GeI_2, 13573-08-5; $BrCH_2CH_2Br$, 106-93-4; $Me_2Ge(Cl)(CH_2)_2Ge(Cl)Me_2$, 63746-65-6; $Me_2Ge(H)(CH_2)_2Ge(H)Me_2$, 120926-65-0; $Me_2Ge(nH)CH_2Ge(H)Me_2$, 106651-96-1; Me_3GeH, 1449-63-4; Me_4Ge, 865-52-1; $(Me_3GeCH_2GeMe_2)_2O$, 119796-07-5; $Me_2(C_6H_5)SiCH_2Cl$, 1833-51-8; $Me_2Si(Cl)CH_2Cl$, 1719-57-9; $Me_2(C_6H_5)SiCH_2SiCH)Me_2$, 27374-20-5; $Me_2(Br)SiCH_2Si(Br)mE_2$, 999-95-1; $Me_2(H)SiCH_2Si(H)Me_2$, 18163-84-3; Me_2SiHCl, 1066-35-9; $Me_2GeCH_2GeMe_2CH_2$, 24329-46-2; Et_2GeH_2, 1631-46-5; GeI_4, 13450-95-8; *t*-$BuPCl_2$, 25979-07-1; $C_6H_5PCl_2$, 644-97-3; Et_2GeCl_2, 13314-52-8; Me_3SnCl, 1066-45-1; $Me_2Ge(I)CH_2Ge(I)Me_2$, 106652-01-1; $Me_2Ge(Br)CH_2Ge(Br)Me_2$, 106652-02-2; $Me_2Ge(Cl)CH_2Ge(Cl)Me_2$, 98187-50-9; (*t*-BuP)$_3$, 61695-12-3; $(C_6H_5P)_5$, 3376-52-1; $Me_2Ge(I)CH_2CH_2Ge(I)Me_2$, 120926-66-1; $Me_2Ge(Br)CH_2CH_2Ge(Br)Me_2$, 120926-67-2; (*t*-BuP)$_4$, 5995-07-3.

Synthesis of (Alkoxymethyl)zirconocene Chlorides: Stereochemistry of Carbon–Carbon Bond Formation in a Zirconocene-Wittig Rearrangement

Stephen L. Buchwald,* Ralph B. Nielsen, and John C. Dewan

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 2, 1988

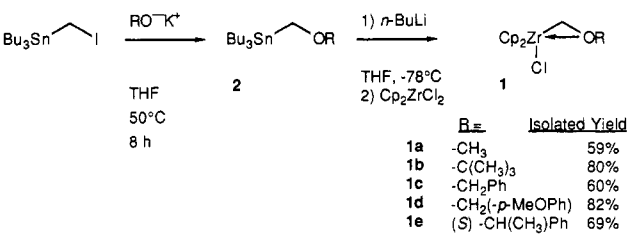
A series of (alkoxymethyl)zirconocene chlorides (**1**, $Cp_2Zr(Cl)CH_2OR$, Cp = η^5-C_5H_5) has been prepared by treatment of Cp_2ZrCl_2 with (alkoxymethyl)lithium reagents. Compound **1c**, $Cp_2Zr(Cl)CH_2OCH_2C_6H_5$, crystallizes in the orthorhombic space group *Pbca*, with a = 15.417 (9) Å, b = 18.249 (9) Å, c = 11.746 (8) Å, and Z = 8. The X-ray crystal structure shows that the alkoxymethyl ligand is η^2, with a significant Zr–O interaction. Compounds **1** with R = benzyl or substituted benzyl undergo a Wittig rearrangement when heated to give products **3** ($Cp_2Zr(Cl)OCH_2R$). The activation parameters that were determined for the transformation, the effects of substituents on the rate of the reaction, the identity of the reaction's side products, and the retention of configuration at the benzylic carbon are all consistent with the formation of a short-lived radical pair intermediate.

As part of a study directed toward the development of general synthetic routes to transition metal aldehyde complexes, we have synthesized a variety of (alkoxymethyl)zirconocene chlorides (**1**), as shown in Scheme I. Compounds **1** are crystalline, air- and moisture-sensitive solids. They exhibit ^{1}H NMR, ^{13}C NMR, IR spectra, and combustion analyses or high-resolution mass spectra that are consistent with the structures as shown. They are obtained in good to excellent yield by treatment of zirconocene dichloride with 1 equiv of an (alkoxymethyl)lithium, which is generated by treatment of an (alkoxymethyl)tributylstannane with *n*-butyllithium.[1] The stannanes **2a–e** are readily prepared by treatment of (iodomethyl)tributylstannane[2] with the appropriate potassium alkoxide or by treatment of (tributylstannyl)lithium[1] with a chloromethyl alkyl ether.

Compounds **1a** and **1b** are unaffected by heating to 110 °C for 8 h, but when the (benzyloxy)methyl compound **1c** is heated, it undergoes a rapid rearrangement to form a mixture of products, in which the (phenethyloxy)-zirconocene chloride (**3c**) predominates (ca. 70%, see Scheme II). The identify of **3c** was confirmed by an independent synthesis from Cp_2ZrCl_2 and phenethyl alcohol. Because of our interest in transition-metal-mediated carbon–carbon bond-forming reactions, we decided to further investigate this rearrangement.

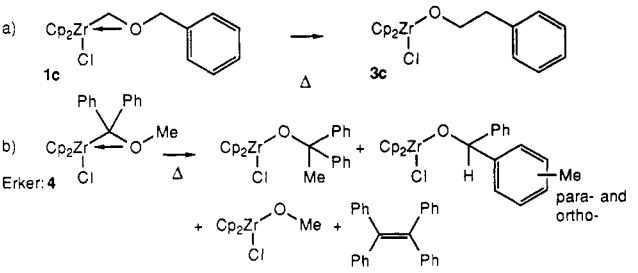
It should be noted that Erker[3] has reported the preparation of the α-(zirconocenyl)benzhydryl methyl ether **4**

Scheme I



	R =	Isolated Yield
1a	$-CH_3$	59%
1b	$-C(CH_3)_3$	80%
1c	$-CH_2Ph$	60%
1d	$-CH_2$(*p*-MeOPh)	82%
1e	(*S*) $-CH(CH_3)Ph$	69%

Scheme II



shown in Scheme II, and he found that it undergoes a similar rearrangement to give a mixture of products, including the Wittig-rearranged alkoxide. A similar product mixture also resulted from the reaction of the dimeric zirconocene–benzophenone complex with alkyl halides.[3b,c] As our study was being completed, Erker reported[3e] an alternate synthesis and the X-ray crystal structure of the methoxymethyl compound **1a**, and the methoxymethyl ligand was found to be η^2 in the crystal, despite examples of related ligands that are η^1.[4] Several lines of evidence had indicated to us that the alkoxymethyl ligands of **1a–e**

(1) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.
(2) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151.
(3) (a) Erker, G.; Dorf, U.; Atwood, J. J.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251. (b) Erker, G.; Rosenfeldt, F. *Tetrahedron Lett.* **1981**, *22*, 1379. (c) Erker, G.; Rosenfeldt, F. *Tetrahedron* **1982**, *38*, 1285. (d) Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1982**, *224*, 29. (e) Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403. (f) Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *338*, C4. (g) Erker, G.; Schlund, R.; Albrecht, M.; Sarter, C. *J. Organomet. Chem.* **1988**, *353*, C27.

(4) Young, S. Y.; Olmstead, M. M.; Knudsen, M. J.; Schore, N. E. *Organometallics* **1985**, *4*, 1432.

0276-7333/89/2308-1593$01.50/0

Table I. Kinetic Measurements for the Rearrangement of 1c–e

tube	compd	amount, mg	solv, μL	T, °C	$\tau_{1/2}$,[a] min	$10^{-4}k_{obsd}$, s (σ)
A	**1c**	19	550	80.4	68.0 (±1.2)	1.70 (0.01)
B	**1c**	19	550	80.4	68.0 (±1.2)	1.70 (0.01)
C	**1c**	19	550	80.4	68.4 (±1.2)	1.69 (0.01)
D	**1c**	19	550	90.4	20.5 (±0.3)	5.64 (0.03)
E	**1c**	19	550	90.4	20.0 (±0.5)	5.76 (0.05)
F	**1c**	19	550	90.4	19.5 (±0.4)	5.93 (0.04)
G	**1c**	19	550	100.4	6.9 (±0.2)	16.8 (0.01)
H	**1c**	19	550	100.4	6.8 (±0.3)	16.9 (0.02)
J	**1c**	19	550	100.4	7.7 (±0.3)	15.0 (0.02)
K	**1d**	19	550	90.4	26.1 (±1.2)	4.43 (0.07)
L	**1d**	19	550	90.4	25.5 (±0.7)	4.53 (0.04)
M	**1d**	19	550	90.4	26.0 (±0.4)	4.44 (0.02)
N	**1e**	20	580	100.7	1.5 (±0.2)	74 (3)

[a] Values in parentheses correspond to $\pm 3\sigma$.

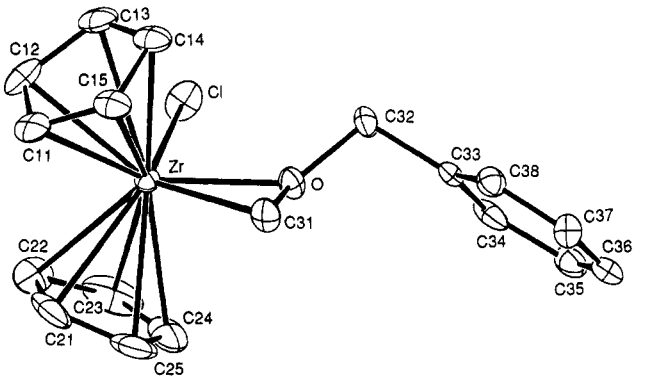


Figure 1. Molecular structure of **1c**.

are also η^2 in solution as shown in Figure 1. First, in the ^{1}H NMR spectra of **1**, protons bound to the carbon neighboring the oxygen (i.e. the benzylic protons of **1c**) are deshielded substantially (0.4–1.2 ppm) compared to analogous η^1 compounds such as the stannane starting materials. Second, treatment of compounds **1a–e** with trimethylsilyl iodide (TMSI)[5a,b] leads to quantitative and very rapid (less than 10 min) formation of the corresponding (alkoxymethyl)zirconocene iodides. In contrast to this, simple alkylzirconocene chlorides such as Cp_2Zr(Cl)Me undergo this transformation only very slowly ($\tau_{1/2} \approx 20$ h at 25 °C).[5c] This large rate enhancement for electrophilic halide exchange is consistent with the η^2 structure proposed for **1**, which would have greater electron density at the metal center. The remarkable fact that excess TMSI fails to cleave the R–O bond of what is formally a methyl, *tert*-butyl, or benzyl ether[5b] appears to be a result of the substantially reduced nucleophilicity of the coordinated oxygen. The X-ray crystal structure of **1c** (Figure 1) conclusively shows that the ligand adopts an η^2-O-inside conformation in a manner similar to that observed by Erker[3e] for **1a** and reminiscent of that seen in η^2-acyl complexes[6] and zirconocene–formaldehyde complexes.[7]

Activation parameters for the rearrangement of **1c** were obtained by using ^{1}H NMR in toluene-d_8 solution at 80–110 °C. The disappearance of **1c** follows first-order kinetics with $\Delta H^\ddagger = 28.9 \pm 1.5$ kcal/mol and $\Delta S^\ddagger = +5.6 \pm 4.2$ eu, which at 90 °C corresponds to $\Delta G^\ddagger = 26.8$ kcal/mol and $\tau_{1/2} = 20.0 \pm 0.6$ min. The first-order kinetics and slightly positive entropy of activation are consistent with a simple unimolecular rearrangement.

In order to further probe the mechanism of this transformation, we prepared the *p*-methoxy compound **1d** and the optically active methyl-substituted compound **1e** (>97% ee of the (*S*)-(−)-isomer). If the R–O bond of **1** is polarized or ionized in the transition state, the electron-donating substituent of **1d** should have a significant effect on the rate of the rearrangement. The methyl group of **1e** should also affect the rate of the reaction if the transition state involves ionization or homolysis of the R–O bond, and the chiral center acts as a stereochemical probe to determine whether the reaction proceeds with retention, inversion, or racemization.

Table II. Positional Parameters for 1c

atom	x	y	z
Zr	0.30549 (4)	0.09512 (3)	0.31848 (5)
Cl	0.33258 (13)	0.18152 (11)	0.48611 (16)
O	0.2187 (3)	0.1872 (2)	0.2785 (4)
C(11)	0.4236 (5)	0.0281 (4)	0.2148 (7)
C(12)	0.4622 (5)	0.0597 (5)	0.3138 (8)
C(13)	0.4624 (5)	0.1376 (5)	0.2952 (8)
C(14)	0.4213 (5)	0.1522 (4)	0.1918 (8)
C(15)	0.3982 (5)	0.0849 (4)	0.1412 (7)
C(21)	0.2611 (8)	−0.0358 (4)	0.3282 (12)
C(22)	0.2912 (7)	−0.0156 (8)	0.4421 (15)
C(23)	0.2246 (11)	0.0343 (7)	0.4813 (9)
C(24)	0.1665 (7)	0.0424 (5)	0.4002 (13)
C(25)	0.1845 (7)	0.0007 (5)	0.3074 (10)
C(31)	0.2167 (5)	0.1403 (4)	0.1784 (6)
C(32)	0.2226 (4)	0.2665 (3)	0.2661 (7)
C(33)	0.1334 (4)	0.2942 (3)	0.2330 (6)
C(34)	0.0718 (5)	0.3123 (4)	0.3179 (7)
C(35)	−0.0112 (5)	0.3388 (4)	0.2822 (8)
C(36)	−0.0320 (5)	0.3447 (4)	0.1652 (9)
C(37)	0.0291 (5)	0.3265 (4)	0.0844 (8)
C(38)	0.1115 (5)	0.3027 (4)	0.1175 (6)

Table III. Bond Distances (Å) for 1c

Cl–Zr	2.557 (2)	C(13)–C(12)	1.440 (12)
O–Zr	2.198 (4)	C(14)–C(13)	1.396 (11)
C(11)–Zr	2.509 (7)	C(15)–C(14)	1.409 (10)
C(12)–Zr	2.501 (7)	C(11)–C(15)	1.406 (11)
C(13)–Zr	2.555 (7)	C(22)–C(21)	1.463 (17)
C(14)–Zr	2.547 (7)	C(23)–C(22)	1.448 (16)
C(15)–Zr	2.533 (7)	C(24)–C(23)	1.315 (15)
C(21)–Zr	2.489 (8)	C(25)–C(24)	1.358 (14)
C(22)–Zr	2.498 (8)	C(21)–C(25)	1.378 (13)
C(23)–Zr	2.538 (9)	C(33)–C(32)	1.519 (9)
C(24)–Zr	2.538 (8)	C(34)–C(33)	1.416 (10)
C(25)–Zr	2.542 (8)	C(35)–C(34)	1.431 (11)
C(31)–Zr	2.294 (7)	C(36)–C(35)	1.415 (12)
C(31)–O	1.455 (8)	C(37)–C(36)	1.378 (11)
C(32)–O	1.456 (7)	C(38)–C(37)	1.398 (10)
C(12)–C(11)	1.427 (11)	C(38)–C(33)	1.406 (10)

(5) (a) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331. (b) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. (c) Buchwald, S. L.; Chang, V. L., unpublished results.

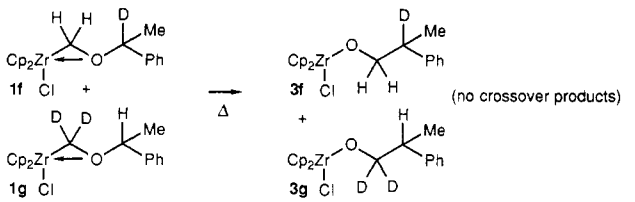
(6) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

(7) (a) Kropp, K.; Skibbe, V.; Erker, G.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, G. *J. Am. Chem. Soc.* **1983**, *105*, 1690.

Table IV. Bond Angles (deg) for 1c

Cl-Zr-O	78.0 (1)	C(24)-Zr-O	81.8 (3)
O-Zr-C(31)	37.7 (3)	C(25)-Zr-O	93.5 (3)
C(11)-Zr-Cl	123.8 (2)	C(33)-C(32)-O	108.7 (5)
C(12)-Zr-Cl	91.9 (2)	C(32)-O-C(31)	120.3 (5)
C(13)-Zr-Cl	74.9 (2)	Zr-O-C(31)	74.7 (3)
C(14)-Zr-Cl	94.8 (2)	Zr-O-C(32)	139.2 (4)
C(15)-Zr-Cl	125.9 (2)	C(32)-C(33)-C(34)	120.4 (7)
C(21)-Zr-Cl	127.0 (3)	C(32)-C(33)-C(38)	120.1 (6)
C(22)-Zr-Cl	93.8 (5)	C(38)-C(33)-C(34)	119.5 (7)
C(23)-Zr-Cl	76.7 (3)	C(15)-C(11)-C(12)	108.6 (7)
C(24)-Zr-Cl	94.6 (3)	C(11)-C(12)-C(13)	106.1 (8)
C(25)-Zr-Cl	125.2 (3)	C(12)-C(13)-C(14)	108.7 (6)
C(11)-Zr-O	135.3 (2)	C(13)-C(14)-C(15)	108.4 (7)
C(12)-Zr-O	141.3 (2)	C(14)-C(15)-C(11)	108.3 (7)
C(13)-Zr-O	108.7 (2)	C(25)-C(21)-C(22)	108.1 (10)
C(14)-Zr-O	89.4 (2)	C(21)-C(22)-C(23)	103.0 (9)
C(15)-Zr-O	102.9 (2)	C(22)-C(23)-C(24)	108.9 (11)
C(21)-Zr-O	125.2 (3)	C(23)-C(24)-C(25)	112.3 (10)
C(22)-Zr-O	133.5 (3)	C(24)-C(25)-C(21)	107.7 (10)
C(23)-Zr-O	101.3 (4)		

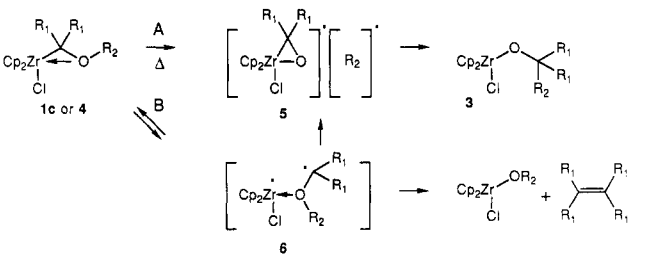
Scheme III



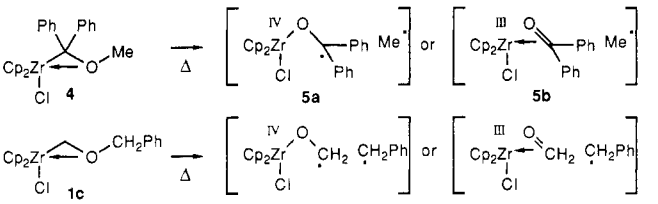
Compounds **1d** and **1e** rearrange upon heating to give product mixtures analogous to that obtained from **1c**. At 90 °C the half-life of **1d** is 25.9 ± 0.3 min, which is only slightly slower than the rate observed for **1c**. At 100 °C the observed half-life for **1e** is 1.5 ± 0.2 min, which is noticeably shorter than the half-life of 7.1 ± 0.6 min observed for **1c** at the same temperature. These relative reaction rates are inconsistent with a rate-determining ionization of **1** and are what should be expected for a rate-determining homolysis of the R–O bond (see Table I).

Capillary GC analysis of the organic products obtained by aqueous HCl hydrolysis of the products of thermolysis of **1c** also suggests the presence of radical intermediates. In addition to phenethyl alcohol (70%, from **3c**) and methyl benzyl ether (6%, from protonolysis of **1c**) is found bibenzyl (13%), which presumably comes from coupling of benzyl radicals.[8] No detectable amounts of benzyl chloride were observed, although it is a product that might be expected to form by abstraction of chlorine by the benzyl radical. Examination of the 2-phenyl-1-propanol obtained from hydrolysis of **3e** showed 70% ee of the *S*-(−) enantiomer, indicating that the major reaction pathway, as has been demonstrated for Wittig rearrangements involving main-group metals such as lithium,[9] proceeds with retention of configuration. Apparently the Zr(III)/benzyl radical pair is very short-lived, and recombination is fast relative to rotation of the benzyl radical. The deuterium-labeled compounds **1f** and **1g** (Scheme III) were prepared in order to determine whether the partial racemization in the rearrangement of **1e** might be due to a competing intermolecular pathway. Thermolysis of a 1:1 mixture of **1f** and **1g**, followed by hydrolysis and analysis of the 2-phenyl-1-propanol formed, showed only mono- and dideuterated compound and no detectable unlabeled or trideuterated material. This indicates that the reaction is >97% intramolecular. Therefore, the partial racemization is not attributable to a competing intermolecular mechanism.

Scheme IV



Scheme V



The aryl ring methylated side products[3b,c] observed in the rearrangement of Erker's complex **4** are consistent with homolysis of the R–O bond and the formation of intermediate zirconocene–benzophenone ketyl and methyl radicals. It is interesting to note that the (benzyloxy)methyl compound **1c** also undergoes homolysis to form radical intermediates, even though it lacks the two radical stabilizing α-phenyl substituents of **4**. Two possible reaction pathways are consistent with the observed behavior of **1c–e** and Erker's diphenyl-substituted complex **4**, as outlined in Scheme IV. Pathway A involves direct homolytic cleavage of a benzylic C–O bond to yield radical pair **5**. This radical pair can undergo recombination in the solvent cage to yield **3**, or it can diffuse to form bibenzyl and unknown organometallic side products. Pathway B involves a potentially reversible homolysis of a Zr–C bond, resulting in a Zr(III) diradical **6**, which may rearrange to form **5**. If **6** is sufficiently long-lived, it may couple in an intermolecular fashion to give olefin products and an alkoxyzirconocene chloride. The rearrangement of complex **4** is suggestive of pathway B because the product distribution is temperature dependent, and the products include tetraphenylethylene and chloromethoxyzirconocene as well as the "normal" alkoxide product **3**. Presumably the phenyl substituents stabilize intermediate **6**, and the formation of a high-energy methyl radical disfavors conversion of **6** to **5**. The lack of olefin byproducts in the rearrangement of **1c–e** is more suggestive of pathway A, although the intermediacy of **6** has not been ruled out.

A comparison of the radical pair intermediate **5** for the reaction of both **4** and **1c** is shown in Scheme V. The two phenyl substituents of **4** would tend to favor **5a** over **5b**, and the reactivity of a carbon-centered radical such as **5a** is consistent with the formation of ring-methylated products. However, the facile rearrangement of **1c** to form an unsubstituted zirconocene–formaldehyde ketyl implies that much of the stabilization in this case may be metal-centered and that the radical more closely resembles a Zr(III)–formaldehyde complex. The stability of the benzyl radical is an important factor, and the failure of the methoxymethyl complex **1a** and the *tert*-butoxymethyl complex **1b** to rearrange illustrates the necessity of having

(8) Good precedent exists that coupling of benzyl radicals is fast relative to H abstraction in toluene solvent. Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401. Buchwald, S. L.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 1766.

(9) Schollkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 763. Felkin, H.; Frajerman, C. *Tetrahedron Lett.* **1977**, 3485.

efficient radical-stabilizing substituents.

Experimental Section

General Data. All manipulations were conducted under nitrogen or argon atmosphere by using standard Schlenk techniques or in a Vacuum Atmospheres Co. drybox. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker WM-250, Bruker WM-270, Varian XL-300, Varian XL-400, and Varian VXR-500 Fourier transform spectrometers. IR spectra were recorded on an IBM IR/30S Fourier transform spectrometer. Gas chromatography analyses were performed on a Hewlett-Packard 5890 gas chromatograph with FID detector using a 25-m capillary column with cross-linked SE-30 as stationary phase. Gas chromatography/mass spectrum analyses were obtained by using a Hewlett-Packard System 5990A GC/MS. Electron-impact mass spectra and high-resolution mass determinations (HRMS) were recorded on a Finnegan MAT System 8200. Combustion analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI; Schwarzkopf Microanalytical Laboratory, Woodside, NY; or Desert Analytics, Tucson, AZ.

Tetrahydrofuran, benzene, diethyl ether, hexane, toluene-d_8, and benzene-d_6 were distilled or vacuum transferred from sodium/benzophenone ketyl. Cp_2ZrCl_2 was purchased from Boulder Scientific Inc., Mead, CO. CD_2I_2 (98.5% D),[10] TMSI,[5b] Bu_3SnLi,[1] and Bu_3SnCH_2I[2] were prepared according to published procedures. All other reagents were available from commercial sources.

Preparation of (Alkoxymethyl)stannanes. 2a. To a solution of KO-*t*-Bu (2.24 g, 20 mmol) in THF (15 mL) was added methanol (1.2 mL, 30 mmol) and Bu_3SnCH_2I (6.46 g, 15 mmol).[2] The mixture was stirred at 50 °C for 12 h and was then opened to air and poured into 200 mL of hexane. Extraction of the organic layer with 1 N HCl and 5% $NaHCO_3$, drying over $MgSO_4$, and evaporation of solvent gave **2a** (4.98 g, 99%): ^1H NMR (250 MHz, C_6D_6) δ 0.85–1.70 (m, 27 H), 3.20 (s, 3 H), 3.69 (s, tin satellites, J = 7.4 Hz, 2 H); $^{13}C\{^1H\}$ NMR (67.9 MHz, C_6D_6) δ 9.20, 13.86, 27.65, 29.54, 63.32, 64.29; IR (neat) 2957, 2925, 2872, 2856, 2806, 1465, 1376, 1094 cm^{-1}.

2b. To a solution of KO-*t*-Bu (4.49 g, 40 mmol) in THF (15 mL) was added Bu_3SnCH_2I (5.17 g, 12 mmol). The mixture was stirred at 50 °C for 12 h and was then opened to air and poured into 200 mL of hexane. Extraction of the organic layer with 1 N HCl/NaCl, drying over $MgSO_4$, evaporation, and Kugelrohr distillation (120 °C, 0.05 mm) yielded **2**: (4.43 g, 98%): ^1H NMR (250 MHz, C_6D_6) δ 0.80–1.10 (m, 15 H), 1.13 (s, 9 H), 1.16–1.75 (m, 12 H), 3.57 (s, tin satellites, J = 11 Hz, 2 H); $^{13}C\{^1H\}$ NMR (67.9 MHz, C_6D_6) δ 9.19, 13.95, 26.86, 27.64, 29.57, 50.37, 73.74; IR (neat) 2957, 2924, 2872, 2855, 1584, 1465, 1384, 1376, 1360, 1188, 1072, 1047, 1020, 858 cm^{-1}; HRMS calcd for $C_{17}H_{38}OSn$ 376.1941, found 376.1943 ± 0.0009 amu.

2c. Stannane **2c** has been synthesized from Bu_3SnCH_2I and $PhCH_2ONa$.[1] The following method is simpler on a larger scale. To a 0 °C solution of 20 mmol of Bu_3SnLi[1] in THF (150 mL) was added $ClCH_2OCH_2Ph$ (7.0 mL, 50 mmol, Aldrich). After 5 min at 0 °C, the mixture was opened to air and poured into 400 mL of hexane. Extraction of the organic layer with 1 N HCl/NaCl and 5% $NaHCO_3$, drying over $MgSO_4$, evaporation, and vacuum distillation (130–140 °C, 1 mm) yielded **2c** (20.26 g, 98%): ^1H NMR (250 MHz, $CDCl_3$) δ 0.80–1.10 (m, 15 H), 1.20–1.70 (m, 12 H), 3.75 (s, tin satellites, J = 10 Hz, 2 H), 4.42 (s, 2 H), 7.3–7.5 (m, 5 H); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 9.01, 13.71, 27.31, 29.16, 61.46, 76.57, 127.26, 127.47, 128.15, 138.94; IR (neat) 2956, 2926, 2871, 2853, 1464, 1454, 1376, 1360, 1084, 1067, 1028, 733, 696 cm^{-1}.

2d. To a 0 °C solution of KO-*t*-Bu (1.69 g, 15 mmol) in THF (10 mL) was added *p*-methoxybenzyl alcohol (2.76 g, 20 mmol). After 10 min, Bu_3SnCH_2I (4.30 g, 10 mmol) was added. The mixture was heated for 5 h at 45 °C, and the mixture was opened to air and poured into 60 mL of hexane. Extraction of the organic layer with 1 N HCl/NaCl, drying over $MgSO_4$, and evaporation yielded an oil that was purified by flash chromatography on silica gel (2% ether/hexane) to give **2d** (3.79 g, 86%): ^1H NMR (300 MHz, $CDCl_3$) δ 0.80–1.05 (m, 15 H), 1.20–1.60 (m, 12 H), 3.72 (s, tin satellites, J = 9 Hz, 2H), 3.81 (s, 3 H), 4.34 (s, 2 H), 6.87 (d, J = 9 Hz, 2 H), 7.23 (d, J = 9 Hz, 2 H); $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$) δ 9.03, 13.70, 27.31, 29.15, 55.23, 61.12, 113.59, 129.10, 131.05, 159.00; IR (neat) 2956, 2926, 2871, 2853, 1613, 1587, 1514, 1465, 1376, 1359, 1302, 1248, 1181, 1172, 1069, 1040, 821 cm^{-1}; HRMS calcd for $C_{21}H_{38}O_2Sn$ 440.1890, found 440.1897 ± 0.0009 amu.

2e. To a slurry of KH (0.722 g, 18 mmol) in THF (20 mL) was added dropwise (*S*)-(−)-*sec*-phenethyl alcohol (1.95 g, 16 mmol, $[\alpha]D^{20}$ = −41.3 (neat)). After 5 min Bu_3SnCH_2I (6.88 g, 16 mmol) was added dropwise. The mixture was heated to 60 °C for 1 h and was then poured into 200 mL of hexane in air. Extraction with 1 N HCl/NaCl and 5% $NaHCO_3$, drying over $MgSO_4$, and evaporation yielded an oil which was purified by flash chromatography on silica gel (2% ether/hexane) to give **2e** (4.25 g, 66%); d = 1.10 g/mL; $[\alpha]_D^{20}$ = −26.6 (neat); ^1H NMR (300 MHz, $CDCl_3$) δ 0.80–1.10 (m, 15 H), 1.20–1.75 (m, 15 H), 3.58 (ab of m, 2 H), 4.19 (q, J = 6.5 Hz, 1 H), 7.25–7.45 (m, 5 H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ 9.09, 13.83, 24.16, 27.38, 29.21, 59.37, 82.01, 126.19, 127.01, 128.16, 144.35; IR (neat) 2957, 2926, 2871, 2854, 1465, 1455, 1376, 1368, 1085, 1041, 1003, 875, 760, 700 cm^{-1}; HRMS calcd for $C_{21}H_{38}OSn$ 424.1941, found 424.1937 ± 0.0006 amu.

2f. To a 0 °C solution of $LiAlD_4$ (0.230 g, 5.5 mmol) in ether (20 mL) was added dropwise acetophenone (2.40 g, 20 mmol). The mixture was warmed to room temperature for 15 min. Ether (50 mL) was added, and the solution was extracted with 1 N HCl, dried over Na_2SO_4, and evaporated to give 1-deuterio-*sec*-phenethyl alcohol (2.36 g, 96%). The deuterated alcohol (1.72 g, 14 mmol) was added to a solution of KO-*t*-Bu (1.01 g, 9 mmol) in THF (10 mL). After 10 min, Bu_3SnCH_2I (3.45 g, 8 mmol) was added and the mixture stirred at 50 °C for 6 h. The reaction was opened to air and poured into 60 mL of hexane, and the organic layer was extracted with 1 N HCl, dried over $MgSO_4$, and evaporated, and the crude product was purified by flash chromatography on silica gel (2% ether/hexane) to give **2f** (1.74 g, 51%): ^1H NMR (300 MHz, $CDCl_3$) δ 0.85–1.15 (m, 15 H), 1.20–1.36 (m, 6 H), 1.36 (s, 3 H), 1.37–1.65 (m, 6 H), 3.55 (ab of m, 2 H), 7.20–7.40 (m, 5 H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ 9.03, 13.68, 23.84, 27.30, 29.14, 59.33, 81.50 (3 lines, weak), 126.30, 127.09, 128.21, 144.47.

2g. Bu_3SnCD_2I was prepared by using CD_2I_2[10] and the procedure of Seyferth and Andrews.[2] Reaction of (±)-*sec*-phenethyl alcohol and Bu_3SnCD_2I as in the preparation of **2f** yielded **2g** (2.51 g, 74%); ^1H NMR (300 MHz, $CDCl_3$) δ 0.85–1.05 (m, 15 H), 1.20–1.65 (m, 15 H), 4.16 (q, J = 6.6 Hz, 1 H), 7.20–7.40 (m, 5 H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ 9.00, 13.70, 24.03, 27.31, 29.19, 81.97, 126.29, 127.11, 128.22, 144.56.

General Procedure for the Preparation of Compounds 1a–g. Cp_2ZrCl_2 (0.730 g 2.50 mmol) was dissolved in THF (25 mL) and cooled with stirring to −78 °C. To a solution of the (alkoxymethyl)stannane **2** (2.88 mmol) in 15 mL of THF at −78 °C was added dropwise *n*-BuLi (2.88 mmol, ca. 1.6 M in hexane). After 5 min, the transmetalation mixture was added very rapidly via cannula into the Cp_2ZrCl_2 solution. After 30 min, the reaction was warmed to room temperature and the solvent was evaporated to yield two immiscible oils (the product **1** and Bu_4Sn). **1** solidified after continued evaporation, and the solid was then washed with 3 × 2 mL of hexane to remove most of the Bu_4Sn. The solid was extracted into 10 mL of benzene and filtered to remove LiCl. Evaporation of the solvent yielded **1** as a solid, which was washed with 3 × 2 mL of hexane and vacuum dried.

1a. From a 5-mmol scale reaction, 0.890 g (59%) **1a** was obtained as a white powder. ^1H NMR and ^{13}C NMR are identical with that previously reported.[3e]

1b. From a 5-mmol scale reaction, 1.39 g (80%) of **1b** was obtained as a white solid: ^1H NMR (300 MHz, C_6D_6) δ 1.18 (s, 9 H), 2.28 (s, 2 H), 5.74 (s, 10 H); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6) δ 28.16, 56.31, 84.48, 109.77; IR (KBr) 3101, 3083, 2972, 2932, 2868, 1442, 1390, 1367, 1260, 1245, 1164, 1130, 1017, 942, 918, 828, 801, 740, 532, 502, 425 cm^{-1}; HRMS calcd for $C_{15}H_{21}OZr$ (M^+ − Cl) 307.0635, found 307.0634 ± 0.0006 amu. Anal. Calcd for $C_{15}H_{21}ClOZr$: C, 52.37; H, 6.15. Found: C, 52.24; H, 6.20.

1c. From a 5-mmol scale reaction, 1.13 g (60%) of **1c** was obtained as a pale yellow solid: ^1H NMR (400 MHz, C_6D_6) δ 2.48 (s, 2 H), 4.63 (s, 2 H), 5.66 (s, 10 H), 7.05–7.30 (m, 5 H); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6) δ 64.90, 77.10, 109.55, 128.52, 128.80,

(10) Takaya, H.; Suzuki, T.; Kumagai, Y.; Yamakawa, M.; Noyori, R. *J. Org. Chem.* **1981**, *46*, 2846.

129.86, 136.15; IR (KBr) 3115, 2976, 2930, 2880, 2860, 1498, 1456, 1441, 1360, 1213, 1113, 1014, 982, 967, 924, 806, 795, 757, 704, 614, 484, 429 cm^{-1}. Anal. Calcd for $C_{18}H_{19}ClOZr$: C, 57.19; H, 5.07. Found: C, 57.38; H, 5.27.

1d. Reaction according to the general procedure yielded 0.840 g (82%) of **1d** as a white powder: ^1H NMR (300 MHz, C_6D_6) δ 2.47 (s, 2 H), 3.25 (s, 3 H), 4.66 (s, 2 H), 5.68 (s, 10 H), 6.76 (d, J = 9 Hz, 2 H), 7.26 (d, J = 9 Hz, 2 H); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6) δ 54.76, 63.54, 76.50, 109.57, 114.04, 131.88, 160.67; IR (KBr) 3113, 2963, 2931, 2866, 2835, 1613, 1585, 1515, 1438, 1370, 1303, 1260, 1245, 1180, 1173, 1119, 1110, 1028, 1016, 962, 929, 811, 799, 570, 528, 457, 440 cm^{-1}; HRMS calcd for $C_{19}H_{21}O_2Zr$ (M^+ - Cl) 371.0585, found 371.0584 ± 0.0006 amu. Anal. Calcd for $C_{19}H_{21}ClO_2Zr$: C, 55.93; H, 5.18. Found: C, 55.73; H, 5.23.

1e. Reaction according to the general procedure yielded 0.680 g (69%) of **1e** as a white solid: $[\alpha]_D^{20}$ = –66.3 (c = 4.8, benzene). ^1H NMR (400 MHz, C_6D_6) δ 1.41 (d, J = 7 Hz, 3 H), 2.08 (s, 1 H), 2.36 (s, 1 H), 5.23 (q, J = 7 Hz, 1 H), 5.59 (s, 5 H), 5.68 (s, 5 H), 7.05–7.40 (m, 5 H); $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6) δ 19.60, 57.06, 81.34, 109.53, 109.70, 128.41, 128.75, 128.89, 139.13; IR (KBr) 3104, 3087, 2989, 2935, 1493, 1455, 1379, 1358, 1286, 1210, 1119, 1106, 1045, 1023, 1013, 1005, 986, 926, 907, 837, 814, 804, 781, 740, 705, 530, 485 cm^{-1}; HRMS calcd for $C_{19}H_{21}OZr$ (M^+ - Cl) 355.0635, found 355.0636 ± 0.0005 amu. Anal. Calcd for $C_{19}H_{21}ClOZr$: C, 58.21; H, 5.40. Found: C, 58.33; H, 5.58.

1f. Reaction according to the general procedure yielded 0.400 g (41%) of **1f** as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 1.40 (s, 3 H), 2.08 (s, 1 H), 2.35 (s, 1 H), 5.59 (s, 5 H), 5.68 (s, 5 H), 7.05–7.40 (m, 5 H).

1g. Reaction according to the general procedure yielded 0.520 g (53%) of **1g** as a white solid: ^1H NMR (400 MHz, C_6D_6) δ 1.41 (d, J = 6 Hz, 3 H), 5.22 (q, J = 6 Hz, 1 H), 5.59 (s, 5 H), 5.68 (s, 5 H), 7.05–7.40 (m, 5 H).

Thermolysis of 1c, 1d, and 1e. Rate Measurements. NMR samples were prepared in 5-mm NMR tubes by using 0.550 mL of toluene-d_8 as solvent, as indicated below. To each tube was added 0.002–0.004 mL of mesitylene as an internal standard. The samples were heated in the NMR probe. During the reactions, the relative integrals of the entire Cp region (δ 5.6–6.4) and several reference peaks remained essentially constant. After complete reaction, no precipitated material was visible, and the solutions remained clear and colorless, indicating that essentially all products remained in solution and were observed in the spectrum. In all cases, both the disappearance of **1** (δ 5.63 for **1c**) and the formation of **3** (δ 5.93 for **3c**) followed first-order kinetics. Also, the ratio of **3** to the other cyclopentadienyl-containing side products (δ 5.95–6.30) remained constant throughout the reaction. Because of partial signal overlap of **3** and other reaction products, the disappearance of **1** could be monitored with slightly more accuracy than the appearance of **3**. Activation parameters for the reaction of **1c** were calculated from the observed rate constants for samples A–J. ^1H NMR data (300 MHz, toluene-d_8) for 3c–e are as follows: **3c**; δ 2.55 (t, J = 8 Hz, 2 H), 4.01 (t, J = 8 Hz, 2 H), 5.83 (s, 10 H), 6.8–7.2 (m, 5 H); **3d**; δ 2.58 (t, J = 5.5 Hz, 2 H), 3.44 (s, 3 H), 4.06 (t, J = 5.5 Hz, 2 H), 5.91 (s, 10 H), 6.78 (d, J = 6.3 Hz, 2 H), 7.01 (d, J = 6.3 Hz, 2 H); **3e**; δ 1.15 (d, J = 5.7 Hz, 3 H), 2.72 (m, 1 H), 3.96 (m, 2 H), 5.89 (s, 5 H), 5.90 (s, 5 H), 7.05–7.31 (m, 5 H).

Alternate Preparation of 3c. Phenethyl alcohol (0.611 g, 5 mmol) and ttriethylamine (0.77 mL, 5.5 mmol) were added to a solution of Cp_2ZrCl_2 (1.46 g, 5 mmol) in 10 mL of benzene at room temperature. The resulting suspension was stirred for 20 min, filtered to remove triethylamine hydrochloride, and the solvent was evaporated. The solid product was washed with 2 × 5 mL hexane and vacuum dried to yield 1.50 g (80%) **3c** as a white powder. The ^1H NMR is identical with that observed above after thermolysis of **1c**; $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 40.23, 76.30, 113.47, 126.40, 128.52, 129.53, 139.90. Anal. Calcd for $C_{18}H_{19}ClOZr$: C, 57.19; H, 5.07. Found: C, 57.11; H, 5.07.

Analysis of Organic Products from the Rearrangement of 1c. A solution of **1c** (75 mg) in 1.5 mL of toluene with 0.010 mL of dodecane (as internal standard) was heated to 110 °C for 40 min. The solution was cooled to room temperature, and 20 mL of gaseous HCl was added, followed by 1 mL of hexane and 2 mL of water. Analysis of the organic layer by capillary GC showed 70% phenethyl alcohol, 5.8% benzyl methyl ether, and 13.2% bibenzyl (molar ratios, by comparison to authentic samples and after correction for detector response). Benzyl methyl ether and bibenzyl were also observed by ^1H NMR after thermolysis of **1c** (δ 3.28 (s), 2.90 (s), respectively, 300 MHz, toluene-d_8).

Thermolysis of 1e. A solution of **1e** (0.196 g, 0.5 mmol) in benzene (10 mL) was heated in a sealed tube to 80 °C for 1.5 h. The solvent was evaporated to ca. 1-mL volume, acetyl chloride (0.071 mL, 1 mmol) was added, and the reaction was heated to 80 °C for 15 min. Isolation of the product by flash chromatography on silica gel (5% ether/hexane) yielded 44.6 mg (50%) 1-acetoxy-2-phenylpropane, identical by GC and ^1H NMR to material prepared from commercially obtained 2-phenyl-1-propanol and acetyl chloride.

The material was found to contain 70% ee of the S enantiomer (the acetate of (*S*)-(–)-2-phenyl-1-propanol) by ^1H NMR with tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]-europium(III) (Eu(hfc)$_3$, Aldrich) as chiral shift reagent. A sample of 10 mg of the acetate in C_6D_6, after addition of 25–50 mg of shift reagent, showed resolution of the benzylic methyl protons into two signals. Homonuclear decoupling of the benzylic proton (to collapse the methyl signals from doublets to singlets) and integration of the methyl signals indicated 70% ee of the enantiomer corresponding to the downfield signal. Under identical conditions, racemic material showed the expected 1:1 ratio of signals. An independently prepared sample of 2-phenyl-1-propanol (57% ee of the R-(+) enantiomer by optical rotation, $[\alpha]_D^{25}$ = +10.8 (c = 0.83))[11] was converted to the acetate with acetyl chloride/triethylamine. ^1H NMR measurement with Eu(hfc)$_3$ as above showed the material to have a 62% ee of the enantiomer corresponding to the upfield methyl signal. The upfield signal therefore corresponds to the R enantiomer and the downfield signal to the S.

Crossover Experiment—Thermolysis of 1f and 1g. A solution of **1f** and **1g** (0.098 g each, 0.5 mmol total) in benzene (10 mL) was heated in a sealed tube to 80 °C for 2 h. The solvent was evaporated, and to the residue was added a mixture of 10 mL of ethyl ether and 10 mL of 6 N HCl. The mixture was stirred for 10 min, and the organic layer was dried over $MgSO_4$. This solution and a reference solution of unlabeled 2-phenyl-1 propanol were analyzed by GC/MS. The unlabeled material exhibits M^+ = 136 (12.0%) and $M^+ + 1$ = 137 (1.3%), while the labeled material exhibits m/z = 137 (11.5%), 138 (10.8%), and 139 (1.5%). The absence of m/z = 136 and the magnitude of m/z = 139 relative to m/z = 137 and 138 indicate that no crossover occurred. Given the sensitivity of the instrument, no more than 3% crossover may have remained undetected.

Crystallography. Suitable crystals were obtained by slow evaporation of a CH_2Cl_2/hexane solution of **1c**. X-ray data were collected at –65 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation. Data collection, reduction, and refinement procedures have been described elsewhere.[12] A total of 3766 reflections ($+h$, $+k$, $+l$) were collected in the range $3° \le 2\theta \le 55°$ with the 2366 having $I_0 > 2\sigma(I_0)$ being used in the structure refinement which was by full-matrix least-squares techniques (190 variables) using SHELX-76. Final R_1 = 0.061 and R_2 = 0.065. Hydrogen atoms were ignored while all other atoms were refined anisotropically. The final difference Fourier map contained no chemically significant electron density. The structure was solved by using the MITHRIL direct methods package.[13] Final positional parameters, bond lengths, and bond angles are given in Tables II, III, and IV, respectively.

Crystal data: a = 15.417 (9) Å, b = 18.249 (9)) Å, c = 11.746 (8) Å; V = 3304.68 Å^3, orthorhombic space group $Pbca$; Z = 8; mol wt = 378.0; ρ(calcd) = 1.519 g cm^{-3}; μ = 7.3 cm^{-1}. A semi-empirical absorption correction was applied.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank

(11) Suzuki, T.; Katayama, E.; Matsumoto, T.; Tsuchihashi, G. *Tetrahedron Lett.* **1984**, *25*, 3715.
(12) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.
(13) Gilmore, C. J. *J. Appl. Cryst.* **1984**, *17*, 42.

the Henry and Camille Dreyfus foundation for the award of a Distinguished New Faculty Grant (S.L.B.), the National Science Foundation for a Predoctoral Fellowship (R.B.N.), and the Biomedical Research Support-Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10RR02243).

Registry No. **1a**, 109031-61-0; **1b**, 120410-89-1; **1c**, 120410-90-4; **1d**, 120445-27-4; **1e**, 120410-91-5; **1f**, 120410-92-6; **1g**, 120410-93-7; **2a**, 27490-32-0; **2b**, 87996-30-3; **2c**, 66222-28-4; **2d**, 120385-24-2; **2e**, 120385-25-3; **2f**, 120385-26-4; **2g**, 120385-27-5; **3c**, 120410-94-8; **3d**, 120410-95-9; **3e**, 120410-96-0; Bu_3SnCH_2I, 66222-29-5; Bu_3SnCD_2I, 120385-28-6; Bu_3SnLi, 4226-01-1; MeOh, 67-56-1; $ClCH_2OCH_2Ph$, 3587-60-8; Cp_2ZrCl_2, 1291-32-3; *p*-methoxybenzyl alcohol, 105-13-5; (*S*)-(−)-*sec*-phenethyl alcohol, 1445-91-6; acetophenone, 98-86-2; 1-deuterio-*sec*-phenethyl alcohol, 3101-96-0; (±)-*sec*-phenethyl alcohol, 13323-81-4; phenethyl alcohol, 60-12-8; (*S*)-1-acetoxy-2-phenyl propane, 50373-50-7; (*R*)-1-acetoxy-2-phenyl propane, 73308-18-6.

Supplementary Material Available: A table listing final positional and thermal parameters (1 page); a listing of final observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Photochemistry of (η^5-Cyclopentadienyl)tetracarbonylvanadium in Frozen Gas Matrices at ca. 12 K. Infrared Spectroscopic Evidence for Species Arising from Carbon Monoxide Ejection and Ring Dechelation Processes

Ramli B. Hitam† and Antony J. Rest*

Department of Chemistry, The University, Southampton SO9 5NH, United Kingdom

Received June 17, 1988

Infrared spectroscopic evidence, including ^{13}CO labeling and energy-factored force-field fitting of terminal metal carbonyl stretching vibrations, is presented showing that irradiation of $V(\eta^5\text{-}C_5H_5)(CO)_4$ at high dilution in frozen gas matrices at ca. 12 K results in two types of reversible process. One process (Ar, CH_4) is ejection of CO to yield the species $V(\eta^5\text{-}C_5H_5)(CO)_n$ (n = 1–3) that may be related to the dissociative pathways proposed for thermal and photochemical substitution reactions in solution at 298 K. The second process (Ar, CH_4, N_2, and CO) is proposed to involve a change in the ring hapticity with the formation of $V(\eta^3\text{-}C_5H_5)(CO)_4$ and probably $V(\eta^3\text{-}C_5H_5)(CO)_5$ (CO matrices). The detection of these ring dechelation species suggests that the contribution of a S_N2 pathway to the solution substitution reactions should be reevaluated. In reactive and doped matrices (N_2, C_2H_4 doped CH_4) irradiation yielded $V(\eta^5\text{-}C_5H_5)(CO)_3(N_2)$, $V(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_4)$, and *trans*-$V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$ species.

The photolability of $V(\eta^5\text{-}C_5H_5)(CO)_4$ has been employed in preparing a variety of $V(\eta^5\text{-}C_5H_5)(CO)_{4-m}L_m$ complexes by irradiating $V(\eta^5\text{-}C_5H_5)(CO)_4$ in the presence of L. In the case of monodentate ligands, e.g. L = diene,[1] PPh_3,[2-4] $P(n\text{-}Bu)_3$,[5] PH_3,[6] or EMe_2 (E = S, Te),[7] the products are monosubstituted complexes of the type $V(\eta^5\text{-}C_5H_5)(CO)_3L$. Photoreactions with bidentate phosphines (L-L), e.g. L-L = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 4)[8] or $PhP(CH_2CH_2PPh_2)_2$,[9] gave disubstituted complexes of the type *cis*-$V(\eta^5\text{-}C_5H_5)(CO)_2(L\text{-}L)$. A bidentate amine ligand NN*, a Schiffs base formed by condensation of 2-formylpyridine and 1-amino-1-methyltoluene, also formed a disubstitution product, $V(\eta^5\text{-}C_5H_5)(CO)_2(NN^*)$, when irradiated with $V(\eta^5\text{-}C_5H_5)(CO)_4$ in tetrahydrofuran (THF).[10] Irradiation of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in the presence of acetylenes (RC≡CR′), e.g. R = H and R′ = H, *n*-Pr, *n*-Bu, or CMe_3[3] and R = R′ = Ph,[11-13] C_6F_5,[12] Me,[13] or $SiMe_3$,[13] has afforded the acetylene complexes $V(\eta^5\text{-}C_5H_5)(CO)_2(RC{\equiv}CR')$. The only bis(acetylene) complex is $V(\eta^5\text{-}C_5H_5)(CO)(PhC{\equiv}CPh)_2$ which was formed on treating $V(\eta^5\text{-}C_5H_5)(CO)_2(PhC{\equiv}CPh)$ with a further mole of PhC≡CPh. Interestingly, acetylenes can stabilize highly electron-deficient species, e.g. $V(\eta^5\text{-}C_5H_5)(CO)(PhC{\equiv}CPh)^2$ and $V(\eta^5\text{-}C_5H_5)(CO)(F_5C_6C{\equiv}CC_6F_5)$.[12]

Kinetic studies of the thermal substitution reactions of $V(\eta^5\text{-}C_5H_5)(CO)_4$ with a variety of phosphines and phosphites have suggested that the reactions proceed by dissociative paths in which loss of a CO ligand is the rate-determining step.[14] Although the quantum yield data for the photochemical reaction of $V(\eta^5\text{-}C_5H_5)(CO)_4$ with PPh_3 was consistent with an associative path, this was ruled out because it seemed unlikely that a sterically crowded 20-electron intermediate, $V(\eta^5\text{-}C_5H_5)(CO)_4(PPh_3)$, could be formed.[4] Instead, the photosubstitution reactions of $V(\eta^5\text{-}C_5H_5)(CO)_4$ have been proposed to involve dissociative

† Present address: Department of Chemistry, Universiti Teknologi Malaysia, Kampus Sekudai, Karung Berkunci 791, 80990 Johor Bahru, Malaysia.

(1) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401.
(2) Tsumura, R.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1901.
(3) Kinney, R. J.; Jones, W. D.; Bergmann, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.
(4) Alway, D. G.; Barnett, K., W. *Inorg. Chem.* **1980**, *19*, 779.
(5) Fischer, E. O.; Schneider, R. J. J. *Angew. Chem. Int. Ed. Engl.* **1968**, *6*, 569.
(6) Fischer, E. O.; Louis, E.; Schneider, R. J. *J. Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 136.
(7) Belforte, A.; Calderazzo, F.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1985**, *115*, 71.
(8) Rehder, D.; Dahlenburg, L.; Müller, I. *J. Organomet. Chem.* **1976**, *122*, 53.
(9) Müller, I.; Rehder, D. *J. Organomet. Chem.* **1977**, *139*, 293.
(10) Hoch, M.; Rehder, D. *Inorg. Chim. Acta* **1986**, *115*, L23.
(11) Nesmeyanov, A. N. *Adv. Organomet. Chem.* **1972**, *10*, 56.
(12) Foust, D. F.; Rausch, M. D. *J. Organomet. Chem.* **1982**, *239*, 321.
(13) Alt, H. G.; Engelhardt, H. E. *Z. Naturforsch., B* **1985**, *40B*, 1134.
(14) Faber, G. C. Angelici, R. J. *Inorg. Chem.* **1970**, *9*, 1586.

0276-7333/89/2308-1598$01.50/0