

Communications

The First Eight-Electron-Bonded *t*-Bu-DAB Complex.^{1,2} C-C Coupling of Two *t*-Bu-DAB Ligands on Mn. X-ray Structure of Mn₂(CO)₆(*t*-Bu-IAE), Hexacarbonylbis[1-(*tert*-butylimino)-2-(*tert*-butylamino)ethane]dimanganese, Containing a Novel, Asymmetrically Bridging, Eight-Electron-Donating IAE Ligand

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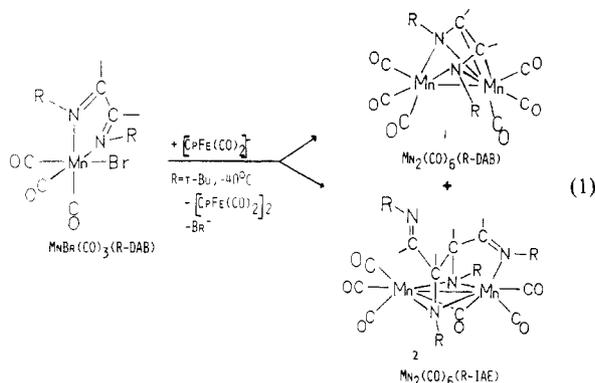
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Summary: Reaction of [CpFe(CO)₂]⁻ (Cp = η⁵-C₅H₅) with MnBr(CO)₃(*t*-Bu-DAB) yields the novel homodinuclear complexes Mn₂(CO)₆(*t*-Bu-DAB) (1) (10%) and Mn₂(CO)₆(*t*-Bu-IAE)² (2) (ca. 40%), together with [CpFe(CO)₂]₂. The α-dilimine ligand in 1 is eight-electron bonded, which is unprecedented for *t*-Bu-DAB; the X-ray crystal of 2 shows a *t*-Bu-IAE ligand formed by a reductive C-C coupling of two *t*-Bu-DAB ligands and acting as an asymmetrically bridging, eight-electron donor.

Coordination of R-DAB ligands,² either to one metal or to different metals at the same time, may result in activation of the α-diimine skeleton. For the latter, multi-site-bonded R-DAB complexes, this activation can lead to C-C, C-H, N-C, or N-H bond formation.³ Such multi-site-bonded R-DAB complexes are synthesized by reacting polynuclear carbonyls with R-DAB as well as by reacting carbonyl metalates with R-DAB-containing metal bromides.

Examples of this latter strategy are the reactions of MBr(CO)₃(R-DAB) (M = Mn, Re) with either one of the

following metalates: [Mn(CO)₅]⁻, [Co(CO)₄]⁻, or [HFe(CO)₄]⁻.⁴ As expected, the formation of dinuclear mixed-metal R-DAB complexes indeed occurs, presumably via a simple substitution reaction. We now report the reaction⁵ of [CpFe(CO)₂]⁻ (Cp = η⁵-C₅H₅) with MnBr(CO)₃(*t*-Bu-DAB) which reaction yields, rather than the expected mixed-metal complexes, only homodinuclear compounds: i.e., [CpFe(CO)₂]₂ (ca. 90% yield), in addition to Mn₂(CO)₆(*t*-Bu-DAB) (1) (less than 10% yield) and Mn₂(CO)₆(*t*-Bu-IAE)² (2) (ca. 40% yield); see eq 1.



The stoichiometry of complex 1 has been derived from the analytical and FD mass spectroscopic data,⁷ IR spectroscopy in the V(CO) region⁷ indicates that only terminal CO groups are present, while the NMR results⁷ are in line with an eight-electron-bonding mode for the *t*-Bu-DAB ligand.³ A very likely geometry of 1 is schematically presented in eq 1 and is analogous to that found for Mn₂(CO)₆(Me-DAB{Me,Me}) for which complex an X-ray crystal structure has been determined.⁸ The eight-electron-bonding mode of the α-diimine ligand in 1 shows that

(4) (a) Staal, L. H.; Keijsper, J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* 1979, 175, 73. (b) Staal, L. H.; Keijsper, J.; van Koten, G.; Vrieze, K.; Cras, J. A.; Bosman, W. P. *Inorg. Chem.* 1981, 20, 555. (c) Keijsper, J.; Grimberg, P.; van Koten, G.; Vrieze, K.; Kodice-Prodic, B.; Spek, A. L. *Organometallics* 1985, 4, 438. See also: ref 3b,d.

(5) A THF solution (50 mL) of [CpFe(CO)₂]⁻ was obtained from 3 mmol of CpFe(CO)₂ and NaK_{2,3} as described in the literature.^{6a} This solution was cooled to -40 °C and slowly added (in ca. 0.3 h) to 3 mmol of MnBr(CO)₃(*t*-Bu-DAB)^{6b} under additional stirring. After being stirred for 1 h at -40 °C, the solution was brought to room temperature and the THF was evaporated in vacuo. The resulting mixture was purified by column chromatography (silica). With hexane as eluent, 1 was obtained, giving ca. 10% (based on Mn) of orange crystals, when recrystallized at -80 °C from pentane. Elution with hexane/diethyl ether (1/1) and diethyl ether gave a large red-brown fraction containing [CpFe(CO)₂]₂ as evidenced by FD mass and IR spectroscopy. Elution with diethyl ether/THF (1/1) gave a very air-sensitive orange-red fraction, which was collected. Recrystallization from dichloromethane/diethyl ether (1/2) yielded 2 in ca. 40% yield (based on Mn). For analytical and spectroscopic data of 1 and 2, see ref 7 and 9.

(6) (a) Ellis, J. E.; Flom, A. E. *J. Organomet. Chem.* 1975, 99, 263. (b) Staal, L. H.; Oskam, A.; Vrieze, K. *ibid.* 1979, 170, 235.

(7) Spectroscopic data of Mn₂(CO)₆(*t*-Bu-DAB) (1). IR (CO) in hexane solution: 2025 (m), 1996 (s), 1938 (s), 1932 (s), 1918 (s) cm⁻¹. ¹H NMR (multiplicity, integral) in CDCl₃ solution, in ppm relative to SiMe₄: 6.45 (s, 1 H), 1.36 (s, 9 H). ¹³C NMR (assignment) in toluene-*d*₆ solution, in ppm relative to SiMe₄: 103.4 (imine C), 63.5 (NCMe₂), 34.4 (CH₃). FD mass, *m/z* value of highest peak in isotope pattern (calculated mass): 446 (446.2). Anal. Found (Calcd): C, 42.92 (43.07), H, 4.53 (4.52), N, 5.97 (6.28).

(8) Mn₂(CO)₆(Me-DAB{Me,Me}) has been prepared in 7% yield from the reaction of [Mn(CO)₄(CNMe)]⁻ with MeI: Adams, R. D. *J. Am. Chem. Soc.* 1980, 102, 7476.

(1) Part 14. For earlier parts, see, e.g., ref 3 and 4.

(2) R-DAB stands for 1,4-disubstituted 1,4-diaza-1,3-butadiene, RN=CHCH=NR, while RN=C(R₁)C(R₂)=NR is abbreviated as R-DAB{R₁,R₂}. See: van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* 1982, 21, 151. R-IAE stands for bis[(R-imino)(R-amino)ethane], RN=CHC(H)(NR)C(H)(NR)CH=NR; see ref 3a.

(3) (a) For C-C coupling reactions: Staal, L. H.; Polm, L. H.; Balk, R. W.; van Koten, G.; Vrieze, K.; Brouwers, A. M. F. *Inorg. Chem.* 1980, 19, 3343. Staal, L. H.; van Koten, G.; Vrieze, K.; van Santen, B.; Stam, C. H. *ibid.* 1981, 20, 3598. Staal, L. H.; Oskam, A.; Vrieze, K.; Roosendaal, E.; Schenk, H. *ibid.* 1979, 18, 1634. Keijsper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Abbel, G.; Stam, C. H. *ibid.* 1984, 23, 2142. (b) For C-H coupling reactions: Keijsper, J.; Grimberg, P.; van Koten, G.; Vrieze, K.; Christopherson, M.; Stam, C. H. *Inorg. Chim. Acta*, accepted for publication. (c) For N-C coupling reactions: Polm, L. H.; van Koten, G.; Vrieze, K.; Stam, C. H.; van Tunen, W. C. J. *J. Chem. Soc., Chem. Commun.* 1983, 1177. (d) For N-H coupling reactions: Keijsper, J.; Mul, J.; van Koten, G.; Vrieze, K.; Ubbels, H. C.; Stam, C. H. *Organometallics* 1984, 3, 1732.

t-Bu-DAB can act as an eight-electron-donor ligand just as, e.g., the *c*-Hx and *i*-Pr derivatives. Earlier, it has been tentatively suggested that for *t*-Bu-DAB eight-electron-coordination is thermodynamically unfavorable and indeed until now, no examples of isolated eight-electron-bonded complexes have been found although six-electron-bonded complexes have been observed.² The present results, however, indicate that eight-electron coordination for *t*-Bu-DAB can be accomplished when the proper kinetic pathway is applied.

Complex 2 has been characterized by analytical and spectroscopic techniques⁹ and its molecular geometry has been established by an X-ray diffraction study (see Figure 1).¹⁰ The metal carbonyl part of this complex consists of a (CO)₃Mn(μ-CO)Mn(CO)₂ unit with a rather short Mn-Mn single bond length of 2.585 (6) Å. The C(4)O(4) carbonyl is of the semibridging type with an asymmetry factor of $\alpha = 0.3$.¹¹ The two former *t*-Bu-DAB ligands, i.e., N(1)C(7)C(8)N(2) and N(3)C(9)C(10)N(4), are C-C coupled (C(7)-C(9) = 1.58 (2) Å), thus forming a new *t*-Bu-IAE ligand. Surprisingly, this ligand acts as an eight-electron donor that asymmetrically bridges the Mn-Mn bond via two bridging amine N atoms (N(1), N(3)) and via one σ -N-bonded imine N atom (N(2)). The other imine N(4) atom is clearly not coordinated to Mn. So far, in other dinuclear R-IAE, complexes, i.e., Ru₂(CO)₅(R-IAE) and Mo₂(CO)₆(R-IAE), the R-IAE ligand has acted as a symmetrically bridging, 10-electron donor.^{3a,12} Interestingly, the central N(1)C(7)C(9)N(3) part of the ligand in 2 is almost flat (maximum deviation from 1 *s*-plane: 0.1 Å), and it closely resembles an analogous NCCN part in (μ -H)FeMn(CO)₆(N(*p*-Tol)CH₂CH₂N(*p*-Tol)), also obtained from a reduction of two imine bonds.^{3b}

The IR spectrum of 2 in hexane solution shows four CO stretching frequencies in the terminal region and one, with a very small intensity, that can be assigned to the bridging carbonyl. The IR spectrum of the solid (KBr pellet), however, reveals the CO of the latter more pronounced at 1850 cm⁻¹.

(9) Spectroscopic data of Mn₂(CO)₆(*t*-Bu-IAE) (2), see ref 7 for an explanation of the used form. IR (CO) in hexane solution: 2019 (m), 1987 (s), 1926 (s), 1905 (m), 1875 (vw) cm⁻¹. ¹H NMR in toluene-*d*₆ solution, in ppm: 8.59 (d, 1 H, *J* = 2 Hz), 8.04 (d, 1 H, *J* = 2 Hz), 4.43 (d, 1 H, *J* = 2 Hz), 3.11 (d, 1 H, *J* = 2 Hz), 1.53 (s, 18 H), 1.18 (s, 18 H). ¹³C NMR in toluene-*d*₆ solution, in ppm: 184.7, 166.1 (imine C), 75.3, 65.9, 64.0, 62.3, 62.1, 58.3 (amine C and NCMe₃), 31.4, 29.7 (CH₃). FD mass: *m/z* 614, 307 (614.5). Anal. Found (Calcd): C, 50.20 (50.82), H, 6.64 (6.56), N, 8.62 (9.12).

(10) (a) Crystal data of 2: C₂₈H₄₀Mn₂N₄O₆, *M* = 614.5, orthorhombic, space group P2₁2₁2₁, *Z* = 4, *a* = 16.878 (7) Å, *b* = 19.394 (9) Å, *c* = 9.084 (3) Å, *d*_{calc} = 1.37 g cm⁻³, μ = 8.6 cm⁻¹, crystal dimensions 0.50 × 0.33 × 0.08 mm; total number of accessible reflections, measured on a Nonius CAD 4 diffractometer, using graphite-monochromatized Mo K α radiation (1.1 < θ < 22°), 2082; observed reflections (>2.5 σ (*I*)) used in the refinement, 114.1. The number of reflections is rather small because of poor crystal quality. The structure was solved by the heavy-atom technique. After isotropic block-diagonal least-squares refinement an empirical absorption correction was applied.^{10b} The refinement was continued anisotropically, with the H atoms fixed at their calculated position, resulting in an *R* value of 0.056 (*R*_w = 0.087). Refinement of the inverted structure resulted in *R* = 0.053 (*R*_w = 0.083), implying that this structure represented the correct absolute configuration for the crystal used. The coordinates (supplementary material) refer to this structure. A weighting scheme of $w = 1/(5.2 + F_o + 0.034F_o^2)$ was used. The final difference synthesis showed excursions between -0.2 and +0.3 e/Å³. Computations used,^{10c} atomic scattering factors, and anomalous dispersion correction for Mn^{10d} were taken from the literature. (b) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1983, A39, 158. (c) Stewart, J. M. "The X-RAY 76 - system", Report TR-466, Computer Science Center, University of Maryland: College Park, MD, 1976. (d) "International Tables for X-ray crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(11) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* 1980, 19, 2096.

(12) Van Koten, G.; Jastrzebski, J. T. B. J.; Vrieze, K. J. *Organomet. Chem.* 1983, 250, 49 and references therein.

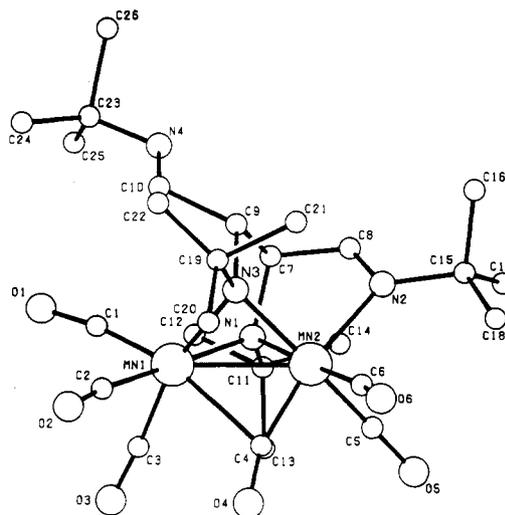


Figure 1. The molecular geometry of Mn₂(CO)₆(*t*-Bu-IAE) with some important bond lengths in angstroms and bond angles in degree (esd): Mn(1)-Mn(2) = 2.585 (6), Mn(1)-N(1) = 2.04 (1), Mn(1)-N(3) = 2.03 (1), Mn(2)-N(1) = 2.04 (1), Mn(2)-N(2) = 2.06 (1), Mn(2)-N(3) = 2.16 (1), Mn(1)-C(4) = 2.34(2), Mn(2)-C(4) = 1.81 (2), Mn-C(10) = 1.79 (2) (mean), N(1)-C(7) = 1.47 (2), C(7)-C(9) = 1.58 (2), C(9)-C(3) = 1.42 (2), C(9)-C(10) = 1.50 (3), N(4)-C(10) = 1.29 (2), C(7)-C(8) = 1.54 (3), N(2)-C(8) = 1.31 (3), C-O = 1.16 (2) (mean), N-C(*t*-Bu) = 1.53 (3) (mean), C-C(*t*-Bu) = 1.53 (4) (mean); Mn(1)-C(4)-O(4) = 122 (1), Mn(2)-C(4)-O(4) = 162(1), Mn-C-O(terminal) = 171 (3) (mean), N(1)-C(7)-C(8) = 110 (1), N(1)-C(7)-C(9) = 105 (1), C(7)-C(8)-N(2) = 117 (2), C(7)-C(9)-N(3) = 105 (1), C(7)-C(9)-C(10) = 108 (1), C(9)-C(10)-N(4) = 120 (2), C(8)-C(7)-C(9) = 104 (1), N-C-C(*t*-Bu) = 110 (4) (mean), C-C-C(*t*-Bu) = 109 (2) (mean). Standard deviation of the mean value is calculated by $\sigma = \{\sum_i(X_i - \bar{X})^2/(N - 1)\}^{1/2}$.

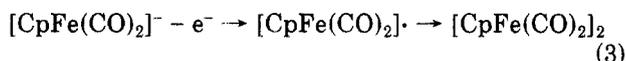
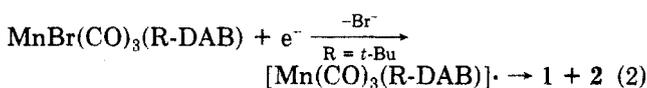
The ¹H NMR spectrum of 2 shows only two inequivalent *t*-Bu groupings and four inequivalent NC(H) protons, all appearing as doublets. Two of these doublets are observed in the imine region near 8 ppm and two at about 4 ppm. The ¹³C NMR data are likewise: two inequivalent *t*-Bu signals and four inequivalent imine C signals. These features most likely arise from an intramolecular exchange reaction. In this reaction a Mn(1)-N(4) bond is formed and the Mn(2)-N(2) one broken, while the bridging C-(4)O(4) carbonyl group becomes terminally bonded to Mn(2) and is replaced by a bridging C(3)O(3) group (see Figure 1 for the atom numbering). A likely intermediate in this exchange process is a complex containing a 10-electron-bonded *t*-Bu-IAE ligand in which both imine N atoms are coordinated, while the Mn-Mn single bond is absent.¹³ In Ru₂(CO)₅(R-IAE) this latter bonding situation is present, and in fact, such a bonding situation has been anticipated for a complex with the stoichiometry of 2.

As the result of the above described exchange reaction, the *t*-Bu groupings, evidently being in the fast exchange, give two signals: one for both C=N-*t*-Bu parts and one for both C-N-*t*-Bu parts. The four NC(H) groupings, still being in the slow exchange as the result of a large chemical shift difference, give rise to four signals. A further strong indication for the existence of the proposed exchange process is that when in the ¹H NMR spectrum the doublet at 8.59 ppm is irradiated, the imine proton signal at 8.04

(13) Another possible, electron-precise, intermediate may be a six-electron-bonded *t*-Bu-IAE complex, i.e., a complex in which both imine N atoms are not coordinated and containing a Mn-Mn double bond. In Fe₂(CO)₈L₂ with L₂ representing two C(imine)-C(imine) coupled α -imino ketones, an analogous six-electron-bonding mode is present; i.e., both amino functions are bridging the Fe-Fe bond while the two keto functions are not coordinated: De Cian, A.; Weiss, R. *J. Chem. Soc., Chem. Commun.* 1976, 249.

ppm vanishes, probably as the result of spin saturation transfer. The signal at 3.11 ppm then appears as a singlet while the signal at 4.43 ppm remains a doublet.¹⁴ These data^{14a} indicate that the signal at 8.59 ppm is coupled to that at 3.11 ppm. Moreover, they show that the rate of the intramolecular exchange reaction is less than 150 Hz, being the chemical shift difference in Hz between the two imine signals. Unfortunately, temperature-dependent measurements are severely hindered by decomposition above 30 °C and precipitation below -10 °C. Evidently, more experiments are needed to get a clear picture of the dynamic behavior of **2** in solution.

Generally for a reaction of a metalate (M^-) with a metal halide, several reaction routes have to be considered.¹⁵ Until now, reactions of M^- with $MnBr(CO)_3(R-DAB)$ have yielded heterodinuclear $MnM-R-DAB$ complexes only, which results can be interpreted on basis of simple substitution reactions.^{4,16} In the present reaction, however, only homodinuclear compounds are obtained. A likely reaction route¹⁷ involves an electron transfer mechanism and is outlined in eq 2 and 3. The $[Mn(CO)_3(t-Bu-DAB)]^-$



radical, which possibility of existence has been proven in 2-Me-THF at 230 K, has spin density on Mn ($a_{Mn} = 9.53$ G) and on the imine N and C atoms ($a_N = 7.40$ and $a_H = 4.75$ G).¹⁸ Mn-Mn coupling, followed by elimination of one *t*-Bu-DAB ligand and coordination of the two imine bonds of the other, then may yield **1**, while C-C coupling may yield the IAE complex **2**.¹⁹ It seems not possible to convert **2** into **1** (or vice versa) which excludes the possibility that **2** is formed first via a coupling reaction after which **1** is formed as the result of an elimination reaction.

The following conclusions can be drawn from these results: i, *t*-Bu-DAB can act as an eight-electron donor ligand; ii, *t*-Bu-IAE formation is possible on Mn, probably via an electron-transfer mechanism;¹⁹ iii, *t*-Bu-IAE can act as an asymmetrically bridging, eight-electron donor.²⁰

Acknowledgment. We thank the Netherland Foundation for Chemical Research (S.O.N.) and the Netherland

(14) (a) Alternatively, irradiation of the doublet at 4.43 ppm causes disappearance of the signal at 3.11 ppm, while the signal at 8.04 ppm appears as a singlet and that at 8.59 ppm still as a doublet. This indicates that the signal at 4.43 ppm is coupled to that at 8.04 ppm. (b) For an analogous spin saturation transfer in a coupled system see, e.g., Fung, B. M. *J. Chem. Phys.* 1967, 47, 1409.

(15) (a) Dessy, R. E.; Weissman *J. Am. Chem. Soc.* 1966, 88, 5124. (b) Dessy, R. E.; Weissman, *Ibid.* 1966, 88, 5129.

(16) Interestingly, however, is that when the R-DAB containing metalate $[Mo(CO)_4(R-DAB)]^-$ is oxidized by $MnBr(CO)_3(R'-DAB)$, the C-C coupled product $Mo_2(CO)_6(R-IAE)$ is obtained after an oxidative CO elimination, together with a dinuclear Mn_2 species.^{3a} This oxidation reaction closely resembles the present reaction with $[Mo(CO)_4(R-DAB)]^-$ probably playing the electron-donating role of $[CpFe(CO)_2]^-$, and it seems therefore worthwhile to characterize carefully the Mn_2 product obtained in this reaction.^{3a}

(17) Another possible reaction route involves a substitution reaction, yielding a $(t-Bu-DAB)(CO)_3MnFeCp(CO)_2$ complex, followed by a redistribution reaction¹⁵ that affords the $[CpFe(CO)_2]_2$ dimer and a $[Mn(CO)_3(t-Bu-DAB)]^-$ anion. The latter anion may react with the starting complex to yield finally **1** and **2**.

(18) Kokkes, M. W.; Stufkens, D. J.; Oskam, A., to be submitted for publication.

(19) It is interesting to note that R-IAE formation in the reaction of R-DAB with Et_2Zn proceeds via a $[EtZn(R-DAB)]^-$ radical.¹²

(20) Until now, R-IAE formation has only been observed on Mo, Ru,^{3a} and Zn,¹² and in all complexes so far, R-IAE has acted as a symmetrically bridging, 10-electron-donating ligand.

Organization for Pure Research (Z.W.O.) for their financial support.

Registry No. 1, 96481-47-9; 2, 96455-74-2; $[CpFe(CO)_2]_2$, 12154-95-9; $[CpFe(CO)_2]^-$, 12107-09-4; $[Mn(CO)_3(t-Bu-DAB)]^-$, 96455-75-3; $MnBr(CO)_3(t-Bu-DAB)$, 70749-13-2.

Supplementary Material Available: Tables of atomic coordinates, all geometric data, anisotropic thermal parameters, and structure factors (21 pages). Ordering information is given on any current masthead.

A Novel Rearrangement of α -Zirconocenyl Thioethers

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Summary: The thermolysis of $(\eta^5-C_5H_5)_2Zr(C_6H_5)[CH(Si(CH_3)_3)SCH_3]$ (**2**) in toluene solution follows first-order kinetics to give $(\eta^5-C_5H_5)_2Zr(SCH_3)[CH(Si(CH_3)_3)C_6H_5]$ (**4**), whereas under similar conditions $(\eta^5-C_5H_5)_2ZrX[CH(Si(CH_3)_3)SCH_3]$, X = Cl, CH₃, and CH₂C₆H₅, were found to be unreactive. A mechanism is put forward to account for the rearrangement of complex **2** to **4**, which also accounts for the observed lack of this reactivity pattern for $(\eta^5-C_5H_5)_2ZrX[CH(Si(CH_3)_3)SCH_3]$ under these conditions. Further thermolysis of complex **4** produces benzyltrimethylsilane and an as yet unidentified yellow precipitate.

Early-transition-metal alkyl complexes have been shown in recent years to exhibit a rich and varied chemistry. As a part of our investigation of the effect of α -heteroatom substituents on the reactivity of alkyl complexes of the early transition metals we have investigated the thermolysis of α -zirconocenyl thioethers.¹ Preliminary results of this study are reported here. The high oxygen affinity of Zr(IV) in Cp_2ZrR_2 and Cp^*ZrR_2 derivatives has been found in recent years to figure prominently in zirconocene chemistry. The reactivity of α -zirconocenyl ethers² and zirconocene- η^2 -acyl,³ η^2 -ketone,^{2b,3c,4} and η^2 -ketene complexes⁵ are dominated by the electrophilic nature of zirconium. We have found that the reactivity of α -zirconocenyl thioethers is sufficiently attenuated that these complexes are indefinitely stable in the dark at room temperature in contrast to the analogous α -zirconocenyl ether $Cp_2ZrCl[C(C_6H_5)_2OCH_3]$ which Erker et al.² have reported to be unstable with a half-life of 48 h at room temperature.

Many of these new α -zirconocenyl thioethers require prolonged heating in solution to undergo significant de-

(1) (a) Mintz, E. A.; Ward, A. S. 15th Central Regional Meeting of the American Chemical Society, Oxford, OH, May 1983; American Chemical Society: Washington, DC, 1983; Abstract No. 137. (b) Mintz, E. A.; Ward, A. S.; Lindeman, J. A. 186th National Meeting of the American Chemical Society: Washington, DC, August 1983; American Chemical Society: Washington, DC, 1983; Abstract No. INOR 339.

(2) (a) Erker, G.; Rosenfeldt, F. *Tetrahedron Lett.* 1981, 22, 1379-1382. (b) Erker, G.; Rosenfeldt, F. *Tetrahedron* 1982, 38, 1285-1291.

(3) (a) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* 1977, 1946-1950. (b) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 605-606. (c) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* 1982, 224, 29-42. (d) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* 1980, 102, 1747-1748. (e) Erker, G. *Acc. Chem. Res.* 1984, 17, 103-109.

(4) Rosenfeldt, F.; Erker, G. *Tetrahedron Lett.* 1980, 21, 1637-1640.

(5) (a) Straus, J. E.; Grubbs, R. H. *J. Am. Chem. Soc.* 1982, 104, 5499-5500. (b) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiera, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* 1983, 105, 2068-2070.