Table II. Spectral Data

species	^{11}B NMR chem shifts,^{a} ppm		IR, cm^{-1} (BH region)
	B_{base}	B_{apex}	
$[(C_6H_5)_3PCH_3][B_5H_8]$	−15.2	−51.5	2475 (s, br), 1945 (w), 1845 (w)
$[(C_6H_5)_3PCH_3][BrB_5H_7]$	−13.23	37.30	2497 (s, br), 2238 (w)
$[(C_6H_5)_3PCH_3][B_6H_9]$	10.43	−49.72	not recorded
$[P(C_6H_5)(CH_3)[C_2B_4H_7]$	7.1(1), −5.5(2)	−55.0	2475 (s, br), 1800 (w)

^{a}Spectra run in CD_2Cl_2 at −50 °C; numbers in parentheses indicate relative areas.

7.16; B, 12.30. Found: C, 68.83; H, 7.12; B, 12.73. The 96.3-MHz ^{11}B NMR spectrum at −78 °C in CD_2Cl_2 exhibits a doublet at −55.0 ppm (J = 155 Hz) assigned to the apical boron atom and two singlets at 6.7 and −5.9 ppm attributed to B(4,6) and B(5), respectively. The 300-MHz proton NMR spectrum consists of a multiplet at 7.8 ppm and a doublet at 2.74 ppm (J = 13 Hz) assigned to the phenyl and methyl protons, respectively, on $[(C_6H_5)_3PCH_3]^+$, a singlet at −5.0 ppm and a 1:1:1:1 quartet at −1.97 ppm (J = 155 Hz) arising from the bridge hydrogen and the apical terminal hydrogen, respectively, and a singlet at 4.93 ppm attributed to the hydrogens on the carbons of the carborane cage. Two broad overlapping resonances at 3.4 and 2.0 ppm with area ratios of 2:1 are assigned to the hydrogens attached to the basal boron atoms. The 121.5-MHz ^{31}P NMR spectrum exhibits a sharp resonance at 21.8 ppm. The IR spectrum includes a strong band at 2475 cm^{-1} (BH_{term}) and a weak band at 1800 cm^{-1} (BH_{bridge}).

Results and Discussion

The boranes B_5H_9, B_6H_{10}, $C_2B_4H_8$, and 1-BrB_5H_7 were easily deprotonated in the ylide solution, and the results are summarized in Table I. The first three boranes afford white solids that are stable for several hours in the absence of air and moisture. Spectral data for the species are given in Table II.

2,3-Dimethyldicarbahexaborane(8) did not react with the ylide, and we presume that the inductive effect of the methyl groups reduces the acidity of the carborane such that deprotonation does not occur. $(CH_3)_2C_2B_4H_6$ is easily deprotonated with NaH, as others have noted.[19,20] The reaction between 1-BrB_5H_8 and $(C_6H_5)_3PCH_2$ is much more complicated than those of the other species. If the reaction is carried out exactly as it was for $C_2B_4H_8$, two products appear to be formed, one a white powder and the other a yellow oil. We were not able to separate and identify these species satisfactorily, and the eventual elemental analysis of the two species gave inconclusive results. The relative quantities of the two species appeared to be temperature dependent, suggesting that perhaps some thermal reaction or arrangement occurs. A possibility is that there are two simultaneous reactions occurring: deprotonation and adduct formation. A third possibility is that these two products may interconvert according to

$$[(C_6H_5)_3PCH_3][B_5H_7Br] \rightarrow [(C_6H_5P)_3PCH_3\cdots B_5H_8Br]$$

Another possible side reaction, which has precedent in the chemistry of bromoboranes,[17] is the elimination of $[(C_6H_5)_3PCH_3]Br$ from either the adduct or the salt to form higher boranes according to

$$[(C_6H_5)_3PCH_3]B_5H_7Br \rightarrow [(C_6H_5)_3PCH_3]Br + \text{“}B_5H_7\text{”}$$

$$\text{“}B_5H_7\text{”} \rightarrow \text{higher boranes} + H_2$$

"B_5H_7" could form $B_{10}H_{14}$ or any of a series of higher boranes. The final product mixture always contained materials that we presumed to be higher boranes. Their ^{11}B NMR spectra were complex but resembled spectra of mixtures of higher boranes. Allowing the reaction to proceed in an NMR tube and monitoring it by NMR were not easy, since 1-BrB_5H_8 rearranges to the 2-isomer in ethers, as noted previously.[21] Because the ylide is not soluble in other solvents such as C_5H_{12} or CH_2Cl_2, the reaction could not be followed in these. The $[1\text{-}BrB_5H_7]^-$ salt was prepared by carrying out the reaction with the ylide at −78 °C and isolating the product without warming the reaction mixture above −78 °C until the solvent-free solid was isolated. This substance was a yellowish solid, and its spectral and other data are given in Tables I and II. In order to demonstrate that deprotonation took place at −78 °C, the reaction between 1-BrB_5H_8 and $(C_6H_5)_3PCH_2$ was allowed to proceed at that temperature and then to warm slowly to room temperature while the spectrum was monitored. In the range −80 to −20 °C, the separation between the two ^{11}B resonances did not change although there was a small (0.46 ppm) shift upfield. The spectrum of the parent 1-BrB_5H_8 under the same conditions has different peak separations and chemical shifts. At −20 °C, significant decomposition had taken place; however, the spectrum still resembled that of the anion. The resultant salt is much less stable than the other $[(C_6H_5)_3PCH_2]^+$ salts reported herein.

In summary, intermediate boranes react with methylidenetriphenylphosphorane to give products resulting from deprotonation of the borane. The yields are quite low, and thus, the reaction is not a useful method for directly preparing the stable borane salts and will not serve as an alternative to methods using alkali-metal hydrides.

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Registry No. $[(C_6H_5)_3PCH_3]Br$, 1779-49-3; $[(C_6H_5)_3PCH_3]I$, 2065-66-9; B_5H_9, 19624-22-7; $C_2B_4H_8$, 18972-20-8; $(CH_3)_2C_2B_4H_6$, 20741-68-8; B_6H_{10}, 23777-80-2; 1-BrB_5H_8, 23753-67-5; $[(C_6H_5)_3PCH_3][C_2B_4H_7]$, 118043-04-2; $(C_6H_5)_3PCH_2$, 3487-44-3; $[(C_6H_5)_3PCH_3][B_5H_8]$, 67495-88-9; $[(C_6H_5)_3PCH_3][BrB_5H_7]$, 118043-02-0; $[(C_6H_5)_3PCH_3][B_6H_9]$, 57298-52-9.

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Synthesis of $Cp_2Ti[C\equiv CSi(CH_3)_3]_2$ and Synthesis and Molecular Structure of $[Cp_2TiC\equiv CSi(CH_3)_3]_2$

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Titanium compounds of the general type $Cp_2Ti[C\equiv CR]_2$, where R = alkyl or aryl substituents, have been synthesized and shown to exhibit limited stability.[1-4] These alkynyltitanium complexes have been characterized by various methods, including IR spectroscopy (which revealed a $\nu_{C\equiv C}$ absorption in the range 2040–2000 cm^{-1}), elemental analyses, and NMR spectroscopy.

The reaction of titanium(III) complexes with acetylides has proven more interesting. Teuben found that the reaction of $[Cp_2TiCl]_2$ with $Na[C\equiv C(Ph)]$ resulted in the formation of a green material that no longer exhibited a $\nu_{C\equiv C}$ stretch.[2] A dimeric species was proposed as the structure in which the acetylene group acted as a σ donor to one metal center and a bridging group with the adjacent titanium atom.[2] It was later determined by Stucky that the complex had actually undergone an oxidative coupling reaction to form μ-(1-3η:2-4η-*trans*,*trans*-1,4-diphenyl-

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butadiene)bis(bis(η^5-methylcyclopentadienyl)titanium) (**1**).[5] The titanium atoms were found to be bridge bonded to alternate carbons on the butadiene. Unfortunately the low solubility of the compound made collection of NMR spectra impossible.

We were interested in the synthesis of stable alkynyltitanium complexes that would have several sites of reactivity. Furthermore, it was believed that (trimethylsilyl)acetylene would provide these characteristics since the electron-releasing silicon moiety would stabilize the alkyne and could later be removed by a variety of methods.[6] We wish to report the synthesis and corrected NMR data for $Cp_2Ti[C{\equiv}CSi(CH_3)_3]_2$ (**2**) and the synthesis and characterization for a new dimeric species $\{Cp_2TiC{\equiv}CSi(CH_3)_3\}_2$ (**3**) where the acetylene group acts as both σ and π donor.

Experimental Section

All manipulations were carried out under inert atmosphere with standard Schlenk techniques.[7] Solvents were dried by standard procedures and distilled under dry nitrogen prior to use. Infrared spectra were recorded by using KBr pellets on a Beckman Model FT1100 FT-IR instrument. ^1H and ^{13}C NMR spectra were recorded on a Brüker AM360 FT-NMR instrument operating at 360.135 and 90.566 MHz, respectively. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Cp_2TiCl_2, $HC{\equiv}CSi(CH_3)_3$, and Na metal were purchased from Aldrich Chemical Co. and used without further purification. Neutral chromatography grade alumina was obtained from Fisher Chemical and used without modification, and $[Cp_2TiCl]_2$ was prepared according to literature methods.[8]

Preparation of $Cp_2Ti[C{\equiv}CSi(CH_3)_3]_2$ (2). An ether slurry of $NaC{\equiv}CSi(CH_3)_3$ was prepared by the addition of 0.6 g (6 mmol) of $HC{\equiv}CSi(CH_3)_3$ to excess Na metal in ether. The mixture was refluxed for 2 h and then cooled to room temperature. The sodium acetylide suspension was then added, dropwise, to Cp_2TiCl_2 (0.75 g, 3 mmol) in 40 mL of ether at 0 °C. The solution slowly changed color from red to orange and was allowed to stir at room temperature for 12 h. The mixture was filtered and the solvent removed in vacuo to yield the crude orange solid, which could be purified by column chromatography (alumina, neutral) eluting first in heptane to remove organic byproducts followed by toluene to elute the product (1.22 g, 32.8% yield; mp 150–155 °C dec). Infrared spectral data (in KBr, cm^{-1}): 3103 (m), 2955 (m), 2924 (w, sh), 2009 (w), 1420 (m), 1246 (s), 1022 (m), 836 (s), 821 (s), 757 (m), 684 (s), 605 (w). Mass spectrum (70 eV): $(Cp_2Ti[C{\equiv}CSi(CH_3)_3]_2)^+$, m/e 372; $(Cp_2Ti[C{\equiv}CSi(CH_3)_3])^+$, m/e 275; $(Cp_2Ti)^+$, m/e 178. NMR for $Cp_2Ti[C_\alpha{\equiv}C_\beta Si(CH_3)_3]_2$. ^1H NMR (360.134 MHz, C_6D_6, $Si(CH_3)_4$ reference): Cp, 6.02 (s) ppm; $Si(CH_3)_3$, 0.22 (s) ppm. ^{13}C NMR (90.556 MHz, C_6D_6, $Si(CH_3)_4$ reference): C_α, 171.84 (s) ppm; C_β, 133.85 (s) ppm; Cp, 113.95 (s) ppm; $Si(CH_3)_3$, 1.09 (s) ppm.

Preparation of $[Cp_2TiC{\equiv}CSi(CH_3)_3]_2$ (3). An ether mixture of $NaC{\equiv}CSi(CH_3)_3$ (prepared as described for **2**) was added dropwise to $[Cp_2TiCl]_2$ (1.47 g, 3 mmol) in 40 mL of ether at 0 °C. The solution immediately changed color from green to deep red on addition of the acetylide. The mixture was allowed to stir at room temperature for an additional 12 h. The reaction mixture was concentrated to 20 mL and transferred to a neutral alumina column. Organic byproducts were eluted with hexane, and the product (a dark red band) was eluted with toluene. The solvent was removed in vacuo and yielded burgundy crystals (mp 250–255 °C) in 23% yield (0.38 g). Infrared spectral data (in KBr, cm^{-1}): 3105 (w), 2955 (w), 1798 (m), 1241 (m), 1051 (m), 843 (s), 819 (s), 795 (s), 752 (m). Mass spectrum (70 eV): $(\{Cp_2TiC{\equiv}CSi(CH_3)_3\}_2)^+$, m/e 550; $(Cp_2TiC{\equiv}CSi(CH_3)_3)^+$, m/e 275; $(Cp_2TiC{\equiv}C)^+$, m/e 202; $(Cp_2Ti)^+$, m/e 178. NMR for $\{Cp_2TiC_\alpha{\equiv}C_\beta Si(CH_3)_3\}_2$. ^1H NMR (360.134 MHz, C_6D_6, $Si(CH_3)_4$ reference): Cp, 5.14 (s) ppm; $Si(CH_3)_3$, 0.27 (s) ppm. $^{13}C\{^1H\}$ NMR (90.556 MHz, C_6D_6, $Si(CH_3)_4$ reference): C_α, 236.79 (s) ppm; C_β, 142.85 (s) ppm; Cp, 104.38 (s) ppm; $Si(CH_3)_3$, 2.15 (s) ppm.

Collection and Reduction of X-ray Data for 3. A deep red crystal, obtained from a toluene solution, was coated in epoxy and mounted on a thin glass fiber on a Picker FACS-1 diffractometer modified by Professor C. E. Strouse of this department. Systematic absences were found for $0k0$ reflections for which $k \neq 2n$ and $h0l$ reflections for which $h + l \neq 2n$. Unit cell parameters were determined from a least-squares fit of 19 accurately centered reflections ($9.9 < 2\theta < 20.2°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table I. Data were collected at 25 °C in a θ–2θ scan mode. Three intense reflections (510, 014, 02$\bar{5}$) were monitored every 97 reflections to check stability. Intensities of these reflections decreased gradually during the course of the experiment, and then dropped sharply, after about two-thirds of the collection had been completed. Of the 2379 unique reflections measured, 1207 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz, polarization, and decay effects. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement, MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, DeClercq, and Woolfson); SHELX76 (Sheldrick); ORTEP (Johnson).

Table I. Summary of Crystallographic Data for $[Cp_2TiC{\equiv}CSi(CH_3)_3]_2$

cryst syst	monoclinic	ρ(calcd), g cm^{-3}	1.23
space group	$P2_1/n$	μ, cm^{-1}	6.3 (not applied)
a, Å	11.249 (1)	no. of unique reflcns	2379
b, Å	8.426 (1)	no. of obsd reflcns ($I > 3\sigma(I)$)	1207
c, Å	15.307 (2)		
b, deg	90.582 (3)	2θ max, deg	55
V, $Å^3$	1459	data collcd	$+h,+k,\pm l$
Z	4	no. of params refined	145
formula	$C_{30}H_{38}Si_2Ti_2$	GOF	2.26
mol wt	550.67	R, %	7.2
		R_w, %	8.5

Table II. Atomic Parameters for **3**[a]

atom	x	y	z	u,[b] $Å^2$
Tl(1)	0.3813 (1)	0.0646 (2)	0.0667 (1)	0.046
Sl(1)	0.8029 (3)	0.2034 (3)	0.0949 (2)	0.064
C(1)	0.5626 (9)	0.0894 (9)	0.0577 (4)	0.042
C(2)	0.6724 (10)	0.1025 (10)	0.0468 (5)	0.053
C(3)	0.7454 (11)	0.3243 (17)	0.1887 (8)	0.133
C(4)	0.8755 (10)	0.3390 (13)	0.0164 (8)	0.107
C(5)	0.9176 (9)	0.0638 (12)	0.1349 (6)	0.080
C(6)	0.4269 (12)	0.0159 (13)	0.2185 (5)	0.118
C(7)	0.4540 (12)	−0.1270 (13)	0.1742 (5)	0.088
C(8)	0.3465 (12)	−0.1892 (13)	0.1392 (5)	0.074
C(9)	0.2530 (12)	−0.0847 (13)	0.1620 (5)	0.090
C(10)	0.3027 (12)	0.0421 (13)	0.2110 (5)	0.125
C(11)	0.4043 (7)	0.3217 (9)	−0.0010 (7)	0.077
C(12)	0.3756 (7)	0.3477 (9)	0.0878 (7)	0.0930
C(13)	0.2587 (7)	0.2905 (9)	0.1015 (7)	0.088
C(14)	0.2152 (7)	0.2292 (9)	0.0211 (7)	0.092
C(15)	0.3052 (7)	0.2485 (9)	−0.0422 (7)	0.074

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. [b] Defined as $(1/8\pi^2)B_{equiv}$, where B_{equiv} for an anisotropic atom is as defined by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610.

Solution and Refinement of the Structure of 3. Atoms were located by use of MULTAN80. All calculations were performed on the VAX 11/750 crystallographic computer. All H atoms were included in calculated positions (C–H = 1.0 Å) in structure factor calculations with an assigned u value of 0.15 or 0.10 $Å^2$ for methyl and non-methyl H, respectively. H parameters were not refined. Both cyclopentadienyl ligands were constrained to be perfect pentagons, C–C = 1.42 Å. Anisotropic temperature factors were refined for all nonhydrogen atoms. Scattering factors for H were obtained from Stewart et al.[9] and for other atoms were taken from ref 10. The maxima and minima on a final difference electron density map were 0.2 e $Å^{-3}$. Final positional and thermal parameters are shown in Table II for non-hydrogen atoms, and anisotropic thermal parameters for those atoms are given in Table IS of the supplemental material.

Discussion

Compound **2** is isolated as a golden yellow solid that is soluble in polar or aromatic solvents and can be handled in ambient atmosphere for limited periods of time (1–2 h). The infrared spectrum reveals an absorption at 2009 cm^{-1}, which is assigned

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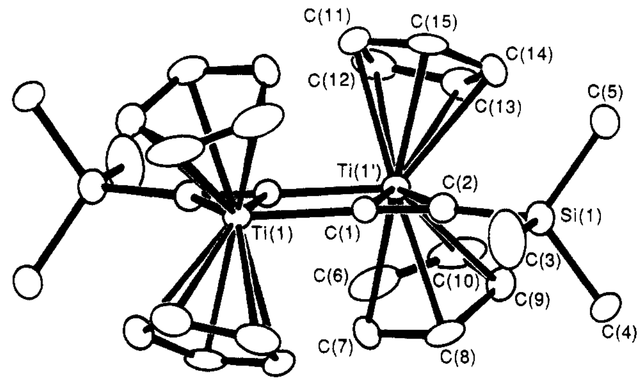

Figure 1. ORTEP representation of $[Cp_2TiC{\equiv}CSi(CH_3)_3]_2$ (**3**) with H atoms omitted. Ellipsoids are drawn with 20% probability.

to the $\nu_{C\equiv C}$ stretch. The mass spectrum confirms the proposed formulation.

The assignment of the ^{13}C NMR is consistent with those of other alkynyltitanium complexes[4] where the downfield signal is assigned to the carbon directly bonded to the metal. It should be noted that Wrackmeyer and co-workers reported the ^{13}C NMR spectrum for a compound that was believed to be **2**.[4] The ^{13}C NMR data reported by Wrackmeyer do not agree with the values reported here for **2**, but do agree well with the values for **3**.[11]

The dimer, **3**, is comprised of dark burgundy crystals that are soluble in organic solvents and can be handled in ambient atmosphere for limited periods of time (1–2 h). The infrared spectrum exhibits a medium-intensity absorption at 1789 cm^{-1}, which is assigned to the $\nu_{C\equiv C}$ stretch. The shift to lower wavenumber is consistent with the coordination of the acetylenic group with the adjacent metal atom.[12] The mass spectrum confirms the dimeric structure; both the parent ion (*m/e* 550) and the expected mass for the monomer (*m/e* 275) are observed. The complex is expected to contain two formal titanium(III) centers and, therefore, exhibit paramagnetism; however, it is diamagnetic at room temperature. The observed diamagnetism may be due to an antiferromagnetic coupling since similar behavior is observed in other Ti(III) systems at reduced temperatures.[13] For the compounds $[Cp_2Ti(X)]_2$ (X = Cl, Br), it is found that as the Ti–Ti distance decreases the antiferromagnetic coupling increases. The ^{13}C NMR spectrum exhibits a strongly deshielded signal at 236.79 (s) ppm, which is assigned to C_α. The C_β is assigned to a singlet at 142.85 (s) ppm. The trimethylsilyl carbons appear as a singlet at 2.15 ppm.

The X-ray crystal structure of **3** supports the spectroscopic data. As shown in Figure 1, **3** is a dimeric molecule that exhibits a center of inversion. The titanium atom, in this case, is bonded directly to the C(1) atom and to the adjacent acetylenic group. One interesting feature of **3** is the fact that the acetylenic groups do not couple as in the structure reported by Stucky.[5] The structure indicates that the acetylenes are engaged in both σ and π bonding with the titanium metal. Selected bond distances and angles are shown in Table III.

The Ti(1)–Ti(1)′ distance is 3.550 (3) Å. This is shorter than the reported distance in $[Cp_2Ti(Cl)]_2$ (3.926 (3) Å) or $[Cp_2Ti(Br)]_2$ (4.125 (4) Å).[13] The C(1)–C(1)′ distance is 2.706 (16) Å. The C–C single bond distance in **1** is much shorter, only 1.485 (4) Å.[5] The Ti(1)–C(1) bond is 2.056 (11) Å, which is shorter than the Ti–CH$_3$ bond for $(\eta^5\text{-indenyl})_2Ti(CH_3)_2$, which is 2.21 (2) Å.[14] The Ti–C bond distance of **3** more closely matches those for the sp^2-hybridized carbons of **1** where the distances are 2.107 (7) and 2.230 (7) Å.[5] The Ti–C(1)′ and Ti–C(2)′ bond distances are 2.395 (7) and 2.312 (8) Å, respectively. These distances are longer than the bond distances reported for $Cp_2Ti(CO)(\eta^2\text{-}(C_6H_5)C{\equiv}C(C_6H_5))$ (**4**) where the Ti–C distances are 2.107 (7) and 2.230 (7) Å.[15] The centroid to metal distances (Cp(1)–Ti and Cp(2)–Ti) are 2.099 (1) and 2.096 (2) Å. These are typical of η^5-Cp bond distances. The Cp–Ti distances for **4** are 2.083 and 2.084 Å.[12] The C(1)–C(2) bond distance is 1.253 (15) Å, which is similar to that reported for **4** where the C≡C bond distance is 1.285 (10) Å.

Table III. Selected Bond Distances and Angles for **3**

A. Bond Distances (Å)

Ti(1)–C(1)	2.056 (11)	Ti(1)–C(6)	2.410 (8)
Ti(1)–C(7)	2.440 (10)	Ti(1)–C(8)	2.442 (11)
Ti(1)–C(9)	2.415 (11)	Ti(1)–C(10)	2.394 (9)
Ti(1)–C(11)	2.417 (8)	Ti(1)–C(12)	2.408 (8)
Ti(1)–C(13)	2.413 (8)	Ti(1)–C(14)	2.424 (8)
Ti(1)–C(15)	2.427 (9)	Ti(1)–Cp(1)	2.099 (1)
Ti(1)–Cp(2)	2.096 (2)	Ti(1)–C(1)′	2.395 (7)
Ti(1)–C(2)′	2.312 (8)	Si(1)–C(2)	1.844 (11)
Si(1)–C(3)	1.881 (13)	Si(1)–C(4)	1.852 (12)
Si(1)–C(5)	1.845 (10)	C(1)–C(2)	1.253 (15)
C(1)–Ti(1)′	2.395 (7)	C(2)–Ti(1)′	2.312 (8)
Ti(1)–Ti(1)′	3.550 (3)	C(1)–C(1)′	2.706 (16)

B. Bond Angles (deg)

C(1)–Ti(1)–Cp(1)	104.5 (2)	C(1)–Ti(1)–Cp(2)	105.1 (2)
C(1)–Ti(1)–C(1)′	74.5 (3)	C(1)–Ti(1)–C(2)′	105.3 (3)
Cp(1)–Ti(1)–Cp(2)	129.0 (1)	Cp(1)–Ti(1)–C(1)′	114.3 (2)
Cp(1)–Ti(1)–C(2)′	105.4 (2)	Cp(2)–Ti(1)–C(1)′	113.1 (2)
Cp(2)–Ti(1)–C(2)′	105.6 (2)	C(1)′–Ti(1)–C(2)′	30.8 (3)
C(2)–Si(1)–C(3)	106.0 (5)	C(2)–Si(1)–C(4)	112.3 (5)
C(2)–Si(1)–C(5)	112.9 (4)	C(3)–Si(1)–C(4)	108.6 (5)
C(3)–Si(1)–C(5)	109.7 (5)	C(4)–Si(1)–C(5)	107.3 (5)
Ti(1)–C(1)–C(2)	176.1 (7)	Ti(1)–C(1)–Ti(1)′	105.5 (3)
C(2)–C(1)–Ti(1)′	70.9 (6)	Si(1)–C(2)–C(1)	140.3 (8)
Si(1)–C(2)–Ti(1)′	141.4 (5)	C(1)–C(2)–Ti(1)′	78.2 (6)

The Ti(1)–C(1)–C(2) bond angle is essentially linear at 176.1 (7)°. The C(1)–C(2)–Si(1) bond angle is 140.3 (8)°. This distortion is believed to be the result of the side-on bonding of the adjacent titanium atom to the acetylenic group. Such distortion is consistent with the previously reported structure for **4** in which the $C{\equiv}C(C_6H_5)$ bond angles are 138.8 (7) and 145.8 (7)°. The Cp(1)–Ti–Cp(2) angle is 129.0 (1)° which is smaller than that in **3**, which has a bond angle of 133.5 (5)°.

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Supplementary Material Available: Tables IS and IIS, listing positional and thermal parameters, and Table IIIS, listing distances, angles, and torsion angles (16 pages); Table IVS, listing calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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[11] Wrackmeyer in ref 4 reports the ^{13}C NMR data (C_6D_6, $Si(CH_3)_4$ as follows: C_α, 236.1 ppm; C_β, 143.1 ppm; Cp, 104.1 ppm; $Si(CH_3)_3$, 1.8 ppm.

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Encapsulated Phosphides: $Ru_8(CO)_{21}(\mu_6\text{-}P)(\mu_4\text{-}PPh)(\mu_2\text{-}PPh_2)$, a Molecule with a Six-Coordinate Phosphorus Atom in a Condensed Cluster

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Although an extensive chemistry has been developed for μ_2-diorganophosphido (R_2P)[1] and μ_n-phosphinidene (n = 2–4) (RP)[2]

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