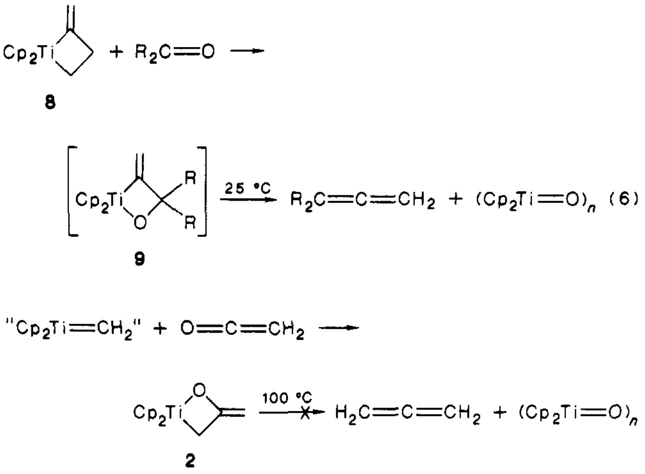
Organometallics 1988, 7, 782–784

tallaoxacycles in early metal olefin epoxidation and alkylidene transfer reactions have never been observed. Most striking is the comparison of the stable 3-alkylidene complexes **2** and **6** to the isomeric 2-methylene complexes such as **9** that are formed in the reaction of the precursor to $Cp_2Ti{=}C{=}CR_2$ (**8**) with ketones and aldehydes. Complex **9** is unstable at room temperature (eq 6).[17]



At least two major factors are considered to account for this difference. If the transition state for the cleavage of the metallaoxacycle is similar to that for the cleavage of the corresponding metallacyclobutanes, the ring must reach a planar geometry for the reaction to occur.[18] As indicated above, the 3-methylene-metallaoxacyclobutanes are puckered and there is a significant barrier to flattening. The 2-methylene isomers cannot pucker and maintain normal angles and bond distances. The differences in the barriers to planarity could account for a significant part of the difference in stabilities between the two isomers. In all the examples where **9** is a proposed intermediate, the β-carbon is substituted with alkyl groups. Substitution in this position has been shown to significantly destabilize the corresponding metallacyclobutanes[19] due to significant steric interactions between the β-substituent and the cyclopentadienyl ligands. Therefore, there is significantly greater relief of steric strain when **9** cleaves to allene and the titanocene oxide than when **2** or **6** reacts to yield the same products. We propose that these 3-alkylidene metallaoxacycles are more stable than the 2-alkylidene isomer due to the combined ability to pucker to increase bonding by donation of the oxygen lone pair electrons to the titanium center and to the absence of steric crowding due to the planar sp^2 β-carbon.

Acknowledgment. We wish to acknowledge the financial support of the Department of Energy (DE-FG03-85ER135452) and the National Science Foundation (CHE 8520517).

Registry No. **1**, 66320-88-5; **2**, 112681-97-7; **5**, 12099-30-8; **6**, 112681-98-8; **7**, 75687-68-2; $CH_2S(O)(CH_3)_2$, 70775-39-2; Cp_2TiCl_2, 1271-19-8; $O{=}C{=}CPh_2$, 525-06-4; $Cp_2TiCH_2C(CH_3)_2CH_2$, 80122-07-2; 1,1-diphenyl-2-propanone, 781-35-1; acetone, 67-64-1.

---

(17) Buchwald, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490.
(18) Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880.
(19) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

Synthesis, Characterization, and Reactivity of Several Unusual Trinuclear Clusters Containing Either Rhodium or Cobalt and the Cyclopentadienyl or Pentamethylcyclopentadienyl Ligands

Craig E. Barnes* and Michelle R. Dial

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Received September 25, 1987

Summary: Exposure of various mono- and dinuclear carbonyl complexes of rhodium and cobalt to the bis(ethylene) complex $CpCo(C_2H_4)_2$ gives rise to several new trinuclear clusters of the form $(Cp^*M)_{3-n}(CpCo)_n(\mu_3\text{-}CO)_2$ (n = 1, 2; M = Co, Rh) in high yield. These 46e clusters exhibit paramagnetically shifted ^{1}H NMR spectra and readily engage in the reversible transfer of a cyclopentadienyl cobalt fragment to suitable organometallic acceptors.

Recently, a series of unsaturated trinuclear cluster complexes of the form $Cp^*_3MM'M''(\mu_3\text{-}CO)_2$ have been described which exhibit interesting electronic properties.[1,2] These complexes are unusual in that they contain three low-valent, electron-rich metals in a highly electron-deficient cluster arrangement (46 electron count). Depending on the metals and substitution on the cyclopentadienyl rings, several different high- and low-spin electron configurations have been reported for these complexes.[1a,2a–c] Herein we report on a broadly applicable synthetic methodology for the synthesis of a wide variety of this type of trinuclear cluster containing at least one CpCo fragment. Preliminary characterization of the electronic states of several new examples of these clusters is also presented along with initial investigations into their reactions with carbon monoxide and several organometallic complexes.

---

(1) (a) Herrmann, W. A.; Barnes, C. E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1985**, *4*, 172–180. (b) Hörlein, R.; Herrmann, W. A.; Barnes, C. E.; Weber, C.; Krüger, C.; Ziegler, M. L.; Zahn, T. *J. Organomet. Chem.* **1987**, *321*, 257–272. (c) Herrmann, W. A.; Barnes, C. E.; Serrano, R.; Koumboris, B. *J. Organomet. Chem.* **1983**, *256*, C30–C34.

(2) (a) Green, M.; Hankey, D. R.; Howard, J. A. K.; Louca, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 757–758. (b) Bray, A. C.; Green, M.; Hankey, D.; Howard, J.; Johnson, O.; Stone, F. G. A. *J. Organomet. Chem.* **1985**, *281*, C12–C16. (c) Olsen, W. L.; Stacy, A. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 7646–7656. (d) Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1555–1561. (e) Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Orpen, A. G.; Stone, F. G. A. *Ibid.* **1984**, 2757–2763. (f) Farrugia, L. J.; Jeffery, J. C.; Marsden, C.; Stone, F. G. A. *Ibid.* **1985**, 645–650. (g) Jeffery, J. C.; Marsden, C.; Stone, F. G. A. *Ibid.* **1985**, 1315–1321. (h) Barr, R. D.; Green, M.; Marsden, K.; Stone, F. G. A.; Woodward, P. *Ibid.* **1983**, 507–512. (i) Carriedo, G. A.; Howard, J. A. K.; Stone, F. G. A. *J. Organomet. Chem.* **1983**, *250*, C28–C32. (j) Brun, P.; Dawkins, G. M.; Green, M.; Miles, A. D.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 926–927. (k) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89–99 and references therein. (l) Boag, N. M.; Green, M.; Mills, R. M. Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1171–1173. (m) Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1309–1319. (n) Green, M.; Howard, J. A. K.; Pain, G. N.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1327–1331. (o) Mague, J. T. *J. Organomet. Chem.* **1986**, *305*, 1–198. (p) Bedard, R. L.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5924–5932. (q) Bedard, R. L.; Dahl, L. F. *Ibid.* **1986**, *108*, 5933–5948. (r) Olson, W. L.; Dahl, L. F. *Ibid.* **1986**, *108*, 7657–7663. (s) Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978**, *17*, 772–774. (t) Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L.; Shore, S. G. *Organometallics*, **1987**, *6*, 274–283. (u) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521–1531. (v) Zonnevylle, M. C.; Silvestre, J.; Hoffmann, R. *Ibid.* **1986**, *108*, 1509–1517. (w) Uchtman, V. A. *J. Am. Chem. Soc.* **1969**, *91*, 3763–3769. (x) Strouse, C. E.; Dahl, L. F. *Discuss. Faraday Soc.* **1969**, *No. 47*, 93–106. (y) Byers, L. R.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1981**, *103*, 1942–1951.

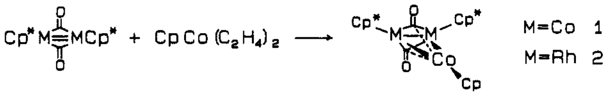
0276-7333/88/2307-0782$01.50/0

Table I. ^{1}H NMR (δ) and IR Spectral Data for Complexes 1–4

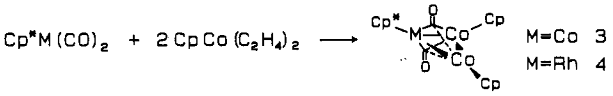
Complex	^{1}H NMR^a		IR (cm^{-1})	
	Cp	Cp*	CH_2Cl_2	KBr
1	−55.4	−7.2	1690	1686
2	−41.9	−10.8	1680	1690
3	−11.2	−2.2	1688	1699
4	3.6	0.3	1675	1702

[a] C_6D_6, 24 °C; signals upfield of TMS are negative.

The sythetic scheme for the construction of virtually any trinuclear complex which contains at least one CpCo fragment is summarized in eq 1 and 2.

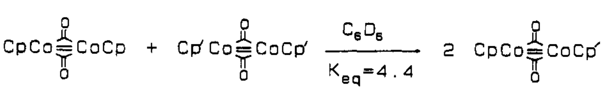


(1)

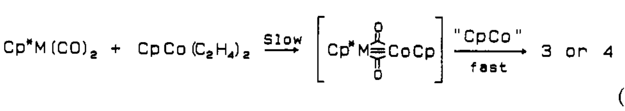


(2)

The bis(ethylene) complex $CpCo(C_2H_4)_2$[3] reacts under mild conditions with a variety of carbonyl-containing species losing 2 equiv of ethylene and formally adding the CpCo fragment (isolobal with CH^+) to the existing complex. In this way both 1 and 2 are synthesized in high yield simply by mixing hexane/ether solutions of the unsaturated dinuclear species and $CpCo(C_2H_4)_2$ under stringent anaerobic conditions.[4] The trinuclear complexes containing two CpCo fragments (3 and 4) require a slightly different approach involving careful inverse addition of the mononuclear dicarbonyl to at least 2 equiv of the bis(ethylene) complex. Attempts to make the unsaturated dinuclear complexes Cp*M(μ-CO)$_2$CoCp (M = Co, Rh) have been unsuccessful. Instead, good yields of the known [Cp*M(μ-CO)]$_2$ complexes are isolated under all conditions investigated. We believe that the mixed Cp/Cp* complexes Cp*M(μ-CO)$_2$CoCp (M = Co, Rh) are unstable under these conditions toward a type of metathesis reaction first reported by Hersh and Bergman[5] for the analogous Cp and methyl Cp complexes involving cobalt as illustrated in eq 3.[6] The success of the inverse addition reaction relies on the fact that the second addition of a CpCo fragment across the face of the unobserved dinuclear species is fast relative to the bimolecular metathesis reaction (eq 4).[1a]



(3)



(4)

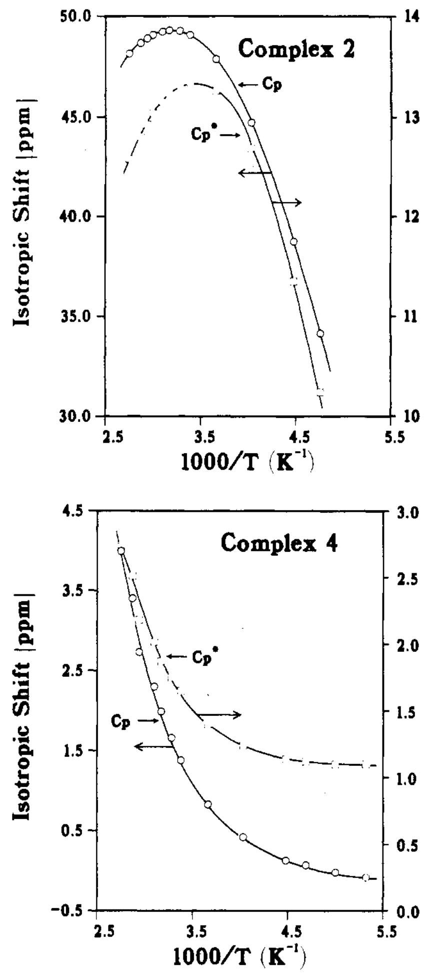


Figure 1. Absolute value of the paramagnetically derived shift (δ) as a function of inverse temperature for complexes 2 and 4 in toluene-d_8. The paramagnetically derived shift is calculated from the following equation: $\delta_{\text{observed}} = \delta_{\text{diamagnetic}} - \delta_{\text{paramagnetic}}$. The limiting diamagnetic shifts for the Cp and Cp* ring protons are esimated to be 5 and 2 ppm, respectively.

Room-temperature ^{1}H NMR and IR spectral data for complexes 1 through 4 are summarized in Table I.

The CO stretching frequencies are observed between 1705 and 1675 cm^{-1}. In the cases of 1 and 2, where the stretching frequencies for the dinuclear precursors are known,[7] addition of the CpCo fragment causes a 40–50 cm^{-1} reduction in these frequencies. These data are consistent with either triply bridging or semi-triply bridging geometries for the carbonyl ligands. In the latter case, the carbonyl ligands remain associated with one edge of the metal triangle (μ_2) but are canted over the plane toward the third metal atom in a μ_3 bonding mode. Both geometries have been observed in similar trinuclear systems[1,2] and have been described theoretically.[8]

Two observations are apparent from the ^{1}H NMR data: (1) The large upfield shifts (all but those for 4 are above TMS) of the signals for the Cp and Cp* protons are strong evidence for the presence of unpaired electrons in these complexes. (2) Regardless of the combination of Cp or Cp* rings in the complex, only one signal is observed for each. Careful integration indicates that all the protons of the

---

(3) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 295–311. Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716–717; *Angew. Chem. Suppl.* **1983**, 1005–1016.

(4) Satisfactory C and H elemental analyses have been obtained for all new complexes described in this report and are provided as supplementary material to this manuscript.

(5) Hersh, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *105*, 5846–5859.

(6) The complex Cp*Ir(μ-CO)$_2$CoCp is unique in this regard as it shows no tendency whatsoever to metathesize to the corresponding homometal dinuclear complexes, cf. ref 1a,b.

(7) The CO stretching frequencies for [Cp*Rh(μ-CO)]$_2$ and [Cp*Co(μ-CO)]$_2$ measured in CH_2Cl_2 are 1717 and 1740 cm^{-1}, respectively. See also Nutton, A.; Maitlis, P. M. *J. Organomet. Chem.* **1979**, *166*, C21–C22. Ilenda, C. S.; Shore, N. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1781.

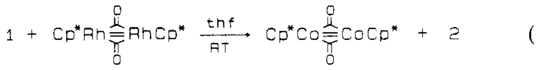
(8) Pinhas, A.; Albright, T.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29–49.

rings are accounted for in these signals (Cp(H):Cp*(H) = 1:6 for 1 and 2 and 2:3 for 3 and 4). This behavior is consistent with the carbonyl ligands engaging in a fast fluxional shuttling around the edges of the triangular core.[9]

To more fully characterize the paramagnetism of these complexes, we investigated the temperature dependence of their proton NMR spectra. As has been observed previously,[1a] complex 1 exhibits a strict linear relationship between the shift and inverse temperature. This type of behavior is consistent with a $S = 1$ triplet formulation for the complex over the temperature range studied (±90 °C). Plots of ^{1}H shift versus $1/T$ for complexes 2 and 4 are shown in Figure 1. For the rhodium–dicobalt cluster 4, as the temperature is lowered, the paramagnetically derived shift goes asymptotically to zero (diamagnetic position) consistent with a ground-state singlet formulation with low-lying, thermally available triplet states. Clusters 2 and 3 exhibit similar though somewhat unusual shift versus $1/T$ behaviors as shown for 2. A maximum paramagnetic shift is observed in both cases with the shift falling off at both higher and lower temperatures. Although a detailed description of the electronic structures for 1–4 cannot be made with the data in hand, their complex and seemingly incongruent properties may all be explained by a ground-state singlet formulation with thermally accessible, low-lying triplet states.[10] Detailed magnetic susceptibility studies are in progress to determine the precise origin of these interesting electronic effects.

Preliminary investigations into the reactions of these cluster complexes with various ligands and organometallic complexes reveal the following patterns: (1) One CpCo fragment is easily lost upon exposure to dioxygen with the concomitant formation of the parent dinuclear complex in the case of 1 and 2. (2) The trinuclear framework remains intact when complexes 1–4 are exposed to carbon monoxide. The resulting tricarbonyl adducts 5–8 conform to one of the known structure types for these complexes.[11]

Finally, complexes 1–4 appear to function as CpCo transfer agents when exposed to appropriate organometallic acceptors. For example, complex 1 cleanly transfers a CpCo fragment to $[\text{Cp*Rh}(\mu\text{-CO})]_2$ in THF at room temperature over several hours as shown in eq 5.



$$1 + \text{Cp*Rh}\overset{\text{O}}{\underset{\text{O}}{\equiv}}\text{RhCp*} \xrightarrow[\text{RT}]{\text{thf}} \text{Cp*Co}\overset{\text{O}}{\underset{\text{O}}{\equiv}}\text{CoCp*} + 2 \qquad (5)$$

These reactions appear to be under equilibrium control. The equilibrium constant for the reaction of 1 with $[\text{Cp*Rh}(\mu\text{-CO})]_2$ is 4.2 at room temperature in THF-d_8. Equilibrium and rate studies are underway to characterize this CpCo transfer reaction.[12]

From the results reported here both the underlying electronic structures and the reactivities exhibited by this class of trinuclear complexes appear to be a sensitive function of several factors including the metals involved, the number of Cp and Cp* ligands associated with the cluster, the type of incoming ligand, and the reaction conditions. With the synthetic approach described herein we are currently exploring other combinations of metals and ligands within the trinuclear framework as well as the diverse types of reactivity these clusters exhibit in an attempt to more fully understand their chemistry.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corp. for partial support of this research. We acknowledge generous loans of rhodium metal starting materials from Johnson Matthey, Inc.

Registry No. 1, 112532-12-4; 2, 112532-13-5; 3, 112532-14-6; 4, 112532-15-7; $\text{CpCo(C}_2\text{H}_4)_2$, 69393-67-5; $\text{Cp*Co}(\mu\text{-CO})_2\text{CoCp*}$, 69657-52-9; $\text{Cp*Rh}(\mu\text{-CO})_2\text{RhCp*}$, 69728-34-3; Cp*Co(CO)_2, 12129-77-0; Cp*Rh(CO)_2, 32627-01-3.

Supplementary Material Available: Tables of observed ^{1}H NMR shifts versus temperature for complexes 1 through 4 and elemental analysis data for complexes 1 through 8 (2 pages). Ordering information is given on any current masthead page.

---

(9) For a more detailed discussion of this type of behavior, cf. ref 1a.

(10) Behavior similar to 4 has been reported by Dahl and co-workers.[2c] It is also possible that these complexes exhibit both high- and low-spin ground-state electron configurations. See ref 8 for a discussion of the possible ground states for these clusters.

(11) Three distinct structural types for $\text{Cp}_3\text{M}_3\text{(CO)}_3$ (M = Co, Rh) complexes have been described. Following the designations of R. J. Lawson and J. R. Shapley (*Inorg. Chem.* **1978**, *17*, 772–774), these are C_{3v} $(\text{MCp})_3(\mu\text{-CO})_3$, C_s $(\text{MCp})_3(\mu_3\text{-CO})(\mu\text{-CO})_2$, and C_s $(\text{MCp})_3(\mu\text{-CO})_2\text{(CO)}$. Complexes 1 through 4 form the C_s $(\text{MCp})_3(\mu_3\text{-CO})(\mu\text{-CO})_2$ with CO: **5** (from 1), IR (CH_2Cl_2) 1815 (s), 1765 (m), 1665 (s) cm^{-1}, ^{1}H NMR (C_6D_6, 90 MHz) δ 4.703 (s, 5 H), 1.466 (s, 30 H); **6** (from **2**) IR (CH_2Cl_2) 1815 (s), 1770 (m), 1730 (w), 1655 (s) cm^{-1}, ^{1}H NMR (C_6D_6) δ 4.689 (s, 5 H), 1.627 (s, 30 H); **7** (from **3**) IR (KBr) 1830 (s), 1780 (s), 1685 (sh), 1675 (s) cm^{-1}, ^{1}H NMR (C_6D_6) δ 4.62 (s, 10 H), 1.390 (s, 15 H); **8** (from **4**) IR (KBr) 1800 (s), 1760 (s), 1650 (s) cm^{-1}, ^{1}H NMR (C_6D_6) δ 4.62 (s, 10 H), 1.56 (s, 15 H.

(12) Garrou, P. E. *Adv. Organometallic. Chem.* **1984**, *23*, 95–127. Horvath, I. T.; Zsolnai, L.; Huttner, G.; *Organometallics* **1986**, *5*, 180–182.

Transition-Metal Silyl Complexes. 22.[1] Anionic Silyl Complexes, $L_nM\text{-SiR}_3^-$, as Equivalents to L_nM^{2-} in Synthesis. A Novel Route to Carbene Complexes

Uwe Kirchgässner and Ulrich Schubert*

Institut für Anorganische Chemie der Universität
Am Hubland, D-8700 Würzburg, Germany

Received October 23, 1987

Summary: Cyclopropenylidene complexes are obtained by reaction of anionic silyl complexes $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{(CO)}_2\text{MnSiMePh}_2]^-$ or $[(\text{Ph}_3\text{P})(\text{CO})_3\text{FeSiMePh}_2]^-$ with 3,3-dichloro-1,2-diphenylcyclopropene. The structure of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Mn}{=}\overline{\text{C}{-}\text{CPh}{=}\text{C}}\text{Ph}$ (1) has been determined by X-ray diffraction.

Whereas the chemistry of simple metal carbonyl anions is well-established, the reactivity of anionic transition-metal silyl complexes has only recently attracted some attention. They readily react with organic and inorganic halides and therefore are useful precursors to silyl-substituted complexes with metal–carbon, metal–metal, or metal–metalloid bonds.[2,3] Beyond such substitution reactions, the reactivity of the silyl ligand renders additional preparative applications possible. When $[\text{MeCp}(\text{CO})_2\text{MnSiR}_3]^-$ (MeCp = η^5-$\text{CH}_3\text{C}_5\text{H}_4$) is reacted with Ph_3PAuCl or $(\text{picoline})_2\text{PtCl}_2$ in the presence of moist picoline, binuclear complexes with hydrogen-bridged metal–metal bonds are formed,[4] the anionic silyl complex

---

(1) Part 21: Schubert, U.; Müller, J. *J. Organomet. Chem.*, in press.

(2) (a) Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 2559; **1970**, 3147. (b) Graham, W. A. G.; Jetz, W. *Inorg. Chem.* **1971**, *10*, 1647. (c) Blakeney, A. J.; Johnson, D. L.; Donovan, P. W.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 4415. (d) Schubert, U.; Kunz, E.; Knorr, M.; Müller, J. *Chem. Ber.* **1987**, *120*, 1079. (e) Colomer, E.; Corriu, R. J. P.; Vioux, A. *J. Organomet. Chem.* **1984**, *267*, 107. (f) Carré, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. *Organometallics* **1984**, *3*, 970. (g) Schubert, U.; Kunz, E. *J. Organomet. Chem.* **1986**, *303*, C1.

(3) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

(4) Kunz, E.; Müller, J.; Schubert, U. *J. Organomet. Chem.* **1987**, *320*, C11.