

Table V. Bond Lengths (Å) and Bond Angles (deg) for $\text{CpFeI}(\text{CO})\{\text{CMe}_2(\text{CH}_2)_2\text{O}\}$ (7)

(a) Bond Lengths			
I(1)-Fe(1)	2.608 (12)	Fe(1)-C(1)	1.729 (35)
Fe(1)-C(2)	2.058 (33)	Fe(1)-C(3)	2.092 (33)
Fe(1)-C(4)	2.128 (35)	Fe(1)-C(5)	2.173 (36)
Fe(1)-C(6)	2.084 (34)	Fe(1)-C(7)	1.903 (33)
O(1)-C(1)	1.138 (42)	O(2)-C(7)	1.349 (35)
O(2)-C(10)	1.509 (37)	C(2)-C(3)	1.354 (46)
C(2)-C(6)	1.355 (42)	C(3)-C(4)	1.429 (46)
C(4)-C(5)	1.435 (45)	C(5)-C(6)	1.428 (45)
C(7)-C(8)	1.483 (49)	C(8)-C(9)	1.584 (47)
C(8)-C(11)	1.506 (42)	C(8)-C(12)	1.472 (42)
C(9)-C(10)	1.480 (49)		
(b) Bond Angles			
I(1)-Fe(1)-C(1)	95.0 (11)	I(1)-Fe(1)-C(7)	87.4 (9)
C(1)-Fe(1)-C(7)	95.5 (15)	Fe(1)-C(1)-O(1)	175.0 (32)
C(3)-C(2)-C(6)	113.6 (30)	C(2)-C(3)-C(4)	106.2 (28)
C(3)-C(4)-C(5)	106.9 (28)	C(4)-C(5)-C(6)	106.9 (27)
C(2)-C(6)-C(5)	106.1 (27)	C(7)-O(2)-C(10)	114.1 (23)
Fe(1)-C(7)-O(2)	113.9 (23)	Fe(1)-C(7)-C(8)	136.2 (22)
O(2)-C(7)-C(8)	109.7 (25)	C(7)-C(8)-C(9)	100.2 (25)
C(7)-C(8)-C(11)	105.9 (26)	C(9)-C(8)-C(11)	109.4 (25)
C(7)-C(8)-C(12)	115.5 (26)	C(9)-C(8)-C(12)	111.1 (27)
C(11)-C(8)-C(12)	113.8 (27)	C(8)-C(9)-C(10)	107.2 (29)
O(2)-C(10)-C(9)	99.8 (24)		

and corrected for Lorentz and polarization effects. Two check reflections monitored once every 100 measurements showed no evidence of decay. No absorption correction was necessary because of the small size of the crystal. The structure was solved by Patterson and difference Fourier methods and refined by cascade blocked-diagonal least squares (254 refined parameters) with use of the SHELXTL suite of programs on a NOVA 3 computer. The weighting scheme was $w = [\sigma^2(|F|) + gF^2]^{-1}$ with $g = 0.0011$. Hydrogen atoms were inserted at calculated positions and con-

strained to ride on their neighboring heavy atoms. Their thermal parameters were fixed at 1.2 times those for the neighboring heavy atoms. The structures are illustrated in Figure 1; details are given in Tables II and III and in the supplementary material (hydrogen atom positional parameters, anisotropic thermal vibrational parameters with esd's, observed structure amplitudes and calculated structure factors).

$\text{CpFeI}(\text{CO})\{\text{CMe}_2(\text{CH}_2)_2\text{O}\}$ (7). The 916 observed reflections were corrected for Lorentz effects, for polarization effects, and for absorption on the basis of azimuthal scans. The structure was solved by standard Patterson and Fourier techniques and refined by blocked-cascade least-squares methods to a final $R = 0.1241$, with allowance for the anisotropic thermal vibration of iron and iodine only. Complex scattering factors were taken from the program package SHELXTL (as implemented on the NOVA 3 computer) used for the refinement. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters linked to those of the supporting atom. The weighting scheme was $w = [\sigma^2(|F|) + gF^2]^{-1}$ with $g = 0.0005$. The structure is illustrated in Figure 8; details are given in Tables IV and V and in the supplementary material (hydrogen atom positional parameters, anisotropic thermal vibrational parameters with esd's, observed structure amplitudes and calculated structure factors).

Acknowledgment. We are pleased to acknowledge the SERC and the Royal Society for financial support. The Royal Society is also acknowledged for a 1983 Research Fellowship (to C.E.H.), and the SERC is also acknowledged for a Research Studentship (to C.R.). We thank the reviewers for perceptive comments.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for 4 and 7 (3 pages); tables of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Notes

Carbon-Carbon Bond Formation by Coupling of Two Phenylethynyl Ligands in an Organolanthanide System

William J. Evans,* Roy A. Keyer, and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, Irvine, California 92717

Received March 8, 1990

Summary: $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhC}_4\text{Ph})$, a crystallographically characterized complex that previously has been isolated from the reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ with $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$, can be obtained from organosamarium precursors derived from $\text{PhC}\equiv\text{CH}$. $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhC}_4\text{Ph})$ is formed from the reaction of $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-H})]_2$ with $\text{PhC}\equiv\text{CH}$, from the thermolysis of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}\equiv\text{CPh})(\text{THF})$ at 80–145 °C, from the reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm}$ with $\text{PhC}\equiv\text{CH}$, and from the reaction of $(\text{C}_5\text{Me}_5)_2\text{Sm}[\text{CH}(\text{SiMe}_3)_2]$ with $\text{PhC}\equiv\text{CH}$, a reaction that has been reported to form $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-C}\equiv\text{CPh})]_2$.

Ligand-coupling reactions constitute one of the important classes of metal-mediated transformations in organometallic chemistry.¹ For example, the formation of

a new bond between two reductively eliminated ligands plays an important role in many metal-based catalytic cycles. Comparable processes are not common in organolanthanide chemistry.²⁻⁶ For monometallic complexes, simple reductive elimination is not possible since none of

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.

(2) Forsberg, J. H.; Moeller, T. In *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Moeller, T., Krueker, U., Schleitzer-Rust, E., Eds.; Springer-Verlag: Berlin, 1983; Part D6, pp 137-282.

(3) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 21.

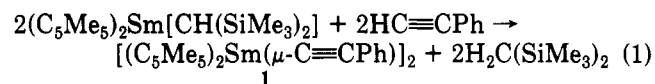
(4) Schumann, H.; Genthe, W. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, 1985; Vol. 7, Chapter 53, and references therein.

(5) Evans, W. J. *Adv. Organomet. Chem.* 1985, 24, 131-177.

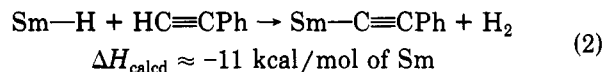
(6) Evans, W. J. *Polyhedron* 1987, 6, 803-835.

the lanthanides have accessible two-electron-redox couples.⁷ For bimetallic complexes of the type $[(C_5R_5)_2Ln](\mu-R')(\mu-R'')[Ln(C_5R_5)_2]$ ($R = H, Me; R', R'' = \text{alkyl, aryl, hydride, halide, pseudohalide ligands}$) in which a two-electron process could occur, $R-R'$ coupling has not been observed. Such coupling may be electrostatically inhibited because both R and R' may carry a partial negative charge when attached to the electropositive lanthanide. We now report the first example of an organolanthanide reaction in which a carbon-carbon bond is formed by coupling two ligands in the system, in this case, two phenylethyne ligands.

The genesis of this project was the report of the synthesis of $[(C_5Me_5)_2Sm(\mu-C\equiv CPh)]_2$ (**1**; eq 1) as part of a thermochemical study⁸ of $(C_5Me_5)_2Sm$ complexes.⁶ The



heat of iodinolysis of **1** was used to calculate the bond disruption enthalpy for the $(C_5Me_5)_2Sm-C\equiv CPh$ bond, and it was noted "that the bridging nature of the μ -alkynyl bonding in **1** (i.e., **1**) has not greatly affected the metal-alkynyl bond strength".⁸ The thermochemical data were used to predict that $[(C_5Me_5)_2Sm(\mu-H)]_2$ ^{9,10} would react with $PhC\equiv CH$ to form **1** according to eq 2.



Although eqs 1 and 2 are reasonable on the basis of prior organolanthanide chemistry,^{3-6,11-13} the dimeric, bridged structure proposed for **1** was unusual in light of the close-packed-tetrahedral arrangement of four C_5Me_5 rings found in $[(C_5Me_5)_2Sm(\mu-H)]_2$ (**2**).^{9,14} Replacement of the hydride ligands in **2** with phenylalkynyl bridges as proposed in **1** would generate a very sterically crowded molecule. Previously, substitution of chloride for hydride in **2** was found¹⁵ to form the trimer $[(C_5Me_5)_2Sm(\mu-Cl)]_3$ instead of $[(C_5Me_5)_2Sm(\mu-Cl)]_2$, the analogue of **2**. An alternative structure for **1** seemed possible since no $\nu_{C\equiv C}$ stretch was observed in the infrared spectrum, in contrast to the spectra for the crystallographically characterized, sterically less crowded $[(C_5H_5)_2Er(\mu-C\equiv CMe_3)]_2$ ¹² ($\nu_{C\equiv C} = 2050 \text{ cm}^{-1}$) and yellow $[(MeC_5H_4)_2Sm(\mu-C\equiv CMe_3)]_2$ ¹⁶ ($\nu_{C\equiv C} = 2035 \text{ cm}^{-1}$). An alternative structure for the red complex **1** was the red, crystallographically characterized complex $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC_4Ph)$ (**3**), obtained from $(C_5Me_5)_2Sm(THF)_2$ and $PhC\equiv CC\equiv CPh$.¹⁷ Complex **3** has both the exact elemental composition and molecular weight as **1**, it similarly lacks the $\nu_{C\equiv C}$ stretch in the IR spectrum, and its ¹H NMR spectrum, although reported

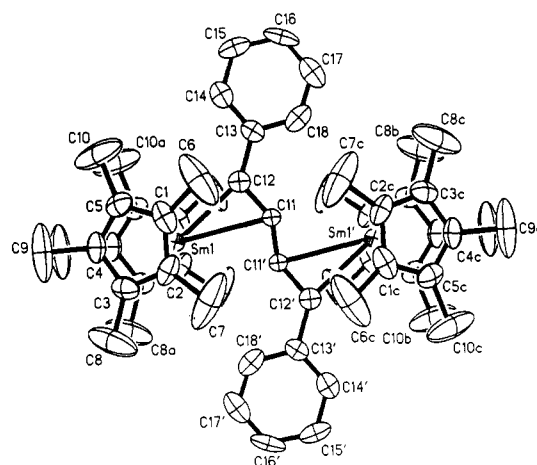
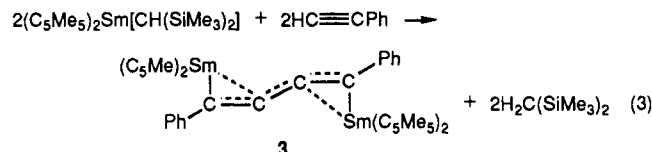


Figure 1. ORTEP diagram of $[(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC_4Ph)\cdot 2C_6H_6$ with probability ellipsoids at the 30% level. Important bond distances and angles are as follows: C(11)-C(12), 1.363 (17) Å; C(11)-C(11'), 1.298 (19) Å; C(12)-C(11)-C(11'), 146.9 (10)°; Sm(1)-C(12), 2.505 (9) Å; Sm(1)-C(11), 2.807 (8) Å; Sm(1)-C(11'), 2.963 (9) Å; Sm-C(C_5Me_5) average, 2.71 (1) Å.

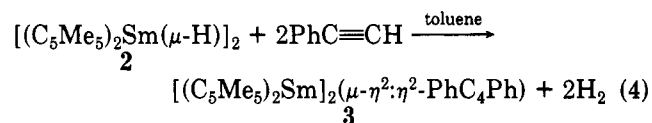
in a different solvent, is similar. To determine if the product of reactions 1 and 2 was **3**, not **1**, NMR and crystallographic studies were carried out as described below and the formation of **3** from a fully characterized (phenylethyne)samarium complex was investigated.

Results and Discussion

The ¹H NMR spectrum of **3** in toluene-*d*₈ corresponds exactly to that reported for **1**. Reaction 1 was repeated according to the literature method⁸ to obtain the ¹³C NMR spectrum of **1**, which also corresponded exactly to that of **3**. Hence, eq 1 should be written as shown in eq 3. The



reaction of $[(C_5Me_5)_2Sm(\mu-H)]_2$ with $HC\equiv CPh$ (i.e., eq 2) was examined, and the product, which forms in quantitative yield upon mixing, was identified as **3** and not **1** by NMR spectroscopy and by single crystal X-ray diffraction (eq 4).



Complex **3** was also prepared from yellow-orange, crystallographically characterized $(C_5Me_5)_2Sm(C\equiv CPh)(THF)$ (**4**).¹⁸ Over 3 days, **3** is formed in 40% yield from **4** at 120 °C in benzene in a sealed tube (eq 5). This $2(C_5Me_5)_2Sm(C\equiv CPh)(THF) \rightarrow [(C_5Me_5)_2Sm]_2(\mu-\eta^2:\eta^2-PhC_4Ph) + 2THF$ (**5**)

reaction product was also crystallographically identified (Figure 1). Reaction 5 is not an equilibrium, since pure samples of **3** do not convert back to **4** in THF at 120 °C, although they do transform to other products. At 145 °C in toluene, **4** converts to **3** quantitatively in 14 h. Complex

(18) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. *Organometallics* 1990, 9, 2124-2130.

(7) Morss, L. R. *Chem. Rev.* 1976, 76, 827-841.

(8) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* 1989, 111, 7844-7853.

(9) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* 1983, 105, 1401-1403.

(10) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8091-8103.

(11) Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.* 1980, 202, C6-C8.

(12) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* 1981, 20, 4115-4119.

(13) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* 1984, 106, 1291-1300.

(14) Ortiz, J. V.; Hoffmann, R. *Inorg. Chem.* 1985, 24, 2095-2104.

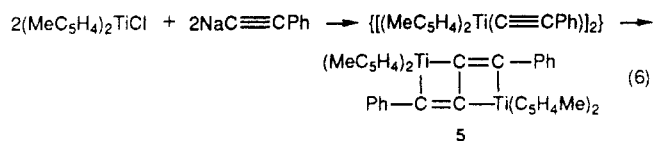
(15) Evans, W. J.; Drummond, D. K.; Grate, J. W.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* 1987, 109, 3928-3936.

(16) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* 1983, 2, 709-714.

(17) Evans, W. J.; Keyser, R. A.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* 1987, 837-838.

3 can also be prepared from the divalent $(C_5Me_5)_2Sm^{19}$ and $PhC\equiv CH$.

Equations 3–5 represent the first examples of lanthanide-mediated coupling of alkynide ligands. Oxidative coupling of terminal alkynes to diynes with use of cuprous salts and an oxidant is well-known, and numerous variations have been reported.^{20,21} The oxidative coupling most closely related to eqs 3–5 is shown in eq 6.^{21,22} Equations



3–5 differ from eq 6 in that **3** formally contains a butadiyne dianion and trivalent metals, whereas **5** formally contains a butadiyne tertaanion and tetravalent titanium. In the titanium study,²¹ it was stated that the reaction of “ $NaC\equiv CPh$ and Cp_2TiCl might be envisaged to occur with reduction to Cp_2Ti^{II} along with coupling of $PhC\equiv C^{\bullet}$ and reaction of the coupled product with Cp_2Ti^{III} ”. The reaction of $(MeC_5H_4)_2Ti$ with 1,4-diphenylbutadiyne was independently shown to form **5**. Spectral evidence for a Ti(III) alkynide intermediate in reaction 6 was obtained,²³ and rearrangement of electrons in this intermediate to form **5** involving “internal reduction and oxidation” was discussed.²¹ The mechanism of the samarium reaction, which accomplishes an equivalent coupling, has not yet been determined.

These results demonstrate that, under the proper conditions, C–C bond formation can be achieved by coupling organic ligands in organolanthanide systems. These results also illustrate the importance of considering steric effects in the f-element area.⁶ Reactions that are thermodynamically reasonable may not yield the expected products²⁴ due to steric constraints, and these same steric factors may allow unexpected reactions to occur. The mechanism of this phenylethynyl coupling reaction and the possibility that the reaction is fostered by the steric environment provided by the four C_5Me_5 rings of two $(C_5Me_5)_2Sm$ groups²⁵ are under study.

Experimental Section

The complexes described below were handled under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab)

(19) (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272. (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285–1291.

(20) (a) Glaser, C. *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422. (b) Cadiot, P.; Chodkiewicz, W. In *The Chemistry of Acetylenes*; Viehe, G. H., Ed.; Marcel Dekker: New York, 1969; Chapter 9. (c) Shostakovski, M. F.; Bogdanova, A. V. In *The Chemistry of Diacetylenes*; Wiley: New York, 1974. (d) Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225–328. (e) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247–254.

(21) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376–1382.

(22) Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87–93.

(23) See also: Erker, G.; Fromberg, W.; Mynott, R.; Gabor, B.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463–465. Wood, G. L.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1989**, *28*, 382–384.

(24) Although $[(C_5Me_5)_2Sm(\mu-C\equiv CPh)]_2$ was not observed in these reactions, the presence of $(C_5Me_5)_2Sm(C\equiv CPh)$ units in some form is suggested by the fact that when reaction 4 is run at $-78^\circ C$ and the system is quenched with THF, some $(C_5Me_5)_2Sm(C\equiv CPh)(THF)$ ¹⁸ is formed along with **3**. Asymmetric bridged alkynide complexes of empirical composition $(C_5Me_5)_2Sm(C\equiv CPh)$ may be possible. Cf. $(C_5Me_5)_2ClY(\mu-Cl)Y(C_5Me_5)_2$ (Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554–559) and ref 15.

(25) (a) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219–223. (b) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314–2324.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-PhC\equiv CPh) \cdot 2C_6H_6$ (A) and $[(C_5Me_5)_2Sm]_2(\mu-\eta^2-\eta^2-PhC\equiv CPh) \cdot 2C_6H_6$ (B)

	A	B
formula	$C_{70}H_{96}Sm_2$	$C_{68}H_{92}Sm_2$
fw	1228.1	1200.0
temp, K	173	296
cryst syst	monoclinic	monoclinic
space group	$P2_1/m$	$C2/m$
a, Å	15.0826 (14)	15.3735 (16)
b, Å	13.9339 (12)	13.9572 (14)
c, Å	15.5179 (12)	14.9786 (16)
β , deg	114.795 (7)	112.720
V, Å ³	2960.6 (4)	2964.6 (5)
Z	2	2
D_{calc} , Mg/m ³	1.378	1.344
diffractometer	Nicolet P3 (R3m/V system)	Syntex P2 ₁ (R3m/V system)
radiation	Mo K α ($\lambda =$ 0.710730 Å)	Mo K α ($\lambda =$ 0.710730 Å)
monochromator	highly oriented graphite	highly oriented graphite
data collected	+h,+k, \pm l	+h,+k, \pm l
scan type	θ -2 θ	θ -2 θ
scan width, deg	1.2 + K α separation	1.2 + K α separation
scan speed, deg/min	3.0 (in ω)	2.0 (in ω)
2 θ range, deg	4.0–50.0	4.0–50.0
μ (Mo K α), mm ⁻¹	2.01	2.01
abs cor	semiempirical (ψ -scan method)	semiempirical (ψ -scan method)
no. of rflns collected	5709	2866
no. of rflns with $ F_o > 0$	5148	2596
no. of variables	361	172
R_F , R_{wF} , %	5.3, 6.5	5.1, 6.4
goodness of fit	1.54	1.08

techniques. Solvents were purified as previously described.²⁶ $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$,⁸ $[(C_5Me_5)_2Sm(\mu-H)]_2$,⁹ $(C_5Me_5)_2Sm(C\equiv CPh)(THF)$,¹⁸ and $(C_5Me_5)_2Sm^{19}$ were prepared according to the literature methods. $(C_5Me_5)_2Sm$ must be handled in an ether-free glovebox. $PhC\equiv CH$ was dried over 4A molecular sieves and vacuum-transferred before use. Physical measurements were obtained as previously described.^{26,27} The reaction of $(C_5Me_5)_2Sm[CH(SiMe_3)_2]$ with $HC\equiv CPh$ was conducted as described in the literature.⁸

Synthesis of 3 from $[(C_5Me_5)_2Sm(\mu-H)]_2$. In an ether-free glovebox, $PhC\equiv CH$ (13 μ L, 0.12 mmol) was syringed into an orange toluene solution (5 mL) of $[(C_5Me_5)_2Sm(\mu-H)]_2$ (50 mg, 0.059 mmol). The stirred solution turned red within 5 min. After 10 min, the solvent was removed with a rotary evaporator to leave the red **3** in quantitative yield as shown by NMR spectroscopy (C_6D_6). Crystals for X-ray analysis were grown by the slow evaporation of benzene at room temperature.

Synthesis of 3 from $(C_5Me_5)_2Sm(C\equiv CPh)(THF)$. In the glovebox, a yellow toluene- d_8 solution of $(C_5Me_5)_2Sm(C\equiv CPh)(THF)$ (17.6 mM) was placed in an NMR tube. The tube was cooled with a liquid-nitrogen bath, degassed, and sealed. After 14 h at $145^\circ C$, **3** was formed in quantitative yield (by ¹H NMR spectroscopy). Formation of **3** has been observed under similar conditions at temperature as low as $80^\circ C$, although the reaction is much slower and the yield is not quantitative. Crystals suitable for X-ray crystallography were isolated from an NMR sample of $(C_5Me_5)_2Sm(C\equiv CPh)(THF)$ in benzene that was heated to $120^\circ C$ and then cooled.

Synthesis of 3 from $(C_5Me_5)_2Sm$. In an ether-free glovebox, $PhC\equiv CH$ (13 μ L, 0.12 mmol) was syringed into a green toluene solution (5 mL) of $(C_5Me_5)_2Sm$ (50 mg, 0.12 mmol). Gas evolution was observed, and the solution turned red within 5 min. The reaction mixture was stirred for 10 min, and the solvent was

(26) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671–1679.

(27) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.

removed by rotary evaporation. The yield of **3** was shown to be quantitative by ^1H NMR spectroscopy in C_6D_6 .

Crystallographic Data for the Product of the $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-H})_2]/\text{PhC}\equiv\text{CH}$ Reaction. A dark red crystal of approximate dimensions $0.23 \times 0.27 \times 0.30$ mm was immersed in Paratone-N (lube oil additive), mounted on a glass fiber, and transferred to the Nicolet P3 diffractometer, which is equipped with a modified LT-2 apparatus. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (173 K) intensity data were carried out with use of standard techniques similar to those of Churchill.²⁸

All 5709 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflections with $I(\text{net}) < 0$ were assigned the value $|F_o| = 0$. Careful examination of a preliminary data set revealed the systematic extinction $0k0$ for $k = 2n + 1$; the diffraction symmetry was $2/m$. The two possible monoclinic space groups are the noncentrosymmetric $P2_1$ (C_2^2 , No. 4) or the centrosymmetric $P2_1/m$ (C_{2h}^2 , No. 11). The latter was chosen and subsequently shown to be correct by successful solution and refinement of the structure.

All crystallographic calculations were carried out with use of either a locally modified version of the UCLA Crystallographic Computing Package²⁹ or the SHELXTL PLUS program set.³⁰ The analytical scattering factors for neutral atoms were used throughout the analysis;^{31a} both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion^{31b} were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0010(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atom contributions were included by using a riding model with $d(\text{C-H}) = 0.96 \text{ \AA}$ and $U(\text{iso}) = 0.08 \text{ \AA}^2$. Refinement of positional and anisotropic thermal parameters led to convergence with $R_F = 5.3\%$, $R_{wF} = 6.5\%$, and $\text{GOF} = 1.54$ for 361 variables refined against all 5148 unique data ($R_F = 4.1\%$ and $R_{wF} = 5.9\%$ for those 4296 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference-Fourier map was devoid of significant features; $\rho(\text{max}) = 1.38 \text{ e \AA}^{-3}$.

The molecule lies on the mirror plane at $y = 3/4$ and contains two toluene solvent molecules in the lattice. At the onset of this study, it was expected that the complex would be crystallographically identical with the previously studied $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhC}_4\text{Ph})\cdot 2\text{C}_6\text{H}_5\text{Me}$.¹⁷ However, this is not the case. The latter complex crystallizes in space group $C2/m$ with the molecule sitting on a mirror plane ($y = 0$) containing the samarium atom and the carbon atoms of the PhC_4Ph unit.¹⁷ The 2-fold rotation axis is located at the centroid of the $\text{C}(2)\text{-C}(2')$ bond. The toluene solvent molecule is positioned such that the plane of the arene ring is perpendicular to the mirror plane with the methyl carbon lying on the mirror.

In the crystal studied here, the samarium atoms and carbon atoms of the PhC_4Ph unit also lie on the mirror plane ($y = 3/4$), but the toluene solvent molecules cannot be related by a 2-fold rotation axis. One toluene molecule (defined by $\text{C}(37)\text{-C}(41)$) lies

perpendicular to the mirror plane (as above¹⁷) with the methyl carbon on the mirror. However, the toluene defined by $\text{C}(42)\text{-C}(45)$ is situated such that no atoms lie on the mirror plane; therefore, the methyl carbon, $\text{C}(45)$, is disordered. The methyl carbon and corresponding hydrogen atoms were assigned site occupancy factors of 0.5. No attempt was made to account for the "missing" hydrogen atom resulting from the disordered methyl carbon. Were it not for the orientation of this solvent molecule, one could expect both structures to be crystallographically identical.

The centrosymmetric space group $P2_1/m$ requires that the pentamethylcyclopentadienyl ligands maintain an eclipsed rather than staggered orientation. It is evident from the ORTEP diagram (supplementary material, part 2) and the thermal parameters that there is a high degree of librational motion associated with these ligands. Difference-Fourier syntheses based on an isotropic model failed to reveal significant electron density that could be assigned to a disordered model. Refinement in the noncentrosymmetric space group $P2_1$, which does not contain a mirror plane, also resulted in a model with eclipsed rings. It was, therefore, decided that the model is best described as centrosymmetric and ordered, albeit with a propensity toward having disordered pentamethylcyclopentadienyl ligands.

Crystallographic Data for the Product of the Thermolysis of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{C}\equiv\text{CPh})(\text{THF})$. A red crystal of approximate dimensions $0.12 \times 0.23 \times 0.27$ mm was inserted into a thin-walled glass capillary under an inert (N_2) atmosphere and mounted on the Syntex P2₁ diffractometer. Subsequent setup operations, collection of room-temperature (296 K) intensity data, data reduction, and refinement of the crystal structure were carried out as described above.

Careful examination of a preliminary data set revealed the systematic extinction hkl for $h + k = 2n + 1$. The diffraction symmetry was $2/m$. Three monoclinic space groups are possible: $C2$, Cm , and $C2/m$. With the expectation that this complex is identical with $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhC}_4\text{Ph})\cdot 2\text{C}_6\text{H}_5\text{Me}$ ¹⁷ except that benzene rather than toluene is incorporated into the lattice, the last centrosymmetric space group $C2/m$ (C_{2h}^2 , No. 12) was chosen and subsequently shown to be correct.

The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.002(|F_o|)^2$. Refinement of positional and anisotropic thermal parameters led to convergence with $R_F = 5.1\%$, $R_{wF} = 6.4\%$, and $\text{GOF} = 1.08$ for 172 variables refined against all 2596 unique data ($R_F = 3.8\%$ and $R_{wF} = 5.6\%$ for those 2173 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference-Fourier map yielded $\rho(\text{max}) = 1.54 \text{ e \AA}^{-3}$.

The molecule lies on a mirror plane; $y = 0$ for samarium and the carbon atoms of the PhC_4Ph unit. The benzene solvent molecules lie about the mirror plane. However, no atoms are located directly on the mirror. Except for the difference in lattice solvent, the structure is the same as that of $[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-PhC}_4\text{Ph})\cdot 2\text{C}_6\text{H}_5\text{Me}$.¹⁷

Acknowledgment. We thank the National Science Foundation for support for this research. Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495.

Supplementary Material Available: ORTEP diagrams and tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (29 pages); tables of observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

(28) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(29) UCLA Crystallographic Computing Package; University of California: Los Angeles, CA, 1981. Strouse, C. Personal communication.

(30) Nicolet Instrument Corp., Madison, WI, 1988.

(31) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; pp 99-101; (b) *Ibid.*, pp 149-150.