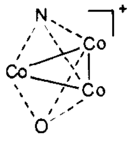
statistical distribution of label. For Co_4NO^+ the ratio of $Co_4(^{18}O)(^{16}O)^+$:$Co_4(^{18}O)_2$ is 1.7:1.

The isotopic distribution for Co_3NO^+ may have consequences rooted in the geometry of the $Co_3(N)(O)^+$ species where the nitride and oxide reside in positions above and below a triangular Co_3 nucleus **1**.[25] In such a configuration, the preferential elmination of $N^{18}O$ upon reaction with $^{18}O_2$ can easily be envisioned.



1

The above results clearly show that nitric oxide undergoes dissociative chemisorption on Co_3^+ and Co_4^+ in analogy with surface chemistry.[8,9] The effect additional NO and CO ligands have on dissociative chemisorption of nitric oxide on these small cobalt clusters is currently under investigation as well as their reactivity. These results will yield information on the molecular level for reactions of relevance to both surface chemistry and catalysis. In addition we are also probing the nature of the unreactive portion of Co_2NO^+ (with dioxygen) and studying a variety of other cluster–nitric oxide complexes. These limited results demonstrate that nitric oxide has a rich and varied chemistry with small gas-phase transition-metal cluster ions just as it has on metal surfaces and organometallic clusters.

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

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[25] Triangular, M_3 clusters containing a triply bridging oxygen atom are known. See, for example: Cercotti, A.; Resconi, L. *J. Organomet. Chem.* **1983**, *249*, C35 and reference cited therein.

Carbon–Carbon Bond Activation via β-Alkyl Elimination. Reversible Branching of 1,4-Pentadienes Catalyzed by Scandocene Hydride Derivatives

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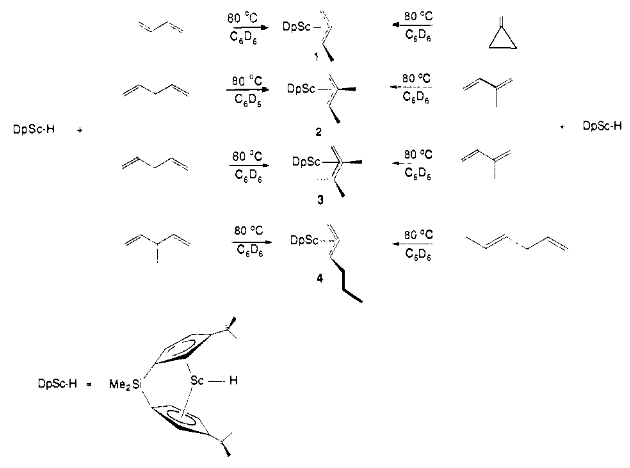
Although impressive advances have recently been made in activating the carbon–hydrogen bonds of hydrocarbons,[1] the activation of carbon–carbon bonds by soluble transition-metal complexes remains one of the most prominent challenges in organometallic chemistry. Since classical approaches to hydrocarbon rearrangements involve acid-promoted carbocation chemistry, we have explored the possibility that highly Lewis acidic, early transition-metal alkyls and hydrides could effect C–C bond-forming or -breaking processes for simple hydrocarbons. We report herein that a scandocene hydride complex catalyzes the reversible branching and cyclization of 1,4-pentadienes. The key feature responsible for this unusual reactivity is reversible olefin insertion/β-alkyl elimination.

Scheme I



Permethylscandocene alkyls, $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$, rapidly polymerize ethylene but undergo preferential σ bond metathesis with α olefins (eq 1).[2] Unfavorable steric interactions between the

$$(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R + CH_2{=}CHR' \rightarrow (\eta^5\text{-}C_5Me_5)_2Sc\text{-}CH{=}CHR' + R\text{-}H \quad (1)$$

olefin substituent and an $(\eta^5\text{-}C_5Me_5)$ ligand appear to prevent coordination of the olefin π bond, so that attack at a vinylic C–H bond occurs to the exclusion of insertion. We have therefore prepared some less sterically hindered scandocene derivatives, including $[Me_2Si(\eta^5\text{-}C_5H_3CMe_3)_2]Sc\text{-}R$, "DpSc-R", (R = H, alkyl, etc.) (Scheme I). The starting material, $(DpSc\text{-}Cl)_n$,[3] is obtained in ca. 55% yield via treatment of $ScCl_3\cdot(THF)_3$ (THF = tetrahydrofuran) with $Li_2[Me_2Si(C_5H_3CMe_3)_2]$ in toluene. The trimethylsilylmethyl derivative, $DpSc\text{-}CH_2SiMe_3$, is prepared (60%) by treatment of $(DpSc\text{-}Cl)_n$ with trimethylsilyllithium. The dimeric hydride derivative $(DpSc\text{-}H)_2$[4] is obtained (quantitatively, ^1H NMR; isolated 70%) by hydrogenolysis of $DpSc\text{-}CH_2SiMe_3$.

Butadiene, 1,4-pentadiene, 2-methyl-1,4-pentadiene, and 3-methyl-1,4-pentadiene react with $(DpSc\text{-}H)_2$ (most likely via the monomer, DpSc-H) to afford the allyl derivatives **1**, **2**, **3**, and **4** (Scheme I), which were independently prepared by treating $(DpSc\text{-}H)_2$ with methylenecyclopropane isoprene, 2,3-dimethylbutadiene, and 1,4-hexadiene.[5] We tentatively interpret these results according to the mechanisms shown in Schemes II and III. Addition of the 1,4-pentadienes to the Sc–H bond of DpSc–H, followed by intramolecular olefin insertion affords cyclopropylmethyl- or cyclobutylmethylscandium intermediates. The methyl branch is introduced (or removed) by β-alkyl elimination in the alternative sense. β-H elimination and readdition to DpSc–H subsequently yields the stable allyl compound in each case.

Both cyclopropylmethyl and cyclobutylmethyl intermediates are required to accommodate all of the observed rearrangements. The symmetry for **5c**, **6a**, and **6b** precludes skeletal rearrangement, since β-alkyl elimination may occur by only one pathway, namely

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[1] For recent reviews see, for example: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Green, M. L. H. *Pure Appl. Chem.* **1985**, *57*, 1897. (c) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (d) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

[2] (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Burger, B. J.; Thompson, M. E.; Bercaw, J. E., manuscript in preparation.

[3] Of the two possible isomeric forms (*meso* and *d,l*), these procedures afford only *meso*. See Supplementary Material for ^1H and ^{13}C NMR data and elemental analyses.

[4] Calcd for $C_{20}H_{31}SiSc$: C, 69.73; H, 9.07. Found: C, 69.80; H, 8.98. ^1H NMR (benzene-d_6, 90 MHz) δ 0.21 (s, 3 H), 0.82 (s, 3 H), 1.21 (s, 18 H), 6.27 (m, 2 H), 6.67 (m, 2 H), 7.33 (M, 2 H) (Sc–*H* not located, presumably due to ^{45}Sc quadrupolar broadening). MW (ebulliometry) = 717. Calcd for dimer 688.

[5] On the basis of the discussion which follows, branching of 1,4-hexadiene would be expected if addition of DpSc–H to the internal double bond occurs faster than isomerization to 2,4-hexadiene. However, monitoring the formation of **4** reveals that DpSc–H rapidly catalyzes isomerization of 1,4-hexadiene to 2,4-hexadiene (^{13}C and ^1H NMR), presumably via $[CH_3CH(DpSc)CH_2CH{=}CHCH_3]$. Formation of **4** from reaction of 2,4-hexadiene with DpSc–H occurs much more slowly. See footnote 13.

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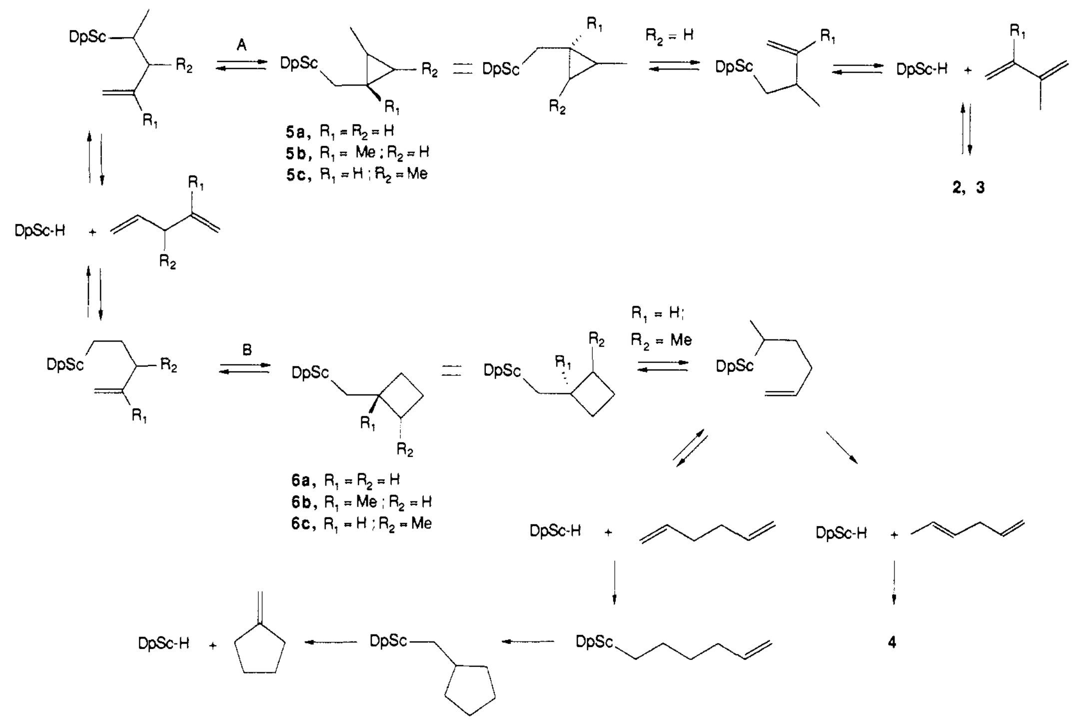
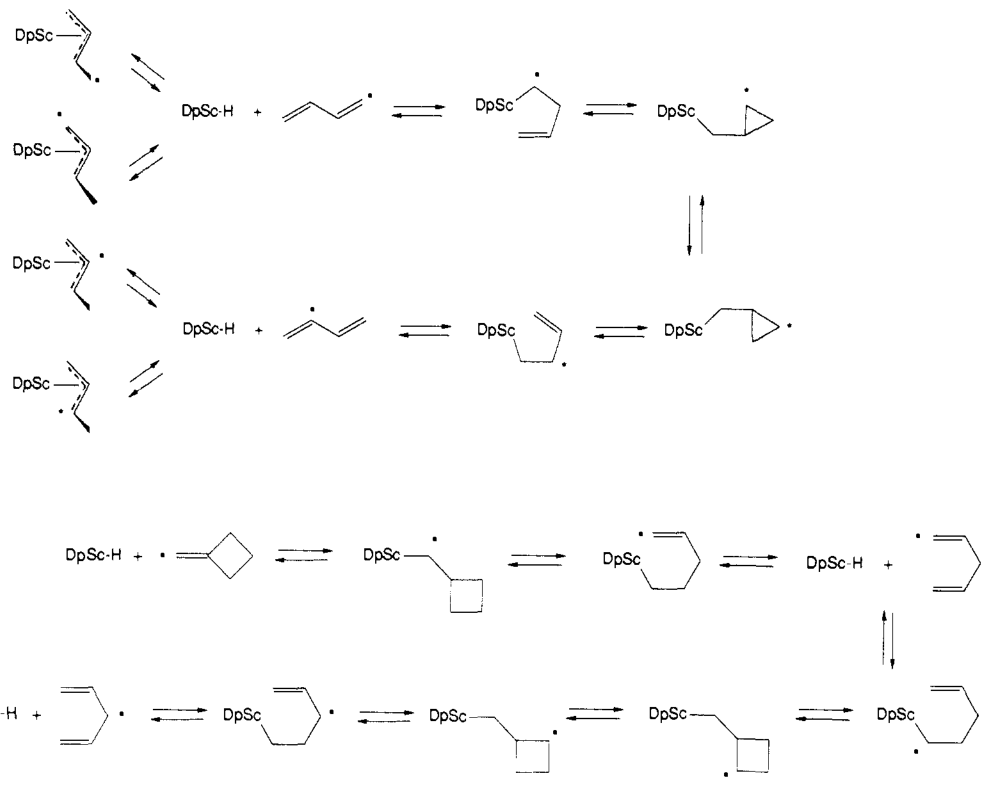
Scheme II



Scheme III



the reverse that followed in their formation. Moreover, the occurrence of this degenerate rearrangement (step A, Scheme II), even for the parent cyclopropylmethyl derivative, is evident from scrambling of the ^{13}C label into all four crotyl positions of DpSc(η^3-CH$_2$CHCHCH$_3$) (^{13}C NMR) when (DpSc–H)$_2$ is treated with ^{13}CH$_2$=CHCH=CH$_2$ (Scheme III).[6] The occurrence of degenerate rearrangement for the parent cyclobutylmethyl derivative (step B, Scheme II) is similarly demonstrated by the catalytic ring opening and scrambling (25 °C, 3 days) of the ^{13}C label of the exocyclic methylene carbon of methylenecyclobutane to yield specifically 1,4-pentadiene-*1,3,5*-$^{13}C_1$ (Scheme III).[7] The intermediacy of interconverting cyclopropylcarbinyl ⇄ allylcarbinyl complexes was invoked for the rearrangements of car-

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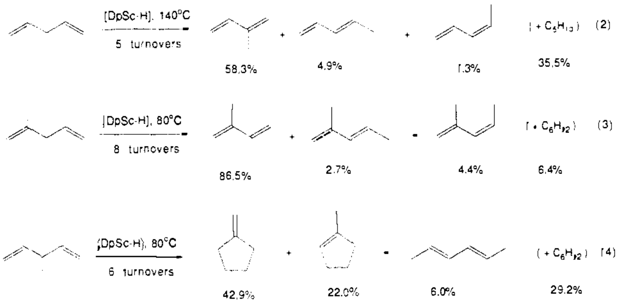
(6) The formation of DpSc(η^3-CH$_2$CHCHCH$_3$)-$^{13}C_1$ occurs after 2 h at 80 °C. Scrambling the ^{13}C label into the internal positions of the allyl group requires heating of isolated DpSc(η^3-CH$_2$CHCHCH$_3$)-$^{13}C_1$ at 140 °C for several hours. DpSc(η^3-CH$_2$CHCHCH$_3$) reacts with excess butadiene at 140 °C to yield unidentified products.

(7) At 25 °C the only scandium compound observed by ^{1}H NMR during the scrambling of the ^{13}C label is (DpSc–H)$_2$. However, if the sample is heated to 80 °C DpSc(η^3-CH$_2$C(CH$_3$)CHCH$_3$) (2-$^{13}C_1$) is quantitatively formed, consistent with the mechanism proposed in Scheme II.

bocation and lithio or Grignard reagent reported by Roberts et al.[8] Similar mechanisms have been proposed by Miller et al. for $\{NiCl_2(PBu_3)_2/AlCl(CH_2CHMe_2)_2\}$-catalyzed skeletal rearrangements of 1,4-dienes,[9] by Atkins, Johnson, et al. for some homoallylcobalt complexes,[10] and by Flood et al. for some cyclobutylmethylplatinum derivatives.[11]

Catalytic reactions can also be performed with DpSc–H when excess 1,4-pentadienes (eq 2–4) are introduced, although after several turnovers significant amounts of hydrogenation products are formed, most likely accompanied by metalation of the Dp ligands. The remarkable catalytic conversion of 3-methyl-1,4-pentadiene to methylenecyclopentane and its isomer, methyl cyclopentene, is readily accommodated as shown in Scheme II.



These observations implicate the reverse of olefin insertion into Sc–C bonds, namely β-alkyl elimination,[12] as a relatively facile process in this system. The scope of these transformations[13] as well as the factors responsible for the high selectivity of the catalytic rearrangements[14] are presently under study.

Acknowledgment. This work was supported by the USDOE Office of Energy Research, Office of Basic Energy Sciences (Grant no. DE-FG03-85ER13431), and by the Shell Company Foundation which are gratefully acknowledged. We thank Professors Dennis Dougherty and John Roberts and Dr. Jay Labinger for helpful discussions.

Supplementary Material Available: Table consisting of ^1H and ^{13}C NMR spectral, analytical, infrared, and GC data together with a description of a representative experiment (5 pages). Ordering information is given on any current masthead page.

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(8) (a) Cox, E. F.; Caserio, M. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 2719. (b) Silver, M. S.; Caserio, M. C.; Rice, H. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 3671. (c) Patel, D. J.; Hamilton, C. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 5144. (d) Maercker, A.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1742. (e) Howden, M. E. H.; Maercker, A.; Burdon, J.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1732. (f) Kover, W. B.; Roberts, J. D. *J. Am. Chem. Soc.* **1979**, *91*, 3687.

(9) (a) Miller, R. G.; Pinke, P. A.; Stauffer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211. (b) Pinke, P. A.; Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4221. (c) Pinke, P. A.; Stauffer, R. D.; Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4229. (d) Golden, H. J.; Baker, D. J.; Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4235.

(10) Atkins, M. P.; Golding, B. T.; Bury, A.; Johnson, M. D.; Sellars, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3630.

(11) (a) Flood, T. C.; Bitler, S. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (b) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795.

(12) Watson first reported β-alkyl elimination may be competitive with β-H elimination for some closely related permethyllutetiocene derivatives: (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

(13) On the basis of these rather limited results the branching reaction appears to be restricted to α, ω (diterminal) dienes. With an internal double bond simple isomerization to the linear, conjugated diene results (e.g., for 1,4-hexadiene; footnote 5). Apparently, unfavorable steric interactions greatly slows addition of Sc–H to the internal olefin relative to addition to terminal olefin and precludes the intramolecular cyclization (via insertion of an internal olefin into a DpSc–C bond) required for branching (step B, Scheme II).

(14) For example, in eq 2 the equilibrium concentrations are estimated as the following: 1,4-pentadiene (0.05%), *cis*-piperylene (40.5%), *trans*-piperylene (27.6%), and isoprene (31.8%) at 413 K (Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969; pp 330–334). The relative percentages of these isomers obtained are as follows: 1,4-pentadiene (<0.03%), *cis*-piperylene (2.0%), *trans*-piperylene (7.6%), and isoprene (90.4%) at 413 K.

Solid-State and Solution Structure of Dilithium Trimethyl((phenylsulfonyl)methyl)silane, a True Dilithiomethane Derivative[†]

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The dilithiosulfones $Li_2[C(R^1)-SO_2R^2]$ (**1**) represent potential dilithioalkane derivatives of the type $Li_2C(R^1)R^2$ (**2**)[1] with a preparative useful functional group and are therefore of particular synthetic and structural interest.[2] Despite many reports of their formation based on chemical evidence,[3] only recently with the title compound **1a** ($R^1 = SiMe_3$, $R^2 = Ph$) the first dilithiosulfone could be isolated and unequivocally characterized by ^{13}C and ^1H NMR spectroscopy.[4]

We now report results of a combined X-ray and NMR investigation which show that **1a** is a *true geminal dilithio compound* of the type **2** in the solid state as well as in solution. No such structural informations on compounds of this type were previously available.[1,5]

Metalation of trimethyl((phenylsulfonyl)methyl)silane (**3**) with 2 equiv of *n*-butyllithium (*n*-BuLi) in tetrahydrofuran (THF) at −90 °C to 25 °C in the *presence of Li_2O gave prismoide crystals* of the sparingly soluble $(\mathbf{1a})_6{\cdot}Li_2O{\cdot}(thf)_{10}$ complex.[4] The X-ray structure analysis[6] shows a hexamer (C_i) with six THF molecules and one Li_2O molecule (Figure 1). Four THF molecules lie between the hexamers. Around the unique O atom in the center of symmetry is an octahedral array of Li atoms, two of which (Li5 and Li5A) make no contact to the dianionic C atoms C1A, C1B, and C1C and symmetry-related C1AA, C1BA, and C1CA. Six dianions of **1a** featuring three different conformations in regard to the C(α)–S bond are grouped around the Li octahedron and linked together through four-membered O–Li–O–Li and six-membered Li–C–Li–O–S–O rings, among others. The *three different dianionic C atoms are each coordinated at least to two Li atoms* with the coordination geometry and connectivity shown in Figure 2. C1C and C1A are both weakly bound, if at all, to

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[†] Dedicated to Professor Klaus Hafner on the occasion of his 60th birthday.

(1) Maercker, A.; Theis, M. *Top. Curr. Chem.* **1987**, *138*, 1 and references therein.

(2) For the solid-state structure of monolithiosulfones, see: Gais, H.-J.; Vollhardt, J.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 939 and references therein.

(3) (a) Truce, W. E.; Christensen, L. W. *J. Chem. Soc., Chem. Commun.* **1971**, 588. (b) Bosworth, N.; Magnus, P. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2319. (c) Tanaka, K.; Matsui, S.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3619. (d) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* **1980**, *21*, 4727. (e) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 610. (f) Eisch, J. J.; Dua, S. K.; Behrooz, M. *J. Org. Chem.* **1985**, *50*, 3676. (g) Hendrickson, J. J.; Boudreaux, G. J.; Palumbo, P. S. *J. Am. Chem. Soc.* **1986**, *108*, 2358. (h) McCombie, S. W.; Shankar, B. B.; Ganguly, A. K.; Padwa, A.; Bullock, W. H.; Dyszlewski, A. D. *Tetrahedron Lett.* **1987**, *28*, 4127 and citations in ref 4, footnote 4.

(4) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 696.

(5) For a cursory note about the solid-state structure of $Li_2C(C{\equiv}C\text{-}t\text{-}Bu)_2$, see: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(6) Crystal data for $(\mathbf{1a})_6{\cdot}Li_2O{\cdot}(thf)_{10}$ are given in the Supplementary Material.

0002-7863/88/1510-0978$01.50/0