

Sterically accelerated carbon-carbon bond formation at hafnium: Formation and structure of $\text{Hf}(\eta^5\text{-C}_7\text{H}_{11})[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]$ (R = iso-Pr) via coupling of coordinated allyl butadiene fragments

Michael D. Fryzuk, T. S. Haddad, and Steven J. Rettig

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An interesting aspect of complexes 1 and 2 is the relative position of the two phosphine ligands. In dithioformate complexes $\text{MX}(\text{S}_2\text{CH})(\text{CO})(\text{PR}_3)_2$ ($\text{M} = \text{Ru}$ or Os , $\text{X} = \text{Cl}$ or Br , and $\text{R} = \text{Ph}$, Ph_2Me , or PhMe_2), the cis isomer is formed in a first step but the trans isomer is observed after lengths of heating in benzene.² Moreover, the cis and trans isomers were detected in phosphonodithiocarboxylate complexes $[\text{RuH}(\text{CO})(\text{S}_2\text{CPR}_3)(\text{PCy}_3)_2][\text{BPh}_4]$ ($\text{R} = \text{Cy}$ or Et) synthesized at moderated temperatures.³ The cis isomer of complex $\text{IrCl}_2(\text{S}_2\text{CH})(\text{PPh}_3)_2$ was also obtained from the reaction of (trans chlorides) $\text{IrCl}_2(\text{PPh}_3)_3$ with carbon disulfide in boiling benzene, but the cis \rightarrow trans isomerization was not observed.² From spectroscopic data of the crude complexes 1 and 2 only one isomeric form seems to be formed even in solution at room temperature after several days. In order to determine the relative position of the phosphines and to confirm the nature of the dithiocarboxylate ligand in complexes 1 and 2, a X-ray diffraction study was undertaken.¹² Suitable single crystals of 1 were obtained from a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution.

The molecular structure of 1 is shown in Figure 1. One important feature of the molecule is the cis disposition of the two phosphines with a $\text{P}(1)\text{-Ru-P}(2)$ angle of 108.4° . The two phosphorus, the ruthenium, and the two sulfurs are in a plane forming with $\text{C}(1)$ and Cl a very distorted octahedral geometry around of the metallic center. The $\text{C}(1)\text{-O}(1)$ distance is very short (1.02 \AA), perhaps influenced by the nearly trans position of the Cl ligand ($170.6(3)^\circ$). A similar situation was observed in the complex $\text{OsCl}(\text{CO})(\text{HC}=\text{CHPh})(\text{P-}i\text{-Pr}_3)_2$.¹³ The ruthenium-sulfur distances are different ($2.52(2)$ and $2.35(2) \text{ \AA}$) as well as the ruthenium-phosphorus bonds ($2.43(2)$ and $2.39(2) \text{ \AA}$).

It is interesting to note that the shorter Ru-S distance is pseudotrans to the longer Ru-P distance and vice versa, suggesting a trans effect between the ligands. The related dithiocarbamate ligands frequently are not symmetrically bonded to metals.¹⁴ The $\text{S}(1)\text{-Ru-S}(2)$ angle ($72.4(7)^\circ$) is similar to those observed in other octahedral (dithioformato)ruthenium complexes.^{15,16} The rest of the di-

thiocarboxylate ligand was easily identified by spectroscopic techniques (IR and ^1H NMR), but in the crystallographic study of 1, the $\text{C}(3)\text{-C}(4)$ double bond appears significantly short ($1.252(1) \text{ \AA}$) compared with others.⁷

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Registry No. 1, 113161-98-1; 2, 113161-99-2; $\text{Ru}(\text{CO})\text{Cl}(\text{HC}=\text{CHPh})(\text{PPh}_3)_2$, 109800-33-1; $\text{Ru}(\text{CO})\text{Cl}(\text{HC}=\text{CH-}t\text{-Bu})(\text{PPh}_3)_2$, 113161-97-0; CS_2 , 75-15-0.

Supplementary Material Available: Tables of final atomic coordinates and final anisotropic thermal parameters for $\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CHC}=\text{CHC}(\text{C}_6\text{H}_5))(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (5 pages); a listing of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

Sterically Accelerated Carbon-Carbon Bond Formation at Hafnium: Formation and Structure of $\text{Hf}(\eta^5\text{-C}_7\text{H}_{11})[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]$ ($\text{R} = i\text{-Pr}$) via Coupling of Coordinated Allyl and Butadiene Fragments

Michael D. Fryzuk,* T. S. Haddad, and Steven J. Rettig†

Department of Chemistry, University of British Columbia
2036 Main Mall
Vancouver, British Columbia, Canada V6T 1Y6

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Summary: A unique coupling of an allyl and a butadiene ligand occurs within the coordination sphere of hafnium to generate an $\eta^5\text{-C}_7\text{H}_{11}$ fragment. The reaction is accelerated by the presence of bulkier ancillary phosphines.

Carbon-carbon bond-forming reactions are probably the single most important transformation in synthetic organic methodology.¹ Of particular interest are such reactions that occur in the coordination sphere of a transition-metal complex since the resulting stereoselectivity of the process can often be fine-tuned by changes in the ancillary ligands at that metal center.² In the course of examining the fundamental chemistry of "lower" oxidation states of the group 4 metals, we discovered a simple C-C coupling/rearrangement reaction at hafnium which is accelerated by increasing the steric bulk of the ancillary ligand.

Since phosphine donors are relatively rare³ as ancillary ligands for early metal complexes, we have developed a mixed donor system of the formula $\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2$ which binds in a tridentate fashion to zirconium and

(12) Crystal data: $\text{C}_{46}\text{H}_{37}\text{ClO}_2\text{P}_2\text{S}_2\text{Ru}$; M , 867.6; monoclinic; $a = 15.09(2)$, $b = 16.531(5)$, $c = 17.96(2) \text{ \AA}$; $\beta = 106.18(12)^\circ$; $V = 4302.7(8) \text{ \AA}^3$ (by least-squares refinement on a CAD-4 diffractometer for 25 automatically centered reflections, $\lambda = 0.7107 \text{ \AA}$); space group Cc ; $Z = 4$; $D_{\text{calc}} = 1.28 \text{ g cm}^{-3}$; poor crystal ($0.1 \times 0.1 \times 0.2 \text{ mm}$); $\mu(\text{Mo K}\alpha) = 11.7 \text{ cm}^{-1}$. Data collection and processing. Intensity data were recorded by the $w\text{-}2\theta$ scan technique. A total of 7747 reflections with $1 < \theta < 25^\circ$ were measured; 1300 were considered observed ($I > 2\sigma(I)$). No measurable intensities were obtained at high resolution. Absorption corrections were made (Walker, N.; Stuart, P. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1983, A39, 158-166). Structure Determination. Ru atom was located from a Patterson map. The other atoms except hydrogens were found in successive Fourier syntheses. The hydrogen atoms were located by geometrical calculations. Because of the low resolution, it was impossible to refine the whole of structure and part of the atoms were fixed. Anisotropic temperature factors were applied to Ru, P, Cl, and S. Unit weights were applied to every reflection (Martinez-Ripoll, M.; Cano, F. H. PESOS, Instituto Rocasolano, CSIC, Madrid). The refinement converged at $R = 0.10$ ($R_w = 0.109$) for observed reflections only. Calculations were performed with the XRAY70 System (Stewart, J. M.; Kundell, F. A.; Baldwin, J. C. The XRAY70 System, Computer Science Center, University of Maryland, College Park, MD, 1974). Atomic scattering dispersion correction factors for Ru, P, Cl, and S were chosen from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. 4. The molecule plot was drawn with PLUTO (Motherwell, S.; Clegg, B. PLUTO, Program for plotting molecular and crystal structures, 1978, Cambridge Data Center, Cambridge England).

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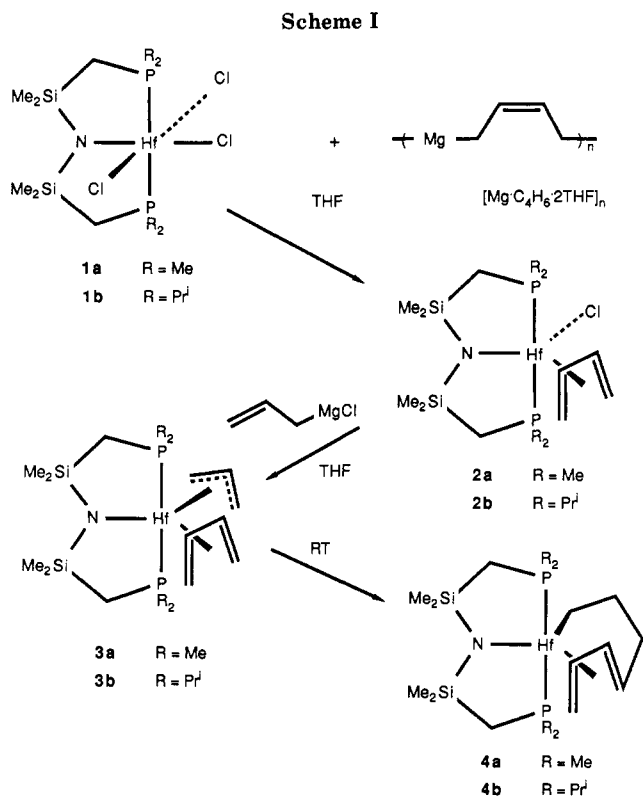
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hafnium.⁴ In particular, the two hafnium(IV) derivatives, $\text{HfCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]$ (**1a**) and $\text{HfCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{P-}i\text{-Pr}_2)_2]$ (**1b**) are versatile starting materials with different steric demands by virtue of the substituents on the phosphorus donors. For example, reaction of $\text{HfCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]$ (**1**) with magnesium butadiene,⁵ $\text{Mg}\cdot\text{C}_4\text{H}_6\cdot 2\text{THF}$, generates the orange, formally hafnium(II) 1,3-butadiene complexes⁶ $\text{HfCl}(\eta^4\text{-C}_4\text{H}_6)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]$ (**R = Me, 2a; R = *i*-Pr, 2b**). The remaining chloride can be substituted by reaction with allyllithiums or Grignard reagents. Of particular interest is the reaction with allylmagnesium chloride. With $\text{HfCl}(\eta^4\text{-C}_4\text{H}_6)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]$ (**2a**), the less sterically crowded complex, the allyl derivative $\text{Hf}(\eta^3\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_6)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]$ (**3a**), can be spectroscopically characterized. Over a period of 5–6 days in solution, however, **3a** decomposes to a purple material, **4a**, which has the same molecular formulation as **3a** but completely different solution spectroscopic properties (vide infra). The reaction of allylmagnesium chloride with the more bulky derivative $\text{HfCl}(\eta^4\text{-C}_4\text{H}_6)[\text{N}(\text{SiMe}_2\text{CH}_2\text{P-}i\text{-Pr}_2)_2]$ (**2b**) gives the analogous ultimate purple product **4b** after *only 1 h*; the corresponding allyl intermediate **3b** is detectable

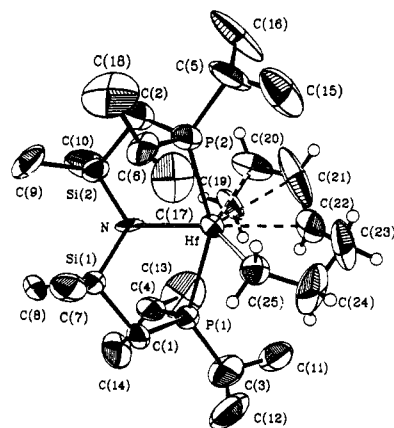
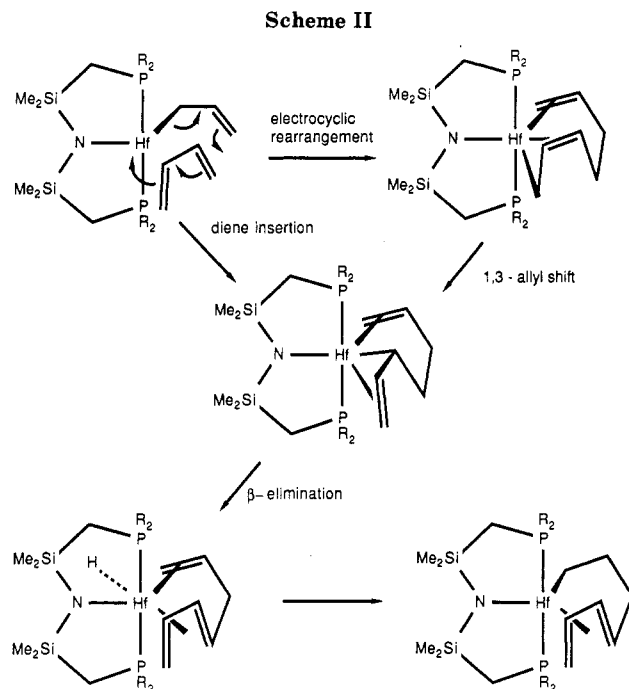


Figure 1. The molecular structure of **4b**. Selected distances (Å): Hf–P1, 2.767 (6); Hf–P2, 2.812 (6); Hf–N, 2.129 (13); Hf–B (B is the diene centroid), 2.10 (2); Hf–C19, 2.32 (2); Hf–C20, 2.36 (2); Hf–C21, 2.56 (3); Hf–C22, 2.58 (3); Hf–C25, 2.22 (3); C19–C20, 1.43 (3); C20–C21, 1.45 (5); C21–C22, 1.36 (5). Selected angles (deg): P1–Hf–P2, 150.3 (2); N–Hf–B (B is the diene centroid), 140.3 (6); C25–Hf–B, 103.4 (8); N–Hf–C25, 115.9 (8); C19–C20–C21, 120 (3); C20–C21–C22, 118 (4); C21–C22–C23, 122 (4); C22–C23–C24, 107 (2); C23–C24–C25, 110 (3).



and its conversion to **4b** can be followed spectroscopically. This is summarized in Scheme I.

The identity of the ultimate product in these reactions was established by a combination of single-crystal X-ray analysis and NMR spectroscopy. The solid-state structure⁷ of the isopropyl derivative $\text{Hf}(\eta^5\text{-C}_7\text{H}_{11})[\text{N}(\text{SiMe}_2\text{CH}_2\text{P-}i\text{-Pr}_2)_2]$ (**4b**) is shown in Figure 1. Not only have the allyl and the butadiene ligands coupled to generate a C_7H_{11} fragment, but there has also been a proton transfer from the diene unit to the allyl moiety. The solution data, in particular, the 2D ^1H – ^{13}C heterocorrelation spectrum confirms that the solid-state structure is maintained in solution. Also of interest is the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of both **4a** and **4b** which show an AX pattern (doublet of doublets, $^2J_{\text{P-P}} = 65\text{--}76$ Hz) due to the inequivalent, static phosphorus donors. The observable intermediate allyl-butadiene **3a** displays ^1H NMR resonance completely in

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(7) Crystals of **4b** are tetragonal with $a = b = 10.2288$ (5) Å, $c = 30.247$ (2) Å, $Z = 4$, and space group $P4_1$. The structure was solved by Patterson and Fourier methods and was refined by full-matrix least-squares procedures to $R = 0.052$ and $R_w = 0.046$ for 1809 independent absorption-corrected reflections with $I \geq \sigma(I)$ collected at 22 °C with Cu K α radiation on an Enraf-Nonius CAD4-F diffractometer. Hydrogen atoms were fixed in idealized positions. Refinement of the mirror-image structures in $P4_1$ resulted in slightly higher residuals.

accord with a rotating η^4 -butadiene ligand⁶ and an AX₄ pattern for the fluxional allyl unit.

Possible mechanisms to account for the formation of the observed product are shown in Scheme II. The intermediate allyl-butadiene **3** can undergo a formal electrocyclic rearrangement to generate an olefin allylic C₇ fragment; a 1,3-shift of the hafnium to the more substituted end of the allylic moiety allows for a β -elimination and subsequent hydride addition across the terminal olefin functionality to generate the observed species. Another plausible route is the direct insertion of one end of the butadiene ligand into the hafnium-carbon bond of the allyl moiety followed by β -elimination and hydride addition. The fact that the intermediate allyl-butadiene complex **3b** with the more hindered isopropyl substituents is only transiently observed suggests that the acceleration in product formation is due to relief of steric strain in the intermediate by coupling of the two hydrocarbon units.

This coupling of an allyl unit with a 1,3-butadiene fragment appears to be unique.⁸ The analogous cyclopentadienylzirconium complex (η^5 -C₅H₅)Zr(allyl)(butadiene) is apparently stable and not subject to this coupling reaction.⁹ Interestingly, the use of the bulkier pentamethylcyclopentadienyl ancillary ligand also allows for the isolation of similar complexes of the formula (η^5 -C₅Me₅)-M(1-Me-allyl)(butadiene) (M = Zr and Hf), with no reported¹⁰ evidence for carbon-carbon bond formation. These observations clearly show that the choice of the ancillary ligands is crucial for observing this reaction sequence; in addition, fine-tuning the rate of this coupling/rearrangement is also possible by modifying the steric demands of the amido-phosphine donors.

Further investigations of this unusual coupling/rearrangement reaction are underway. We are particularly interested in the diastereoselectivity of the transformation when the reaction involves substituted allyl and diene ligands.

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Registry No. **1a**, 94481-25-1; **1b**, 113773-38-9; **2a**, 113686-58-1; **2b**, 113686-59-2; **3a**, 113686-60-5; **3b**, 113725-86-3; **4a**, 113703-95-0; **4b**, 113703-96-1; Mg·C₄H₆·2THF, 60300-64-3.

Supplementary Material Available: Preparative experimental details, microanalytical, ¹H, ¹³C, and ³¹P NMR data for all new compounds, stereoview of **4b**, and tables of final positional and isotropic thermal parameters, calculated hydrogen coordinates and isotropic thermal parameters, final anisotropic thermal parameters, bond lengths, bond angles, and intraannular torsion angles (15 pages); a listing of measured and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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A New Route to 1,4-Disilabenzenes and 1,4-Disilabarrelenes

Akira Sekiguchi,¹ Gregory R. Gillette, and Robert West*

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

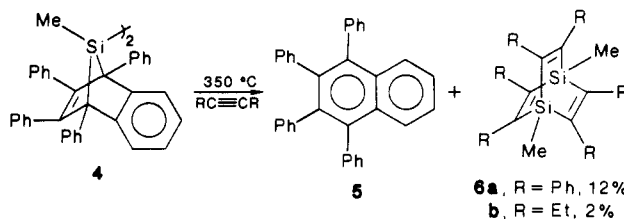
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Summary: Heating bi(7-silanorboranadien-7-yl) **4** with diphenylacetylene at 350 °C produces 1,4-disilabarrelene **6a**. The X-ray crystal structure of **6a** is reported. Thermolysis of **4** in the presence of 3-hexyne also produces small amounts of the corresponding 1,4-disilabarrelene. Mechanisms for the formation of these products are proposed; the probable immediate precursor is a 1,4-disilabenzene.

Earlier papers from these laboratories^{2,3} have described the isolation of trapped products believed to arise from hexamethyl-1,4-disilabenzene,⁴ including several 1,4-disilabarrelenes. Photolysis or thermolysis of the 9,10-bridged anthracene compound **1** or thermolysis of the *cis*-1,4-disilacyclohexadiene **2** in the presence of acetylenes led to disilabarrelenes **3a-c** (Scheme I).

We now report synthesis of disilabarrelenes by another route, starting from the bi(7-silanorborandien-7-yl) compound **4** previously described as a synthon for dimethyldisilyne, MeSi≡SiMe.⁵ Thermolysis of **4** (1.82 mmol) with diphenylacetylene (18.4 mmol) and ca. 1 g of benzene in a sealed tube at 350 °C for 2 h gave a mixture that was chromatographed on silica gel (hexane/benzene, 3:1), affording 1,2,3,4-tetraphenylnaphthalene (**5**) (1.21 g, 77%) and disilabarrelene **6a** (136 mg, 12%) as the sole silicon-containing product.⁶ Similar thermolysis of **4** with 3-hexyne also led to the formation of the corresponding disilabarrelene **6b** (ca. 2%) along with **5**.⁷ The structure of **6a**, determined by X-ray crystallography, is shown in Figure 1.⁸



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(6) **6a**: mp > 300 °C; ¹H NMR (CDCl₃, 200 MHz) δ 0.13 (s, 6 H, SiMe), 6.78-6.95 (m) and 6.95-7.21 (m) (total of 30 aromatic protons in the ratio 2:3); ¹³C NMR (CDCl₃) δ -8.36 (SiMe), 125.35 (aromatic C), 127.79 (aromatic C), 127.82 (aromatic C), 141.90 (aromatic C) and 160.05 (olefinic C); ²⁹Si NMR (CDCl₃) 16.9 ppm; high resolution mass, *m/e* 620.2335, calcd for C₄₄H₃₆Si₂, *m/e* 620.2355.

(7) Compound **6b** was isolated by preparative GLC: mp 71-72 °C; NMR (CDCl₃) δ 0.59 (s, 6 H, SiMe), 0.86 (t, 18 H, CCH₃) and 2.29 (q, 11 H, C=CCH₂); high-resolution mass, *m/e* 332.2365, calcd for C₂₀H₃₆Si₂, *m/e* 332.2355.