promote the ring opening of coordinated thiophenes.[13] We have recently reported an unusual example of the ring-opening oligomerization of DMT by 1, which appears to be initiated by nucleophilic attack of a free molecule of DMT upon the bridging DMT ligand.[2] Studies of the ring opening of the bridging DMT ligand by other nucleophiles are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for both of the structural analyses (19 pages); tables of structure factors (36 pages). Ordering information is given on any current masthead page.

---

(12) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394. (c) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11. (d) Prins, R.; De Beer, V. H. H.; Somorjai, G. A. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 1.

(13) (a) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359. (b) Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909.

Transformation of Heteroatom-Substituted Alkynes into Substituted Vinylidene Ligands Accompanied by CO Insertion

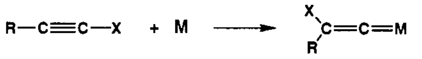
Richard D. Adams,* Gong Chen, Linfeng Chen, Michael P. Pompeo, and Jianguo Yin

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received April 25, 1991

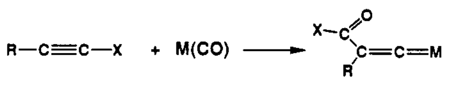
Summary: The reactions of $Mn_2(CO)_9NCMe$ (**1**) with the alkynes $MeC{\equiv}CX$ (X = OEt, NMe_2) have yielded the substituted bridging vinylidene complexes $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)C{=}O(X)]$ (**2a**, X = OEt; **2b**, X = NMe_2) in 39% and 10% yields, respectively, by a rearrangement of the alkyne accompanied by a CO insertion. Compound **2b** also adds 1 equiv of $MeC{\equiv}CNMe_2$ to form the complex $Mn_2(CO)_7[\mu\text{-}CC(Me)C(NMe_2)C(Me)C{=}O(NMe_2)]$ (**3**) in 50% yield, which contains a four-membered carbocyclic ring.

While there are many examples of the metal-assisted transformation of terminal alkynes into vinylidene ligands,[1] there are relatively few that involve the shift of a non-hydrogen heteroatomic grouping (eq 1).[2-5] We now wish to report the first examples of this transformation involving the substituents OEt and NMe_2 with R = Me in which the shift is also accompanied by a CO insertion (eq 2).



(1)

$X = PPh_2$, SMe, Cl, Br, I



(2)

X = OEt, NMe_2

From the reaction of $Mn_2(CO)_9NCMe$[6] (1; 300 mg, 0.744 mmol) with $MeC{\equiv}COEt$ (0.177 mL, 1.86 mmol) at 25 °C in 150 mL of hexane solvent for 24 h, we have isolated by TLC the new yellow compound $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)\text{-}$

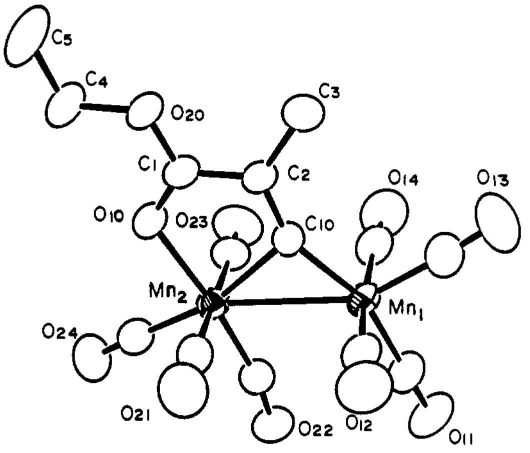
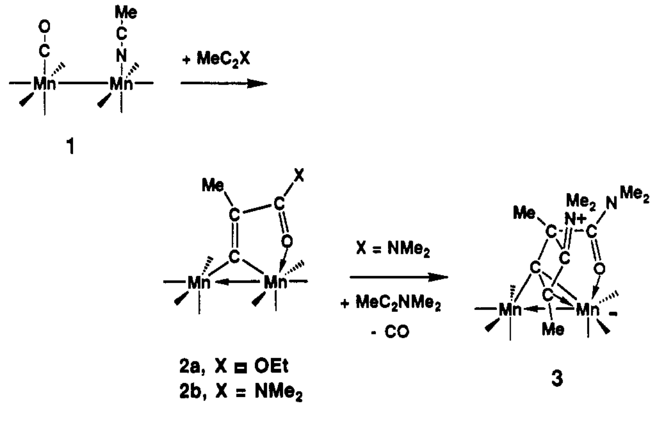


Figure 1. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)C{=}O(OEt)]$ (**2a**). Selected interatomic distances (Å) are Mn(1)-Mn(2) = 2.9147 (6), Mn(1)-C(10) = 1.874 (2), Mn(2)-C(10) = 2.125 (2), Mn(2)-O(10) = 2.068 (2), C(10)-C(2) = 1.339 (3), C(1)-C(2) = 1.440 (3), and C(1)-O(10) = 1.249 (3).

Scheme I



---

(1) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(2) Fogg, D. E.; MacLaughlin, S. A.; Kwek, K.; Cherkas, A. A.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1988**, *352*, C17.

(3) Miller, D. C.; Angelici, R. J. *Organometallics* **1991**, *10*, 79.

(4) Hund, H.-U.; Berke, H. *J. Organomet. Chem.* **1989**, *371*, 311.

(5) Horvath, I. T.; Palyi, G.; Marko, L.; Andreetti, G. *J. Chem. Soc.* **1979**, 1054.

(6) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53.

0276-7333/91/2310-2541$02.50/0

C=O(OEt)] (**2a**) in 39% yield.[7] Compound **2a** was characterized by IR, ^{1}H NMR, and X-ray diffraction analyses.[8] An ORTEP drawing of the molecular structure of **2a** is shown in Figure 1. The molecule contains two mutually bonded manganese atoms (Mn–Mn = 2.9147 (6) Å), with each containing four carbonyl ligands. The most interesting ligand is the bridging C=C(Me)C=O(OEt) grouping. Carbon C(10) bridges the metal atoms asymmetrically (Mn(1)–C(10) = 1.874 (2) Å and Mn(2)–C(10) = 2.125 (2) Å). The C(10)–C(2) distance of 1.339 (3) Å is indicative of a double bond as found in vinylidene ligands.[1] Oxygen O(10) is part of an ethyl ester grouping that is coordinated to Mn(1) (Mn(1)–O(10) = 2.068 (2) Å, ν(CO) = 1581 cm^{-1}). The ^{1}H NMR spectrum of **2a** shows resonances at δ = 4.27 (q, $J_{\text{H-H}}$ = 7.1 Hz, OCH_2), 2.25 (s, C*Me*), and 1.32 (t, $J_{\text{H-H}}$ = 7.1 Hz, CH$_2$CH_3) and is consistent with the observed structure. The composition of the vinylidene ligand shows that it is a combination of one CO grouping and one molecule of MeC$_2$OEt. The manner in which the components were combined was established by a ^{13}C labeling study. A sample of **1** enriched to approximately 45% with ^{13}CO was converted to **2a*** and then analyzed by ^{13}C and ^{1}H NMR spectroscopy. In addition to the strong resonances of the CO ligands,[9] the ^{13}C{^{1}H} NMR spectrum of **2a*** showed one strong resonance located at 184.00 ppm. On the basis of shift this could be attributed reasonably either to the metal-bonded vinylidene carbon C(10)[1] or to the ester carbon C(1). However, its assignment to the C(1) site was unambiguously established by the observation of three-bond C–H coupling to both the methylene group C(4) ($^3J_{\text{C-H}}$ = 2.75 Hz) and the methyl group C(3) ($^3J_{\text{C-H}}$ = 3.36 Hz) in the ^{1}H NMR spectrum.[10] Details of the mechanism of the formation of the vinylidene ligand have not yet been established, but a process involving an oxidative-addition-induced cleavage of the OEt group from the alkyne and a CO insertion to form a metallo carboxylate followed by a transfer of the carboxylate grouping to the methyl-substituted carbon of the alkyne fragment is expected.

The reaction of **1** with MeC$_2$NMe$_2$ was similar to that with MeC$_2$OEt. The product Mn$_2$(CO)$_8$[μ-C=C(Me)C=O(NMe$_2$)] (**2b**) was obtained in 10% yield together with the second product Mn$_2$(CO)$_7$[μ-CC(Me)C(NMe$_2$)C(Me)-C=O(NMe$_2$)] (**3**) in 46% yield from the reaction of **1** (45 mg, 0.11 mmol) with MeC≡CNMe$_2$ (26 μL, 0.25 mmol) at 40 °C in hexane solvent for 45 min. Both products have been characterized by IR, ^{1}H NMR, mass spectral, and X-ray diffraction analyses.[8,11] The structure of **2b** is analogous to that of **2a** but contains an O-coordinated amido grouping instead of the O-coordinated ester grouping.

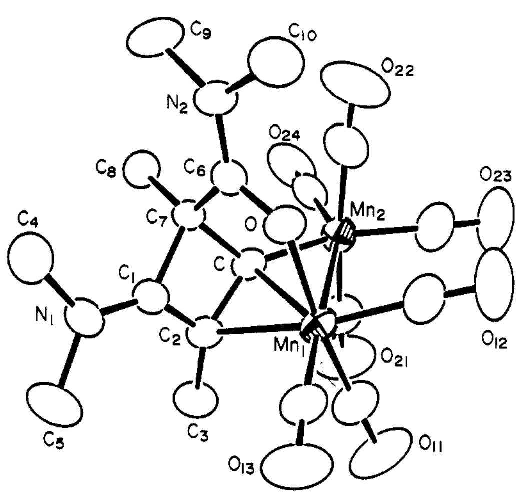


Figure 2. ORTEP diagram of Mn$_2$(CO)$_7$[μ-CC(Me)C(NMe$_2$)C(Me)C=O(NMe$_2$)] (**3**). Selected interatomic distances (Å) are Mn(1)–Mn(2) = 2.8104 (8), Mn(1)–C = 2.094 (3), Mn(2)–C = 1.941 (3), Mn(1)–O = 2.064 (2), Mn(1)–C(2) = 2.263 (3), C–C(7) = 1.590 (4), C–C(2) = 1.450 (4), C(1)–C(2) = 1.414 (4), C(1)–N(1) = 1.301 (4), C(6)–C(7) = 1.518 (4), C(6)–O = 1.257 (4), and C(6)–N(2) = 1.325 (4).

An ORTEP drawing of **3** is shown in Figure 2. This molecule also contains two mutually bonded manganese atoms (Mn–Mn = 2.8104 (8) Å). Mn(1) has three carbonyl ligands while Mn(2) has four. This molecule contains a CC(Me)C(NMe$_2$)CMeC=O(NMe$_2$) ligand with the carbon C bridging the metal atoms. A four-membered carbocyclic ring (atoms C, C(7), C(1), and C(2)) contains a dimethylamino substituent on C(1) and an amido group on C(7) that has its oxygen atom coordinated to Mn(1) (ν(CO) = 1583 cm^{-1}). Compound **3** can be obtained directly from **2b** in 50% yield by reaction with MeC≡CNMe$_2$ at 35 °C, thus confirming that **2b** is an intermediate in its formation. This unusual reaction evidently involves the formation of a four-membered carbocyclic ring by the addition of the ynamine C–C triple bond across the vinylidene C(10)–C(2) double bond in **2b**. It is known that ynamines will undergo (2 + 2) cycloaddition reactions with electrophilic olefins.[12] These results are summarized in Scheme I. The cycloaddition should result in the formation of a cyclobutenylidene ligand with a double bond between the atoms C(1) and C(2). Although the C(1)–C(2) distance (1.414 (4) Å) is consistent with this formulation, there is also a strong donation of electron density from C(2) to Mn(1) (Mn(1)–C(2) = 2.263 (3) Å). This interaction permits the metal atoms to achieve 18-electron configurations but results in the formation of a formal negative charge on Mn(1), a positive charge on N(1), and a donor–acceptor bond be-

---

[7] IR ν(CO) for **2a** in hexane: 2098 (w), 2058 (s), 2018 (vs), 2003 (s), 1981 (m), 1961 (s), 1932 (w), 1581 (w) cm^{-1}. Crystal data for **2a**: space group $P\bar{1}$, a = 10.3802 (8) Å, b = 11.852 (2) Å, c = 7.217 (1) Å, α = 91.29 (1)°, β = 91.16 (1)°, γ = 98.40 (1)°, Z = 2, 2482 reflections, R = 0.027 (5). Anal. Calcd (found): C, 37.67 (37.50); H, 1.79 (1.17).

[8] Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. Structure solutions and refinements were made on a VAXstation 3520 computer by using the TEXSAN structure-solving program library (v5.0) of Molecular Structure Corp., The Woodlands, TX.

[9] The ^{13}C NMR spectrum of **2a*** taken in CDCl$_3$ showed resonances at 222.75 (1 CO), 221.65 (1 CO), 214.67 (1 CO), 213.16 (2 CO), 213.98 (1 CO), 209.14 (2 CO), and 184.00 (1 C) ppm. The ^{1}H NMR spectrum of **2a*** taken in acetone-d_6 showed resonances at 4.41 (q, $J_{\text{H-H}}$ = 7.1 Hz, OCH_2), 2.29 (s, CMe), and 1.34 (t, $J_{\text{H-H}}$ = 7.1 Hz, CH$_2$CH_3) ppm. The resonances at 4.41 and 2.29 ppm showed ^{13}C satellites with $^3J_{\text{C-H}}$ = 2.75 and 3.36 Hz, respectively.

[10] (a) Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 175. (b) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, U.K., 1966; Vol. 2, Table 12.34.

[11] The products were separated by TLC on silica gel. IR ν(CO) for **2b** in hexane: 2094 (w), 2053 (s), 2013 (vs), 1997 (s), 1989 (m), 1953 (s), 1928 (w), 1554 (w) cm^{-1}. IR ν(CO) for **3** in CH$_2$Cl$_2$: 2036 (m), 1974 (s), 1933 (s, br), 1894 (w), 1583 (w), 1622 (w, C=N). ^{1}H NMR in acetone-d_6 for **2b**: δ 3.34 (s, br, NMe), 3.07 (s, br, NMe), 2.65 (s, CMe). ^{1}H NMR in acetone-d_6 for **3**: δ 3.53 (s, NMe), 3.33 (s, NMe), 3.07 (s, NMe), 2.78 (s, NMe), 1.98 (s, CMe), 1.93 (s, CMe). Crystal data for **2b**: space group $P\bar{1}$, a = 10.422 (1) Å, b = 10.628 (2) Å, c = 8.934 (1) Å, α = 113.74 (1)°, β = 97.55 (1)°, γ = 93.27 (1)°, Z = 4, 1931 reflections, R = 0.027. Details on the structure of **2b** will be provided in the full report on this work. Crystal data for **3**: space group $P2_1/c$, a = 11.976 (2) Å, b = 10.092 (2) Å, c = 18.429 (3) Å, β = 107.18 (5)°, Z = 4, 2155 reflections, R = 0.027. The mass spectrum for **2b** shows the parent ion plus ions corresponding to the loss of each of eight CO ligands. The mass spectrum of **3** showed a weak parent ion (M$^+$) with stronger ions M$^+$ – x(CO) (x = 1, 4–7). Anal. Calcd (found): C, 43.22 (43.34); H, 3.63 (3.40); N, 6.00 (5.65).

[12] Ficini, J. *Tetrahedron* **1976**, *32*, 1449.

tween the metal atoms, as shown in Scheme I.

Acknowledgment. These studies were supported by the U.S. Department of Energy under Grant No. DEFG84ER13296.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for the structural analyses of **2a** and **3** (16 pages); tables of structure factors (32 pages). Ordering information is given on any current masthead page.

Organolanthanide-Catalyzed Dehydrogenative Coupling of Silanes. Mechanistic Implications

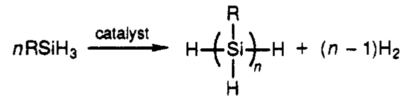
Craig M. Forsyth, Steven P. Nolan, and Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

Received June 4, 1991

Summary: Organolanthanide complexes of the type Cp'_2LnR ($Cp' = \eta^5$-Me_5C_5; Ln = La, Nd, Sm, Y, Lu; R = H, $CH(SiMe_3)_2$), $Me_2SiCp''_2LnR$ ($Cp'' = \eta^5$-Me_4C_5; Ln = Nd; R = $CH(SiMe_3)_2$), Cp'_2Sm, and $Cp'_2Sm(THF)_2$ catalyze the rapid dehydrogenative oligomerization of $PhSiH_3$. Kinetic and mechanistic arguments exclude the importance of metal-centered redox processes in the catalytic cycle and support instead "four-center" "heterolytic" bond-scission/bond-forming sequences.

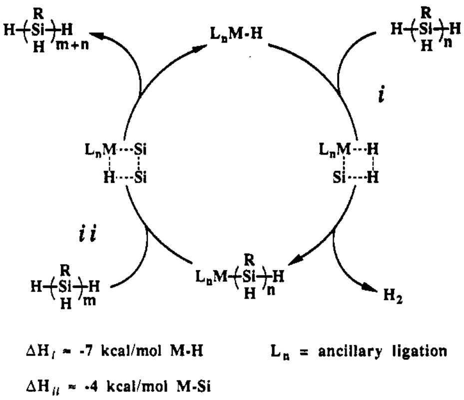
Polyorganosilanes are of considerable current interest as ceramic precursors, third-order NLO materials, deep-UV photoresists, conductive polymers, and photoconductors.[1] A major advance in polyorganosilane synthesis was Harrod's discovery of the catalytic dehydrogenative oligomerization/polymerization of organosilanes effected by organo-group 4 complexes (e.g., eq 1).[2,3] Key unresolved



$$nRSiH_3 \xrightarrow{\text{catalyst}} H\!\left(\begin{matrix}R\\ |\\ Si\\ |\\ H\end{matrix}\right)_{\!n}\!H + (n-1)H_2 \qquad (1)$$

mechanistic issues in such catalytic cycles concern the importance of oxidative addition/reductive elimination sequences,[2-4] the intermediacy of silylene complexes,[2,5] the importance of free radical processes,[2f] or the dominance of four-center heterolytic M–Si/M–H transposition processes (Scheme I). The latter scenario is supported by Tilley's recent characterization of several group four-centered stoichiometric model reactions[6] and thermochemical results,[7] which indicate (for closely analogous M = U) that the steps in Scheme I possess no significant thermodynamic impediments. If Scheme I were indeed valid, metal centers incapable of oxidative addition/reductive elimination sequences, which possess only one possible metal-Si/H σ functionality, and for which other four-center processes are typically facile, might be expected to be catalytically competent. We report here, in an application of this test, that electrophilic organolanthanides of the type $Cp'_2LnR/Me_2SiCp''_2LnR$ ($Cp' = \eta^5$-Me_5C_5; $Cp'' = \eta^5$-Me_4C_5; Ln = lanthanide; R = hydrocarbon, hydride)[8,9] are highly active for eq 1, some initial catalytic phenomenology, and initial kinetic/mechanistic observations.[10]

Scheme I



---

(1) (a) Miller, R. D. *Angew. Chem., Int. Ed. Engl. Adv. Mater.* **1989**, *28*, 1733–1740. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359–1410. (c) West, R.; Maxka, J. *ACS Symp. Ser.* **1988**, *360*, 6–20. (d) Miller, R. D.; Rabolt, J. F.; Sooriyakumaran, R.; Fleming, W.; Fickes, G. N.; Farmer, B. L.; Kuzmany, H. *ACS Symp. Ser.* **1988**, *360*, 43–60. (e) Matyjaszewski, M.; Chen, Y. L.; Kim, H. K. *ACS Symp. Ser.* **1988**, *360*, 78–88. (f) Worsfold, D. J. *ACS Symp. Ser.* **1988**, *360*, 101–111. (g) Baumert, J.-C.; Bjorklund, G. C.; Jundt, D. H.; Jurich, M. C.; Looser, H.; Miller, R. D.; Rabaolt, J.; Sooriyakumaran, R.; Swalen, J. D.; Twieg, R. *J. Appl. Phys. Lett.* **1988**, *53*, 1147–1149.

(2) (a) Gauvin, F.; Harrod, J. F. *Polym. Prepr.* **1991**, *32*, 439–440. (b) Mu, Y.; Aitken, C.; Coté, B.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1991**, *69*, 264–276. (c) Harrod, J. F.; Mu, Y.; Coté, B. *Polym. Prepr.* **1990**, *31*, 228–229. (d) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732–1736. (e) Harrod, J. F. *ACS Symp. Ser.* **1988**, *360*, 89–100. (f) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381–1387. (g) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11–C13. (h) Aiken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059–4066.

(3) (a) Campbell, W. H.; Hilty, T. K.; Yurga, L. *Organometallics* **1989**, *8*, 2615–2618. (b) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885–1893.

(4) (a) Corey, J. Y.; Zhu, X. H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924–930. (b) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590–1591. (c) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595–1596. (d) Ojima, I.; Inaba, S. D.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7–C8.

(5) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897–902.

(6) (a) Walzer, J. F.; Woo, H. G.; Tilley, T. D. *Polym. Prepr.* **1991**, *32*, 441–442. (b) Tilley, T. D.; Woo, H.-G. *Polym. Prepr.* **1990**, *31*, 228–229. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37–51. (d) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043–8044.

(7) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450–1457.

(8) (a) Mauermann, H.; Marks, T. J. *Organometallics* **1985**, *4*, 200–202. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (c) Jeske, G.; Schock, L. E.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118.

(9) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–55.

(10) (a) Communicated in part: Marks, T. J. First International Conference on f-Elements, Leuven, Sept 4–7, 1990. (b) While this work was nearing completion, Cp'_2LuMe-catalyzed dehydrogenative silane polymerization was also reported by P. L. Watson: Watson, P. L., First International Conference on f-Elements, Leuven, Sept 4–7, 1990. See also: Watson, P. L.; Tebbe, F. N. U.S. Patent 4,965,386, Oct 23, 1990; *Chem. Abstr.* **1991**, *114*, 123331p.

0276-7333/91/2310-2543$02.50/0