Synthesis and Solution Behavior of (Tetraisopropylcyclopentadienyl)calcium Acetylide Complexes. Molecular Structure of $\{[(C_3H_7)_4C_5H]Ca(\mu\text{-}C{\equiv}CPh)(thf)\}_2$

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The reaction of $(Cp^{4i})Ca[N(SiMe_3)_2](thf)$ (Cp^{4i} = $(i\text{-}Pr)_4C_5H$) (**1**) with several terminal alkynes HC≡CR in either toluene or hexanes produces the corresponding calcium acetylide complexes $(Cp^{4i})Ca[C{\equiv}CR](thf)$ (**2**) (R = Ph (**2a**), Fc (**2b**), $SiMe_3$ (**2c**), $Si(i\text{-}Pr)_3$ (**2d**), $SiPh_3$ (**2e**)) in good yield. The $(Cp^{4i})Ca[C{\equiv}CR](thf)$ complexes do not react with excess alkyne. $(Cp^{4i})Ca[C{\equiv}CPh](thf)$ crystallizes from toluene as an acetylide-bridged dimer, $[(Cp^{4i})Ca[\mu\text{-}C{\equiv}CPh)(thf)]_2{\cdot}C_7H_8$, with a pentahapto $[Cp^{4i}]^-$ ligand and a terminal THF ligand on each calcium. The calcium−carbon bond distances for the bridging $[C{\equiv}CPh]^-$ ligands are 2.551(8) and 2.521(7) Å; the average Ca−C(ring) bond distance is 2.713(15) Å. As with other $(Cp^{4i})CaX(thf)_n$ complexes, the $(Cp^{4i})Ca[C{\equiv}CR](thf)$ compounds are kinetically stabilized against disproportionation in the solid state and in THF solution; $(Cp^{4i})Ca[C{\equiv}CSi(i\text{-}Pr)_3](thf)$ is also indefinitely stable in aromatic solutions. Slow but substantial dissociation of the THF ligand in $(Cp^{4i})Ca[C{\equiv}CR](thf)$ (R = Ph, Fc, $SiMe_3$) occurs over several days in aromatic solution, leading to partial disproportionation of the complexes into $(Cp^{4i})_2Ca$ and $\{Ca[C{\equiv}CR]\}_n$. THF dissociation is even more pronounced in aromatic solutions of $(Cp^{4i})Ca[C{\equiv}CSiPh_3](thf)$, leading to rapid disproportionation in minutes. Attempts to isolate the unsolvated complex $\{(Cp^{4i})Ca[C{\equiv}CPh]\}_n$ (**3a**) are frustrated by its facile disproportionation at elevated temperatures.

Introduction

During the last decade, interest in the organometallic chemistry of the heavier alkaline-earth metals calcium, strontium and barium has centered largely on compounds containing bulky cyclopentadienyl rings with alkyl or phenyl substituents.[1,2] Analogous complexes containing other types of polyhapto organic ligands (e.g., pentadienyls,[3] carboranes,[4−6] or dienes[7]) are rare, and those containing σ-bonded alkyl ligands are poorly understood. Although compounds such as $Ca(CH_3)_2$ and $Sr(C_2H_5)_2$ are described in the older literature,[8] they are in general thermally unstable and inadequately characterized. Only one crystallographically authenticated σ-bonded complex of this type is known, $Ca[CH(SiMe_3)_2]_2(dioxane)_2$;[9] other reasonably well-characterized examples are limited to those with the bulky $[Ph_3C]^-$ ligand (e.g., $Ca(CPh_3)_2(thf)_x$,[10,11] $Ca(CPh_3)Cl(thf)_x$[11,12]) and the polymeric bis(alkynyl) compounds $[Ae(C{\equiv}CPh)_2(thf)_x]_n$ (Ae = Ca, Sr, Ba).[11,13]

Despite the limited data available on isolated heavy group 2 compounds containing σ-bonded carbon ligands, various alkyl-substituted complexes have shown promise as novel reagents in organic synthesis. For example, σ-bonded allylbarium compounds have been found to be highly regio- and stereospecific allylation agents for carbonyl compounds,[14,15] organocalcium reagents derived from halogenated polystyrenes react with electrophiles to yield functionalized polymers,[16] and nitrous oxide has been found to react with several phenylcalcium reagents to produce azobenzenes.[17] Improved understanding of heavy alkaline-earth−carbon σ bonding could lead to the development of additional useful reagents.

We recently found that the $[(Cp^{4i})Ca(thf)]$ (Cp^{4i} = $(i\text{-}Pr)_4C_5H$) fragment serves as a stabilizing moiety in organocalcium chemistry and blocks Schlenk-type disproportionation reactions.[18] It is therefore a logical

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Table 1. Comparison of ν(C≡C) for (Cp^{4i})Ca[C≡CR](thf) and R−C≡C−H[a]

R	ν(C≡C) (cm^{-1}) (Cp^{4i})Ca[C≡CR](thf)	ν(C≡C) (cm^{-1}) R−C≡C−H	$\Delta\nu$ (cm^{-1})
Ph (**2a**)	2043	2110	67
Fc (**2b**)	2042	2105	63
$SiMe_3$ (**2c**)	1991	2037	46
Si(*i*-Pr)$_3$ (**2d**)	1968	2032	64
$SiPh_3$ (**2e**)	1985	2035	50

[a] The spectra of (Cp^{4i})Ca[C≡CR](thf) and $Ph_3SiC{\equiv}CH$ were obtained as KBr pellets; the spectra of the remaining alkynes were obtained as thin films.

substrate for the detailed investigation of Ca−C σ-bonded complexes. We have focused our initial efforts on acetylide complexes to permit direct comparison with corresponding lanthanide derivatives (Cp′$_2$LnC≡CR), which in certain instances have shown remarkable chemistry.[19−24] In addition, the availability of the organocalcium amide (Cp^{4i})Ca[N(SiMe$_3$)$_2$](thf)[18] provides a direct high-yield route to these complexes through protonolysis reactions. We report our results with the synthesis and characterization of several (cyclopentadienyl)calcium acetylide complexes.

Experimental Section

General Experimental Considerations. All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques. Proton and carbon (^{13}C) NMR spectra were obtained on a Bruker NR-300 spectrometer at 300 and 75.5 MHz, respectively, and were referenced to the residual proton and ^{13}C resonances of C_6D_6 (δ 7.15 and 128.0) or THF-d_8 (δ 3.58). Assignments in the ^{13}C NMR spectra were made with the help of DEPT pulse experiments. Infrared data were obtained on a Perkin-Elmer 1600 Series FT-IR spectrometer; these data are tabulated in Table 1. KBr pellets for IR spectroscopy were prepared as previously described.[25] Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Materials. (Cp^{4i})Ca[N(SiMe$_3$)$_2$](thf) (**1**)[18] (Cp^{4i} = (*i*-Pr)$_4$C$_5$H) and ferrocenylacetylene (FcC≡CH)[26] were prepared using literature procedures. Commercial samples (Aldrich) of phenylacetylene, (trimethylsilyl)acetylene, and (triisopropylsilyl)acetylene were vacuum distilled and dried over molecular sieves before use; (triphenylsilyl)acetylene was used as received. Solvents for reactions were distilled under nitrogen from sodium or potassium benzophenone ketyl. NMR solvents were vacuum distilled from Na/K (22/78) alloy and stored over molecular sieves.

Synthesis of (Cp^{4i})Ca[C≡CPh](thf) (2a). A sample of **1** (160 mg, 0.32 mmol) was dissolved in 5 mL of toluene in an Erlenmeyer flask. To this was added an excess of PhC≡CH (70 mg, 0.69 mmol) with a pipet. The solution was then shaken for 2 min and set aside. Upon standing for 2 h, a colorless crystalline solid precipitated from solution. The toluene supernatant was removed by decantation, and the solid was dried briefly under vacuum to give 120 mg (77% yield) of **2a** as a toluene solvate (Cp^{4i})Ca[C≡CPh](thf)·$^1/_2$(C_7H_8) (mp 120−126 °C). Anal. Calcd for $C_{32.5}H_{46}CaO$: C, 79.21; H, 9.41. Found: C, 78.98; H, 9.17. The toluene could be removed by placing the compound under vacuum (10^{-2} Torr) for 6 h or by heating the solid to 60 °C for 2 h. ^{1}H NMR (C_6D_6): δ 7.57 (d, J = 8.0 Hz, 2 H, *o*-Ph); 7.12 (t, J = 7.5 Hz, 2 H, *m*-Ph); 7.00 (t, J = 7.5 Hz, 1 H, *p*-Ph); 5.90 (s, 1 H, ring-C*H*); 3.84 (t, J = 6.5 Hz, 4 H, α-C_4H_8O); 3.39 (septet, J = 7.2 Hz, 2 H, C*H*Me$_2$); 3.22 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$); 1.66 (d, J = 7.2 Hz, 6 H, CH_3); 1.58 (d, J = 7.1 Hz, 6 H, CH_3); 1.44 (d, J = 6.7 Hz, 6 H, CH_3); 1.41 (m, 4 H, β-C_4H_8O); 1.32 (d, J = 6.6 Hz, 6 H, CH_3). ^{1}H NMR (THF-d_8): δ 7.00−7.30 (m, 5 H, *o*,*m*,*p*-Ph); 5.57 (s, 1 H, ring-C*H*); 3.62 (m, 4 H, α-C_4H_8O); 3.15 (septet, J = 7.2 Hz, 2 H, C*H*Me$_2$); 2.98 (septet, J = 6.7 Hz, 2 H, C*H*Me$_2$); 1.77 (m, 4 H, β-C_4H_8O); 1.41 (d, J = 6.9 Hz, 6 H, CH_3); 1.31 (d, J = 7.2 Hz, 6 H, CH_3); 1.24 (d, J = 6.6 Hz, 6 H, CH_3); 0.99 (d, J = 6.5 Hz, 6 H, CH_3). ^{13}C NMR (C_6D_6): δ 134.7 (*C*≡CPh); 131.7 (*o*-Ph); 129.3 (ring-*C*CHMe$_2$); 128.4 (*m*-Ph); 127.6 (*p*-Ph); 126.0 (C≡C−*C*(Ph)); 124.0 (ring-*C*CHMe$_2$); 121.2 (C≡*C*Ph); 99.3 (ring-*C*H); 69.7 (α-C_4H_8O); 27.5 (*C*HMe$_2$); 27.4 (*C*HMe$_2$); 27.3 (*C*H$_3$); 25.4 (3 *C*H$_3$ peaks and β-C_4H_8O). The crystal used for the X-ray structural analysis of (Cp^{4i})Ca[C≡CPh](thf)·$^1/_2$(C_7H_8) was taken directly from the reaction mixture before removal of the toluene.

Synthesis of (Cp^{4i})Ca[C≡CFc](thf) (2b). An Erlenmeyer flask was charged with **1** (174 mg, 0.344 mmol) dissolved in 4 mL of toluene. To this was added FcC≡CH (72 mg, 0.343 mmol) dissolved in 2 mL of toluene. The solution was then shaken for 2 min and set aside. Upon standing for 4 h, an orange microcrystalline solid precipitated from solution. The toluene supernatant was removed with a pipet, and the precipitate was dried under vacuum to give 110 mg of **2b** (mp 155−160 °C). An additional 25 mg of product was obtained by adding 15 mL of hexane to the toluene filtrate and subsequently isolating and drying the orange precipitate, for a total yield of 70%. Anal. Calcd for $C_{33}H_{46}CaFeO$: C, 71.46; H, 8.36. Found: C, 70.58; H, 8.11. ^{1}H NMR (C_6D_6): δ 5.94 (s, 1 H, ring-C*H*); 4.45 (t, J = 1.8 Hz, 2 H, α-C_5H_4); 4.22 (s, 5 H, C_5H_5); 3.98 (t, J = 1.8 Hz, 2 H, β-C_5H_4); 3.79 (t, J = 6.5 Hz, 4 H, α-C_4H_8O); 3.45 (septet, J = 7.2 Hz, 2 H, C*H*Me$_2$); 3.30 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$); 1.73 (d, J = 7.2 Hz, 6 H, CH_3); 1.64 (d, J = 7.2 Hz, 6 H, CH_3); 1.54 (d, J = 6.8 Hz, 6 H, CH_3); 1.42 (d, J = 6.6 Hz, 6 H, CH_3); 1.40 (t, J = 6.5 Hz, 4 H, β-C_4H_8O). ^{13}C NMR (C_6D_6): δ 132.5 (*C*≡CFc); 127.4 (ring-*C*CHMe$_2$); 123.9 (ring-*C*CHMe$_2$); 118.4 (C≡*C*Fc); 99.6 (ring-*C*H); 71.1 (α-C_5H_4); 70.2 (C_5H_5); 69.6 (α-C_4H_8O); 69.0 (C≡C−*C*(Fc)); 68.3 (β-C_5H_4); 27.5 (*C*HMe$_2$); 27.4 (*C*HMe$_2$); 27.3 (*C*H$_3$); 26.0 (*C*H$_3$); 25.8 (*C*H$_3$); 25.7 (*C*H$_3$); 25.4 (β-C_4H_8O).

Synthesis of (Cp^{4i})Ca[C≡CSiMe$_3$](thf) (2c). To a suspension of **1** (100 mg, 0.20 mmol) in 3 mL of hexanes was added an excess of $Me_3SiC{\equiv}CH$ (55 mg, 0.36 mmol) with a pipet. The reaction flask was shaken for 2 min, during which time the solution became clear. The reaction was then allowed to stand for 12 h, resulting in the precipitation of a white microcrystalline solid. The hexanes solution was removed with a pipet and the solid dried briefly under vacuum to give 70 mg (80% yield) of **2c** (mp 140−145 °C). Anal. Calcd for $C_{26}H_{46}CaOSi$: C, 70.52; H, 10.47. Found: C, 68.13; H, 10.04. (A similarly low value for carbon was obtained in an analysis on a different sample of **2c**; this is a frequent problem with organoalkaline-earth complexes.[27−30]) ^{1}H NMR (C_6D_6): δ 5.92 (s, 1 H, ring-C*H*); 3.80 (t, J = 6.5 Hz, 4 H, α-C_4H_8O); 3.37 (septet, J = 7.2 Hz, 2 H, C*H*Me$_2$); 3.26 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$); 1.64 (d, J = 7.2 Hz, 6 H, CH_3); 1.57 (d, J = 7.1 Hz, 6 H, CH_3); 1.50 (d, J = 6.8 Hz, 6 H, CH_3); 1.42 (t, J = 6.5

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Hz, 4 H, β-C_4H_8O); 1.38 (d, J = 6.7 Hz, 6 H, CH_3); 0.25 (s, 9 H, Si(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 163.3 (*C*≡CSiMe$_3$); 128.7 (C≡*C*SiMe$_3$); 127.4 (ring-*C*CHMe$_2$); 124.0 (ring-*C*CHMe$_2$); 99.4 (ring-*C*H); 69.7 (α-C_4H_8O); 27.5 (*C*HMe$_2$); 27.4 (*C*HMe$_2$); 27.3 (*C*H$_3$); 26.0 (*C*H$_3$); 25.8 (*C*H$_3$); 25.7 (*C*H$_3$); 25.3 (β-C_4H_8O); 0.8 (Si(*C*H$_3$)$_3$).

Synthesis of (Cp^{4i})Ca[C≡CSi(*i*-Pr)$_3$](thf) (2d). A sample of **1** (0.21 g, 0.42 mmol) was dissolved in 5 mL of hexanes in an Erlenmeyer flask; to this was added a solution of (*i*-Pr)$_3$SiC≡CH (78 mg, 0.43 mmol) in 2 mL of hexanes. The reaction flask was shaken for 2 min and then concentrated under vacuum to a volume of ca. 3 mL. On standing for 6 h, a white microcrystalline solid precipitated from solution. The hexanes was removed with a pipet and the solid dried briefly under vacuum to give 166 mg (64% yield) of **2d** (mp 118−123 °C). Anal. Calcd for $C_{32}H_{50}CaOSi$: C, 72.94; H, 11.09. Found: C, 72.88; H, 11.00. ^{1}H NMR (C_6D_6): δ 6.11 (s, 1 H, ring-C*H*); 3.76 (t, J = 6.5 Hz, 4 H, α-C_4H_8O); 3.39 (septet, J = 7.2 Hz, 2 H, C*H*Me$_2$); 3.26 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$); 1.64 (d, J = 7.2 Hz, 6 H, C*H*$_3$); 1.54 (d, J = 6.9 Hz, 12 H, C*H*$_3$); 1.52 (partially obscured septet, 3H, SiC*H*(CH$_3$)$_2$); 1.39 (d, J = 7.2 Hz, 10 H, C*H*$_3$ and β-C_4H_8O); 1.27 (d, 18 H, SiCH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 160.0 (*C*≡CSi(*i*-Pr)$_3$); 127.8 (ring-*C*CHMe$_2$); 124.8 (ring-*C*CHMe$_2$); 124.4 (C≡*C*Si(*i*-Pr)$_3$); 100.8 (ring-*C*H); 69.3 (α-C_4H_8O); 27.5 (*C*HMe$_2$); 27.2 (*C*HMe$_2$); 26.6 (*C*H$_3$); 26.1 (*C*H$_3$); 25.8 (*C*H$_3$); 25.5 (*C*H$_3$); 25.3 (β-C_4H_8O); 19.2 (SiCH-(*C*H$_3$)$_2$); 12.6 (Si*C*H(CH$_3$)$_2$).

Synthesis of (Cp^{4i})Ca[C≡CSiPh$_3$](thf) (2e). To a solution of **1** (140 mg, 0.28 mmol) in 7 mL of hexanes was added 3 mL of a hexanes solution of Ph$_3$SiC≡CH (78 mg, 0.27 mmol). A white solid immediately began to precipitate. The reaction flask was shaken for 2 min and then allowed to stand for 2 h. The hexanes solution was removed with a pipet, and the remaining solid was allowed to dry overnight at ambient pressure to give 140 mg (82% yield) of **2e** (mp 165−168 °C). Anal. Calcd for $C_{41}H_{52}CaOSi$: C, 78.29; H, 8.33. Found: C, 77.86; H, 8.39. ^{1}H NMR (C_6D_6) (see below): δ 7.83 (m, 6 H, *o*-Ph); 7.23 (m, 9 H, *m*,*p*-Ph); 5.95 (s, 1 H, ring-C*H*); 3.57 (br s, 4 H, α-C_4H_8O); 3.26 (septet, J = 7.1 Hz, 2 H, C*H*Me$_2$); 3.14 (septet, J = 6.7 Hz, 2 H, C*H*Me$_2$); 1.54 (d, J = 7.1 Hz, 6 H, C*H*$_3$); 1.47 (d, J = 7.0 Hz, 6 H, C*H*$_3$); 1.39 (d, J = 6.6 Hz, 6 H, C*H*$_3$); 1.25 (d, J = 6.7 Hz, 6 H, C*H*$_3$); 1.21 (m, 4 H, β-C_4H_8O). ^{1}H NMR (THF-d_8): δ 7.67 (m, 6 H, *o*-Ph); 7.23 (m, 9 H, *m*,*p*-Ph); 5.58 (s, 1 H, ring-C*H*); 3.61 (m, 4 H, α-C_4H_8O); 3.22 (septet, J = 7.2 Hz, 2 H, C*H*Me$_2$); 3.13 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$); 1.77 (m, 4 H, β-C_4H_8O); 1.45 (d, J = 7.2 Hz, 6 H, C*H*$_3$); 1.36 (d, J = 7.1 Hz, 6 H, C*H*$_3$); 1.35 (d, J = 6.8 Hz, 6 H, C*H*$_3$); 1.09 (d, J = 6.7 Hz, 6 H, C*H*$_3$). ^{13}C NMR (THF-d_8): δ 178.3 (*C*≡CSiPh$_3$); 136.8 (Si*C*(Ph)); 136.4 (*o*-Ph); 129.2 (*p*-Ph); 127.9 (*m*-Ph); 127.4 (ring-*C*CHMe$_2$); 124.0 (ring-*C*CHMe$_2$); 105.4 (C≡*C*SiPh$_3$); 98.7 (ring-*C*H); 68.2 (α-C_4H_8O); 27.8 (*C*HMe$_2$); 27.7 (*C*HMe$_2$); 27.2 (*C*H$_3$); 26.4 (β-C_4H_8O); 25.5 (*C*H$_3$); 25.3 (*C*H$_3$); 25.2 (*C*H$_3$). Dissolution of **2e** in C_6D_6 produces significant amounts (20−40%) of the unsolvated complex [(Cp^{4i})Ca-(C≡CSiPh$_3$)]$_n$ (**3e**), as determined by ^{1}H NMR. The unsolvated complex partly disproportionates into (Cp^{4i})$_2$Ca and [Ca-(C≡CSiPh$_3$)$_2$]$_n$ over several days. ^{1}H NMR (C_6D_6) resonances attributable to **3e**: δ 7.97 (m, 6 H, *o*-Ph); 7.25 (m, 9 H, *m*,*p*-Ph); 6.31 (s, 1 H, ring-C*H*); 1.97 (d, J = 6.7 Hz, 6 H, C*H*$_3$); 1.69 (d, J = 6.8 Hz, 6 H, C*H*$_3$); 1.64 (d, J = 7.1 Hz, 6 H, C*H*$_3$); 1.57 (d, J = 7.2 Hz, 6 H, C*H*$_3$); the C*H*Me$_2$ resonances are obscured by the C*H*Me$_2$ and α-C_4H_8O peaks of **2e**.

Thermal Conversion of 2a into (Cp^{4i})$_2$Ca and [Ca-(C≡CPh)$_2$]$_n$. A sublimation flask containing a 140 mg sample of **2a** was evacuated to 10^{-6} Torr and heated to 130 °C for 4 h. Subsequent spectroscopic analysis of the solid (100 mg) indicated that it was a mixture of (Cp^{4i})$_2$Ca (identified by ^{1}H NMR (C_6D_6)[25] and {Ca[C≡CPh]$_2$}$_n$ (identified by FT-IR (KBr)).[13] A second sample (100 mg) of **2a** that was heated to 90 °C at 10^{-6} Torr for 4 h only partly converted to (Cp^{4i})$_2$Ca and {Ca-[C≡CPh]$_2$}$_n$; this solid also contained unchanged **2a** (40%) and a new compound, identified as the THF-desolvated complex {(Cp^{4i})Ca[C≡CPh]}$_n$ (**3a**) (15%). Spectroscopic data characteristic of **3a**: ^{1}H NMR (C_6D_6): δ 7.68 (m, 2 H, *o*-Ph); 6.11 (s, 1 H, ring-C*H*); 3.58 (septet, J = 6.8 Hz, 2 H, C*H*Me$_2$); 1.77−1.81 (two overlapping doublets, 12 H, C*H*$_3$); 1.68 (d, J = 7.1 Hz, 6 H, C*H*$_3$); the remaining resonances are obscured by those for **2a** and (Cp^{4i})$_2$Ca.

Table 2. Crystal Data and Summary of X-ray Data Collection for {(Cp^{4i})Ca[C≡CPh](thf)}$_2$·C$_7$H$_8$ (2a)

formula	$C_{32.5}H_{46}CaO$
fw	492.80
cryst dimens, mm	0.20 × 0.25 × 0.90
space group	$P2_1/n$
cell dimens (20 °C)	
a, Å	12.635(3)
b, Å	16.316(3)
c, Å	14.624(2)
β, deg	92.09(1)
V, Å^3	3102.8(9)
Z	2 (dimers)
D(calcd), g/cm^3	1.086
abs coeff, cm^{-1}	19.2
scan speed, deg/min	4.0
scan width	1.42 + 0.30 tan θ
limits of data collcn	6° ≤ 2θ ≤ 120°
tot. reflcns	4921
unique reflcns	4683
no. with $I > 3\sigma(I)$	2444
$R(F)$	0.072
$R_w(F)$	0.091
goodness of fit	3.08
max Δ/σ in final cycle	0.44
max/min peak (final diff map) (e/Å^3)	0.37/−0.23

X-ray Crystallography of {(Cp^{4i})Ca[C≡CPh](thf)}$_2$·C$_7$H$_8$ (2a). A long needle-shaped crystal of **2a** was located and sealed in a glass capillary tube. All measurements were performed on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å). Relevant crystal and data collection parameters for the present study are given in Table 2.

Cell constants and orientation matrices for data collection were obtained from a systematic search of a limited hemisphere of reciprocal space; sets of diffraction maxima corresponding to a monoclinic cell were located whose setting angles were refined by least-squares. The space group $P2_1/n$ was uniquely determined from systematic absences. Subsequent solution and refinement of the structure confirmed this choice.

Data collection was performed using continuous $\omega-2\theta$ scans with stationary backgrounds (peak/bkgd counting time = 2:1). Data were reduced to a unique set of intensities and associated σ values in the usual manner. There was no decay in three standard reflections and ψ-scans of several representative absorptions indicated no need for an absorption correction. The calcium atom was located from a Patterson map and the structure expanded using DIRDIF and Fourier techniques. The asymmetric unit was found to contain half a dimeric complex; the other half was related through an inversion center. A molecule of toluene was found associated with each dimer; it was disordered across an inversion center, and the methyl group was not identified. All non-hydrogen atoms were refined anisotropically. To improve the refinement of the non-hydrogen atoms in the complex, hydrogen atoms were inserted in calculated positions based on packing considerations, and d(C−H) = 0.95 Å; their positions were fixed for the final cycles of refinement. A final difference map was featureless. Selected bond distances and angles are listed in Table 3.

Results and Discussion

Synthesis of (Cp^{4i})Ca[C≡CR](thf). The reaction of (Cp^{4i})Ca[N(SiMe$_3$)$_2$](thf) (**1**) with several terminal alkynes HC≡CR (R = Ph, CpFeC$_5$H$_4$ (Fc), SiMe$_3$, Si(*i*-Pr)$_3$, or SiPh$_3$) in either toluene or hexanes produces the (cyclopentadienyl)calcium acetylide complexes (Cp^{4i})Ca-[C≡CR](thf) (**2**) in good to high yield (eq 1). The

$$(Cp^{4i})Ca[N(SiMe_3)_2](thf) + HC{\equiv}CR \rightarrow (Cp^{4i})Ca[C{\equiv}CR](thf) + HN(SiMe_3)_2 \quad (1)$$

R = Ph (**2a**), $CpFeC_5H_4$ (Fc) (**2b**), $SiMe_3$ (**2c**), $Si(i\text{-}Pr)_3$ (**2d**), $SiPh_3$ (**2e**)

products are isolated as spectroscopically pure, white (orange for **2b**) microcrystalline solids by precipitation directly from the reaction solution, precipitation being brought about by using small volumes (ca. 3−5 mL) of solvent.

This synthetic approach has been previously applied to the synthesis of trivalent bis(cyclopentadienyl)lanthanide alkynyl complexes; i.e., the reaction of $Cp^*_2Ln[N(SiMe_3)_2]$ (Ln = Ce, Nd, Sm) with HC≡CPh in THF generated the corresponding phenylacetylide complexes $Cp^*_2Ln[C{\equiv}CPh](thf)$ in high yield.[19] In contrast to the case for **1**, the $Cp^*_2Ln[N(SiMe_3)_2]$ complexes did not react with HC≡CPh in toluene.

It is notable that the $(Cp^{4i})Ca[C{\equiv}CR](thf)$ complexes do *not* react with excess alkyne (eq 2), either by proton-

$$(Cp^{4i})Ca[C{\equiv}CR](thf) + HC{\equiv}CR \rightarrow \text{no reaction} \quad (2)$$

ation of the $[Cp^{4i}]^-$ ligands or by insertion into the Ca−C bonds. Such inertness of **2** to terminal alkynes contrasts with the protonation of one of the $[Cp^*]^-$ ligands of $Cp^*_2Eu(OEt_2)$ by HC≡CPh in THF to generate $\{Cp^*Eu[C{\equiv}CPh](thf)_2\}_2$.[31] It also distinguishes **2** from several lanthanide and actinide acetylide complexes, which undergo facile insertion reactions with alkynes.[19−24]

Spectroscopic data (^1H, ^{13}C NMR, IR spectroscopy) and elemental analysis for the $(Cp^{4i})Ca[C{\equiv}CR](thf)$ compounds confirmed their proposed formulation. IR spectra for all five complexes contain $\nu(C{\equiv}C)$ bands characteristic of anionic alkynyl ligands coordinated to a d^0 metal, in that they are shifted to lower wavenumbers ($\Delta\nu \approx 60$ cm^{-1}) compared to the neutral alkynes (Table 1).[23,32] Proton and ^{13}C NMR spectra of the complexes display the expected resonances for the $[Cp^{4i}]^-$ and $[C{\equiv}CR]^-$ ligands; the downfield (>118 ppm) shifts observed for the acetylide carbons are indicative of deprotonated alkynes.[22] Additionally, the phenylacetylide derivative **2a** was characterized by X-ray crystallography (see below).

Solution Behavior of $(Cp^{4i})Ca[C{\equiv}CR](thf)$. As found for other $(Cp^{4i})CaX(thf)$ complexes,[18] the (cyclopentadienyl)calcium alkynyl complexes **2** were indefinitely stable with respect to disproportionation as solids and in THF solution. The stability stems from the high oxophilicity of calcium center, which is reluctant to release the coordinated THF ligand, and from the steric bulk of the $[Cp^{4i}]^-$ ring, which prevents the formation of a solvated $(Cp^{4i})_2Ca$ metallocene.[25] Together, these features block the operation of Schlenk-type equilibria (eq 3). However, the solution behavior of the $(Cp^{4i})Ca$-

$$2(Cp^{4i})Ca[C{\equiv}CR](thf) \overset{THF}{\not\rightleftharpoons} (Cp^{4i})_2Ca + \{Ca[C{\equiv}CPh]_2\}_n + 2THF \quad (3)$$

[C≡CR](thf) complexes in noncoordinating solvents depended on the specific substituent on the acetylide ligand. C_6D_6 solutions of **2a**, **2b**, or **2c** monitored for 2−10 days revealed the small (<5%) but reproducible generation of the base-free complexes $\{(Cp^{4i})Ca[C{\equiv}CR]\}_n$ (**3**), which subsequently began to disproportionate slowly into $(Cp^{4i})_2Ca$ (identified by ^1H NMR) and $\{Ca[C{\equiv}CR]_2\}_n$. This behavior contrasts with that of C_6D_6 solutions of the mono(ring) iodide complex $(Cp^{4i})CaI(thf)_n$ (n = 1, 2), which do not show any evidence for THF dissociation for periods up to 2 weeks.[18]

The identification of the $\{(Cp^{4i})Ca[C{\equiv}CR]\}_n$ complexes rests primarily on the downfield shifts of the resonances for the $[Cp^{4i}]^-$ ligands in their proton NMR spectra (C_6D_6) when compared to the THF-solvated analogs. The largest shift is found for the ring proton resonances, which move from ca. 5.9 ppm for **2a**−**c** to 6.11−6.16 ppm for the corresponding $\{(Cp^{4i})Ca[C{\equiv}CR]\}_n$ complexes. A similar shift for this peak (from 5.98 to 6.11 ppm) is found on loss of THF from $(Cp^{4i})CaI(thf)$ to form $[(Cp^{4i})CaI]_n$.[18]

More pronounced (up to 20%) dissociation of THF from **2a**−**c** (and subsequent disproportionation) occurred when toluene solutions of these complexes were placed under a vacuum (10^{-2} Torr) for several minutes, frustrating initial attempts at their isolation and purification. Fortunately, the use of small volumes of solvent in the syntheses allowed for the clean precipitation of the products before significant desolvation could occur. For **2a**,**b**, the toluene solubility is limited enough that these complexes can be isolated from this solvent in good yield. However, the greater toluene solubility of **2c** required the use of hexanes to effect precipitation of the complex in high yield.

An even greater instability of the Ca−THF dative bond in aromatic solution is observed for **2e**. Monitoring the reaction of $HC{\equiv}CSiPh_3$ and **1** in C_6D_6 by ^1H NMR revealed that after only 15 min almost 30% of the initially generated **2e** had lost THF, as evidenced by the presence of resonances for $\{(Cp^{4i})Ca[C{\equiv}CSiPh_3]\}_n$ (**3e**) (ca. 10%) and its disproportionation product $(Cp^{4i})_2Ca$ (ca. 10%).[33] As for **3a**−**c**, the identification of **3e** was based on a characteristic downfield shift in the

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $\{(Cp^{4i})Ca[C{\equiv}CPh](thf)\}_2{\cdot}C_7H_8$ (2a)

Ca(1)···Ca(1′) [a]	3.699(3)	Ca(1)−ring centroid	2.432
C(18)···C(18′)	3.47(2)	Ca(1)−C(18)	2.551(8)
Ca(1)−O(1)	2.385(5)	Ca(1)−C(18′)	2.521(7)
Ca(1)−C(1)	2.659(7)	C(18)−C(19)	1.173(9)
Ca(1)−C(2)	2.680(6)	C−C(Cp ring) (av)	1.415(9)
Ca(1)−C(3)	2.756(7)	C−C(Ph ring) (av)	1.38(1)
Ca(1)−C(4)	2.751(7)	C(Cp ring)−CH (av)	1.52(1)
Ca(1)−C(5)	2.721(7)	CH−CH_3 (av)	1.52(1)
C(18)−Ca(1)−O(1)	91.9(2)	C(18)−Ca(1)−ring centroid	131.4
C(18′)−Ca(1)−O(1)	93.3(2)	C(18′)−Ca(1)−ring centroid	129.2
C(18)−Ca(1)−C(18′)	86.4(2)	O(1)−Ca(1)−ring centroid	114.1
Ca(1)−C(18)−Ca(1′)	93.6(2)	C(18)−C(19)−C(20)	177.2(7)
Ca(1)−C(18)−C(19)	123.7(6)	CH_3−CH−CH_3 (av)	111(1)
Ca(1)−C(18′)−C(19′)	141.7(6)		

planarity of the Cp ring: within 0.008 Å

[a] The primed atoms are related to the unprimed atoms by the following relation: 1 − x, −y, 1 − z.

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(33) The rate of desolvation from **2e** slowed over time; i.e., after 2 days 40% of the initially formed **2e** was desolvated, only 10% more than at 15 min. The concentration of $(Cp^{4i})_2Ca$ increased to ca. 15% during this time, whereas the amount of **3e** remained roughly the same (ca. 10%). The decreasing rate of THF desolvation from **2e** over time is most likely caused by the increasing amount of THF released during the process.

proton NMR resonances for the $[Cp^{4i}]^-$ ligand; the ring proton of this complex resonates at 6.31 ppm, as compared to 5.95 ppm for **2e**. In spite of the increased instability of **2e** in aromatic solution, the complex can still be synthesized in hexanes; it precipitates from solution before desolvation occurs.

In contrast to the other $(Cp^{4i})Ca[C{\equiv}CR](thf)$ derivatives, **2d** is indefinitely stable in aromatic solution; no THF desolvation (and subsequent disproportionation) is observed even when solutions of the complex are placed under a vacuum. Although **2d** does not undergo THF desolvation in toluene, it is invariably isolated from this solvent as a highly viscous oil, which makes purification tedious. Consequently, the isolation of the complex was carried out by precipitation from small amounts of hexanes; the high solubility of **2d** even in this solvent resulted in a reduced yield (ca. 60%) compared to the other (cyclopentadienyl)calcium acetylide complexes.

Attempted Preparation of $\{(Cp^{4i})Ca[C{\equiv}CPh]\}_n$. In an attempt to prepare **3a** quantitatively, a solid sample of **2a** was heated at 130 °C and 10^{-6} Torr for 4 h. (Similar conditions were used in the preparation of $[(Cp^{4i})CaI]_n$ from $(Cp^{4i})CaI(thf)_n$.[8]) However, a proton NMR spectrum (C_6D_6) of the solid after heating displayed only the resonances for $(Cp^{4i})_2Ca$.[25] An FT-IR (KBr) spectrum, besides exhibiting bands for $(Cp^{4i})_2Ca$, also had bands characteristic of the bis(acetylide) complex $\{Ca[C{\equiv}CPh]_2\}_n$ at 2027 (ν(C≡C)), 1595, 1485, 754, and 689 cm^{-1}.[13] Apparently, **2a** is desolvated under these conditions, but the unsolvated complex **3a** is not stable with respect to disproportionation at this temperature and is completely converted into $(Cp^{4i})_2Ca$ and $\{Ca[C{\equiv}CPh]_2\}_n$ (eq 4).

$$2\{(Cp^{4i})Ca[C{\equiv}CPh](thf)\}_n(s) \xrightarrow{130\ °C} (Cp^{4i})_2Ca + \{Ca[C{\equiv}CPh]_2\}_n + n\mathrm{THF} \quad (4)$$

Attempts to desolvate **2a** at lower temperatures to prevent the subsequent thermal disproportionation of **3a** were not successful. For example, a sample of **2a** heated to 90 °C at 10^{-6} Torr for 4 h was only partly desolvated (ca. 60%), and even then more than two-thirds of the generated **3a** had converted into $(Cp^{4i})_2Ca$ and $\{Ca[C{\equiv}CPh]_2\}_n$ (see Experimental Section). Thus, solid **3a** is much more thermally unstable than the corresponding unsolvated (cyclopentadienyl)calcium iodide complex $[(Cp^{4i})CaI]_n$, which does not disproportionate below 210 °C.[18]

Solid-State Structure of $\{(Cp^{4i})Ca[C{\equiv}CPh](thf)\}_2{\cdot}C_7H_8$. A crystal of **2a** deposited from toluene was used to determine its structure by X-ray crystallography. A molecule of toluene was found in the lattice, but it was severely disordered across an inversion center. The inability to accurately model the toluene increased the values of the reliability indices; however, the remainder of the structure was well-behaved. An ORTEP view of **2a** is given in Figure 1; selected bond distances and angles for the complex are listed in Table 3.

The compound is dimeric in the solid state with bridging $[C{\equiv}CPh]^-$ ligands; a pentahapto $[Cp^{4i}]^-$ ring and a THF molecule complete the coordination sphere around each calcium. A similar dimeric structure was found for $[(Cp^{4i})CaI(thf)]_2$,[18] with bridging iodides in place of the acetylide ligands. **2a** represents the first

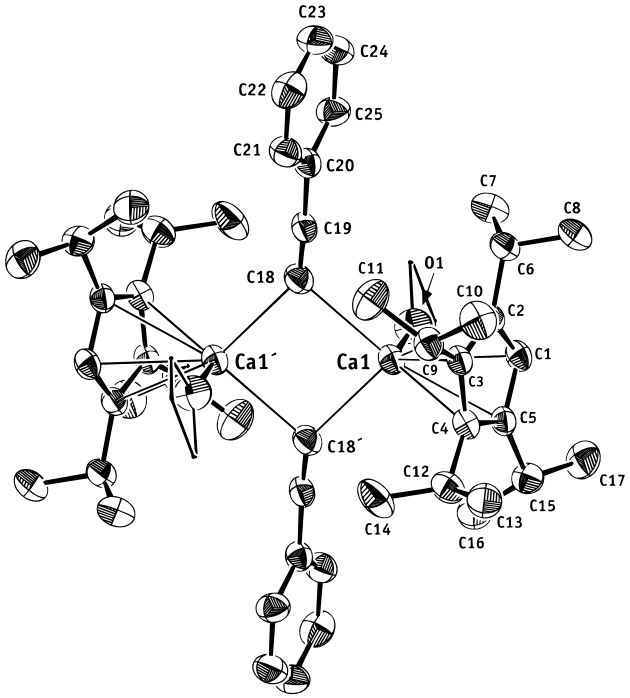

Figure 1. ORTEP diagram of the non-hydrogen atoms of **2a**, illustrating the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level. For clarity, the carbon atoms of the coordinated THF are rendered as dots and the lattice solvent has been omitted.

acetylide complex of a heavy alkaline-earth (Ca−Ba) metal to be characterized by X-ray diffraction.[34−37] Additionally, **2a** is only the second structurally determined organocalcium complex that contains metal−carbon σ-bonds, the other being $Ca[CH(SiMe_3)_2]_2{\cdot}(dioxane)_2$, reported by Lappert and co-workers.[9]

The $[Ca-C]_2$ core of **2a** is only slightly asymmetric, with Ca(1)−C(18) and Ca(1)−C(18)′ distances of 2.551(8) and 2.521(7) Å, and Ca(1)−C(18)−Ca(1)′ and C(18)−Ca(1)−C(18)′ angles of 93.6(2)° and 86.4(2)°, respectively. Although the Ca−C distances cannot be directly compared with any examples from the heavier alkaline-earth metals, they do fall within the range of values seen for M−C bonds in lanthanide complexes with bridging acetylide ligands, once the differences in metal radii are taken into account (Table 4). The short C(18)−C(19) triple-bond distance (1.173(9) Å) and nearly linear C(18)−C(19)−C(20) angle (177.2(7)°) are characteristic of a $[C{\equiv}CPh]^-$ ligand bound to a d^0 metal.[38−40]

The average Ca−C(ring) and Ca−ring centroid distances of 2.713(15) and 2.432 Å in **2a** are marginally longer than those in $[(Cp^{4i})CaI(thf)]_2$ (2.67(2) and 2.376 Å); a similar lengthening is seen for the Ca(1)−O(1)(thf) bond (2.385(5) vs 2.34(1) Å). The longer distances for **2a** presumably arise from an increase in steric

(34) Several structurally characterized beryllium and magnesium alkynyl complexes have been reported, including $[(MeBeC{\equiv}CMe)NMe_3]_2$ (ref 35), $[(MeC{\equiv}C)_2BeNMe_3]_2$ (ref 36), and $(PhC{\equiv}C)_2Mg(tmeda)_2$ (ref 37).

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Table 4. Comparison of the M−C_α Bond Distances in Dimeric Alkaline-Earth, Lanthanide, and Actinide Acetylide Complexes

compd	M−C_α (Å)	metal radius (Å)[a]	effective C_α radius (Å)[b]	ref
$\{(Cp^{4i})Ca[C{\equiv}CPh](thf)\}_2$	2.551(8)	1.00	1.55	this
	2.521(7)		1.52	work
$\{Cp^*Eu[C{\equiv}CPh](thf)_2\}_2$	2.709(7)	1.20	1.51	31
	2.702(7)		1.50	
$\{Cp_2Er[C{\equiv}CC(CH_3)_3]\}_2$	2.47(2)	1.00	1.47	42
	2.42(2)		1.42	
$\{(MeCp)_2Sm[C{\equiv}CC(CH_3)_3]\}_2$	2.55(1)	1.08	1.47	43
$\{((t\text{-}Bu)Cp)_2Sm[C{\equiv}CPh]\}_2$	2.617(13)	1.08	1.54	39
	2.560(11)		1.48	
$\{(PhC(NSiMe_3)_2)_2Y[C{\equiv}CH]\}_2$	2.556(5)	0.90	1.66	23
	2.509(5)		1.61	

[a] Shannon radii.[44] [b] Calculated by subtracting the metal radius from the M−C_α bond distance.

encumbrance at the metal center caused by its shorter Ca−C bridging bonds. An analogous elongation of the metal−Cp′ bond distances occurs in the mono(ring)-calcium complex $\{(Me_4EtC_5)Ca[N\overline{SiMe_2CH_2CH_2SiMe_2}]\}_2$, because of the steric congestion brought about by the bulky bridging amide ligands.[28]

It should be noted that the geometry and metrical parameters of **2a** are very similar to those previously reported for $\{Cp^*Eu[C{\equiv}CPh](thf)_2\}_2$.[31] This observation, along with the structural similarity seen previously for $[(Cp^{4i})CaI(thf)]_2$ and $[Cp^*CaI(thf)_2]_2$,[18] indicates that the combined bulk of a $[Cp^{4i}]^-$ and THF ligand is roughly the same as that for a $[Cp^*]^-$ and two THF ligands. However, the ability of **2a** to exist as an acetylide-bridged dimer suggests that a $[Cp^{4i}]^-$ ring and a THF ligand are not as sterically bulky as *two* $[Cp^*]^-$ ligands, as the severe steric strain present in the lanthanide complexes $\{Cp^*_2Ln[C{\equiv}CR]\}_2$ leads to rapid coupling of the acetylide ligands, forming complexes of the type $[Cp^*_2Ln]_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}RC_4R\}$.[19,22,32]

Ligand Effects on the Kinetic Stability of (Cp^{4i})-Ca[C≡CR(thf). Our initial investigation into the chemistry of mono(cyclopentadienyl)calcium complexes containing $[Cp^{4i}]^-$ ligands yielded three complexes, $(Cp^{4i})CaI(thf)_n$, $(Cp^{4i})Ca[N(SiMe_3)_2](thf)$, and $(Cp^{4i})Ca$-[BHT](thf), which were indefinitely stable with respect to THF dissociation and disproportionation in either aromatics or THF at room temperature.[18] However, the solution behavior of the $(Cp^{4i})Ca[C{\equiv}CR](thf)$ complexes synthesized from the reaction of **1** with terminal acetylenes is much more variable, depending on the specific substituent present on the acetylene ligand. Thus, the synthesis of the $(Cp^{4i})Ca[C{\equiv}CR](thf)$ complexes provided an opportunity to evaluate in greater detail how the nature of the anionic ligand influences the stability of the corresponding mono(cyclopentadienyl) complex.

The complexes **2a**−**c** all are more susceptible than $(Cp^{4i})CaI(thf)$ to the loss of coordinated THF and subsequent disproportionation in aromatic solution; noticeable formation of **3a**−**c** occurs after only a few days. The most likely reason for the increased lability of THF is that these complexes are more sterically crowded at the calcium atom than is $(Cp^{4i})CaI(thf)$; the release of steric pressure through THF dissociation is consequently more energetically favorable. In fact, the solid-state structure of **2a** may be more sterically congested than $[(Cp^{4i})CaI(thf)]_2$, because of the significantly shorter Ca−C bridging bonds in the mono(ring) alkynyl complex when compared with the corresponding Ca−I bridging bonds of $[(Cp^{4i})CaI(thf)]_2$. Their solution behavior thus strongly suggests that **2a**−**c** are dimeric with bridging $[C{\equiv}CR]^-$ ligands in aromatic solution. A higher degree of steric strain at the calcium atom in **3a**, when compared to $[(Cp^{4i})CaI]_n$, may also account for the increased thermal instability toward disproportionation exhibited by solid samples of the former complex.

The above discussion also provides a rationale for the higher rate of dissociation of THF from **2e**; i.e., that this complex is also dimeric in aromatic solution, in spite of the presence of the bulky $SiPh_3$ group on the alkynyl ligand. Once the compound dimerizes, the increased steric strain caused by the bulk of the $[C{\equiv}CSiPh_3]^-$ ligand substantially increases the extent of THF dissociation from **2e** when compared to **2a**, **2b**, or **2c**. It is likely that dissociation of THF would be even more extensive for aromatic solutions of **2e** placed under a vacuum. It should be noted that complete dissociation of THF has been observed in other sterically crowded mono(cyclopentadienyl)calcium complexes; for example, the reaction of $(Me_4EtC_5)CaI(thf)$ with $\{K[N\overline{SiMe_2CH_2CH_2SiMe_2}]\}_2$ yields only $\{(Me_4EtC_5)Ca[N\overline{SiMe_2CH_2CH_2SiMe_2}]\}_2$ on isolation from toluene under vacuum.[28] The THF ligand is lost during this reaction presumably for the same reason it readily dissociates from the calcium in **2e**.

Considering the results for the other $(Cp^{4i})Ca[C{\equiv}CR]$-(thf) complexes, the fact that **2d** does not lose its coordinated THF ligand in toluene solution, and that it displays good hexanes solubility, suggests that it is largely monomeric in aromatic solution, as was previously seen for $(Cp^{4i})Ca[N(SiMe_3)_2](thf)$.[18] The increased steric bulk of the $Si(i\text{-}Pr)_3$ substituent in **2d** probably interferes with dimer formation.[41] The changes between **2d**,**e** illustrate how sensitive the properties of the corresponding $(Cp^{4i})CaX(thf)$ complexes are to the nature of the anionic ligand $[X]^-$.

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Supporting Information Available: Tables of atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(41) Although quantitative steric estimates of $Si(i\text{-}Pr)_3$ relative to $SiPh_3$ do not seem to have been published, the cone angles of $E(i\text{-}Pr)_3$ species are consistently greater than those of EPh_3. See: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348. White, D.; Taverner, B. C.; Leach, P. G. L.; Coville, N. J. *J. Comput. Chem.* **1993**, *14*, 1042−1049.

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