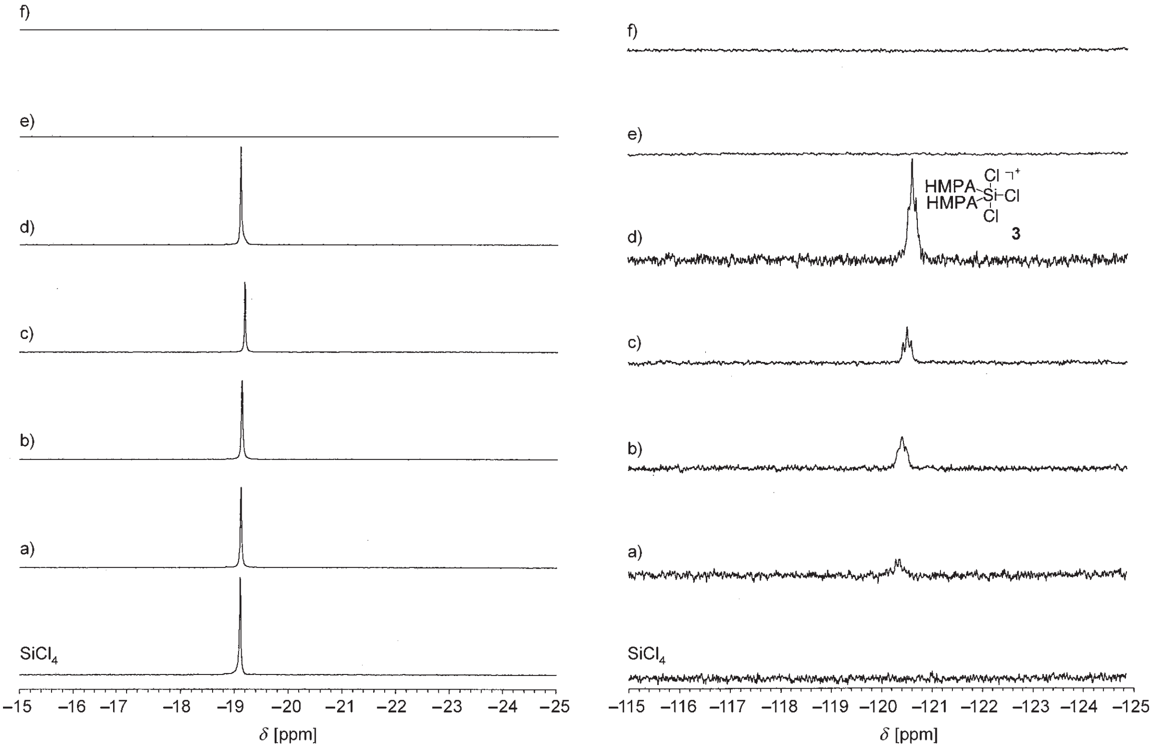

Figure 2. ^{29}Si NMR spectra at −70 °C with different HMPA/$SiCl_4$ ratios. a) 0.2 equiv HMPA, b) 0.5 equiv HMPA, c) 1.0 equiv HMPA, d) 2.0 equiv HMPA, e) 3.0 equiv HMPA, f) 5.5 equiv HMPA. A spectrum with no HMPA ($SiCl_4$ only) is included at the bottom for reference. Upfield plot vertical scales (right) are exaggerated to show the minor component, and are comparable to the right-hand portion of Figure 3. Downfield plot vertical scales (left) are comparable to the left-hand portion of Figure 3.

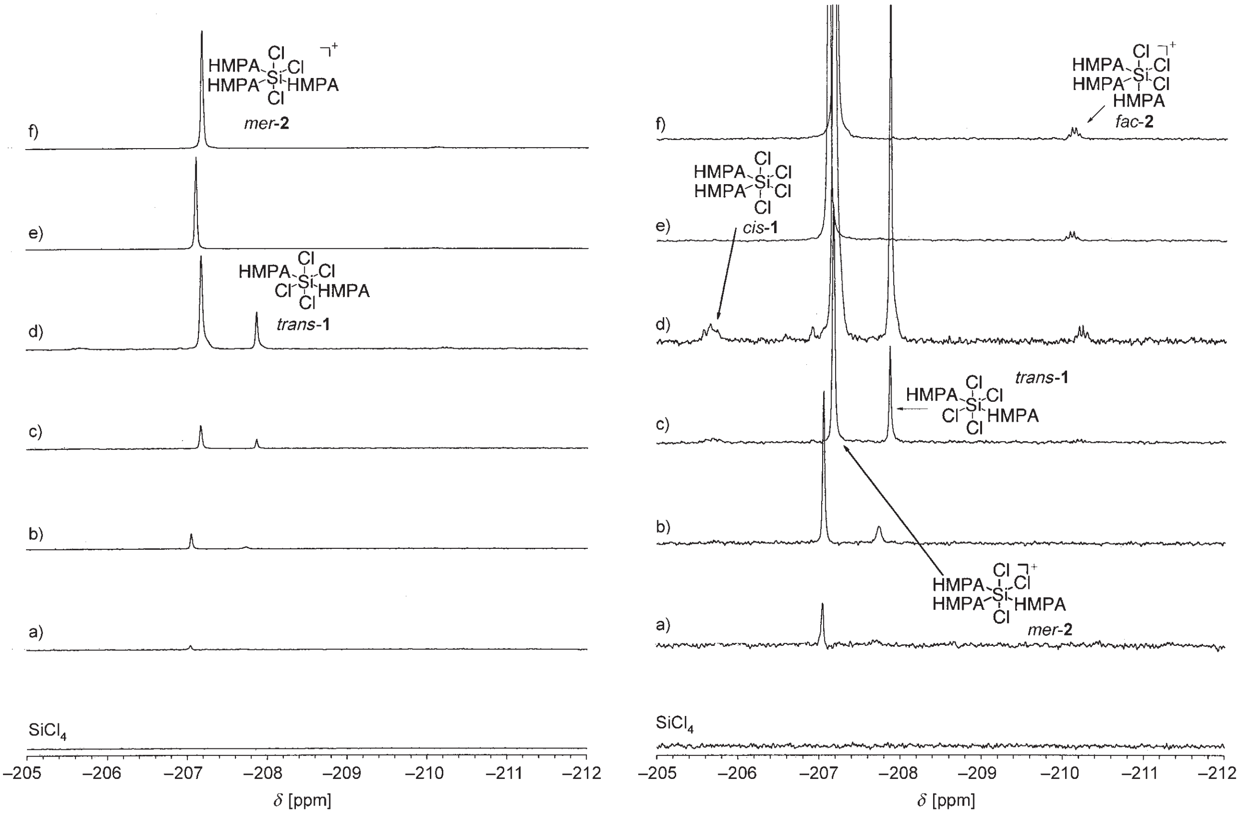

Figure 3. ^{29}Si NMR spectra at −70 °C with different HMPA/SiCl$_4$ ratios. The right-hand series has the vertical scale exaggerated to show minor components; the vertical scale is comparable to the right hand portion of Figure 2. a) 0.2 equiv HMPA, b) 0.5 equiv HMPA, c) 1.0 equiv HMPA, d) 2.0 equiv HMPA, e) 3.0 equiv HMPA, f) 5.5 equiv HMPA. A spectrum with no HPMA (SiCl$_4$ only) is included at the bottom for reference.

three equivalent phosphoramides. Both of the possible cationic complexes with the requisite 3 HMPA•SiCl$_3^+$ Cl$^-$ formula are shown in Figure 4. This resonance corresponds to *fac*-**2**, as all three of the phosphorus atoms in this complex are equivalent. The major resonance in all cases ($\delta = -207$ ppm) is then assigned to *mer*-**2**.[9]

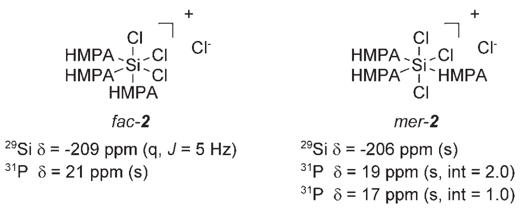

Figure 4. The two possible 3 HMPA•SiCl$_3^+$ Cl$^-$ isomers.

As demonstrated in Figure 3f, g and 2f, g, the ^{29}Si NMR spectra only display two peaks at or above a 3:1 HMPA/SiCl$_4$ ratio. Assigning these two resonances to the two isomers, *fac*- and *mer*-**2** satisfies the 3:1 HMPA/SiCl$_4$ stoichiometry requirement, and is also in complete agreement with the ^{31}P NMR spectrum (See Figure 1e). The minor peak in the ^{31}P NMR spectrum ($\delta = 20.4$ ppm) corresponds to *fac*-**2**, as selectively decoupling this peak in the ^{31}P NMR spectrum leads to the collapse of the ^{29}Si resonance at $\delta = -210$ ppm to a singlet, demonstrating that all three of the phosphoramides are chemical shift equivalent. The other two ^{31}P resonances then correspond to the two different phosphorus environments in *mer*-**2**. The integral ratios of both the ^{31}P and ^{29}Si spectra are also in agreement with a 97:3 ratio of the *mer*-**2**/*fac*-**2** isomers.[10]

If the NMR spectra of the 3:1 HMPA/SiCl$_4$ mixture represent the exclusive formation of *fac*- and *mer*-**2**, it must follow that the *facial* isomer possesses a small P–Si coupling, while the *meridional* isomer does not.[11] Unfortunately, very little is known about phosphoryl–silicon complexes and consequently the signs and magnitudes of their $^2J_{\mathrm{Si,P}}$ coupling constants are not available. A survey of the CCSD provided a handful of structures containing a P=O–silicon linkage, but there are no reports of a $^2J_{\mathrm{P,Si}}$ for these complexes.[12] Our provisional assignment is supported by a series of magnetization transfer experiments on a 5.5:1 HMPA/SiCl$_4$ mixture. These experiments demonstrated that the silicon-bound ^{31}P resonances corresponding to *fac*-**2** and *mer*-**2** exchange with each other, without exchanging with any free HMPA in solution. This supports a facile *intramolecular* phosphoramide exchange pathway that does not involve dissociation of a phosphoramide. The simplest explanation for this intramolecular exchange is isomerization between the *fac*- and *mer*-**2** isomers (i.e., via a Bailar twist[13]).

X-Ray crystallographic structures

2HMPA·SiCl$_4$ (1): To secure further structural information on the nature of the HMPA–SiCl$_4$ complexes, the solid-state structures of crystalline materials were obtained. Addition of hexanes to a 1 M solution of SiCl$_4$ in a mixture of HMPA and methylene chloride yielded large, colorless, cubic crystals. A suitable crystal was chosen for an X-ray diffraction study, which revealed the neutral *trans*-2HMPA·SiCl$_4$ complex shown in Figure 5.[14] The structure of this complex corroborates earlier vibrational and paramagnetic spectroscopic studies[15] of its structure, and the *trans*-relationship of the Lewis basic moieties appears to be general.[16]

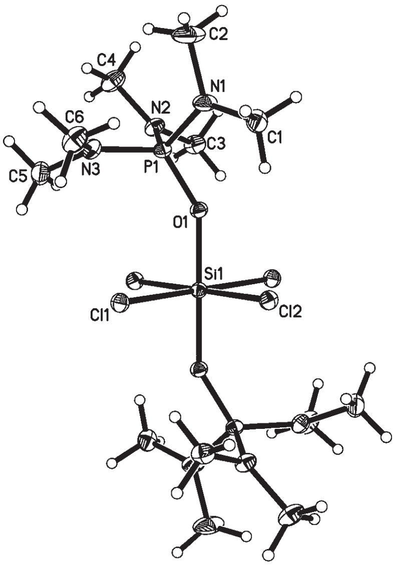

Figure 5. ORTEP representation of the 2HMPA·SiCl$_4$ complex (*trans*-**1**).

The silicon atom of the complex sits on a crystallographic inversion center, with a near-perfect octahedral ligand arrangement (Figure 5). The four chlorine atoms are displayed about the equatorial plane, with the two phosphoramides *trans* to each other.[17] The complex shows a lengthened P–O bond ($\Delta d = 0.048$ Å) as well as shorter P–N bond lengths ($\Delta d = -0.035$ Å for P1–N3 and -0.012 Å for P1–N2 and P1–N1) than in the free phosphoramide (Table 1),[18] while the Si–Cl bonds are lengthened ($\Delta d = +0.19$ and $+0.26$ Å) when compared with SiCl$_4$ (measured by electron diffraction, Si–Cl 2.02 Å).[19]

Interestingly, this complex can be isolated in excellent yield and is a stable colorless powder if stored in an anhydrous environment. Unfortunately, the ^{31}P and ^{29}Si NMR spectra of solutions made from the isolated complex demonstrate that it disproportionates rapidly to give the same components as shown above (Figures 1e, 2e, and 3e), even if the solution is mixed and maintained at −78 °C.

Table 1. Selected bond lengths [Å] and bond angles [°] for *trans*-**1** and *mer*-**2**.

trans-**1**		*mer*-**2**	
Si–Cl1	2.217	Si–Cl1	2.210
Si–Cl2	2.210	Si–Cl2	2.199
		Si–Cl3	2.202
Si–O	1.770	Si–O1	1.766
		Si–O2	1.778
		Si–O3	1.769
P–O	1.523	P1–O1	1.518
		P2–O2	1.523
		P3–O3	1.524
P–N1	1.631	P1–N1	1.611
P–N2	1.630	P1–N2	1.620
P–N3	1.620	P1–N3	1.604
Cl1-Si-Cl2	90.0	Cl1-Si-Cl2	90.9
		Cl1-Si-Cl3	90.8
Si-O-P	148.3	Si-O1-P1	159.0
		Si-O2-P2	147.6
		Si-O3-P3	145.8
Cl1-Si-O	90.0	Cl1-Si-O2	90.4
		Cl1-Si-O3	90.9
		Cl3-Si-O1	88.7

3HMPA·SiCl$_3$$^+$ HCl$_2$$^-$ (2): Upon standing for one week, this solution also yielded a crop of colorless needles, which precipitated from the hexanes phase. These crystals proved to be *mer*-**2**, in which the expected chloride counter anion is replaced with the more complex HCl$_2$$^-$ (Figure 6).[20] This structure is unprecedented, as it is the first report of an ionized Lewis base–silicon complex that does not rely upon a pendant Lewis base.[3] Somewhat surprisingly, all three of the Si–O bonds are similar in length and are comparable in length to those in the neutral 2HMPA·SiCl$_4$ complex. The two Si–Cl bonds that are *anti* to each other in this complex are shorter than those in the neutral complex, however, the Si–Cl bond that is situated *trans* to the phosphoramide is

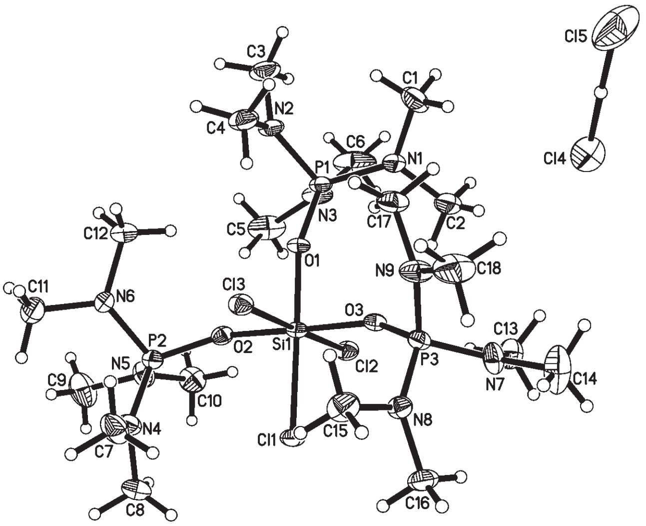

Figure 6. ORTEP representation of the 3HMPA·SiCl$_3$$^+$ Cl-H-Cl$^-$ complex (*mer*-**2**). Full details are available in the Supporting Information.

longer than the other two, and is comparable in length to the Si−Cl bond lengths in the neutral complex.

The cationic complex *mer*-**3** is not only structurally novel, but it also represents compelling evidence for the intermediacy of ligated silicon cations in the phosphoramide-catalyzed reactions of $SiCl_4$. We have posited a central role for these species, but until now have relied solely on kinetic evidence and common ion effects.[2b,21] We now have strong support for this hypothesis and future reports will build on these observations to explain the behavior of chiral bisphosphoramide catalysts.

Conclusion

The solid-state structures of *trans*-**1** and *mer*-**2** have been reported. Complex *trans*-**1** is structurally analogous to the bispyridine•$SiCl_4$ complexes.[16] The complex *mer*-**2** represents the first structure of a hexa-coordinate silicon-centered cation derived from $SiCl_4$. The *mer*-**2** and *fac*-**2** complexes are also the only species observed in solution when three or more equivalents of HMPA (with respect to $SiCl_4$) are present in solution, while they are the major components in solution, at other stoichiometries. Additionally, these observations provide a solid foundation to understand the role of the chiral bisphosphoramide•$SiCl_4$ catalysts, and these results will be reported in due course.

Acknowledgements

We thank the National Science Foundation for generous financial support (NSF CHE-0414440). We thank Dr. Paul Molitor and Dr. Christopher Knight for helpful discussions. We thank Scott R. Wilson and Teresa Prussak-Wieckowska of the UIUC George L. Clark X-Ray Facility for collection and interpretation of X-ray data.

---

[1] a) S. Rendler, M. Oestreich, *Synthesis* **2005**, 1727–1747; b) C. Chuit, R. J. P. Corriu, C. Reye in *Chemistry of Hypervalent Compounds* (Ed.: K. Akiba), Wiley-VCH, New York, **1999**, pp. 81–146; c) M. Kira, C. Zhang in *Chemistry of Hypervalent Compounds* (Ed.: K. Akiba), Wiley-VCH, New York, **1999**, pp. 147–170; d) M. Katsukiyo, A. Hosomi in *Main Group Metals in Organic Synthesis, Vol. 2* (Eds.: H. Yamamoto, K. Oshima), Wiley-VCH, Weinheim, **2004**, p. 409; e) *The Chemistry of Organic Silicon Compounds, Vol. 3* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **2001**; f) C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371–1448; g) S. N. Tandura, M. G. Voronkov, N. V. Alekseev, *Top. Curr. Chem.* **1986**, *131*, 99–189.

[2] a) S. E. Denmark, T. Wynn, G. L. Beutner, *J. Am. Chem. Soc.* **2002**, *124*, 13405–13407; b) S. E. Denmark, G. L. Beutner, T. Wynn, M. D. Eastgate, *J. Am. Chem. Soc.* **2005**, *127*, 3774–3789; c) S. E. Denmark, S. Fujimori in *Modern Aldol Reactions, Vol. 2* (Ed.: R. Mahrwald), Wiley-VCH, Weinheim, **2004**, Chapter 7.

[3] a) W. B. Farnham, R. L. Harlow, *J. Am. Chem. Soc.* **1981**, *103*, 4608–4610; b) W. B. Farnham, J. F. Whitney, *J. Am. Chem. Soc.* **1984**, *106*, 3992–3994; c) I. Kalikhman, O. Girshberg, L. Lameyer, D. Stalke, D. Kost, *Organometallics* **2000**, *19*, 1927–1934; d) D. Kost, I. Kalikhman, *Adv. Organomet. Chem.* **2004**, *50*, 1–106; e) D. Kost, I. Kalikhman in *Chemistry of Organic Silicon Compounds* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, pp. 1339–1445.

[4] Full experimental details and the full set of ^{29}Si and ^{31}P NMR data are included in the Supporting Information.

[5] Additionally, [Cr(dpm)$_3$] (ca. 5 mM) was added to reduce the notoriously long ^{29}Si and ^{31}P relaxation times. All spectra were taken with a minimum of three times the longest T_1 time, to increase the reliability of the integral ratios. In the ^{29}Si spectra, the T_1 for the resonance at $\delta = -207.4$ ppm was 3.5 ± 0.3 s. Therefore, the relaxation delay was set to 10.0 s with a 0.55 s acquisition time, for a total of 10.55 s between pulses. This resonance represented the only peak that could provide a reasonably accurate T_1 value. In the ^{31}P spectra, accurate T_1 values could be measured for all of the peaks in the 5.5:1 HMPA/$SiCl_4$ mixture, and demonstrated that the T_1 values are identical for the three peaks: *mer*-**2**: δ 17.10 ppm ($T_1 = 1.172 \pm 0.006$ s); 18.94 ppm ($T_1 = 1.173 \pm 0.003$ s); *fac*-**2**: δ 20.24 ppm ($T_1 = 1.16 \pm 0.04$ s). The extraordinary equivalence of these values will be discussed below.

[6] Increased ionization of silicon-centered Lewis acid–Lewis base complexes as temperature is lowered appears to be a general phenomenon. See: a) D. Kost, I. Kalikhman, M. Raban, *J. Am. Chem. Soc.* **1995**, *117*, 11512–11522; b) D. Kost, I. Kalikhman, S. Krivonos, D. Stalke, T. Kottke, *J. Am. Chem. Soc.* **1998**, *120*, 4209–4214; c) I. Kalikhman, B. Gostevskii, B. Kertsnus, M. Botoshansky, C. A. Tessier, W. J. Youngs, S. Deuerlein, D. Stalke, D. Kost, *Organometallics* **2007**, *26*, 2652–2658.

[7] While this peak is present in solution until 3.0 equivalents of HMPA have been added, it is always a minor component of the overall composition.

[8] a) J. D. Kennedy, W. McFarlane in *Multinuclear NMR* (Ed.: J. Mason), Plenum Press, New York, **1987**, Chapter 11; b) S. Kobayashi, K. Nishio, *Tetrahedron Lett.* **1993**, *34*, 3453–3456; c) L. Olsson, C. H. Ottosson, D. Cremer, *J. Am. Chem. Soc.* **1995**, *117*, 7460–7479; d) M. Arshadi, D. Johnels, U. Edlund, C.-H. Ottosson, D. Cremer, *J. Am. Chem. Soc.* **1996**, *118*, 5120–5131; e) S. Kobayashi, K. Nishio, *Tetrahedron Lett.* **1993**, *34*, 3453–3456.

[9] Our previous interpretation of a 1:1 mixture of HMPA/$SiCl_4$ must be revisited in light of this new data. We had previously assigned the featureless singlet peak at $\delta = -207$ ppm in the ^{29}Si NMR spectrum as $SiCl_6^{2-}$. Given the interesting new stoichiometric constraint seen here, this assignment must be discounted.

[10] The integral ratios in the ^{31}P NMR spectra are reliable because the spectra are proton decoupled and the T_1 values are nearly identical, see ref. [4].

[11] The presence or absence of $^2J_{P,Si}$ coupling in these compounds is not so surprising if one considers the exchange phenomena seen in these systems. To observe the coupling between two nuclei, any exchange phenomenon must occur a few times slower than the magnitude of the coupling constant. Thus, to observe the five cycles per s coupling constant observed in *fac*-**2**, the exchange phenomenon must occur at a rate slower than about 2 s^{-1}. If the rate of exchange is near this upper limit, coupling constants smaller than ca. 5 Hz would not be observable because of exchange decoupling. In our studies of $SnCl_4$–phosphoramide complexes, we did indeed see different $^2J_{Sn,P}$ coupling constants for different configurations of the complexes (interesting the $^2J_{Sn,P}$ in the *cis* complex is 40 % smaller than in the *trans* complex), but these are much larger couplings and much slower isomerizations. See S. E. Denmark, J. Fu, *J. Am. Chem. Soc.* **2003**, *125*, 2208–2216.

[12] There are many reports of metal–silylene complexes that are solvated by phosphoramides. Some of these species do display a $^2J_{P,Si}$, whose magnitudes are ca. 20–50 Hz. However, other complexes do not have reported coupling constants (For instance, see: C. Zybill, G. Müller, *Organometallics* **1988**, *7*, 1368–1372, where an iron(0)-bound HMPA-coordinated silylene displays a $^2J_{P,Si}$ of 26 Hz, but an analogous chromium(0) complex does not display a measurable coupling constant.). Also, the lower valences of these HMPA-coordinated silylene complexes preclude a direct comparison to this work.

[13] a) B. F. G. Johnson, *Transition Met. Chem.* **1990**, *15*, 493–495; b) P. Râу, N. K. Dutt, *J. Indian Chem. Soc.* **1943**, *20*, 81–92; c) J. C.

Bailar, *J. Inorg. Nucl. Chem.* **1958**, *8*, 165–175; d) J. E. Brady, *Inorg. Chem.* **1969**, *8*, 1208–1209.

[14] CCDC 645343 (*trans*-**1**) and 645345 (*mer*-**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif Data for *trans*-**1**: $C_{12}H_{36}C_{14}N_6O_2P_2Si$, $M_r=528.30$, $0.44\times0.20\times0.08$ mm^3, monoclinic, $P21/n$, $a=8.433(3)$, $b=13.459(4)$, $c=11.177(3)$ Å, $V=1243.2(7)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.411$ Mg m^{-3}, $\mu=0.673$ mm^{-1}, Mo radiation $\lambda=0.71073$ Å, $T=188(2)$ K, $2\theta_{\max}=25.37°$, 2281 independent reflections (12865 measured), Direct methods solution (Bruker SHELXTL) and full-matrix least-squares refinement on F^2 (Bruker SHELXTL) using 130 parameters against 2281 data, observed $R_1=0.0312$, $wR2=0.0652$, residual range 0.283 to -0.301 e Å^{-3}. Data for *mer*-**2**: $C_{18}H_{55}C_{15}N_9O_3P_3Si$, $M_r=743.96$, $0.80\times0.09\times0.05$ mm^3, orthorhombic, $P212121$, a = 8.443(3), b = 18.009(7), $c=23.741(9)$ Å, $V=3610(2)$ $\AA^3$, $Z=4$, $\rho_{\text{calcd}}=1.369$ Mg m^{-3}, $\mu=0.603$ mm^{-1}, Mo radiation $\lambda=0.71073$ Å, $T=188(2)$ K, $2\theta_{\max}=25.40°$, 6627 independent reflections (37581 measured), Direct methods solution (Bruker SHELXTL) and full-matrix least-squares refinement on F^2 (Bruker SHELXTL) using 373 parameters against 6627 data, observed $R_1=0.0409$, $wR2=0.0717$, residual range 0.330 to -0.255 e Å^{-3}.

[15] a) A. I. Andreeva, I. Y. Kuramshin, D. Y. Osokin, I. A. Safin, A. N. Pudovik, A. S. Khramov, *Koord. Khim.* **1977**, *3*, 1192–1195; b) V. P. Feshin, G. V. Dolgushin, I. M. Lazarev, M. G. Voronkov, *Doklady Akademii Nauk SSR* **1987**, *295*, 1415–1419.

[16] a) I. R. Beattie, M. Webster, *J. Chem. Soc.* **1965**, 3672–3678; b) G. A. Ozin, *J. Chem. Soc. D* **1969**, *3*, 104.

[17] The structure reported here is also analogous to the reported di-ligated bispyridine complexes. See: a) O. Bechstein, B. Ziemer, D. Hass, S. I. Trojanov, V. B. Rybakov, G. N. Maso, *Z. Anorg. Allg. Chem.* **1990**, *582*, 211–216; b) K. Hensen, R. Mayr-Stein, B. Spangenberg, M. Bolte, *Acta Crystallogr. Sect. C* **2000**, *56*, 610–613; c) K. Hensen, R. Mayr-Stein, B. Spangenberg, M. Bolte, S. Ruhl, *Z. Naturforsch. B* **2000**, *55*, 248–252.

[18] F. Hartmann, T. Dahlems, D. Mootz, *Z. Kristallogr. New Cryst. Struct.* **1998**, *213*, 639–640.

[19] R. R. Ryan, K. Hedberg, *J. Chem. Phys.* **1969**, *50*, 4986–4995.

[20] a) E. P. Kramarova, A. A. Korlyukov, S. Y. Bylikin, A. G. Shipov, Y. I. Baukov, D. Kost, *Russ. Chem. Bull. Int. Ed.* **2004**, *53*, 1135–1136; b) U. Thewalt, U. Link, *Z. Naturforsch. B* **1991**, *46*, 293–296; c) J. L. Atwood, S. G. Bott, C. M. Means, A. W. Coleman, H. Zhang, M. T. May, *Inorg. Chem.* **1990**, *29*, 467–470.

[21] A full kinetic analysis of the bisphosphoramide•$SiCl_4$ catalyzed aldol addition reactions has been completed and will be reported separately.

Received: September 14, 2007