

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231719442>

Single and double base-induced migrations and rearrangements of group 14 ligand bimetallic complexes, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_m\text{M}(\text{ER}_2)_n\text{M}(\text{CO})_m(\eta^5\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Fe}$ ($m = 2$), W , Mo ($m = 3$); $(\text{ER}_2)_n\ldots$

ARTICLE in ORGANOMETALLICS · SEPTEMBER 1995

Impact Factor: 4.13 · DOI: 10.1021/om00009a033

CITATIONS

33

READS

154

6 AUTHORS, INCLUDING:



José L Mata-Mata

Universidad de Guanajuato

11 PUBLICATIONS 102 CITATIONS

SEE PROFILE

Single and Double Base-Induced Migrations and Rearrangements of Group 14 Ligand Bimetallic Complexes, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_m\text{M}(\text{ER}_2)_n\text{M}(\text{CO})_m(\eta^5\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Fe}$ ($m = 2$), W , Mo ($m = 3$); $(\text{ER}_2)_n = (\text{SiMe}_2)_2, (\text{SiMe}_2)_5, \text{GeMe}_2, \text{SnMe}_2$)

Sneh Sharma,[†] Jorge Cervantes,[‡] Jose Luis Mata-Mata,[‡] Mari-Carmen Brun,[†] Francisco Cervantes-Lee,[†] and Keith H. Pannell*,[†]

Departments of Chemistry, University of Texas at El Paso, El Paso, Texas 79968,
and Universidad de Guanajuato, Guanajuato, GTO 36050 Mexico

Received May 11, 1995[®]

Treatment of the bimetallic complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2(\text{ER}_2)_n$, $\text{Fp}(\text{ER}_2)_n\text{Fp}$ (**1**), $(\text{ER}_2)_n = \text{Si}_2\text{Me}_4$ (**1a**), $\text{Si}_5\text{Me}_{10}$ (**1b**), GeMe_2 (**1c**), and SnMe_2 (**1d**), with 1 equiv of lithium diisopropylamide, LDA, followed by quenching with MeI produced single-migration products $\text{Fp}(\text{ER}_2)_n(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}$, (**2a,c,d** from **1a,c,d**, respectively), and a mixture of single-, **2b**, and double-, $[\text{Me}(\text{CO})_2\text{Fe}(\eta^5\text{-C}_5\text{H}_4)]_2(\text{ER}_2)_n$ (**3b**), migration products from **1b**. Treatment of **1d** with of LDA, added slowly, also produced a novel dimeric complex $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{-SnMe}_2]_2$ (**4**) containing both Fe–Sn and $(\eta^5\text{-C}_5\text{H}_4)\text{-Sn}$ bonds. A single-crystal structure of this latter complex was determined. Treatment of the starting materials (**1a–d**) with 2 equiv of LDA followed by quenching with MeI yielded double-migration products, **3a–d**, in moderate yields, 30%–60%. Quenching the reaction between **1a** and either 1 or 2 equiv of LDA with Me_3SnCl yielded the analogous tin single- and double-migrated derivatives, **5** and **6**. Treatment of the analogous Mo and W tin complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2\text{SnMe}_2$, $\text{M} = \text{Mo}, \text{W}$, with LDA resulted in double-migration products, **7a,b**. However, similar treatment of the related tungsten germanium derivative resulted in cleavage of the W–Ge bond. After the reaction was quenched with MeI, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Me}$ was obtained.

Introduction

Since the report by Dean and Graham illustrating base-induced migrations of Ph_3Ge from Mo and W to the cyclopentadienyl ring in the system $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{-GePh}_3$ ($\text{M} = \text{Mo}, \text{W}$),¹ many other examples of this type of migration reaction have been reported. Thus silyl,² oligosilyl,³ germyl,⁴ stannyl,⁴ and plumbyl⁴ groups have all been shown to undergo such reactions. Certain carbon ligands have also been reported to migrate under similar conditions.⁵

We have observed that the reaction between $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{SiMe}_2\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ and lithium diisopropylamide, LDA, followed by treatment with MeI, resulted in the double-migration product $[\text{MeFe}(\text{CO})_2\text{-(}\eta^5\text{-C}_5\text{H}_4\text{)}]_2\text{SiMe}_2\text{SiMe}_2$.⁶ We now report an extension

of this study to a variety of group 14 bridged bimetallic complexes, $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_m]_2(\text{ER}_2)_n$ ($\text{M} = \text{Fe}, \text{Mo}, \text{W}$; $\text{ER}_2 = \text{Si}_2\text{Me}_4, \text{Si}_5\text{Me}_{10}, \text{GeMe}_2, \text{SnMe}_2$), in which both single and double migrations are possible and were observed under appropriate conditions. Together with the migration chemistry, a complex rearrangement resulted from the treatment of FpSnMe_2Fp with LDA.

Experimental Section

All reactions were performed under inert atmospheres, N_2 or Ar, using dry oxygen-free solvents and reagents. Starting complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_m]_2(\text{ER}_2)_n$ were synthesized using published procedures;^{6–9} LDA was used freshly prepared from $n\text{-BuLi}$ and diisopropylamine; alumina for column chromatography was Fisher 70–200 mesh. NMR spectra were recorded on a Bruker NR 200 MHz multinuclear spectrometer.

Representative synthetic procedures are described below, and the melting points, elemental analyses (performed by Galbraith Laboratories Inc.), and spectral data of the new complexes are recorded in Table 1.

Synthesis of $\text{Si}_2\text{Me}_4[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{SnMe}_3]_2$, **6.** In a 100-mL round-bottomed Schlenk flask was placed 0.32 g (0.68 mmol) of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SiMe}_2\text{SiMe}_2$ in 30 mL of THF. To this solution at 0 °C was added 3 mL (1.68 mmol) of freshly

[†] University of Texas at El Paso.

[‡] Universidad de Guanajuato.

[®] Abstract published in *Advance ACS Abstracts*, August 1, 1995.

(1) Dean, W. K.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1061.
(2) (a) Berryhill, S. R.; Sharenow, B. J. *J. Organomet. Chem.* **1981**, *221*, 143. (b) Thum, G.; Ries, W.; Malisch, W. *J. Organomet. Chem.* **1983**, *252*, C67. (c) Berryhill, S. R.; Clevenger, G. L.; Burdurlu, Y. P. *Organometallics* **1985**, *4*, 1509. (d) Heah, P. C.; Gladysz, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 7636. (e) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc. Chem. Commun.* **1985**, 283. (f) Pannell, K. H.; Rozell, J. M.; Lii, J.; Tien-Mayr, S.-Y. *Organometallics* **1988**, *7*, 2525.

(3) (a) Pannell, K. H.; Hernandez, C.; Cervantes, J.; Cassias, J.; Vincenti, S. P. *Organometallics* **1986**, *5*, 1056. (b) Crocco, J. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1988**, *7*, 2158.

(4) Cervantes, J.; Vincenti, S. P.; Kapoor, R. N.; Pannell, K. H. *Organometallics* **1989**, *8*, 744.

(5) (a) Abbot, S.; Baird, G. J.; Davies, S. G.; Dordor-Hedgcock, I. M.; Maberly, T. D.; Walker, J. C.; Warner, P. J. *Organomet. Chem.* **1985**, *289*, C17. (b) Pannell, K. H.; Vincenti, S. P.; Scott, R. C. *Organometallics* **1987**, *6*, 1593.

(6) Pannell, K. H.; Cervantes, J.; Parkanyi, L.; Cervantes-Lee, F. *Organometallics* **1990**, *9*, 859.

(7) (a) Job, C. R.; Curtis, M. D. *Inorg. Chem.* **1973**, *12*, 2514. (b) Scibelli, J. V.; Curtis, M. D. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 399.

(8) Patil, H. R. H.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 1401.

(9) (a) O'Connor, J.; Corey, E. R. *Inorg. Chem.* **1967**, *6*, 968. (b) Biryukov, B. P.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 488.

Table 1. Spectral Properties for New Complexes^a

(η^5-C₅H₅)Fe(CO)₂SiMe₂SiMe₂(η^5-C₅H₄)Fe(CO)₂Me, 2a	
yield; mp; anal. C, H, calcd (found)	40%; 55 °C; C, 47.14 (46.98); H, 4.99 (5.07)
¹ H	0.3 (SiMe), 0.1 (FeMe), 4.2 (C ₅ H ₅), 4.8, 5.1 (C ₅ H ₄)
¹³ C	-22.4 (FeMe), -2.3 (SiMe), 3.3 (SiFe), 83.1 (C ₅ H ₅), 88, 93 (C ₅ H ₄), 216, 218 (CO)
²⁹ Si	15.9, -16.3
ν (CO)	2010, 1999, 1956, 1948
(η^5-C₅H₅)Fe(CO)₂(SiMe₂)₅(η^5-C₅H₄)Fe(CO)₂Me, 2b	
²⁹ Si	23.1 (Fe-Si), -18.4, -31.3, -38.8, -42.4
(η^5-C₅H₅)Fe(CO)₂GeMe₂(η^5-C₅H₄)Fe(CO)₂Me, 2c	
yield; mp; anal. C, H, calcd (found)	66%; 65 °C; C, 43.38 (43.24); H, 3.85 (3.91)
¹ H	0.45 (FeMe), 0.75 (GeMe), 3.91 (C ₅ H ₅), 4.27, 4.44 (C ₅ H ₄)
¹³ C	-22.4 (FeMe), 5.56 (GeMe), 71.9 (C ₅ H ₅), 83.7, 91.1, 97.9 (C ₅ H ₄), 215.5, 218.6 (CO)
ν (CO)	2002, 1954
(η^5-C₅H₅)Fe(CO)₂SnMe₂(η^5-C₅H₄)Fe(CO)₂Me, 2d	
yield; mp; anal. C, H, calcd (found)	50%; 42 °C; C, 39.52 (38.97); H, 3.51 (3.44)
¹ H	0.49 (FeMe), 0.70 (SnMe), 4.08 (C ₅ H ₅), 4.35, 4.41 (C ₅ H ₄)
¹³ C	-22.6 (FeMe), -4.2 (SnMe), 81.6 (C ₅ H ₅), 82.2, 87.9, 93.6 (C ₅ H ₄), 214.8, 216.6 (CO)
¹¹⁹ Sn	120.0
ν (CO)	2008, 1996, 1951 (bd)
(SiMe₂)₅(η^5-C₅H₄)Fe(CO)₂Me]₂, 3b	
yield; mp; anal. C, H calcd (found)	34%; C, 46.45 (46.12); H, 6.55 (7.01)
¹ H	0.08, 0.10, 0.33, 0.41, (Me), 4.28 (C ₅ H ₄)
²⁹ Si	-18.6, -40.3, -42.9
ν (CO)	1987, 1978, 1941, 1933
GeMe₂(η^5-C₅H₄)Fe(CO)₂Me]₂, 3c	
yield; mp; anal. C, H calcd (found)	29%; yellow-orange oil; C, 44.64 (44.55); H, 4.16 (4.24)
¹ H	0.42 (GeMe), 0.6 (FeMe), 4.3, 4.4 (C ₅ H ₄)
¹³ C	-1.82 (GeMe), -22.7 (FeMe), 87.5, 92.2 (C ₅ H ₄), 217.8 (CO)
ν (CO)	2010, 1957
SnMe₂(η^5-C₅H₄)Fe(CO)₂Me]₂, 3d	
yield; mp; anal. C, H calcd (found)	60%; brown-orange oil; C, 40.74 (40.23); H, 3.79 (4.08)
¹ H	0.1 (SnMe), 0.25 (FeMe), 4.5, 4.7 (η^5 -C ₅ H ₄)
¹³ C	-22.7 (FeMe), -8.8 (SnMe), 88.3, 94.3 (C ₅ H ₄), 217.9 (CO)
¹¹⁹ Sn	-26.6
ν (CO)	2010, 1956
[(η^5-C₅H₄)Fe(CO)₂SnMe₂]₂, 4	
yield; mp; anal. C, H calcd (found)	25%; 158–160 °C; C, 33.29 (33.70); H, 3.10 (3.04)
¹ H	0.50 (Me), 4.28, 4.66 (C ₅ H ₄)
¹³ C	-4.46 (Me), 83.6, 86.8, 91.5 (C ₅ H ₄), 215.5 (CO)
¹¹⁹ Sn	124.2
ν (CO)	1987, 1942
(η^5-C₅H₅)Fe(CO)₂SiMe₂SiMe₂(η^5-C₅H₄)Fe(CO)₂SnMe₃, 5	
yield; mp; anal. C, H calcd (found)	30%; 75 °C; C, 39.85 (39.47); H, 4.77 (5.08)
¹ H	0.28 (SiMe), 0.48 (SnFe), 4.12 (C ₅ H ₅), 4.15, 4.17 (C ₅ H ₄)
¹³ C	-4.8 (SiFe), -3.4 (SiMe), -2.07 (SnMe), 82.7 (C ₅ H ₅), 83.06, 86.8 (C ₅ H ₄), 215.3, 215.6 (CO)
²⁹ Si	16, -16.1
ν (CO)	2010, 1990, 1956, 1940
Si₂Me₄(η^5-C₅H₄)Fe(CO)₂SnMe₃]₂, 6	
yield; mp; anal. C, H calcd (found)	65%; 178 °C; C, 36.22 (36.32); H, 4.81 (4.65)
¹ H	0.28 (SiMe), 0.48 (SnMe), 4.2, 4.22 (C ₅ H ₄)
¹³ C	-2.94 (SnMe), -4.5 (SiMe), 87.4, 89.04 (C ₅ H ₄), 215.8 (CO)
²⁹ Si	-23.2
ν (CO)	1990, 1940
SnMe₂(η^5-C₅H₄)Mo(CO)₃Me]₂, 7a	
yield; mp; anal. C, H calcd (found)	29%; 84–86 °C; C, 36.02 (36.05); H, 3.02 (3.13)
¹ H	0.47 (SnMe), 0.52 (MoMe), 4.6, 4.9 (C ₅ H ₄)
¹³ C	-21.7 (MoMe), -8.2 (SnMe), 92.4, 97.7, 98.7 (C ₅ H ₄), 227.3 (CO)
ν (CO)	2020, 1941, 1934
SnMe₂(η^5-C₅H₄)W(CO)₃Me]₂, 7b	
yield; mp; anal. C, H calcd (found)	41%; 98–100 °C; C, 28.50 (28.57); H, 2.39 (2.30)
¹ H	0.58 (SnMe), 0.7 (WMe), 4.7, 5.0 (C ₅ H ₄)
¹³ C	-34.4 (WMe), -7.9 (SnMe), 90.9, 96.9, 97 (C ₅ H ₄), 216.7 (CO)
ν (CO)	2016, 1933, 1922
SiMeH[(η^5-C₅H₄)Fe(CO)₂Me]₂, 8	
yield; mp; anal. C, H calcd (found)	29%; unstable oil, no analysis
¹ H	0.40 (FeMe), 1.44 (SiMe), 4.3, 4.4 (C ₅ H ₄), 4.8 (Si-H)
¹³ C	-4.8 (SiMe), -22.4 (FeMe), 81.1, 87.4, 93.6 (C ₅ H ₄), 217.8 (CO)
ν (CO)	2010, 1957, 2142 (SiH)

^a NMR spectra were recorded in C₆D₆, and IR spectra were recorded in hexane. Chemical shifts are in δ , and ν (CO) are in cm⁻¹.

prepared LDA in the same solvent. The solution was stirred for 30 min, after which time infrared monitoring indicated the absence of the starting material and the concomitant formation of a species exhibiting $\nu(\text{CO})$ stretching frequencies at 1882, 1867, 1812, and 1753 cm^{-1} . To this solution at 0 °C was added 0.35 g (1.75 mmol) of Me_3SnCl . The solution was stirred for 30 min and warmed to room temperature. Infrared analysis indicated new $\nu(\text{CO})$ bands at 1978 and 1928 cm^{-1} . The solvent was removed *in vacuo*, and the residue was extracted with 50 mL of hexane, filtered, and concentrated to 3 mL, and placed upon a 1 \times 15 cm alumina column. Development of the column with hexane produced a yellow band which was eluted with a 20:80 methylene chloride–hexane solvent mixture. Subsequent to removal of the solvent, recrystallization from hexane yielded complex **6a** as a yellow crystalline solid (0.35 g, 0.44 mmol, 65%).

Synthesis of $\text{GeMe}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}]_2$, **3c.** To 30 mL of a THF solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{GeMe}_2$ (0.3 g, 0.65 mmol) was added 3 mL (1.68 mmol) of a 0.56 M LDA solution at 0 °C. The solution turned deep orange, and after the solution had been stirred for 2 h IR spectroscopy indicated the presence of $\nu(\text{CO})$ bands at 1882, 1867, 1812, and 1753 cm^{-1} . Addition of an excess of MeI resulted in the solution becoming green-brown and exhibiting $\nu(\text{CO})$ bands at 2000 and 1946 cm^{-1} . The solvent was removed, and the residue was extracted into hexane, filtered, concentrated to 5 mL, and placed upon an alumina column, 1 \times 15 cm. Elution with hexane developed a yellow band, which was collected and, after solvent removal, yielded **3c** as a yellow orange oil (0.092 g, 0.19 mmol, 29%).

A similar procedure was used to obtain $\text{SiMeH}[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}]_2$, **8** (29%), and $\text{SnMe}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}]_2$, **3d** (0.24 g, 0.46 mmol, 60%).

Synthesis of $\text{SnMe}_2[(\eta^5\text{-C}_5\text{H}_4)\text{W}(\text{CO})_3\text{Me}]_2$, **7b.** To 30 mL of a THF solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2\text{SnMe}_2$ (0.3 g, 0.36 mmol) was added 3 mL (1.68 mmol) of a 0.56 M LDA solution at 0 °C. The solution turned deep orange, and after the solution had been stirred for 2 h an IR spectrum indicated the presence of $\nu(\text{CO})$ bands at 1894, 1801, and 1712 cm^{-1} . An excess of MeI was added, and after 1 h infrared spectroscopic analysis showed the presence of $\nu(\text{CO})$ bands at 2009, 1970, and 1913 cm^{-1} . The solvent was removed *in vacuo*, and the residue was extracted with 50 mL of hexane, filtered, and, after solvent removal, the residue was dissolved in 5 mL of CH_2Cl_2 and placed on a 1 \times 15 cm alumina column. Elution with hexane developed a yellow band which was recovered and, subsequent to solvent removal and recrystallization from hexane, yielded **7b** as a yellow solid (0.13 g, 0.15 mmol, 42%).

The same synthetic procedure was applied to obtain $\text{SnMe}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_3\text{Me}]_2$, **7a** (26%).

Treatment of FpSnMe_2Fp , **1d, with 1 Equiv of LDA.** To a THF solution (60 mL) of **1d** (1.0 g, 1.99 mmol) was added 4.4 mL of a 0.56 M solution of freshly prepared LDA in THF at 0 °C. There was an immediate color change from yellow to red-orange. The solution was stirred for 1 h, at which time infrared monitoring indicated the formation of new bands at 1980, 1930, 1884, 1868, 1781, and 1750 cm^{-1} showing the formation of a substituted $[\text{Fp}]^-$ salt. This solution was then treated with an excess of MeI at 0 °C, and the resulting solution was warmed to room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in hexane, 10 mL, and placed upon a 2.5 \times 10 cm alumina chromatography column. The resulting yellow band was eluted with hexane and after collection a crude product mixture was obtained. Fractional crystallization from hexane yielded an initial crop of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{SnMe}_2]_2$, **4**, as a yellow crystalline material (0.32 g, 0.49 mmol, 25%). A second crop of crystalline material yielded $\text{FpSnMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}$ (0.51 g, 0.99 mmol, 50%).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{SiMe}_2[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}]_2$, **2a.** To 30 mL of a THF solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SiMe}_2\text{SiMe}_2$ (0.25 g, 0.53 mmol) was added 1 mL (0.56 mmol) of a 0.56 M LDA solution at 0 °C. The solution turned deep orange, and after the solution had been stirred

Table 2. Structure Determination Summary for 4

Crystal Data	
empirical formula	$\text{C}_{18}\text{H}_{20}\text{Fe}_2\text{O}_4\text{Sn}_2$
color; habit	yellow fragment
cryst size (mm^3)	$0.40 \times 0.28 \times 0.40$
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dims	$a = 7.749(2) \text{ \AA}$ $b = 9.161(3) \text{ \AA}$ $c = 15.649(5) \text{ \AA}$ $\alpha = 91.35(3)^\circ$ $\beta = 97.90(2)^\circ$ $\gamma = 103.67(3)^\circ$ $1067.4(6) \text{ \AA}^3$
volume	2
Z	649.4
fw	2.021 Mg/m^3
density (calcd)	3.676 mm^{-1}
abs coeff	624
$F(000)$	
Data Collection	
diffractometer	Siemens R3m/V
radiation	Mo K α ($\lambda = 0.71073 \text{ \AA}$)
temp (K)	295
monochromator	highly oriented graphite crystal
2θ range	$3.5\text{--}45.0^\circ$
scan type	ω
scan speed	variable; $3.00\text{--}15.00 \text{ deg/min. in } \omega$
scan range (ω)	1.20°
bkgd measmt	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
std reflns	3 measd every 97 reflns
index ranges	$0 \leq h \leq 8, -9 \leq k \leq 9, -16 \leq l \leq 16$
no. of reflns colld	3056
no. of independent reflns	2811 ($R_{\text{int}} = 1.06\%$)
no. of obsd reflns	2582 ($F > 3.0\sigma(F)$)
abs cor	semiempirical
min/max transmissn	0.0516/0.0858
Solution and Refinement	
syst used	Siemens SHELXTL PLUS (VMS)
soln	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
abs structure	N/A
extinction cor	$\chi = 0.0102(3)$, where $F^* = \frac{F[1 + 0.002\chi^2/\sin(2\theta)]^{-1/4}}$
hydrogen atoms	riding model, fixed isotropic U
wting scheme	$w^{-1} = \sigma^2(F) + 0.0011F^2$
no. of params refined	236
final R indices (obsd data)	$R = 2.35\%$, $wR = 3.91\%$
R indices (all data)	$R = 2.68\%$, $wR = 4.74\%$
goodness-of-fit	1.04
largest and mean Δ/σ	1.598, 0.455
data-to-param ratio	10.9:1
largest difference peak	0.56 e \AA^{-3}
largest difference hole	-0.47 e \AA^{-3}

for 30 min an IR spectrum exhibited six $\nu(\text{CO})$ bands (1991, 1933, 1882, 1867, 1812, and 1753 cm^{-1}). Addition of an excess of methyl iodide resulted in the formation of a brown-green color and new $\nu(\text{CO})$ bands at 2000, 1991, 1942, and 1937 cm^{-1} . Removal of the solvent *in vacuo* was followed by extraction into a 70:30 hexane–methylene chloride solvent mixture. This solution was filtered, concentrated to 5 mL, and placed upon an alumina column, 1 \times 15 cm. Elution with a hexane–methylene chloride solvent mixture (90:10) developed a yellow band which was collected. Recrystallization from the same solvent mixture yielded **2a** (0.15 g, 0.2 mmol, 38%).

The same procedure was applied to obtain the corresponding Me_3Sn derivative, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SiMe}_2\text{SiMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{SnMe}_3$, **5**.

Structural Determination of 4. Crystallographic data were collected on a Siemens R3m/V single-crystal diffractometer, and the structure was solved using the SHELXTL-PLUS software package. All the relevant data are provided in the accompanying Tables 2–5 and supporting information.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Sn(1)	-6324(1)	-2170(1)	5485(1)	44(1)
Fe(1)	-5012(1)	119(1)	6523(1)	41(1)
O(1)	-5803(6)	-1865(4)	7894(3)	79(2)
O(2)	-1529(5)	-473(5)	6534(3)	86(2)
C(1)	-6692(6)	1201(5)	5759(3)	50(2)
C(2)	-5102(6)	-1905(5)	4316(3)	47(2)
C(3)	-4074(7)	2440(5)	6554(3)	53(2)
C(4)	-5360(8)	2095(6)	7117(3)	59(2)
C(5)	-6956(7)	1304(6)	6624(3)	61(2)
C(6)	-9165(7)	-2634(7)	5025(4)	78(2)
C(7)	-5806(9)	-4219(6)	5980(4)	77(3)
C(8)	-5513(7)	-1090(6)	7347(3)	53(2)
C(9)	-2919(6)	-254(5)	6519(3)	52(2)
Sn(2)	571(1)	5577(1)	8687(1)	44(1)
Fe(2)	1070(1)	7636(1)	9876(1)	40(1)
O(3)	1733(6)	9892(4)	8619(3)	75(2)
O(4)	-2758(5)	7354(4)	9542(3)	72(2)
C(10)	2787(7)	8899(5)	10925(3)	61(2)
C(11)	1349(7)	7940(5)	11214(3)	52(2)
C(12)	1331(6)	6413(5)	10994(3)	44(2)
C(13)	2839(6)	6498(5)	10552(3)	51(2)
C(14)	3723(6)	8030(6)	10493(3)	57(2)
C(15)	2804(8)	4675(7)	8444(4)	76(2)
C(16)	-652(9)	6164(7)	7456(3)	84(3)
C(17)	1465(6)	8972(5)	9106(3)	49(2)
C(18)	-1239(6)	7456(5)	9668(3)	49(2)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U_{ij}* tensor.

Table 4. Selected Bond Lengths (\AA) for 4

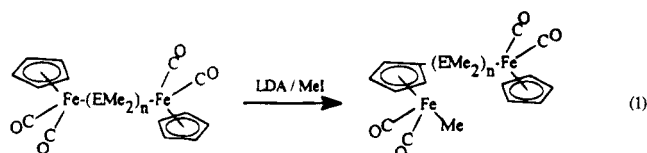
Sn(1)–Fe(1)	2.539(1)	Sn(2)–Fe(2)	2.541(1)
Sn(1)–C(2)	2.166(5)	Sn(2)–C(12)	2.173(4)
Sn(1)–C(7)	2.151(5)	Sn(2)–C(16)	2.165(6)
Fe(1)–C(8)	1.743(5)	Fe(2)–C(17)	1.743(5)

Table 5. Selected Bond Angles (deg) for 4

C(2)–Sn(1)–Fe(1)	110.2(1)	C(12a)–Sn(2)–Fe(2)	109.5(1)
C(6)–Sn(1)–C(7)	106.7(1)	C(15)–Sn(2)–C(16)	107.2(3)
C(8)–Fe(1)–C(9)	92.7(2)	C(17)–Fe(2)–C(18)	92.0(2)

Results and Discussion

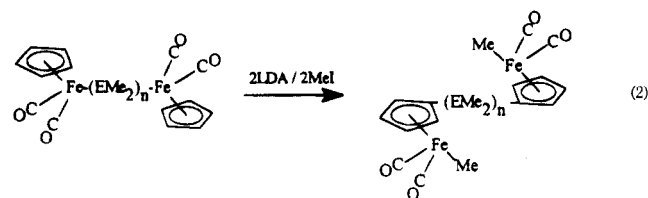
Treatment of the disilyl-, monogermyl-, and monostannyl-bridged bimetallic complexes **1a,c,d** with 1 equiv of LDA resulted in a single migration, such that quenching with MeI resulted in the formation of $\text{Fp}(\text{ER}_2)_n-(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}$, $(\text{ER}_2)_n = \text{Si}_2\text{Me}_4, \text{GeMe}_2, \text{SnMe}_2$, **2a,c,d**, eq 1. Quenching the reaction between **1a** and



LDA with Me_3SnCl resulted in the corresponding trimethyltin complex. NMR analysis of the crude reaction product provided no evidence for significant double migrations in these experiments.

Treatment of the same complexes **1a,c,d** with 2 equiv of lithium diisopropylamide in THF followed by quenching of the resulting metal carbonylate ions with either MeI (and in some cases Me_3SnCl) resulted in the isolation of the corresponding methyl (or stannyl) double-migration products in moderate to good yields, 30%–65%, eq 2.

In the case of the pentasilyl-bridged bimetallic complex, **1b**, treatment with 1 equiv of LDA always resulted



in a mixture of single and double migration. Changing LDA addition rates and temperatures did not change this outcome. We have been able to characterize the single-migration products only by ^{29}Si NMR spectroscopy in these mixtures. Addition of excess LDA, >2 equiv, permitted isolation of the pure double-migration product.

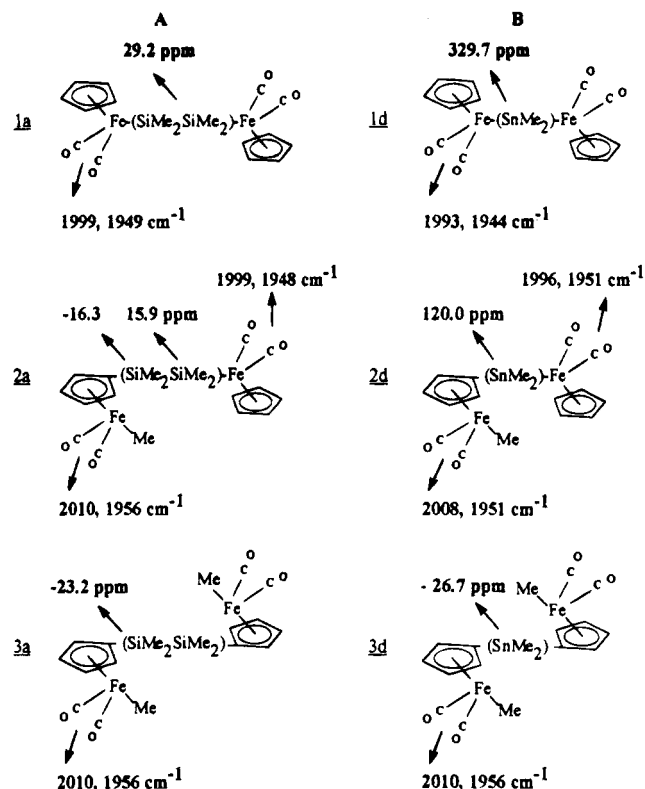
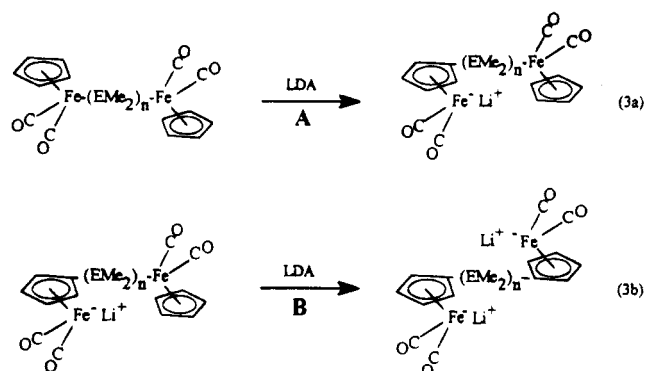


Figure 1. $\nu(\text{CO})$, ^{119}Sn and ^{29}Si NMR data for starting materials and for single- and double-migrated products, **1a,d**, **2a,d**, and **3a,d**.

The above results suggest that when the two Fe centers are close, bridged by only 1 or 2 atoms, initial deprotonation of one cyclopentadienyl ring and migration of the group 14 element to the ring produces an anion that significantly reduces the ability of the second cyclopentadienyl group to deprotonate, i.e., step A (eq 3a) is significantly favored over step B (eq 3b). Only



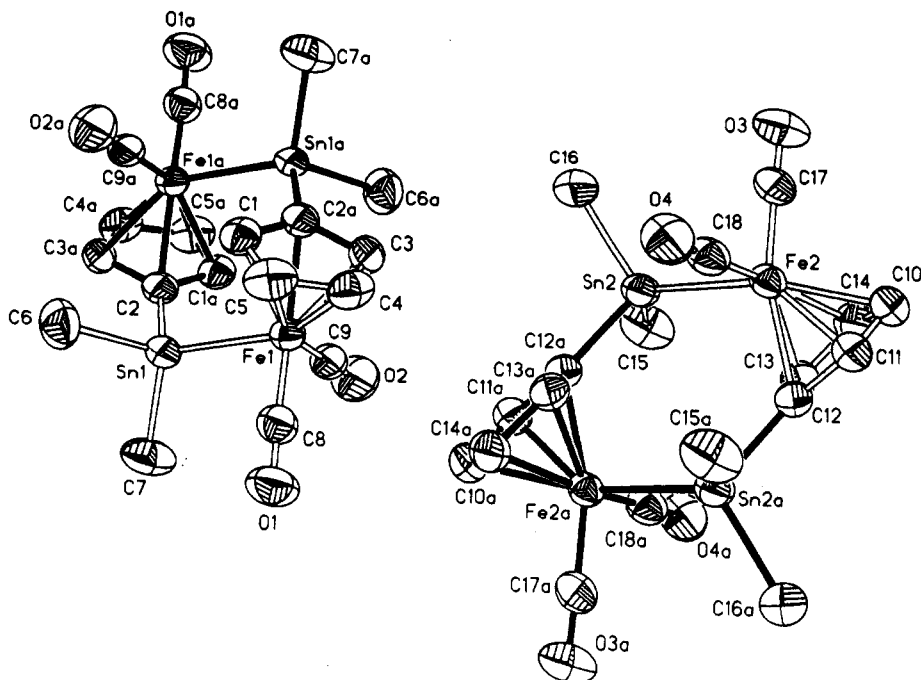


Figure 2. Structure of 4.

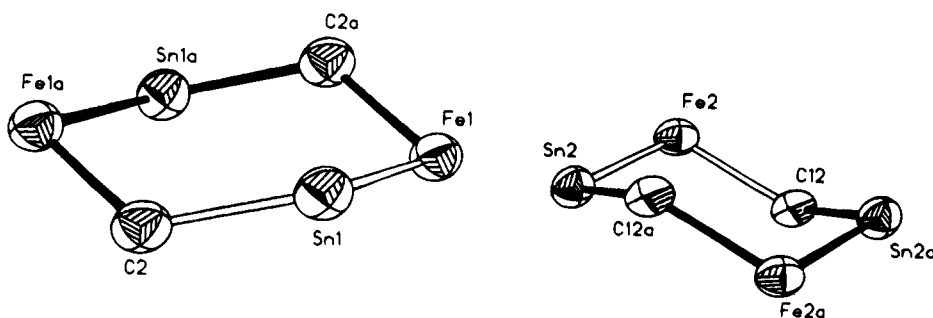


Figure 3. Conformations of the Sn-C-Fe-Sn-C-Fe ring in 4.

upon completion of the first process does the second process, **B**, commence. The inductive effect of negative charge at one end of the bridge may be expected to retard the deprotonation at the other end. A one- or two-atom bridging unit can transmit this effect, but with longer chains the effect is attenuated and the two ends of the complex act as independent and equivalent units.

The spectroscopic data for the new complexes are most informative with respect to detailing the changes in coordination at the transition metal center. Figure 1a illustrates the trends observed for the transformations **1a** → **2a** → **3a**, and Figure 1b does the same from the transformation **1d** → **2d** → **3d**. Thus the infrared stretching frequencies for the CO groups in $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnMe}_2$ at 1993 and 1944 cm^{-1} changed to 2010 and 1956 cm^{-1} upon transformation to the double-migration product $\text{SnMe}_2[(\text{C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{Me}]_2$ that now contains Fe-C bonds. The ^{119}Sn NMR signal for the two complexes changed from 329.7 to -26.7 ppm. Both these observations are in accord with previously reported data, and the spectra of the intermediate single-migration products exhibited bands associated with each "end" of the group 14 bridging ligand.^{4,6} Similarly the IR and ^{29}Si NMR data for the series **1a**, **2a**, and **3a** change in a systematic manner.

Analysis of the crude reaction mixtures using multinuclear NMR and GC/MS sometimes exhibited products from reactions involving the cleavage of the M-Sn and

M-Ge bonds in the starting materials, especially when an excess of LDA was used. Such reactions have been observed previously,⁴ and in the present study the double-migration product was sometimes contaminated with such cleavage products. For example, treatment of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2\text{SnMe}_2$ with an excess of LDA followed by quenching with Me_3SnCl resulted in small amounts of FpSnMe_3 , as determined by ^{119}Sn NMR (+143.5 ppm) and GC/mass spectrometry *via* the intermediacy of Fp^-Li^+ .

A greater amount of the cleavage reaction occurred when we studied the molybdenum complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2\text{SnMe}_2$, and quenching with MeI produced $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Me}$ together with the double-migration product, **7a**. Several purification steps were needed in order to obtain a pure analytical sample of **7a**, hence the relatively low recovered yield. Finally, the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]_2\text{GeMe}_2$ with LDA resulted in cleavage of the W-Ge bond to yield $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Me}]$ upon quenching with MeI.

Formation of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{SnMe}_2]_2$, 4. The reaction between FpSnMe_2Fp and LDA was a complex reaction. Rapid addition of the 2 equiv of base resulted in double migration; however, addition of 1 equivalent resulted in both a single-migration product and the distinctive reaction product 4. The mechanism for the formation of 4 is not clear. Clearly kinetic aspects of the chemistry are involved, including possible participation of intermediates from the Fe-Sn cleavage reactions

noted above; however, one of many speculative processes could be involved.

We obtained crystals of **4** suitable for a single-crystal X-ray analysis, and the structure of the complex is illustrated in Figure 2. It is similar to the analogous silicon complex recently reported by Sun and co-workers from the thermal rearrangement of $[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2(\mu\text{-SiMe}_2\text{SiMe}_2)$.¹⁰ The asymmetric unit consists of two molecular fragments, A and B. Fragment A contains atoms Fe1, Sn1, O1, O2, and C1–C9, and fragment B contains Fe2, Sn2, O3, O4, and C10–C18. Each fragment, through crystallographic symmetry, generates a dimeric molecule having a molecular center of symmetry coinciding with a crystallographic one at $-1/2, 0, 1/2$ for A and at $0, 1/2, 1$ for B. The dimers have similar

conformations but different orientations in the unit cell. The Fe–Sn bond length of 2.539(1) Å is in the normal range for such bonds, and the six-membered ring Fe–C–Sn–Fe–C–Sn assumes a typical chair conformation when viewed in the absence of ancillary atoms for clarity, Figure 3.

Acknowledgment. This research was supported by the R. A. Welch Foundation, Houston, TX; the NSF (Grant No. RII-88-02973); and a joint NSF/CONACyT Collaborative Research Award, No. Int-9002051.

Supporting Information Available: Tables listing anisotropic and isotropic displacement coordinates, H atom coordinates, torsion angles, and bond lengths and bond angles for **4** (7 pages). Ordering information is given on any current masthead page.

OM950341Z

(10) Sun, H.; Xu, S.; Zhou, X.; Wang, H.; Wang, R.; Yao, X. *J. Organomet. Chem.* **1993**, *444*, C41.