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Synthesis and Reactions of Silyl and Germyl Derivatives of Scandocene. Structure of $Cp_2Sc[Si(SiMe_3)_3](THF)$

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The scandocene complexes $Cp_2Sc(ER_3)(THF)$ ($ER_3 = Si(SiMe_3)_3$ (**1**), $Si(SiMe_3)_2Ph$ (**2**), Si^tBuPh_2 (**3**), $SiPh_3$ (**4**), $Ge(SiMe_3)_3$ (**5**)) have been prepared by addition of the appropriate silyl- or germyllithium reagent to $[Cp_2ScCl]_2$. The crystal structure of **1** revealed no unusual distortions in the molecule and a Sc–Si bond length of 2.863(2) Å. These unusually reactive d^0 silyl complexes polymerize ethylene, and **1** reacts with phenylacetylene via σ-bond metathesis to give $HSi(SiMe_3)_3$ and the known acetylide $[Cp_2ScC{\equiv}CPh]_2$. Complexes **1**, **3**, and **5** react with CO via CO–CO coupling processes, to give the scandoxyketene derivatives $(Cp_2ScO)(R_3E)C{=}C{=}O$, which are trapped as the adducts $Cp_2Sc[OC(ER_3)C(L)O]$ (**6**, $ER_3 = Si(SiMe_3)_3$, L = Me-THF; **10**, $ER_3 = Ge(SiMe_3)_3$, L = THF; **11**, $ER_3 = Si(SiMe_3)_3$, L = PMe_2Ph). In nonpolar media, carbonylations of **1**, **3**, and **5** give the enedione diolate structures $[Cp_2ScOC(ER_3)CO]_2$ ($ER_3 = Si(SiMe_3)_3$ (**7**), Si^tBuPh_2 (**8**), $Ge(SiMe_3)_3$ (**9**)). The insertion of CN-2,6-$Me_2C_6H_3$ (CNXyl) into the Sc–Si bond of **1** provides the stable η^2-iminosilaacyl complex $Cp_2Sc[\eta^2\text{-}CN(Xyl)Si(SiMe_3)_3]$ (**12**), which reacts with $PhC{\equiv}CH$ to afford $[Cp_2ScC{\equiv}CPh]_2$ and the formimidoylsilane $HC(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3$ (**13**). Finally, **12** reacts with a second equivalent of CNXyl to form $\{Cp_2ScN(Xyl)C(SiMe_3){=}CN{=}CCMe{=}CHCH{=}CHCMe[Si(SiMe_3)_2]\}$ (**14**), which appears to result from rearrangement of the intermediate ketenimine $(Cp_2ScNXyl)[(Me_3Si)_3Si]C{=}C{=}NXyl$ via (1) migration of $SiMe_3$ from the $Si(SiMe_3)_3$ group to the α-carbon of the ketenimine and (2) addition of the resulting $C{=}Si(SiMe_3)_2$ double bond to an adjacent xylyl ring.

Introduction

Previous investigations in our laboratories have exploited the high reactivity of d^0 metal–silicon bonds toward small molecules. These studies have focused on zirconium,[1] hafnium,[1] niobium,[2] and tantalum[3] d^0 silyl complexes and their reactions with single, double, and triple bonds. This chemistry could prove useful in development of catalytic transformations for silicon compounds, particularly if more reactive metal–silicon-bonded species are discovered. Given the high reactivity associated with hydrido, alkyl, and aryl derivatives of the scandium group and f-block metals,[4] it seemed that more reactive d^0 M–Si bonds might be found in silyl complexes of these metals.

Very few silyl derivatives of the lanthanide, actinide, or scandium group metals have been reported. Schumann and co-workers prepared the first organolanthanide silyl complexes $[Li(dme)_3][Cp_2Ln(SiMe_3)_2]$ (Ln = Sm, Lu) in 1985,[5] while the first report of an organoactinide silyl complex, Cp_3USiPh_3, appeared only recently.[6] In addition, we have recently described a σ-bond metathesis route to the stable lanthanide silyl derivatives $Cp^*{}_2LnSiH(SiMe_3)_2$ (Ln = Nd, Sm).[7] Here we describe the synthesis and characterization of the first scandium silyl and germyl complexes and some aspects of their reaction chemistry. We have previously communicated the unusual reactions

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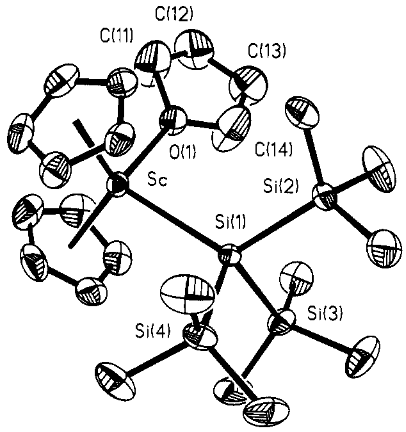
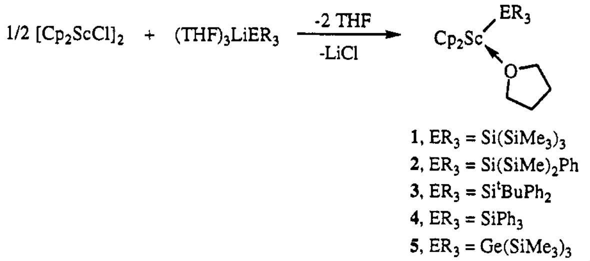


Figure 1. ORTEP view and atom-labeling scheme for $Cp_2Sc[Si(SiMe_3)_3](THF)$ (1).

of $Cp_2Sc[Si(SiMe_3)_3](THF)$ (1) with carbon monoxide and xylyl isocyanide[8a] and the insertion of CO_2 into the Sc–Si bonds of 1 and $Cp_2Sc(Si^tBuPh_2)(THF)$ (3) to give the dimeric silanecarboxylate complexes $[Cp_2Sc(\mu\text{-}O_2CSiR_3)]_2$.[8b]

Results and Discussion

Synthesis of Silyl and Germyl Complexes. The new silyl and germyl complexes were prepared via addition of the appropriate lithium reagent to dimeric scandocene chloride (eq 1).



(1)

The yellow crystalline complexes 1–5 are extremely air- and moisture-sensitive and are soluble in most organic solvents. Pentane was found to be a superior reaction solvent for the synthesis of 1 (compared to toluene and tetrahydrofuran), since it allowed isolation of the product in much higher yield (75%, after crystallization from toluene). With the less soluble lithium silyl $(THF)_3LiSi^tBuPh_2$, toluene was employed as the reaction solvent. Addition of toluene to a mixture of $(THF)_3LiSiPh_3$ and $[Cp_2ScCl]_2$ gave the expected yellow solution, which after filtering and layering with pentane provided yellow microcrystals of a complex that was characterized as 4 by NMR spectroscopy (36% yield). However, combustion analyses for this compound were not reproducible and did not correspond to a formula for 4. We therefore only tentatively characterize this complex as 4 and assume that it does not undergo clean combustion during analysis. Complexes 1–5 are quite thermally stable both in the solid state and in solution. Thermolysis of 1 in benzene-d_6 at 90 °C resulted in formation of $HSi(SiMe_3)_3$, along with unidentified scandium products ($t_{1/2} \approx 24$ h).

Compound 1 crystallizes from toluene in the $P2_1/n$ space group. An ORTEP view of 1 is shown in Figure 1, and geometrical parameters are listed in Table I. The Sc–Si bond length (2.863(2) Å) is shorter than the Sm–Si bond length of 3.052(8) Å in $[Cp^*_2SmSiH(SiMe_3)_2]_2$,[7] by a distance (0.19 Å) that closely reflects the difference in ionic radii between Sc^{3+} and Sm^{3+} (ca. 0.21 Å).[9]

Table I. Selected Bond Distances (Å) and Angles (deg) for 1[a]

(a) Bond Distances			
Sc–Si(1)	2.863(2)	O–C(11)	1.452(5)
Sc–O	2.216(3)	O–C(14)	1.354(5)
Si(1)–Si(2)	2.377(1)	Sc–CNT(1)	2.210
Si(1)–Si(3)	2.364(4)	Sc–CNT(2)	2.205
Si(1)–Si(4)	2.366(1)		
(b) Bond Angles			
O–Sc–Si(1)	95.2(1)	Si(2)–Si(1)–Si(4)	102.1(1)
Sc–Si(1)–Si(2)	120.0(1)	Si(3)–Si(1)–Si(4)	101.9(1)
Sc–Si(1)–Si(3)	119.0(1)	C(14)–O–C(11)	105.0(4)
Sc–Si(1)–Si(4)	110.4(1)	CNT(1)–Sc–CNT(2)	115.3(2)
Si(2)–Si(1)–Si(3)	100.7(1)		

[a] CNT(1) and CNT(2) are the centroids of the $\eta^5\text{-}C_5H_5$ rings.

Reactions with Alkenes and Alkynes. Alkene insertions into metal–carbon and metal–hydrogen bonds of lanthanocene and related derivatives have been studied in connection with alkene polymerization and alkene hydrogenation.[4b,f,e,10] In general, alkene insertions into metal–silicon bonds are thought to be much more difficult,[11] but the zirconium silyls $CpCp^*Zr[Si(SiMe_3)_3]Cl$ and $Cp^*Cl_3MSi(SiMe_3)_3$ (M = Zr, Hf) were found to undergo stoichiometric insertion reactions with 1 equiv of ethylene.[1g]

Addition of ethylene to solutions of 1 results in ethylene polymerization, but no insertion products could be identified by ^1H NMR spectroscopy. All of the silyl complexes 1–5 were found to polymerize ethylene. The molecular weight distributions M_w for polyethylene samples from three different runs with 1 as catalyst varied between 27 000 and 410 000. Correspondingly, the polydispersities (M_w/M_n) ranged from 3.6 to 5.5. The calculated number of polymer chains per catalyst center from these data varied from 0.13 to 1.00. It therefore appears that these polymerizations involve chain transfer, and this is supported further by the observation that unreacted 1 is often observed (by ^1H NMR spectroscopy) after polymerizations in NMR tubes (benzene-d_6) and by the fact that ^1H NMR spectra of the polymers (tetrachloroethane-d_2, 125 °C) contain virtually no evidence for $Si(SiMe_3)_3$ end groups.

Reaction of 1 with propene (15 psi) gave an oily residue which contained $HSi(SiMe_3)_3$, but no propene oligomers were observed by ^1H NMR spectroscopy. Furthermore, no $Cp_2Sc(\eta^3\text{-}C_3H_5)$,[12] which might have formed via σ-bond metathesis reactions of 1 with propene,[4l] was formed. No reaction was observed between 1 and butadiene (excess, benzene-d_6) or cyclohexene (benzene-d_6, 90 °C, 17 h).

Addition of $PhC{\equiv}CH$ to a benzene solution of 1 resulted in quantitative formation of $HSi(SiMe_3)_3$ and a light yellow solid, which was identified as the known acetylide $[Cp_2$-

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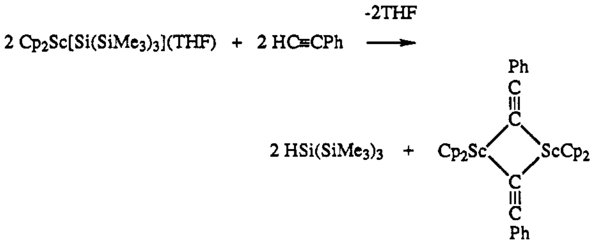
$Sc(C{\equiv}CPh)]_2$[12] (by ^1H NMR and IR spectroscopy; eq 2).

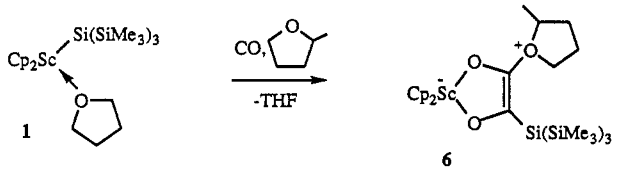


(2)

Similar reactions have been observed between terminal alkynes and $Cp^*{}_2ScH$ or $Cp^*{}_2ScMe$.[41] Under acetylene (15 psi), a benzene solution of 1 was observed (by ^1H NMR spectroscopy) to form $HSi(SiMe_3)_3$ and a small quantity of acetylene oligomers. However, 1 does not react with 2-butyne.

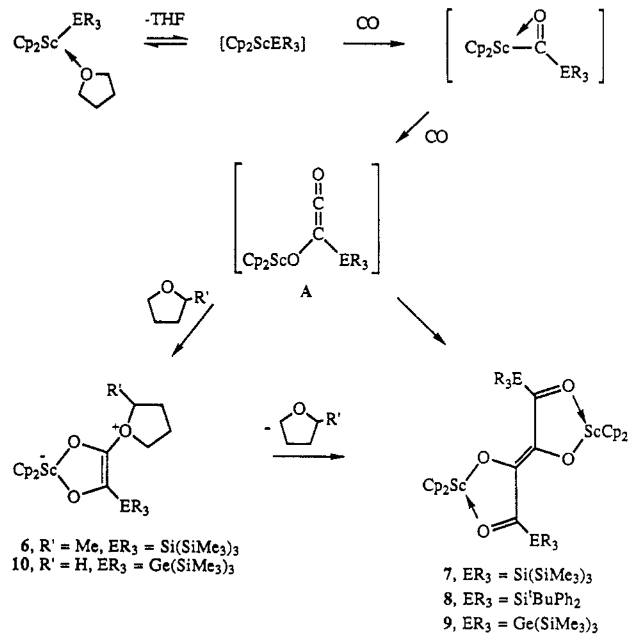
Reactions with Carbon Monoxide. Electron-deficient alkyl and silyl complexes of d^0 metals generally combine with CO or CNR (isocyanides) to form η^2-COR′ and η^2-C(NR)R′ derivatives, respectively.[1a-d,3f,13,14] In some cases these species react further to form products of CO–CO or CNR–CNR coupling.[1b,3f,14] Although transient ketene or ketene-like intermediates may play important roles in these coupling reactions, their elusive nature has left them rather ill-defined. Interestingly, their reaction chemistry seems to vary considerably depending on the nature of the d^0 center, but few of these trends are presently understood. In the course of examining the scandium derivatives described above, we have observed new processes involving CO–CO and CNR–CNR coupling.

Carbonylation of 1 in methyltetrahydrofuran (50 psi of CO) gives an orange solution, which results from clean formation of a new product (6) that was characterized in solution by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of 6-$^{13}C_2$ (prepared from 1 and ^{13}CO) contains doublets at δ 142.21 and 158.57 ($^1J_{CC}$ = 84 Hz), indicating coupling of two CO molecules via formation of a carbon–carbon bond. Since these NMR parameters are in close agreement with those observed for $Cp^*Cl_3Ta[O^{13}C(SiMe_3)^{13}C(2,6\text{-}Me_2NC_5H_3)O]$ (dd, δ 139.7; dd, δ 149.7; $^1J_{CC}$ = 84 Hz),[3f] we characterize 6 as the ketene adduct $Cp_2Sc\{OC[Si(SiMe_3)_3]C(OC_5H_{10})O\}$ (eq 3). Note that an analogous tantalum derivative, $Cp^*Cl_3Ta[OC(SiMe_3)C(OC_5H_{10})O]$, decomposes rapidly via ether cleavage to $Cp^*Cl_3Ta[OCH(SiMe_3)C(O)O(CH_2)_3CH{=}CH_2]$.[3f]

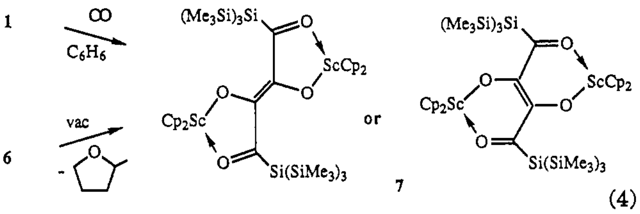


(3)

Scheme I



Removal of solvent from 6 produces a green solid, which exhibits spectroscopic properties distinct from those of the starting compound. This new green complex (7), which can be crystallized from pentane, results from loss of methyltetrahydrofuran from 6 and can also be prepared directly from 1 by carbonylation in nonpolar solvents. The characterization of 7 as an enedione diolate (eq 4) was facilitated by mass spectroscopy and the ^{13}C NMR spectrum of 7-$^{13}C_4$, which exhibits two well-resolved AA′BB′ multiplets centered at 243.97 and 155.89 ppm.[15] The "acylsilane" (SiCO) ^{13}C resonance (δ 243.97) is very close to values that have been observed for free acylsilanes (cf. $Me_3SiCOPh$, which has a ^{13}C chemical shift at δ 236.73[16]). The two possible enedione diolate structures, which cannot be distinguished on the basis of available data, are linkage isomers that in principle may be interconverted by rotation about the C=C double bond. Examples of both structures have been structurally characterized.[14a,c] The lability of methyltetrahydofuran in 6 suggests that formation of 7 occurs by way of dimerization of the ketene $(Cp_2ScO)[(Me_3Si)_3Si]C{=}C{=}O$ (Scheme I).



(4)

Carbonylation of $Cp_2Sc(Si^tBuPh_2)(THF)$ (3) in tetrahydrofuran *initially* gives a green solution, which then turns orange. The orange oil isolated from this reaction contained a complex mixture of products (by ^1H NMR

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(15) For 7-$^{13}C_4$, computer simulation of the ^{13}C spectrum yielded J_{AB} = 48.9 Hz, $J_{BB'}$ = 73.4 Hz, $J_{AB'}$ = 8.8 Hz, $J_{AA'}$ = 0.2 Hz.

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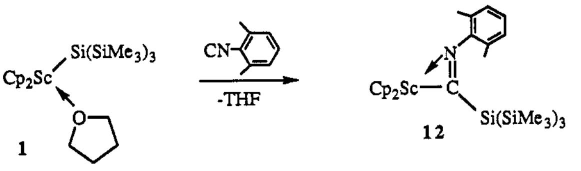
spectroscopy). In benzene, however, the carbonylation cleanly produces the enedione diolate $[Cp_2ScOC(Si^tBuPh_2)CO]_2$ (**8**), isolated as green crystals from pentane. The carbonylation of $Cp_2Sc[Ge(SiMe_3)_3](THF)$ (**5**) is noticeably slower than the comparable reactions of carbon monoxide with silyls **1** and **3** but proceeds to blue solutions of the enedione diolate $[Cp_2ScOC[Ge(SiMe_3)_3]CO]_2$ (**9**), isolated as red crystals from acetonitrile/toluene (5:1). The latter reaction represents, as far as we know, the only example of CO insertion into a transition-metal–germanium bond. Spectroscopic properties for **8** and **9** suggest structures analogous **7**.

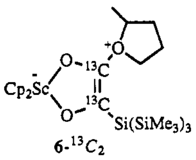
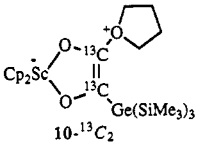
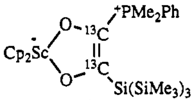
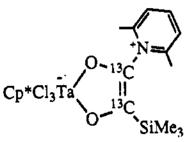
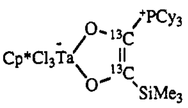
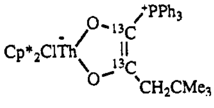
Earlier precedent for the conversions in Scheme I are found in carbonylation studies on $Cp^*Cl_3TaSiMe_3$[3f] and $Cp^*_2ClThCH_2{}^tBu$.[14a] It is presumed that acyls of the type $Cp_2Sc(\eta^2\text{-}COER_3)$ form initially, but we have been unable to detect such an intermediate by monitoring the reaction of **3** with ^{13}CO (which eventually gives **8**-$^{13}C_4$) by NMR spectroscopy at low temperatures. The proposed ketene intermediates (A) have been trapped as the methyltetrahydrofuran adduct **6**-$^{13}C_2$ and as a THF adduct of the germylketene, **10**-$^{13}C_2$. Additionally, **1** reacts with ^{13}CO in the presence of an excess (25 equiv) of PMe_2Ph (benzene-d_6/THF, 1:1) via clean formation of a single product that, on the basis of spectroscopic data, is characterized as the phosphine adduct $Cp_2Sc\{O^{13}C[Si(SiMe_3)_3]^{13}C(PMe_2Ph)O\}$ (**11**-$^{13}C_2$). In the ^{13}C NMR spectrum of **11**-$^{13}C_2$, the diolate carbons appear at δ 115.2 (dd, $^1J_{PC}$ = 104 Hz, $^1J_{CC}$ = 70.6 Hz) and 189.5 (dd, $^2J_{PC}$ = 13.6 Hz, $^1J_{CC}$ = 70.6 Hz). The ^{31}P NMR spectrum exhibits the expected doublet of doublets at δ 4.18 ($^1J_{PC}$ = 104 Hz, $^2J_{PC}$ = 13.6 Hz). Preparative-scale reactions failed to provide **11** in pure form. Interestingly, addition of ^{13}CO to a solution of **5** and PMe_2Ph (excess) resulted only in formation of the THF adduct **10**-$^{13}C_2$. Table II compares ^{13}C NMR parameters for various ketene adducts.

Reactions with CN-2,6-$Me_2C_6H_3$ (CNXyl). The isocyanide CNXyl reacts with **1** to afford an isolable monoinsertion product, the yellow η^2-iminosilaacyl **12** (eq 5). The structure of **12** was assigned by the diagnostic ν(CN) stretching frequency in the infrared spectrum at 1500 cm^{-1} and by a ^{13}C NMR chemical shift for the iminosilaacyl carbon at δ 299.07.[1b,d]

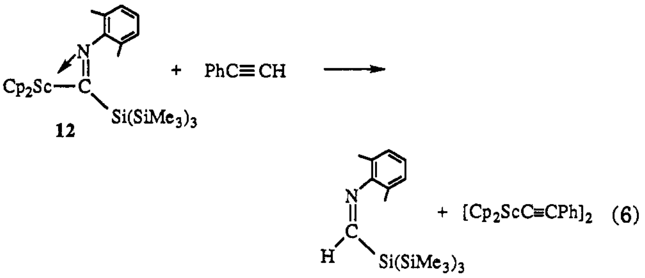


(5)

Table II. Comparison of ^{13}C NMR Parameters for Selected Ketene Adducts

compd	^{13}C NMR shift (δ) C_α	^{13}C NMR shift (δ) C_β	$^1J_{C_\alpha C_\beta}$ (Hz)	ref
 6-$^{13}C_2$	142.2	158.6	84	*a*
 10-$^{13}C_2$	145.1	153.6	86	*a*
 11-$^{13}C_2$	115.2	189.5	71	*a*
	139.7	149.7	83	3f
	136.3	161.0	68	3f
	117.8			16a

[a] This work.



(6)

In general, η^2-iminosilaacyl complexes have proven to be unreactive.[1b,d] However, **12** undergoes Si–C bond cleavage in two processes that have been examined. First, reaction of **12** with phenylacetylene quantitatively gives the known acetylide $[Cp_2Sc(C{\equiv}CPh)]_2$[12] and a second product that we characterize as the formimidoylsilane $HC(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3$ (**13**, eq 6), which sublimes as a white microcrystalline solid. This reaction is somewhat surprising, especially given the fact that the zirconium η^2-iminosilaacyls $Cp_2Zr[\eta^2\text{-}C(SiR_3)N(Xyl)]Cl$ (R = Me, $SiMe_3$) are inert toward $HC{\equiv}CPh$.[17] The scandium iminosilaacyl **12** is probably more reactive because of its more polar metal–carbon bond. Assignment of the structure of **13** is based on its exact-mass spectrum (exact mass calcd 379.2003, found 379.1984) and on comparison to spectroscopic properties for the known (*N*-cyclohexylformimidoyl)trimethylsilane.[18] The ^{13}C NMR shift for the imido carbon appears at δ 182.2 (d, $^1J_{CH}$ = 137.8 Hz). We have reported related reactions, based on acidification of zirconium silaacyl derivatives, as routes to the first examples of formylsilanes, $(Me_3Si)_3SiCHO$[19] and Ph_3SiCHO.[1j]

Addition of 1 equiv of CNXyl to a benzene solution of **12**, or reaction of **1** with 2 equiv of CNXyl, results in formation of the blue complex **14**. The combustion analysis for isolated **14** is consistent with a 1:2 adduct of $Cp_2ScSi(SiMe_3)_3$ with isocyanide, $Cp_2Sc(CNXyl)_2Si(SiMe_3)_3$. The ^1H NMR spectrum for **14** revealed the presence of a rather complex structure, with inequivalent Cp rings and three inequivalent $SiMe_3$ groups in a 1:1:1 ratio. The structure of this compound was determined by

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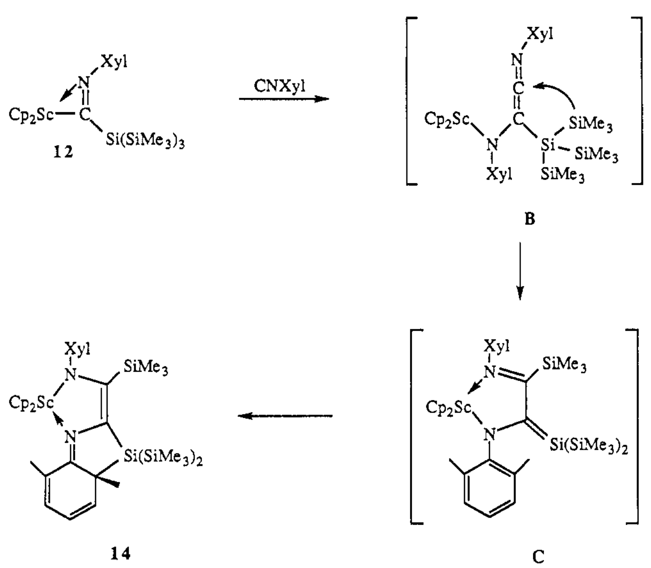
(17) Campion, B. K.; Tilley, T. D. Unpublished results.

(18) Saegusa, T.; Ito, Y.; Kobayashi, S.; Hirota, K. *J. Am. Chem. Soc.* **1967**, *89*, 2240.

(19) Elsner, F. H.; Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 313.

Scheme II



X-ray crystallography,[8a] which provided the structure given in Scheme II.

Thus, compound 14 is composed of three fused rings and is the product of Si–Si bond cleavage in the silyl ligand. A likely mechanism for the formation of 14 is given in Scheme II. On the basis of precedents in η^2-silaacyl chemistry, the η^2-iminosilaacyl group of 12 probably undergoes nucleophilic attack by isocyanide to give a ketenimine intermediate (B).[1b,3f] A closely related ketenimine complex, $Cp_2(Cl)Zr[OC(SiMe_3){=}C{=}NXyl]$, has been characterized.[1b] Migration of a trimethylsilyl group to the α-carbon of the ketenimine ligand would then result in intermediate C, which possesses a reactive Si=C double bond. Ishikawa and co-workers have observed related 1,3-silyl shifts from silicon to carbon, which generate silene (Si=C) intermediates in the coordination sphere of nickel.[20] Cycloaddition of the Si=C double bond in C to the adjacent xylyl ring would then give the connectivity observed for the final product. Attempts to trap the proposed silene intermediate with $(MeO)_3SiH$, Me_3SiOMe, and 2,3-dimethylbutadiene were unsuccessful, but this is not surprising since intramolecular rearrangement of the silene C to 14 should be quite rapid.

Conclusions

In a number of ways, scandocence silyl complexes appear to display reactivity patterns that are comparable to those that have been seen previously for analogous alkyl derivatives. As d^0 metal silyl complexes, the scandium derivatives reported here are among the most reactive. In contrast with many other compounds which contain d^0 M–Si bonds, reactions with alkenes and alkynes occur. Unfortunately, however, direct insertion products have not been detected. The Sc—Si bonds that have been examined also rapidly insert carbon monoxide and xylyl isocyanide to produce insertion products. Comparable processes have been observed in other d^0 systems, but a number of the scandium insertion products described here seem remarkably labile. This is most apparent for the η^2-iminosilaacyl 14, which reacts with a relatively weak acid ($PhC{\equiv}CH$) via cleavage of the Sc—C bond and with CNXyl via a highly unusual sequence that appears to involve migration of a trimethylsilyl group from silicon to the α-carbon of a ketenimine fragment. This chemistry apparently generates a reactive silene (Si=C) group, which adds to an adjacent xylyl ring. We believe that the results reported here are encouraging with respect to the future of scandium group- and lanthanide-silicon chemistry, and efforts in this direction are continuing.

Experimental Section

Manipulations were performed under an inert atmosphere of nitrogen or argon, using Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. ^1H NMR spectra were recorded at 300 MHz with a GE QE-300. ^{29}Si, ^{13}C, and ^{31}P NMR spectra were recorded at 59.6, 75.5, and 121.5 MHz, respectively, on the GE QE-300. Mass spectroscopic analyses were performed by the UC Riverside Mass Spectrometry Laboratory. Carbon monoxide (Linde Specialty Gases), 90% ^{13}C carbon monoxide (MSD), ethylene (Linde Specialty Gases), propene (Aldrich), PMe_2Ph (Aldrich), and 2,6-$Me_2C_6H_3NC$ (Fluka) were used as received. The compounds $[Cp_2ScCl]_2$,[12] $(THF)_3LiE(SiMe_3)_3$ (E = Si,[21] Ge[22]), and $(THF)_3LiSi(SiMe_3)_2Ph$[23] were prepared by literature methods.

$(THF)_3LiSi^tBuPh_2$. Under argon, a tetrahydrofuran (150 mL) solution of $Ph_2{}^tBuSiCl$ (10 g, 0.036 mol) was added dropwise over 1.5 h (after addition of an initial aliquot of 5 mL) to a stirred suspension of lithium wire (1.0 g, 0.14 mol, cut into 3–4-mm pieces) in tetrahydrofuran (20 mL). The red solution was filtered, the volatiles were removed *in vacuo*, and the resulting crude yellow solid was washed with pentane (100 mL) and dried under vacuum to give yellow crystals (mp 61–63 °C) in 79% yield (13.2 g). Cooling the pentane wash (−30 °C) gave an additional 3.0 g of product, for a total yield of 97%. ^1H NMR (benzene-d_6): δ 1.32 (m, 12 H, OCH_2CH_2), 1.47 (s, 9 H, CCH_3), 3.43 (m, 12 H, OCH_2CH_2), 7.18 (m, 2 H, para H), 7.32 (m, 4 H, meta H), 7.96 (d, $^3J_{HH}$ = 6.9 Hz, 4 H, ortho H). ^{13}C NMR (benzene-d_6): δ 20.46 ($SiCCH_3$), 25.39 (t, $^1J_{CH}$ = 133.5 Hz, OCH_2CH_2), 31.95 (q, $^1J_{CH}$ = 123.1 Hz, $SiCCH_3$), 68.30 (t, $^1J_{CH}$ = 149.0 Hz, OCH_2CH_2), 124.40 (dt, $^1J_{CH}$ = 157.3 Hz, $^2J_{CH}$ = 7.5 Hz, para C), meta C obscured by solvent, 137.39 (dt, $^1J_{CH}$ = 154.8 Hz, $^2J_{CH}$ = 7.8 Hz, ortho C), 156.81 (ipso C). ^{29}Si NMR (benzene-d_6, INEPTR): δ 7.54.

$Cp_2Sc[Si(SiMe_3)_3](THF)$ (1). Pentane (115 mL) was added to a mixture of $(THF)_3LiSi(SiMe_3)_3$ (6.80 g, 0.014 mmol) and $[Cp_2ScCl]_2$ (3.10 g, 0.007 mmol), resulting in a bright yellow solution. After the mixture was stirred for 24 h, the volatiles were removed *in vacuo* and the crude yellow solid was extracted into toluene (3 × 30 mL). The combined extracts were cooled (−40 °C) to give the product as yellow crystals (mp 194–196 °C) in 44% yield (3.06 g, 6.18 mmol). Two further crystallizations produced a total yield of 75% (5.40 g, 0.011 mmol). Anal. Calcd for $C_{23}H_{45}OSi_4Sc$: C, 55.82; H, 9.17. Found: C, 55.92; H, 9.03. IR (Nujol, CsI, cm^{-1}): 1235 m, 1015 m, 860 m sh, 830 s, 790 s, 778 s, 670 m, 620 m, 360 w. ^1H NMR (benzene-d_6): δ 0.50 (s, 27 H, $SiCH_3$), 0.98 (m, 4 H, OCH_2CH_2), 2.99 (m, 4 H, OCH_2CH_2), 6.12 (s, 10 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 6.15 ($SiCH_3$), 24.14 (OCH_2CH_2), 70.59 (OCH_2CH_2), 111.53 (C_5H_5). $^{29}Si\{^1H\}$ NMR (benzene-d_6, INEPTR): δ 31.04 ($Si(SiMe_3)_3$), −126.17 ($Si(SiMe_3)_3$).

$Cp_2Sc[Si(SiMe_3)_2Ph](THF)$ (2). Pentane (50 mL) was added to a flask containing $[Cp_2ScCl]_2$ (0.41 g, 0.97 mmol) and freshly isolated $(THF)_3LiSi(SiMe_3)_2Ph$ (0.94 g, 1.98 mmol), to give a bright yellow solution that deposited a yellow solid. After the mixture was stirred for 10 min, the volatiles were removed *in vacuo* and the crude product was extracted into toluene (50 mL). After filtration, the clear yellow solution was concentrated (to ca. 5 mL) and cooled (−40 °C) to give the product as yellow

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(20) (a) Ishikawa, M.; Ono, T.; Saheki, Y.; Minato, A.; Okinoshima, H. *J. Organomet. Chem.* **1989**, *363*, C1. (b) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

(21) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

(22) Brook, A. G.; Abdesaken, F.; Sollradl, H. *J. Organomet. Chem.* **1986**, *299*, 9.

(23) This compound was synthesized using the same procedure reported for $(THF)_3LiSi(SiMe_3)_3$,[21] with $PhSiCl_3$ in place of $SiCl_4$.

crystals (mp 163–166 °C) in 61% yield (0.60 g). The product may also be crystallized from diethyl ether. Anal. Calcd for $C_{26}H_{41}OSi_3Sc$: C, 62.60; H, 8.28. Found: C, 62.18; H, 8.15. IR (Nujol, CsI, cm^{-1}): 1573 w, 1421 w, 1241 s, 1178 w, 1063 w, 1018 s, 832 s, 803 m sh, 790 s, 745 w, 731 m, 706 m, 676 m, 622 m, 471 w, 368 w. ^1H NMR (benzene-d_6): δ 0.51 (s, 18 H, $SiCH_3$), 1.01 (br m, 4 H, $OCH_2CH_2CH_2$), 3.05 (br m, 4 H, OCH_2CH_2), 6.01 (s, 10 H, C_5H_5), 7.13 (m, 1 H, para H), 7.26 (m, 2 H, meta H), 7.73 (m, 2 H, ortho H). ^{13}C NMR (benzene-d_6): δ 4.41 (q, $^1J_{CH}$ = 121.8 Hz, $SiCH_3$), 24.64 (t, $^1J_{CH}$ = 137.2 Hz, OCH_2CH_2), 70.58 (unresolved t, OCH_2CH_2), 111.25, (dt, $^1J_{CH}$ = 159.9 Hz, $^2J_{CH}$ = 7.1 Hz, C_5H_5), 125.16 (dt, $^1J_{CH}$ = 159.1 Hz, $^2J_{CH}$ = 6.8 Hz, para C), 128.29 (d, $^1J_{CH}$ = 158.4 Hz, ortho C), 136.93 (dt, $^1J_{CH}$ = 153.9 Hz, $^2J_{CH}$ = 8.0 Hz, meta C), 149.90 (br s, ipso C). ^{29}Si NMR (benzene-d_6, INEPT): δ −10.14 ($Si(SiMe_3)_3$); the resonance for ($Si(SiMe_3)_3$) was not observed.

$Cp_2Sc(Si^tBuPh_2)(THF)$ (3). Toluene (40 mL) was added to a flask containing both $[Cp_2ScCl]_2$ (1.46 g, 3.46 mmol) and $(THF)_3LiSi^tBuPh_2$ (3.20 g, 6.93 mmol). The resulting yellow-orange solution was stirred for 45 min. After the LiCl was allowed to settle, the solution was filtered and the remaining solids were extracted with more toluene (2 × 15 mL). Concentrating (to <10 mL) and cooling (−30 °C) the combined extracts gave the product as yellow crystals (mp 162–164 °C) in 37% yield (1.26 g). The resulting mother liquors, when layered with pentane, produced an additional 1.14 g (total yield 71%). Anal. Calcd for $C_{30}H_{37}OSiSc$: C, 74.04; H, 7.66. Found: C, 73.65; H, 7.57. IR (Nujol, CsI, cm^{-1}): 1579 w, 1421 m, 1350 w, 1248 w, 1187 w, 1080 m, 1064 w, 1014 s, 861 m, 848 m, 814 s, 799 s, 789 s, 747 s, 740 s, 687 w, 560 br w, 495 m, 478 w, 445 w, 363 m. ^1H NMR (benzene-d_6): δ 0.86 (m, 4 H, OCH_2CH_2), 1.36 (s, 9 H, CCH_3), 2.92 (m, 4 H, OCH_2CH_2), 6.04 (s, 10 H, C_5H_5), 7.22 (m, 2 H, para H), 7.31 (m, 4 H, meta H), 7.80 (d, 4 H, $^3J_{HH}$ = 7.2 Hz, ortho H). ^{13}C NMR (benzene-d_6): δ 23.04 ($SiC(CH_3)_3$), 24.35 (t, $^1J_{CH}$ = 150.1 Hz, OCH_2CH_2), 31.96 (q, $^1J_{CH}$ = 124.4 Hz, $SiC(CH_3)_3$), 71.34 (t, $^1J_{CH}$ = 150.1 Hz, OCH_2CH_2), 111.49 (dt, $^1J_{CH}$ = 168.4 Hz, $^2J_{CH}$ = 6.8 Hz, C_5H_5), 126.34 (dt, $^1J_{CH}$ = 158.5 Hz, $^2J_{CH}$ = 7.2 Hz, para C), 127.18 (dd, $^1J_{CH}$ = 155.8 Hz, $^2J_{CH}$ = 7.0 Hz, ortho C), 137.16 (dt, $^1J_{CH}$ = 155.5 Hz, $^2J_{CH}$ = 7.6 Hz, meta C), 149.90 (ipso C).

$Cp_2Sc(SiPh_3)(THF)$ (4). A procedure similar to that used for 1 was followed, except the resulting yellow toluene solution was layered with pentane and cooled to −30 °C to give yellow microcrystals in 36% yield (0.26 g). ^1H NMR (benzene-d_6): δ 0.84 (m, 4 H, OCH_2CH_2), 2.92 (m, 4 H, OCH_2CH_2), 6.02 (s, 10 H, C_5H_5), 7.13–7.73 (m, 15 H, C_6H_5). ^{13}C NMR (benzene-d_6): δ 111.56 (C_5H_5), 126.83, 130.04, 133.70, 136.20, 136.62, 148.29 (C_6H_5).

$Cp_2Sc[Ge(SiMe_3)_3](THF)$ (5). The same procedure used for 1 was employed, with $[Cp_2ScCl]_2$ (0.38 g, 0.90 mmol) and $(THF)_3LiGe(SiMe_3)_3$ (0.86 g, 1.67 mmol). The product was isolated as yellow crystals (mp 215–217 °C) in 31% yield (0.28 g, 0.52 mmol). This reaction was quantitative by ^1H NMR spectroscopy (benzene-d_6). Anal. Calcd for $C_{23}H_{45}GeOSi_3Sc$: C, 51.22; H, 8.41. Found: C, 51.08; H, 8.38. IR (Nujol, CsI, cm^{-1}): 1250 m, 1235 s, 1171 w, 1019 s, 921 w, 861 s sh, 837 s, 793 s, 782 s, 771 s, 746 w, 672 s, 619 s, 599 w, 358 m, 332 m. ^1H NMR (benzene-d_6): δ 0.54 (s, 27 H, $SiCH_3$), 0.98 (m, 4 H, OCH_2CH_2), 3.01 (m, 4 H, OCH_2CH_2), 6.12 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 6.39 ($SiCH_3$), 24.20 (OCH_2CH_2), 70.82 (OCH_2CH_2), 111.65 (C_5H_5).

Reactions of 1 with Ethylene. In these reactions, 0.050 g of 1 in benzene (25 mL) was transferred to a 100-mL pressure bottle, to which ethylene (50 psi) was admitted. After 24 h, the reaction mixture was filtered to isolate the polyethylene product. Trial 1: 1.15 g of polyethylene, M_n = 75 000, M_w = 410 000, M_w/M_n = 5.5, mol of polymer/mol of catalyst = 0.13. Trial 2: 2.65 g of polyethylene, M_n = 41 000, M_w = 172 000, M_w/M_n = 4.2, mol of polymer/mol of catalyst = 0.64. Trial 3: 0.75 g of polyethylene, M_n = 7500, M_w = 27 000, M_w/M_n = 3.6, mol of polymer/mol of catalyst = 1.00.

$Cp_2Sc\{OC[Si(SiMe_3)_3]C(OC_5H_{10})O\}$ (6-$^{13}C_2$). Compound 1 (40 mg, 0.08 mmol) was dissolved in a mixture of 2-methyltetrahydrofuran (0.3 mL) and benzene-d_6 (0.1 mL) in a 5-mm NMR tube. The tube was attached to a vacuum line, cooled with N_2(l), and evacuated. An excess of (^{13}C)-carbon monoxide was condensed into the tube, and the tube was sealed. The reaction was monitored by ^{13}C NMR spectroscopy at 23 °C. The enolate carbons were observed in the ^{13}C NMR spectrum at δ 142.21 (d, $^1J_{CC}$ = 84 Hz) and δ 158.57 (d, $^1J_{CC}$ = 84 Hz) and were accompanied by the appearance of peaks in the ^1H NMR spectrum at δ 0.12 and 5.94.

$\{Cp_2ScOC[Si(SiMe_3)_3]CO\}_2$ (7). A benzene solution (40 mL) of 1 (0.293 g, 0.59 mmol) was pressurized with CO (50 psi), resulting in rapid color change from yellow to orange and then to green. After 1 h, the volatiles were removed and the crude product was extracted into hexane (25 mL). Concentrating (to ca. 5 mL) and cooling (−78 °C) this solution gave the product as green microcrystals (mp 234–236 °C) in 71% yield (0.201 g). Anal. Calcd for $C_{42}H_{74}O_4Si_8Sc_2$: C, 52.68; H, 7.79. Found: C, 52.40; H, 7.75. IR (Nujol, CsI, cm^{-1}): 1520 w, 1250 s, 1090 s, 1060 w, 1019 m, 835 s, 800 m, 780 s, 771 s, 748 w, 689 m, 650 w, 619 m, 491 m, 430 w, 380 m, 350 w. ^1H NMR (benzene-d_6): δ 0.36 (s, 54 H, $SiCH_3$), 6.24 (s, 20 H, C_5H_5). ^{13}C NMR (benzene-d_6): δ 2.39 ($SiCH_3$), 112.60 (C_5H_5), 155.89 ($OC{=}CO$), 243.96 ($COSi(SiMe_3)_3$). ^{29}Si NMR (benzene-d_6, INEPTR): δ −61.46 ($Si(SiMe_3)_3$), −11.07 ($Si(SiMe_3)_3$). MS (EI): m/e 956 (m^+), 941.3 ($m^+ - CH_3$), 883.2 ($m^+ - SiMe_3$), 507.1 ($m^+ - Cp_2ScOCSi(SiMe_3)_3$).

$\{Cp_2ScO^{13}C[Si(SiMe_3)_3]^{13}CO\}_2$ (7-$^{13}C_4$). The method above was used to obtain the product in 56% yield (0.075 g). IR (Nujol, CsI, cm^{-1}): 1414 m, 1258 w, 1240 m, 1217 m, 1065 sh w, 1050 m, 1017 w, 835 s, 800 m, 782 s, 771 sh m, 605 w, 489 w, 375 w. ^{13}C NMR (benzene-d_6): δ 155.89 (m, $OC{=}CO$), 243.96 (m, $COSi(SiMe_3)_3$). Computer simulation (GENSIM program) gave the following coupling constants: J_{AB} = 48.9 Hz, $J_{BB'}$ = 73.4 Hz, $J_{AB'}$ = 8.8 Hz, $J_{AA'}$ = 0.2 Hz.

$[Cp_2ScOC(Si^tBuPh_2)CO]_2$ (8). A toluene solution (40 mL) of 3 (0.20 g, 0.41 mmol) was pressurized with CO (50 psi), resulting in a rapid color change to green. After 30 min, the volatiles were removed and the crude product was extracted into pentane (4 × 25 mL). Concentrating and cooling (−30 °C) this solution gave the product as green microcrystals (mp 276–277 °C) in 52% yield (0.126 g). IR (benzene-d_6, CaF_2 solution cell, cm^{-1}): 1477 s, 1460 m sh, 1430 w, 1360 w, 1282 s, 1124 s, 1110 m sh, 1100 m sh, 1010 w. ^1H NMR (benzene-d_6): δ 1.17 (s, 18 H, $SiCCH_3$), 5.75 (s, 20 H, C_5H_5), 7.28 (m, 12 H, SiPh), 7.83 (m, 8 H, SiPh). ^{13}C NMR (benzene-d_6): δ 19.05 ($SiCCH_3$), 27.93 ($SiCCH_3$), 112.27 (C_5H_5), 129.45, 133.07, 135.10, 136.22 (SiC_6H_5), 155.57 ($OC{=}CO$), 235.44 ($COSi(SiMe_3)_3$). ^{29}Si NMR (benzene-d_6, INEPTR): δ 49.90.

$\{Cp_2ScOC[Ge(SiMe_3)_3]CO\}_2$ (9). Compound 2 (0.20 g, 0.37 mmol) in benzene (25 mL) was pressurized with CO (50 psi), resulting in a slow color change to blue (red with transmitted light). After 11 h, the volatiles were removed and the crude product was extracted into pentane (25 mL). Concentrating (to ca. 1 mL) and cooling (−78 °C) this solution failed to give a crystalline product. Addition of acetonitrile (5 mL) and enough toluene (ca. 1 mL) to achieve homogeneity allowed crystallization of the product at −30 °C as red prisms (mp 234–236 °C) in 31% yield (0.06 g). Anal. Calcd for $C_{42}H_{74}Ge_2O_4Si_6Sc_2$: C, 48.20; H, 7.13. Found: C, 48.20; H, 7.16. IR (benzene-d_6, CaF_2 solution cell, cm^{-1}): 1528 w, 1467 s, 1400 m, 1245 s, 1072 s, 1058 s sh, 1011 m. ^1H NMR (benzene-d_6): δ 0.34 (s, 54 H, $SiCH_3$), 6.25 (s, 20 H, C_5H_5). ^{13}C NMR (benzene-d_6): δ 2.78 ($SiCH_3$), 112.52 (C_5H_5), 155.59 ($OC{=}CO$), 248.37 ($COGe(SiMe_3)_3$).

$\{Cp_2ScO^{13}C[Ge(SiMe_3)_3]^{13}CO\}_2$ (9-$^{13}C_4$). Following the method for 7-$^{13}C_4$, the reaction of 5 and ^{13}CO was monitored by ^1H and ^{13}C NMR spectroscopy at 23 °C. After 40 h, the reaction had proceeded cleanly to give the product but was only 38% complete. No observable resonance for a silaacyl carbon was detected downfield, and free ^{13}CO was still present. The enedione diolate carbons were observed as AA′BB′ multiplets centered at 153.59 and 248.37 ppm.

$Cp_2Sc\{O^{13}C[Si(SiMe_3)_3]^{13}C(PMe_2Ph)O\}$ (11-$^{13}C_2$). To compound 1 (40 mg, 0.08 mmol) in an NMR tube was added PMe_2Ph (0.14 g, 1.05 mmol), resulting in an orange solution (this suggests coordination of PMe_2Ph to scandium). A small amount of benzene-d_6 was added, followed by THF (ca. 0.2 mL each). On a vacuum line, an excess of ^{13}CO was condensed into the tube, and the tube was flame-sealed. The reaction was monitored by ^{13}C NMR spectroscopy at 23 °C. The enolate carbons for **11**-$^{13}C_2$ were observed at δ 115.19 (dd, $^1J_{PC}$ = 104 Hz, $^1J_{CC}$ = 71 Hz) and 189.54 (d, $^2J_{PC}$ = 14 Hz, $^1J_{CC}$ = 71 Hz). ^{31}P NMR: δ 4.13 (dd, $^1J_{PC}$ = 104 Hz, $^2J_{PC}$ = 14 Hz). Removal of volatiles left an orange residue which, when washed with pentane (5 mL), became yellow-orange. This solid was redissolved in benzene-d_6, and analysis by ^{31}P NMR spectroscopy revealed extensive decomposition of the compound (39% by ^{31}P NMR integration) to a number of phosphorous-containing products.

$Cp_2Sc[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]$ (12). Benzene (35 mL) was added to a flask containing **1** (0.196 g, 0.396 mmol) and 2,6-$Me_2C_6H_3NC$ (0.049 g, 0.374 mmol). The initial red solution gradually turned yellow over 30 min. After the mixture was stirred for 1.5 h, the volatiles were removed *in vacuo* and the crude product was extracted into pentane (25 mL). The resulting yellow-green solution was concentrated and cooled (−30 °C) to give the product (two crystallizations) as yellow crystals (mp 188–191 °C) in 60% yield (0.125 g). Anal. Calcd for $C_{28}H_{46}NSiSc$: C, 60.71; H, 8.37. Found: C, 60.96; H, 8.38. IR (Nujol, CsI, cm^{-1}): 1500 m, 1240 m, 1158 w, 1090 w, 1018 m, 830 s, 810 m, 790 s, 778 s, 771 s, 685 m, 662 m, 385 m. ^{1}H NMR (benzene-d_6): δ 0.22 (s, 27 H, $SiCH_3$), 2.25 (s, 6 H, $C_6H_3CH_3$), 6.12 (s, 10 H, C_5H_5), 6.86 (s, 3 H, C_6H_3). ^{13}C NMR (benzene-d_6): δ 2.89 ($SiCH_3$), 20.05 ($C_6H_3CH_3$), 112.26 (C_5H_5), 125.54, 128.25, 129.50, 155.36 (C_6H_3). ^{29}Si NMR (benzene-d_6, INEPTR): δ −165.67 ($CSi(SiMe_3)_3$), 35.58 ($CSi(SiMe_3)_3$).

$HC[N\text{-}2,6\text{-}Me_2C_6H_3]Si(SiMe_3)_3$ (13). Complex **12** was generated *in situ* via addition of benzene-d_6 (0.4 mL) and 2,6-$Me_2C_6H_3NC$ (0.015 g, 0.11 mmol) to **1** (0.060 g, 0.12 mmol) in an NMR tube. After 10 min, HC≡CPh (12 μL, 0.11 mmol) was syringed into the yellow-green reaction mixture. Immediate precipitation of pale yellow-green $[Cp_2Sc(C{\equiv}CPh)]_2$ was observed, and this solid was separated by decanting the solution. Removal of volatiles left the product as a clear oil. MS (EI): exact mass calcd for $C_{18}H_{37}NSi_4$ 379.2003, found 379.1984; *m/e* 379 (m^+), 306 ($m^+ - SiMe_3$), 204 ($m^+ - Si(SiMe_3)_2$), 175 ($Si(SiMe_3)_2$), 73 ($SiMe_3$). IR (benzene-d_6, CaF_2 solution cell, cm^{-1}): 3280 m, 1571 s, 1245 s, 1180 m. ^{1}H NMR (benzene-d_6): δ 0.26 (s, 27 H, $SiCH_3$), 2.06 (s, 6 H, $C_6H_3CH_3$), 6.92–7.00 (m, 3 H, C_6H_3), 8.50 (s, 1 H, HC(NAr)Si). ^{13}C NMR (benzene-d_6): δ 1.55 (q, $^1J_{CH}$ = 121.9 Hz, $SiCH_3$), 18.80 (dq, $^1J_{CH}$ = 126.8 Hz, $^2J_{CH}$ = 4.4 Hz, $C_6H_3CH_3$), 122.54, 124.64, 126.60 (dt, $^1J_{CH}$ = 114.8 Hz, $^2J_{CH}$ = 7.0 Hz, para C), 129.40, 182.20 (d, $^1J_{CH}$ = 137.8 Hz, HC(NAr)Si). ^{29}Si NMR (benzene-d_6, INEPTR): δ −161.96 ($Si(SiMe_3)_3$), −11.59 ($Si(SiMe_3)_3$). A small amount of product was isolated as a white solid (mp 60–62 °C) by sublimation (90 °C, 10^{-3} Torr).

$Cp_2Sc(C_{27}H_{36}N_2Si_4)$ (14). Compound **1** (0.15 g, 0.30 mmol) and 2,6-$Me_2C_6H_3NC$ (0.080 g, 0.60 mmol) were dissolved in benzene (15 mL) at room temperature, to give an initial red solution which soon turned yellow. During the next 40 min, the solution became green and finally blue. After an additional 1 h of stirring, the volatiles were removed and the gummy residue was extracted into diethyl ether (2 × 15 mL). These extracts were combined, concentrated (to ca. 10 mL), and cooled (−30 °C) to give the product as blue crystals (mp 183–185 °C) in 62% yield (0.125 g). Anal. Calcd for $C_{37}H_{55}N_2Si_4Sc$: C, 64.86; H, 8.09. Found: C, 64.35; H, 8.11. IR (Nujol, CsI, cm^{-1}): 1400 m, 1251 s, 1242 s, 1221 s, 1145 m, 1098 w, 1021 w, 1012 w, 935 w, 839 s, 811 s, 790 s, 781 s, 769 w, 759 m, 690 w, 648 w, 630 w, 61 w, 503 w, 480 w, 330 br w. ^{1}H NMR (benzene-d_6): δ 0.07 (s, 9 H, $SiCH_3$), 0.20 (s, 9 H, $SiCH_3$), 0.35 (s, 9 H, $SiCH_3$), 1.28 (s, 3 H, $CSiCH_3$), 1.82 (s, 3 H, $C{=}CCH_3$), 2.34 (s, 3 H, $C_6H_3CH_3$), 2.38 (s, 3 H, $C_6H_3CH_3$), 5.87 (s, 5 H, C_5H_5), 5.90 (m, 1 H, $C{=}CH$), 6.08 (m, 1 H, $C{=}CH$), 6.22 (s, 5 H, C_5H_5), 6.38 (m, 1 H, $C{=}CH$), 6.90–7.07 (m, 3 H, C_6H_3). ^{13}C NMR (benzene-d_6): δ 2.30 ($SiCH_3$), 2.83 ($SiCH_3$), 3.12 ($SiCH_3$), 21.41, 22.54, 22.82, 25.69, 48.53, 110.55 (C_5H_5), 111.80 (C_5H_5), 120.49, 122.54, 129.08, 129.65, 130.78, 132.98, 134.63, 136.74, 143.79, 155.26, 168.30, 177.51.

X-ray Structure Determination for 1. A yellow crystal of approximate dimensions 0.4 × 0.4 × 0.5 mm was mounted under N_2 in a random orientation in a glass capillary and flame-sealed. Centering of 26 randomly selected reflections with $15° \le 2\theta \le 30°$ provided unit cell data. The selection of the monoclinic cell was confirmed by axial photographs. Data were collected with $\theta/2\theta$ scans ($3° \le 2\theta \le 50°$) at a variable scan speed of 1.50–14.6° min^{-1}, using Mo Kα radiation (λ = 0.710 73 Å), on a Siemens R3m/V automated diffractometer equipped with a highly ordered graphite monochromator. Of the 5982 reflections measured, 5267 were independent (R_{int} = 1.77%) and 3059 were considered observed ($F_o > 6\sigma(F)$). The data were corrected for Lorentz and polarization effects and for a slight decay in the intensity of three check reflections of 1.5%. A semiempirical absorption correction based on the ψ-scan method was employed. The minimum and maximum transmission factors for the correction were 0.543 and 0.569, respectively. The space group $P2_1/n$ was uniquely determined from systematic absences. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. Except for H(1)–H(10), which were located and refined, the hydrogen atoms were placed in idealized, calculated positions (d(C–H) = 0.96 Å), with an independently refined thermal parameter for each of the three groups of hydrogens: R_F = 3.93, R_wF = 4.33, GOF = 1.46, data/parameter 10.3, largest Δ/σ 0.005, and largest difference peak 0.30 e Å^{-3} (located 1.38 Å from O (1)). All calculations utilized the Siemens SHELXTL PLUS computing package (Siemens Analytical X-ray Instruments, Inc., Madison, WI).

Additional data: a = 9.452(4) Å, b = 15.900(5) Å, c = 19.776(6) Å, β = 90.55(3)°, V = 2972(2) Å^3, Z = 4, D_c = 1.107 g cm^{-3}, $F(000)$ = 1072, μ = 0.42 mm^{-1}, T = 296 K, scan range (ω) 1.2° plus Kα separation, background measurement 25% of total scan time, 3 standard reflections measured every 66 reflections, index ranges $0 \le h \le 12$, $0 \le k \le 19$, and $-24 \le l \le 24$, g = 0.000 263 (g is used in the weighting scheme: $w^{-1} = \sigma^2(F) + g(F)^2$), ρ = −0.000 04 (ρ is the extinction correction).

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Supplementary Material Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **1** (8 pages). Ordering information is given on any current masthead page.

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