Contrasting Nonclassical Silicon−Hydrogen Interactions in Niobium and Tantalum Half-Sandwich Complexes: Si−H···M Agostic versus M−H···Si−Cl Interligand Hypervalent Interactions

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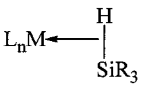
Reaction of [CpM(NAr)(PMe_3)$_2$] (M = Nb, Ta; Ar = 2,6-$C_6H_3iPr_2$) with $HSiClMe_2$ gives two remarkably different nonclassical Si···H···M products depending only on the identity of M; [CpTa(NAr)(H)($SiMe_2Cl$)(PMe_3)] possesses an unusual electron-rich M–H···Si interligand hypervalent interaction while [CpNb{η^3-N(Ar)$SiMe_2$–H}Cl(PMe_3)] is the first example of a β-agostic silylamine Si–H···M interaction showing a "stretched" Si–H bond.

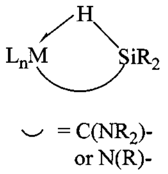
Introduction

The study of complexes possessing interligand interactions is important for developing a better understanding of transition metal-mediated transformations. For example, nonclassical σ-complexes of the type $L_nM(\eta^2\text{-}H{-}X)$ (e.g. X = H, SiR_3, BR_2) serve as models for intermediates in oxidative addition/reductive elimination reactions,[1] while β-agostic L_nM···H−C systems lie on the reaction coordinate for the migratory insertion of alkenes into metal−hydride bonds.[2] Of particular relevance to this contribution are silicon-hydrogen bond complexes of the types **A** (η^2-silane species) and **B** (β-agostic M···H···Si) which are now well-established in the literature. Such metal−hydrogen−silicon interactions can best be described as three-centre, two-electron M···H···Si bonds formally arising from donation of Si−H σ-bond electron density to the metal (often with additional metal-to-Si−H σ* orbital back-donation); the interligand (i.e. Si···H) interactions in **A** and **B** may thus be classified as *electron deficient.*

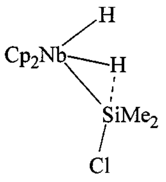
We have recently reported a new type of M···H···Si interligand interaction found in certain niobocene silyl hydride complexes (**C** and **D**) which we classified as an *electron-rich*, interligand hypervalent interaction (IHI).[3] The IHI formally arises from donation of Nb−H bond electron density to the silicon−halogen antibonding orbital. this results in a three-centre, four-electron H···Si−Cl interaction, and in the case of **D** gives a five-centre, six-electron Cl−Si···H···Si−Cl bond. In both **C** and **D** silicon is five coordinate and hypervalent, with H and Cl occupying the apical sites of an approximate trigonal bipyramid. Experimental and theoretical studies by us[3] and others[4] have shown that the presence of a Si−Cl bond *trans* to hydride is crucial to developing shortened H···Si contacts and gives a concomitant lengthening of the Si−Cl bond. Analogous hypervalent interactions between a hydride ligand and a β-positioned silicon (β-IHI) have recently been found by Tilley and co-workers.[5]



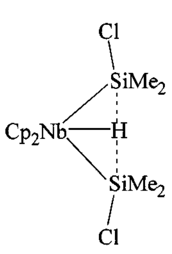
A



B



C



D

Given the current interest and importance of understanding the underlying factors controlling interligand interactions we were interested in finding new examples of complexes with unusual M···H···Si interactions. It is well-estab-

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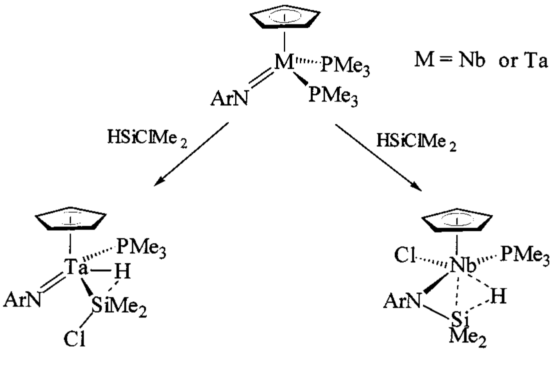
lished that Cp^- and NR^{2-} (R is typically alkyl or aryl) are isolobal fragments,[6] and so complexes of the type $[Cp_2MX_3]$ and $[CpM(NR)(L)(X)_2]$ (M = group 5 metal; X, L = 1- and 2-electron donors) are also isolobal. Suitable group 5 precursor complexes $[CpM(NAr)(PMe_3)_2]$ (M = Nb or Ta; Ar = 2,6-C_6H_3*i*Pr_2) were prepared from the corresponding $[CpM(NAr)Cl_2]$ complexes.[7]

The reactions of $[CpM(NAr)(PMe_3)_2]$ (M = Nb, Ta; Ar = 2,6-C_6H_3*i*Pr_2) with $HSiClMe_2$ (see Scheme 1) give two dramatically different types of complex depending only on the identity of M. These are $[CpTa(NAr)(H)(SiMe_2Cl)(PMe_3)]$ (**1**, 60% isolated yield) and $[CpNb\{\eta^3\text{-}N(Ar)SiMe_2{-}H\}Cl(PMe_3)]$ (**2**, 84% isolated yield), each of which possesses a different type of nonclassical M···H···Si interaction.



1

2

Scheme 1. Reaction of $[CpM(NAr)(PMe_3)_2]$ (M = Nb or Ta; Ar = 2,6-C_6H_3*i*Pr_2) with $HSiClMe_2$

The compound $[CpTa(NAr)(H)(SiMe_2Cl)(PMe_3)]$ (**1**) shows well-defined sets of signals for the Cp, NAr, $SiMe_2$ and PMe_3 ligands in its NMR spectra. The Ta−H resonance appears as a doublet $[^2J(H{-}P) = 64.1\ Hz]$ at δ = 5.13; the unusual low-field shift may be attributed to the anisotropy of the multiple bond to the imido ligand. Compound **1** is a rare example of a stable transition metal hydride complex supported by an imido group.[8] The solution NMR data are consistent with the solid state structure (Figure 1) which shows that the Ta-bound Si, hydride and P atoms all lie in the "bisecting plane" between the Cp and NAr ligands, consistent with the isolobal analogy between $[Cp_2MX_3]$ and $[CpM(NAr)(X)_2L]$. The silicon-bound chlorine atom is approximately *trans* to H(1) and also lies in this plane [maximum deviation from the calculated {Ta(1)−P(1)−H(1)−Si(1)−Cl(1)} least-squares plane = 0.13 Å].

The geometry at Ta in **1** closely resembles that of Nb in the nonclassical complexes $[Cp_2Nb(X)(H)(SiMe_2Cl)]$ (X = H **C** or $SiMe_2Cl$ **D**),[3] assuming that the arylimido group occupies the coordination site of one of the Cp rings. An analogous approximately *trans* position of apical Si−Cl and metal-bound H with the $\{MMe_2\}$ unit formally comprising an equatorial plane was previously observed in **C** and **D**. Recent experimental and theoretical studies have shown that comparatively short M−Si and long Si−Cl bonds are associated with interligand hypervalent interactions between the Si and H ligands.[3] The Si−Cl bond length of 2.177(2) Å in **1** is one of the longest reported for $[L_nM(SiR_2Cl)]$ (R = alkyl, aryl) complexes.[9] Furthermore, it is comparable to that found in the nonclassical complex **C** [Si−Cl = 2.170(2) Å], but significantly longer than that of **D** [Si−Cl = 2.163(1) Å]. The Ta−Si bond of 2.574(1) Å in **1** is the shortest reported to date [avg. 2.638, range 2.611−2.671 Å for six Ta^V nondisordered observations],[10] and is comparable to the Nb−Si bonds in **C** and **D** [Nb−Si = 2.579(2) and 2.597(1) Å, respectively]; these in turn are shorter than in other silyl derivatives of niobocene.[11]

Although the hydride ligand in **1** was crystallographically located and isotropically refined, the characteristically large estimated standard deviations (ca. 0.1 Å) associated with Ta−H and Si−H contacts do not allow for detailed discussion of the Si−H interaction. However, density functional theory (DFT) has conclusively been shown to provide valuable insight into transition metal complexes, including those with metal−hydrogen−ligand interactions.[12] A DFT partial geometry optimisation[13] of **1** allowing only the hydride position to change (starting with non-hydride atom coordinates taken from the X-ray study, and the hydride initially positioned *symmetrically* between Si and P) resulted in a structure with an Si−H contact of 2.158 Å, a P···H distance of 2.469 Å and a Ta−H distance of 1.888 Å. By way of comparison, Si···H contacts of 1.993−2.154 Å were previously calculated for the nonclassical model complexes $[Cp_2Nb(H)(SiH_2Cl)_2]$ and $[Cp_2Nb(H)_2(SiH_2Cl)]$.[3c,4]

Unambiguous experimental verification of the existence of the predicted *direct* Si−H bonding in compound **1** is the observed $^1J(Si{-}H)$ coupling constant of 33 ± 0.5 Hz. This $^1J(Si{-}H)$ is significantly larger then the postulated "nonbonding" value of 20 Hz,[1b] but is somewhat lower than the values (40−60 Hz) usually observed in silane σ-complexes. The observation of a "diminished" Si−H coupling constant in **1** is in complete agreement with our previous report that Si−H bonding through the IHI mechanism mainly involves silicon 3p orbitals.[3c]

In contrast to the formation of the tantalum derivative **1**, reaction of the niobium complex $[CpNb(NAr)(PMe_3)_2]$ with $HSiClMe_2$ gives exclusively $[CpNb\{\eta^3\text{-}N(Ar)SiMe_2{-}H\}Cl(PMe_3)]$ (**2**, see Scheme 1). The ^1H NMR spectrum of **2** shows, in addition to characteristic Cp, Ar, PMe_3 and $SiMe_2$ resonances, a high-field Nb−H resonance at δ = −5.67 indicative of substantial hydridic character.

The IR spectrum of **2** displays a band at 1620 cm^{-1} attributable to vibrations associated with the hydrogen bridging the silicon and niobium atoms. This band is closer to the typical region for ν(Nb−H) in niobocene hydrides (1750−1650 cm^{-1})[11,14] rather than to the typical ν(Si−H) region. For comparison, uncoordinated Si−H bonds exhibit ν(Si−H) bands at about 2100 cm^{-1}, whereas in d^0 Si−H···M β-agostic systems of type **B** this band is shifted to about 1800 cm^{-1}.[15] Therefore, the IR data also establish substantial hydridic character of the niobium-interacting hydrogen. However, the observed $^1J(Si{-}H)$ coupling con-

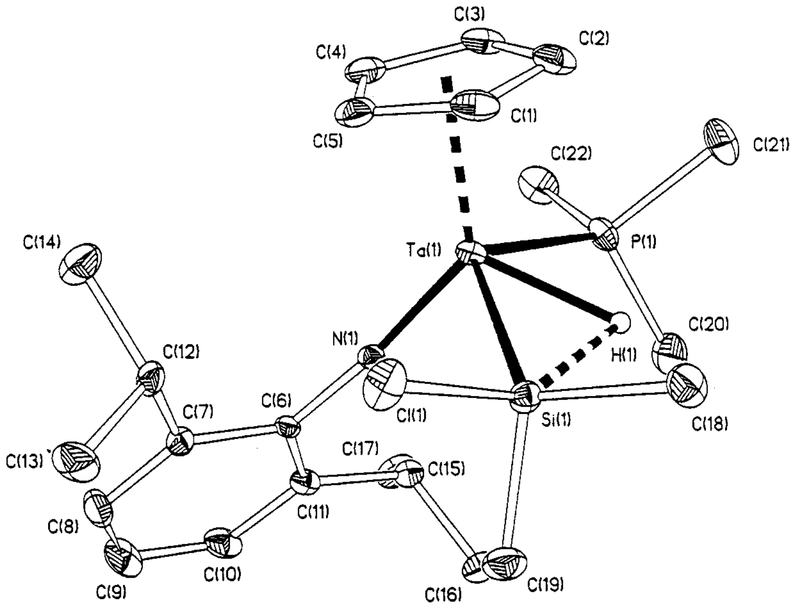
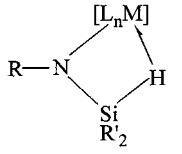


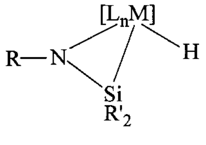
Figure 1. Molecular structure of [CpTa(NAr)(H)(SiMe$_2$Cl)(PMe$_3$)] (**1**); displacement ellipsoids are drawn at the 25% probability level, except for H(1) which is shown as a sphere of arbitrary radius; H atoms except H(1) are excluded for clarity; selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Ta(1)−N(1) 1.821(4), Ta(1)−P(1) 2.550(1), Ta(1)−Si(1) 2.574(1), Cl(1)−Si(1) 2.177(2), Ta(1)−H(1) 1.6(1), Si(1)−H(1) 2.3(1), P(1)−H(1) 2.3(1); P(1)−Ta(1)−Si(1) 120.63(5), Cl(1)−Si(1)−Ta(1) 112.05(7)

stant of 96.6 Hz in **2** unambiguously reveals also direct bonding between this hydride and silicon (and comprehensively rules out the description of **2** as a classical η^2-silanimine hydride complex, **F**). It is noteworthy that this ^1J(Si−H) value is significantly diminished with respect to the values observed for d^0 Si−H···M β-agostic systems [^1J(Si−H) = 113−142 Hz] such as **E**.



β -agostic silylamine

E



silanimine-hydride

F

The X-ray structure of **2** (Figure 2) comprises of a Nb atom ligated by Cp, Cl and PMe$_3$ ligands, and the coordination sphere is completed by an η^3-N(Ar)SiMe$_2$−H ligand. The Nb···H···Si bridging hydrogen atom, H(1), was located from a Fourier difference map and refined isotropically. As for **1**, a DFT partial geometry optimisation[13] was carried out on **2** to assess the predicted position of H(1). All atomic positions were taken from the X-ray structure and the Nb···H···Si bridging hydrogen position was optimised while other atoms were kept fixed. The observed and calculated Nb−H distances are 1.91(5) and 1.931 Å; the corresponding Si−H distances are 1.52(5) and 1.771 Å, respectively. As for **1**, the experimental and theoretical values agree within the uncertainties and approximations associated with the two methods and are supported by the ^{1}H NMR spectroscopic data and ^1J(Si−H) values.

It is interesting to compare the Nb−H and Si−H distances for **2** with those of normal terminal Nb−H bonds (range ca. 1.60 −1.81 Å, depending on the experimental method[11b,14,16]), and with previously reported free or β-agostic Si−H bonds (range ca. 1.42−1.50 Å[15,17]). It is also instructive to consider the Nb(1)−N(1)−Si(1) angle of 89.1(2)° in **2**. This is comparable with M−N−Si angles found previously for silanimine compounds [86.1(1)° and 89.1(2)° for two examples[18]]; these are significantly smaller than the corresponding values for β-agostic (M···H−Si) silylamine (**E**) complexes [range 95.1(1) − 103.4(1)° for four examples[15]].

Therefore the elongated Nb−H and Si−H bonds, contracted Nb−Si−N angles, diminished ^1J(Si−H), along with other NMR and IR spectroscopic data suggest that the bonding in **2** is intermediate between a β-agostic d^2 silylamine (**E**) and a d^0 silanimine-hydride (**F**) structure. The electronic structure from the DFT calculations for **2** is in line with this interpretation and reveals a metal-based HOMO (corresponding formally to a d^2 complex) that is well set up for back-bonding into the Si−H σ* antibonding orbital. Compound **2** may be a useful model of the transition state for the as-yet-unknown migratory insertion of a silanimine into a metal−hydride bond.

In conclusion, the reaction of CpM(NAr)(PMe$_3$)$_2$ (M = Nb, Ta) with HSiClMe$_2$ gives remarkably different nonclassical Si···H···M products depending only on the identity of M. Compound **1** provides further evidence for the existence of electron-rich M−H···Si interligand hypervalent interactions, while compound **2** is the first example of a β-agostic

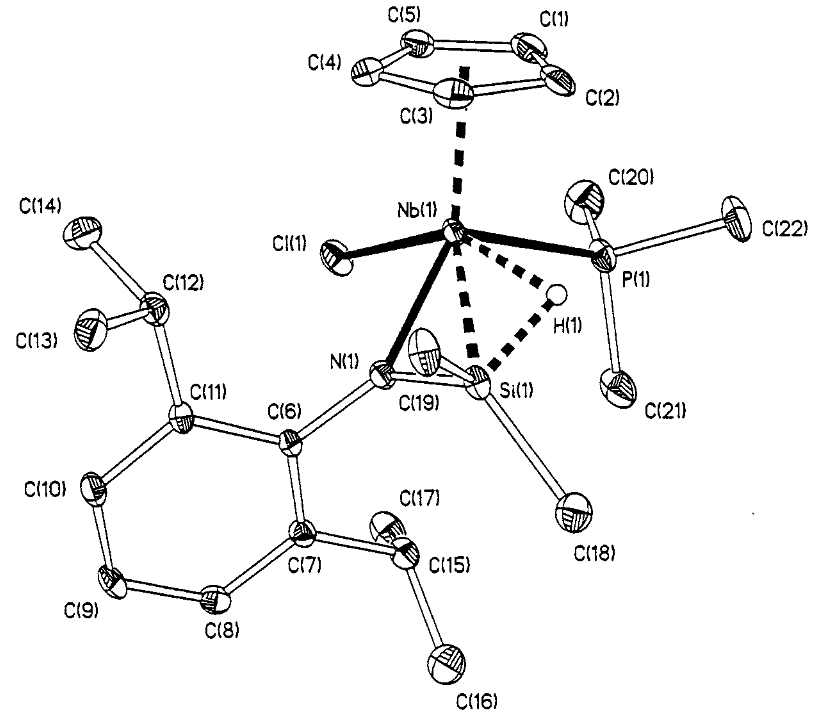


Figure 2. Molecular structure of [CpNb{η^3-N(Ar)SiMe$_2$−H}Cl(PMe$_3$)] (**2**); displacement ellipsoids are drawn at the 30% probability level, except for H(1) which is shown as a sphere of arbitrary radius; H atoms except H(1) are excluded for clarity; selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses: Nb(1)−N(1) 2.051(4), Nb(1)−P(1) 2.552(1), Nb(1)−Si(1) 2.646(1), Nb(1)−Cl(1) 2.497(1), Nb(1)−H(1) 1.91(5), Si(1)−H(1) 1.52(5), Si(1)−N(1) 1.704(4); Nb(1)−N(1)−Si(1) 89.09(16), Si(1)−Nb(1)−P(1) 109.37(5), Si(1)−Nb(1)−Cl(1) 123.42(5)

Si−H···M interaction showing such a "stretched" Si−H bond for a silylamine complex.

Experimental Section

Preparation of [CpTa(NAr)(H)(SiMe$_2$Cl)(PMe$_3$)] (1): To a solution of [CpTa(NAr)(PMe$_3$)$_2$] (1.03 g, 1.10 mmol) in pentane (30 mL) was added HClSiMe$_2$ (0.5 mL). After 14 h a light pink precipitate formed which was filtered off and dried in vacuo. Yield: 0.65 g (61%). − IR (Nujol): 1736 cm^{-1} ν(Ta−H). − ^{1}H NMR ([D$_6$]benzene): δ = 0.90 [d, *J*(H−P) = 8.5 Hz, 9 H, PMe$_3$], 0.95 (s, 3 H, SiMe$_2$), 1.23 (s, 3 H, SiMe$_2$), 1.23 [d, *J*(H−H) = 6.9 Hz, 6 H, CH*Me*$_2$], 1.27 [d, *J*(H−H) = 6.9 Hz, 6 H, CH*Me*$_2$], 4.04 [sept, *J*(H−H) = 6.9 Hz, 2 H, C*H*Me$_2$], 4.52 [d, *J*(H−P) = 1.5 Hz, 5 H, Cp], 5.13 [d, *J*(H−P) = 64.2 Hz, 1 H, Ta−H]. − ^{29}Si{^{1}H-selective} NMR ([D$_6$]benzene): δ = 91.7 [^{1}*J*(H−Si) = 33.3 Hz]. − ^{31}P{^{1}H} NMR ([D$_6$]benzene): δ = −4.3. − $C_{22}H_{38}ClNPSiTa$ (592.0): calcd. C 44.63, H 6.47, N 2.37; found C 44.72, H 6.46, N 2.30.

Preparation of [CpNb{η^3-N(Ar)SiMe$_2$−H}Cl(PMe$_3$)] (2): To a suspension of [CpNb(NAr)(PMe$_3$)$_2$] (1.46 g, 3.09 mmol) in pentane (15 mL) was added HSiClMe$_2$ (1.3 mL, excess). The mixture was kept 5 days to afford large dark-green crystals. These were filtered off, washed with cold pentane and dried in vacuo. Yield: 1.28 g (84%). The solution was reduced in volume to 5 mL and a second crop of **2** (0.20 g) crystallized after 3 days. − IR (Nujol): 1620 cm^{-1} ν(Nb−H). − ^{1}H NMR ([D$_6$]benzene): δ = −5.67 (s, 1 H, Nb−H), 0.22 (d, *J* = 0.9 Hz, 3 H, Si*Me*$_2$), 0.31 [d, *J*(H−P) = 2.0 Hz, 3 H, Si*Me*$_2$], 0.96 [d, *J*(H−P) = 7.8 Hz, 9 H, PMe$_3$], 1.14 (d, *J* = 6.8 Hz, 3 H, CH*Me*$_2$), 1.32 (overlapping 2 × d, *J* = 6.8 Hz, 6 H, 2 × CH*Me*$_2$), 1.50 (d, *J* = 6.7 Hz, 3 H, CH*Me*$_2$), 2.37 (sept, *J* = 6.8 Hz, 1 H, C*H*Me$_2$), 3.33 (sept, *J* = 6.7 Hz, 1 H, C*H*Me$_2$), 4.67 [d, *J*(H−P) 1.7 Hz, 5 H, Cp]. − ^{29}Si{^{1}H-selective} NMR ([D$_6$]benzene): δ = −52.1 [^{1}*J*(H−Si) = 96.6 Hz]. − ^{31}P{^{1}H} NMR ([D$_6$]benzene): δ = 11.5. − $C_{22}H_{38}ClNNbPSi$ (504.0): calcd. C 51.90, H 7.60, N 2.78; found C 51.9, H 7.71, N 2.60.

X-ray Crystallographic Study of 1 and 2: Crystals of **1** were grown from pentane, crystals of **2** from ether. For both structures the data were corrected for Lorentz and polarisation effects. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms except hydride (which was located from Fourier difference synthesis and positionally refined isotropically), were placed in calculated positions and refined in a riding model.

Crystal data for 1: $C_{22}H_{38}ClNPSiTa$, 0.15 × 0.20 × 0.27 mm, monoclinic, space group $P2_1/c$, $a = 15.893(1)$, $b = 9.092(1)$, $c = 19.136(2)$ Å, $\beta = 112.568(3)$°, $V = 2553.47$ Å^3, $\rho = 1.54$ g·cm^{-3}, μ(Mo-K_α) = 4.53 cm^{-1}, $T = 150$ K. Of 23837 data collected (0.96 ≤ θ ≤ 27.53°), 5838 [*R*(int) = 0.050] were independent and 4115 [$I > 3\sigma(I)$] reflections were used in the refinement of 249 parameters. An absorption correction based on multi-scans was applied ($T_{\min}$, $T_{\max}$ = 0.368, 0.615). $R(F) = 0.030$, $R(wF) = 0.035$. Min./max. peaks in final difference map: 1.03/−0.63 e·Å^{-3}.

Crystal Data for 2: $C_{22}H_{38}ClNNbPSi$, 0.19 × 0.17 × 0.14 mm, monoclinic, space group $C2/c$, $a = 31.391(6)$, $b = 10.150(2)$, $c = 16.945(3)$ Å, $\beta = 111.30(3)$°, $V = 5030(2)$ Å^3, $\rho = 1.331$ g·cm^{-3}, μ(Mo-K_α) = 7.04 cm^{-1}, $T = 150(2)$ K. Of 4813 data collected (1.0 ≤ θ < 25.5°), 4437 [*R*(int) = 0.0343] were independent [3557 reflections had $I > 2\sigma(I)$] and were used in the refinement of 313 parameters. An absorption correction (ψ-scans) was applied ($T_{\min}$, $T_{\max}$ = 0.721, 0.913). $R(F) = 0.050$, $R(wF^2) = 0.103$. Min./max. peaks in final difference map: 1.427/−0.868 e·Å^{-3}.

Crystallographic data (excluding structure factors) for the two structures reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-33301 (**1**) and CCDC-33302 (**2**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

DFT Studies: Calculations were performed using the density functional methods of the Amsterdam Density Functional (ADF) code Version 2.3.0.[13a] The basis set used triple-ζ accuracy sets of Slater orbitals with a single polarisation function added to main group atoms. The cores of the atoms were frozen. Vosko, Wilk and Nusair's local exchange correlation potential[13b] was employed with nonlocal exchange corrections by Becke[13c] and nonlocal correlation corrections by Perdew.[13d]

Whereas calculation on the whole "real" complex is unfeasible for us because of the time that it would take, attempted full DFT geometry optimisation of an oversimplified model of **2**, having hydrogen substituents on Si, P and N atoms, converged to a structure with quite different distances between Si and N. This shows (as we found in the chemistry) that substituents are important. Note that in the calculations, all of the distances and angles were chemically realistic, but obviously were more appropriate to a compound further along the reaction coordinate. It is well-known that in certain cases involving "weak" interactions the influence of steric/electronic substituent effects can be crucial.

Acknowledgments

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