mmol; 18%); mp 81 °C. Anal. Calcd for $C_{29}H_{57}B_8Ni_2$ (609.8): C, 57.13; H, 9.42. Found: C, 57.21; H, 9.69. For spectroscopic data, see ref 2.

(η^5-1,4,6-Trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)(η^5-1,3-dimethyl-4,5-diethyl-2,3-dihydro-1,3-diborolyl)nickel (4) and (η^5-1,4,6-Trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)(1,5-cyclooctadiene)nickel Tetrafluoroborate ($5^+BF_4^-$). 1 (70 mg, 0.11 mmol) and 1.3 g (12 mmol) of 1,5-cyclooctadiene in 10 mL of DME are treated dropwise with a dilute solution of $AgBF_4$ in DME until the color changes from green to red-brown. The mixture is filtered, and the solvent is removed in vacuo. Addition of 20 mL of low-boiling petroleum ether allows the extraction of 4 which is purified by distillation at 65 °C (1 Pa) and recrystallization: yield 25 mg (0.06 mmol; 60%); mp 47 °C. Anal. Calcd for $C_{19}H_{37}B_5Ni$ (378.3): C, 60.33; H, 9.86. Found: C, 59.76; H, 9.45. For spectroscopic data of 4, see ref 2.

The residue is dissolved in 1 mL of THF, and $5^+BF_4^-$ is precipitated by the addition of petroleum ether. Recrystallization from DME yields 35 mg of $5^+BF_4^-$ (0.08 mmol, 75%): ^1H NMR (CD_3NO_2) δ −0.12 (s, 3, B–CH_3 apex), 0.42 (s, 6, B–CH_3 basal), 1.32 (t, 6, CH_2CH_3), 2.6 (m, 2, CH_2–CH_3), 2.7 (m, 8, CH_2 (COD)), 2.9 (m, 2, CH_2–CH_3), 5.03 (m, 4, CH (COD)), 5.53 (s, 1, CH); ^{11}B NMR (64.17 MHz, CD_3NO_2) δ 6.3 (br), 1.8 (s, BF_4); FD mass spectrum, m/z (relative intensity) 339 (M^+, 100). Anal. Calcd for $C_{18}H_{32}B_4F_4Ni$ (426.4): C, 50.7; H, 7.56. Found: C, 50.9; H, 7.76.

(μ-η^5-1,3-Dimethyl-4,5-diethyl-2,3-dihydrodiborolyl)(η^5-1,4,6-trimethyl-2,3-diethyl-2,3,5-tricarbahexaboranyl)nickel(η^5-cyclopentadienyl)nickel (8). 4 (80 mg, 0.2 mmol) and 65 mg (0.22 mmol) of $[(C_5H_5)Ni(CO)]_2$ are refluxed in toluene for 3 h. Chromatography on silica gel/petroleum ether and distillation at 100 °C (1 Pa) yield 60 mg (0.12 mmol, 60%) of 8 as a green oil. FD mass spectrum: m/z (relative intensity) 502 (M^+, 100), no fragmentation. EI mass spectrum (70 eV): m/z (relative intensity) 378 (4^+, 20); 148 (tricarbahexaboranyl(1+), 100); 123 ($CpNi^+$, 12). NMR data and assignments, see Tables VII and VIII.

Acknowledgment. This research was supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie and the BASF AG, and by generous grant from the Stiftung Volkswagenwerk. We are grateful to Dr. K. Steinbach (Marburg) and Dr. R. Geist for recording the mass spectra, Dr. P. Kunzelmann and Mrs. G. Rissmann for recording the NMR spectra, and Mr. R. Gänzler for performing elemental analyses.

Registry No. 1, 93782-60-6; 1^-, 116663-32-2; 1^+, 116663-33-3; 3, 81620-71-5; 4, 93782-63-9; 4^-, 116634-57-2; 5, 116634-58-3; 5(BF_4), 116634-53-8; 8, 116634-54-9; 8^-, 116663-34-4; 8^+, 116634-55-0; 8^{2+}, 116634-56-1; $Ni(C_2H_4)_3$, 50696-82-7; $[(C_5H_5)Ni(CO)]_2$, 12170-92-2.

Supplementary Material Available: Tables of atom parameters (with anisotropic thermal parameters and parameters for hydrogen atoms), a complete list of distances and angles, and tables of the best planes (13 pages); listings of structure factors (18 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactions of (1-Ethoxyethyl)zirconocene Chloride, a Stable Acyclic Secondary Zirconocene Alkyl

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

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

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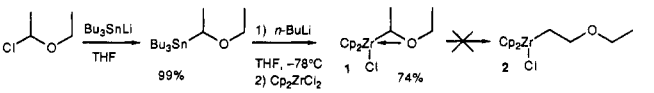
The title compound 1 ($Cp_2Zr(Cl)CH(CH_3)OCH_2CH_3$, Cp = η^5-C_5H_5) has been prepared in good yield by treatment of Cp_2ZrCl_2 with (1-ethoxyethyl)lithium. Compound 1 is the first example of a stable, structurally characterized secondary zirconocene alkyl derivative which shows no tendency to rearrange to the primary alkyl derivative at room temperature. Carbon monoxide and isocyanides react with 1 to give migratory insertion products without rearrangement of the 1-ethoxyethyl fragment. At high temperatures, 1 decomposes to give ethylene and $Cp_2Zr(Cl)OCH_2CH_3$, the same products obtained at ambient conditions from the reaction of Cp_2ZrHCl (Schwartz's reagent) with ethyl vinyl ether.

Hydrozirconation[1] of olefins using Cp_2ZrHCl (Schwartz's reagent) is a well-studied organometallic reaction. A distinctive feature of the hydrozirconation of acyclic olefins is that only primary alkylzirconocene products are observed. The absence of stable secondary alkyls is due both to the greater thermodynamic stability of the primary zirconocene alkyls and to the ease of the β-hydride elimination/hydrozirconation processes which migrate the Cp_2ZrCl fragment to the primary position.[1a] We now report the preparation and X-ray crystal structure of an acyclic secondary alkyl zirconocene chloride stabilized by an α-alkoxy substituent which acts as a ligand for the metal center.

Scheme I



Compound 1, (1-ethoxyethyl)zirconocene chloride, was synthesized in 74% yield (Scheme I) by treatment of Cp_2ZrCl_2 with (1-ethoxyethyl)lithium. The lithium reagent[2] was readily obtained from *n*-butyllithium and (1-

(1) (a) Schwartz, J.; Hart, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 8115. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (c) Negishi, E.; Takahashi, T. *Aldrichchim. Acta* **1985**, *18*, 31 and references therein. (d) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

(2) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

0276-7333/88/2307-2324$01.50/0

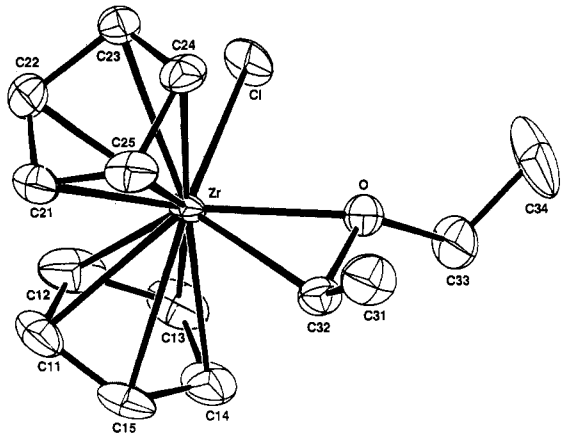
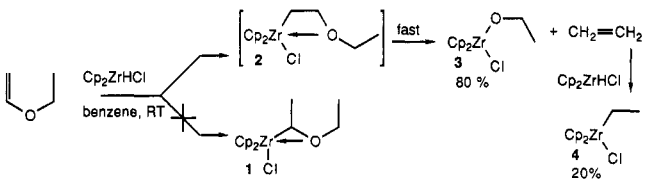


Figure 1. ORTEP diagram showing 1 along with atom-labeling scheme and 30% probability thermal ellipsoids.

Table I. Final Positional Parameters for 1

atom	*x*	*y*	*z*
Zr	0.15801 (9)	0.21171 (6)	−0.07331 (5)
Cl	−0.1689 (3)	0.1553 (2)	−0.05775 (18)
O	0.0148 (8)	0.3449 (5)	−0.1235 (4)
C11	0.3743 (14)	0.0859 (9)	−0.1398 (7)
C12	0.1968 (19)	0.0452 (8)	−0.1492 (8)
C13	0.1063 (14)	0.1048 (11)	−0.2156 (8)
C14	0.2211 (17)	0.1784 (9)	−0.2445 (7)
C15	0.3819 (13)	0.1691 (9)	−0.1980 (7)
C21	0.3966 (11)	0.1883 (8)	0.0484 (6)
C22	0.2458 (13)	0.1261 (8)	0.0744 (5)
C23	0.1048 (12)	0.1926 (7)	0.1008 (5)
C24	0.1640 (12)	0.2919 (8)	0.0864 (5)
C25	0.3455 (12)	0.2895 (9)	0.0545 (5)
C31	0.2423 (16)	0.4704 (8)	−0.0829 (7)
C32	0.2044 (12)	0.3687 (7)	−0.1303 (6)
C33	−0.1059 (15)	0.3675 (10)	−0.2002 (6)
C34	−0.2666 (18)	0.4154 (11)	−0.1671 (9)

Scheme II



ethoxyethyl)tri-*n*-butylstannane, which was prepared in high yield by treatment of 1-chloro-1-ethoxyethane with (tri-*n*-butylstannyl)lithium. Compound **1** is a white crystalline solid that has been fully characterized spectroscopically as well as by combustion analysis, and all data are consistent with the secondary alkyl structure shown. At room temperature in the solid state or in solution, **1** undergoes no perceptible rearrangement to the isomeric primary alkyl derivative **2**.

The X-ray crystal structure of **1** is shown in Figure 1. **1** is clearly an 18-electron complex, with the oxygen atom of the η^2-ethoxyethyl ligand in the central position defined by the cyclopentadienyl rings. The Zr–C, Zr–O, and Zr–Cl bond lengths and the C–Zr–O and O–Zr–Cl angles are very similar to those observed previously for the alkoxymethyl compounds $Cp_2Zr(Cl)CH_2OCH_2Ph$[3] and $Cp_2Zr(Cl)$-CH_2OCH_3.[4]

To determine whether the failure of **1** to isomerize to form **2** was due to an unusual kinetic stability of **1** toward β-hydride elimination or to a thermodynamic stability of **1** over **2**, we set out to prepare **2** independently and see if thermal equilibrium between **1** and **2** could be established. However, attempted preparation of **2** by hydrozirconation of ethyl vinyl ether using Cp_2ZrHCl in benzene resulted in the isolation of only ethoxyzirconocene chloride[5]

Table II. Bond Distances (Å) for 1

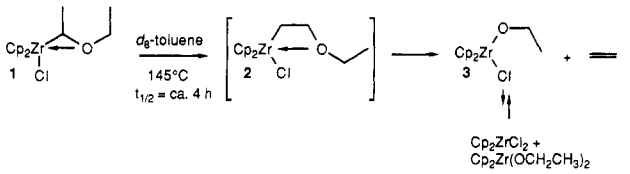
A	B	distance
Cl	Zr	2.5602 (2)
O	Zr	2.197 (6)
C11	Zr	2.522 (9)
C12	Zr	2.499 (10)
C13	Zr	2.526 (10)
C14	Zr	2.552 (9)
C15	Zr	2.523 (8)
C21	Zr	2.509 (8)
C22	Zr	2.501 (8)
C23	Zr	2.553 (8)
C24	Zr	2.538 (8)
C25	Zr	2.528 (8)
C32	Zr	2.282 (9)
C32	O	1.451 (10)
C33	O	1.453 (10)
C12	C11	1.436 (15)
C13	C12	1.413 (16)
C14	C13	1.370 (15)
C15	C14	1.373 (15)
C11	C15	1.396 (14)
C22	C21	1.449 (13)
C23	C22	1.429 (12)
C24	C23	1.415 (13)
C25	C24	1.431 (12)
C21	C25	1.409 (14)
C31	C32	1.548 (13)
C34	C33	1.441 (15)

Table III. Bond Angles (deg) for 1

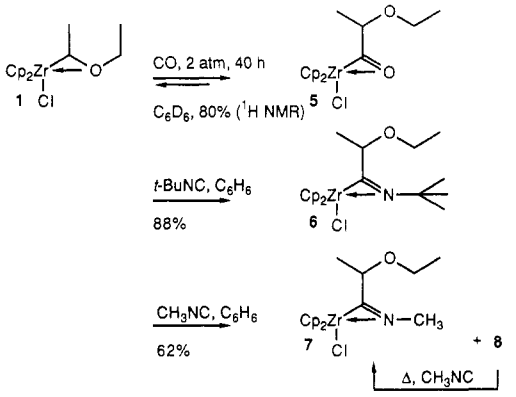
A	B	C	angle
Cl	Zr	O	78.9 (2)
Cl	Zr	C32	117.3 (3)
C11	Zr	Cl	116.5 (3)
C12	Zr	Cl	83.6 (3)
C13	Zr	Cl	76.3 (3)
C14	Zr	Cl	102.3 (3)
C15	Zr	Cl	128.9 (2)
C21	Zr	Cl	124.9 (2)
C22	Zr	Cl	92.0 (2)
C23	Zr	Cl	74.4 (2)
C24	Zr	Cl	93.3 (2)
C25	Zr	Cl	125.4 (2)
C11	Zr	O	136.6 (3)
C12	Zr	O	129.5 (4)
C13	Zr	O	96.9 (3)
C14	Zr	O	85.2 (3)
C15	Zr	O	105.7 (3)
C21	Zr	O	132.2 (3)
C22	Zr	O	140.9 (3)
C23	Zr	O	109.1 (2)
C24	Zr	O	87.8 (3)
C25	Zr	O	99.8 (3)
C34	C33	O	110.6 (8)
C33	O	C32	120.1 (7)
O	C32	C31	109.8 (8)
Zr	C32	C31	132.7 (6)
Zr	C32	O	67.9 (4)
Zr	O	C33	135.8 (7)
Zr	O	C32	74.3 (4)
C15	C11	C12	106.6 (9)
C11	C12	C13	106.6 (10)
C12	C13	C14	108.3 (10)
C13	C14	C15	109.4 (10)
C14	C15	C11	109.1 (10)
C25	C21	C22	109.0 (8)
C21	C22	C23	106.4 (8)
C22	C23	C24	108.4 (8)
C23	C24	C25	108.8 (9)
C24	C25	C21	107.3 (9)

(3) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C., unpublished results.
(4) Erker, G.; Schlund, R.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1403.

Scheme III



Scheme IV



3 in 81% yield (Scheme II). Monitoring this reaction by ^{1}H NMR at ambient temperature in a sealed tube in C_6D_6 solution over a period of 70 min showed no signals attributable to 2 or any other intermediates and only 3 (80%), ethylene, and ethylzirconocene chloride 4 (20%)[6] as products. (In the sealed tube, 4 appears to be formed by a secondary reaction of $Cp_2Zr(H)Cl$ with ethylene.) No detectable amounts of the secondary product 1 were formed, although the compound is stable to the reaction conditions. This product distribution suggests that the hydrozirconation of ethyl vinyl ether proceeds with high kinetic selectivity for the primary product 2, which rapidly undergoes β-alkoxide elimination to give 3 and ethylene as products. Very few β-alkoxide eliminations at transition-metal centers have been reported,[7] but in this case it is not surprising that the process is fast, given a favorable transition-state geometry and the high strength of the Zr–O bond being formed.

The rapid, irreversible decomposition of 2 to form 3 and the kinetic stability of 1 imply that there is an unusually high kinetic barrier for the isomerization of 1 to 2. However, 1 decomposes at elevated temperatures, as shown in Scheme III. Heating 1 in the sealed tube in toluene-d_8 solution at 145 °C leads to complete decomposition of 1 with a halflife of approximately 4 h. After 24 h, the only observed products are ethylene and 3 (70%), as well as zirconocene dichloride (8%) and zirconocene diethoxide[5] (8%), which appear to be formed by disproportionation of 3. These products are consistent with a slow isomerization of 1 to form 2, followed by decomposition of 2 by β-alkoxide elimination.

Although β-hydride elimination from 1 is greatly slowed because no vacant orbital is available at the 18-electron zirconium center, carbon monoxide, and isocyanides react with 1 to give normal migratory insertion products, as shown in Scheme IV. This was unexpected because such migratory insertion reactions are usually extremely slow or do not occur at all for 18-electron zirconocene alkyls.[8] Reaction with 2 atm of CO in C_6D_6 for 40 h produced an 80% yield of the acyl derivative 5, which was observed by ^{1}H and ^{13}C NMR but was not isolated because it decarbonylates[9] when the CO atmosphere is removed. The iminoacyl derivative 6 was isolated in 88% yield after reaction with *tert*-butyl isocyanide for 24 h at room temperature, and 7 was isolated in 62% yield after treatment of 1 with methyl isocyanide for 24 h at 50 °C. Monitoring the *t*-BuNC reaction in $CDCl_3$ by proton NMR showed no appreciable amounts of other species besides 1 and 6, but monitoring the reaction of 1 and methyl isocyanide in $CDCl_3$ showed almost complete conversion of 1 after 3 h at room temperature to a 65:35 mixture of the iminoacyl complex 7 and another species 8, which appears to be a 1:1 adduct of 1 and methyl isocyanide, based on ^{1}H and ^{13}C NMR spectra. Complex 8 is slowly converted to 7 in the presence of excess isocyanide, but after 17 h at room temperature, 9% of 8 still remains, indicating that 8 is not a kinetically competent intermediate for the formation of 7 in the initial 65:35 mixture.

In conclusion, we have prepared and characterized an acyclic alkylzirconocene chloride which is kinetically stabilized by coordination of an α-alkoxy substituent. Although this complex is stable due to its coordinative saturation which inhibits β-hydride elimination, migratory insertion reactions with carbon monoxide and isocyanides can still occur to give the secondary acyl and iminoacyl compounds.

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 a Bruker WM-250, Bruker WM-270, Varian XL-300, or Varian XL-400 Fourier transform spectrometer. IR spectra were recorded on a Mattson Instruments Cygnus 100 Fourier transform spectrometer. Electron-impact mass spectra and high-resolution mass spectra (HRMS) were recorded on a Finnegan MAT System 8200 spectrometer. Combustion analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, Spang Microanalytical Laboratory, Eagle Harbor, MI, or Desert Analytics, Tucson, AZ.

Tetrahydrofuran, benzene, hexane, toluene-d_8, and benzene-d_6 were distilled or vacuum transferred from sodium/benzophenone ketyl. All other reagents were available from commercial sources and were used as received or purified by using conventional procedures.[10]

(1-Ethoxyethyl)tri-*n*-butylstannane. To a stirred 0 °C solution of diisopropylamine (4.6 mL, 32 mmol, Aldrich) in 50 mL of THF under argon was added *n*-BuLi (19.8 mL 1.64 M hexane, 32 mmol, Aldrich). After 15 min, Bu_3SnH (6.6 mL, 25 mmol, Boulder Scientific) was added. After 20 min, 1-chloro-1-ethoxyethane (3 mL, 27.5 mmol) was added, and the mixture was stirred an additional 5 min. Workup with 80 mL of hexane, 50 mL of 1 N HCl/brine, 50 mL of saturated $NaHCO_3$/brine, 50 mL of 1 N HCl/brine, drying over $MgSO_4$, and evaporation gave the stannane (8.99 g, 99%) as a colorless liquid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.80–1.00 (m, 15 H), 1.19 (t, J = 7 Hz, 3 H), 1.25–1.60 (m, 15 H), 3.30–3.50 (m, 2 H), 3.84 (q, J = 7.5 Hz, 1 H); ^{13}C{^{1}H} NMR (69.9 MHz, $CDCl_3$) δ 8.84, 13.63, 15.52, 20.67, 27.46, 29.19, 65.83, 71.67; IR (neat/NaCl) 2956, 2928, 2854, 1458, 1376, 1209, 1149, 1093, 1072, 960, 873, 864, 689, 656 cm^{-1}.

Chlorobis(η^5-2-4-cyclopentadien-1-yl)(1-ethoxyethyl-*C,O*)zirconium (1). In a Schlenk flask under argon, Cp_2ZrCl_2 (2.92 g, 10 mmol, Boulder Scientific) was dissolved in 30 mL of THF and cooled to −78 °C with stirring. In a separate Schlenk

(5) Gray, D. R.; Brubaker, C. J., Jr. *Inorg. Chem.* **1971**, *10*, 2143.
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flask, (1-ethoxyethyl)tri-*n*-butylstannane (4.00 g, 11 mmol, 1.1 equiv) was dissolved in 30 mL of THF at −78 °C, and *n*-BuLi (6.28 mL, 10.5 mmol, 1.05 equiv, 1.67 M hexane, Aldrich) was added dropwise. After 10 min at −78 °C, the metalation mixture was added rapidly via cannula to the zirconocene dichloride solution. The mixture was stirred 1 h at −78 °C, warmed to room temperature, and evaporated to give an oil which solidified on standing. This was washed (using Schlenk filtration) with 2 × 5 mL of hexane to remove the bulk of the Bu_4Sn. Extraction with 20 mL of benzene in two portions, filtration to remove LiCl, evaporation, washing with 2 × 5 mL and 6 × 3.5 mL of hexane, and vacuum drying gave **1** as a white powder: yield 2.44 g (74%); ^{1}H NMR (400 MHz, C_6D_6) δ 1.03 (t, J = 7.2 Hz, 3 H), 1.46 (d, J = 6.0 Hz, 3 H), 2.57 (q, J = 6.0 Hz, 1 H), 3.22 (m, 1 H), 4.09 (m, 1 H), 5.66 (s, 5 H), 5.73 (s, 5 H); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6) δ 16.20, 22.63, 70.94, 76.00, 109.50, 109.99; IR (KBr) 3077, 2975, 2934, 2913, 2874, 2851, 1446, 1384, 136, 1173, 1093, 1027, 904, 831, 813, 798, 754 cm^{-1}. Anal. Calcd for $C_{14}H_{19}ClZr$: C, 50.96; H, 5.80. Found: C, 51.02; H, 5.85.

Hydrozirconation of Ethyl Vinyl Ethyl. Ethyl vinyl ether (0.72 g, 10 mmol, Aldrich) was added to a stirred slurry of Cp_2ZrHCl[1d] (1.28 g, 5 mmol) in 30 mL of benzene in a Schlenk flask under argon. The mixture was stirred for ca. 30 min until the solid Cp_2ZrHCl was consumed. The resulting clear pale yellow solution was evaporated to give a yellow oil which crystallized on extended evaporation. The solid was washed with 5 mL of hexane and vacuum dried to give 1.22 g (81%) of ethoxyzirconocene chloride[6] as a yellow powder: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (t, J = 7.0 Hz, 3 H), 4.06 (q, J = 7.0 Hz, 2 H), 6.296 (s, 10 H).

In an NMR tube were combined 0.65 mL of C_6D_6, ethyl vinyl ether (0.010 mL, 0.11 mmol), and Cp_2ZrHCl (26 mg, 0.1 mmol), and the reaction was monitored by ^{1}H NMR (400 MHz) at room temperature for ca. 70 min, until the reaction was complete. The only species observed were ethylene (δ 5.26 (s)), $Cp_2Zr(OCH_2CH_3)Cl$[5] (80% at completion, δ 0.99 (t, J = 7.2 Hz, 3 H), 3.84 (q, J = 7.2 Hz, 2 H), 5.95 (s, 10 H)), and $Cp_2Zr(CH_2CH_3)Cl$[6] (**4**) (20% at completion, δ 1.1 (q, J = 7 Hz, 2 H), 1.45 (t, J = 7 Hz, 3 H), 5.77 (s, 10 H)).

Thermolysis of 1. In an NMR tube were combined toluene-d_8 (0.7 mL), **1** (20 mg), and mesitylene (0.0025 mL as an internal standard), and the tube was sealed and heated in an oil bath to ca. 145 °C. The reaction was monitored by ^{1}H NMR (400 MHz). Throughout the reaction, the ratio of cyclopentadienyl and mesitylene signals remained constant. After 24 h, no **1** remained, and signals were observed for ethylene (δ 5.26 (s)), $Cp_2Zr(Cl)OCH_2CH_3$[5] (**3**) (70%) (δ 0.992 (t, J = 5.1 Hz, 3 H), 3.833 (q, J = 5.1 Hz, 2 H), 5.938 (s, 10 H)), $Cp_2Zr(OCH_2CH_3)_2$[5] (8%) (δ 1.105 (t, J = 5.4 Hz, 6 H), 3.925 (q, J = 5.4 Hz, 4 H), 5.933 (s, 10 H)), and Cp_2ZrCl_2 (8%) (δ 9.993 (s, 10 H)).

Reaction of 1 with CO: Formation of 5. A solution of **1** (25 mg) in 0.65 mL of C_6D_6 in an NMR tube was freeze–pump–thawed and then placed under 0.5 atm of CO at −196 °C. The tube was sealed and allowed to warm to room temperature. After 40 h, ^{1}H NMR (300 MHz) showed formation of **5** (82% conversion): δ 1.1-1.2 (m, 6 H), 3.3–3.5 (m, 2 H), 3.70 (q, J = 7.5 Hz, 1 H), 5.67 (s, 5 H), 5.70 (s, 5 H). ^{13}C{^{1}H} NMR (100.6 MHz): δ 15.63, 16.90, 65.12, 85.90, 109.52, 109.70, 184.41. Upon removal of CO pressure, **5** decarbonylates over ca. 30 min to form **1**.

Reaction of 1 with *tert*-Butyl Isocyanide. Preparation of 6. In a Schlenk flask under argon, *tert*-butylisocyanide (0.226 mL, 2 mmol) was added to a solution of **1** (330 mg, 1 mmol) in 5 mL of benzene. The reaction was stirred for 24 h at room temperature and evaporated to give a solid product, which was washed with 2 × 5 mL hexane at 0 °C to give 362 mg (88%) of **6** as a white powder: ^{1}H NMR (300 MHz, C_6D_6) δ 1.05–1.15 (m, 6 H), 1.29 (s, 9 H), 3.04 (m, 1 H), 3.35 (m, 1 H), 4.47 (q, J = 6.6 Hz, 1 H) 5.81 (s, 5 H), 5.85 (s, 5 H); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6) δ 15.73, 19.00, 29.50, 62.64, 63.79, 76.89, 108.95, 109.39, 233.61; IR (KBr) 3112, 2985, 2968, 2938, 2927, 2895, 2880, 1650, 1458, 1443, 1401, 1391, 1359, 1326, 1291, 1242, 1229, 1195, 1113, 1085, 1015, 960, 919, 791, 750, 681 cm^{-1}. Anal. Calcd for $C_{19}H_{28}ClNOZr$: C, 55.24; H, 6.83. Found: C, 55.01; H, 6.79.

In an NMR tube were combined 0.60 mL of $CDCl_3$, *tert*-butylisocyanide (0.017 mL, 0.15 mmol) and **1** (25 mg, 0.075 mmol), and the reaction was monitored by ^{1}H NMR (400 MHz) at room temperature until reaction was complete. After 3 h, 12% of starting **1** remained. The only species observed were **1** and **6**: δ 1.35 (t, J = 7 Hz, 3 H), 1.39 (s, 9 H), 1.49 (d, J = 7 Hz, 3 H), 3.49 (m, 1 H), 3.79 (m, 1 H), 4.90 (q, J = 7 Hz, 1 H) 5.89 (s, 5 H), 5.90 (s, 5 H).

Reaction of 1 with Methyl Isocyanide. Preparation of 7. In a Schlenk flask under argon, methyl isocyanide (0.111 mL, 2 mmol) was added to a solution of **1** (330 mg, 1 mmol) in 5 mL of benzene. The reaction was stirred for 4 h at room temperature and 20 h at 50 °C and evaporated to give an oil, which solidified on standing. The solid product was washed with a mixture of 10 mL of hexane and 3 mL of ethyl ether and then with 2 × 2 mL of hexane to give 248 mg of **7** as a white powder in 92% purity by ^{1}H NMR (62% yield). The analytical sample was crystallized from ether: ^{1}H NMR (300 MHz, C_6D_6) δ 1.105 (d, J = 6.9 Hz, 3 H), 1.086 (t, J = 6.6 Hz, 3 H), 3.006 (s, 3 H), 3.06, 3.23 (ab of multiplets, 2 H), 4.106 (q, J = 6.9 Hz, 1 H), 5.737 (s, 5 H), 5.778 (s, 5 H); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6) δ 15.66, 16.96, 34.24, 64.19, 78.60, 109.05, 109.26, 236.85; IR (KBr) 3096, 3085, 2992, 2980, 2922, 2886, 2869, 1661, 1441, 1401, 1387, 1362, 1331, 1154, 1114, 1080, 1028, 1013, 831, 820, 796, 782, 759, 687 cm^{-1}. Anal. Calcd for $C_{16}H_{22}ClNOZr$: C, 51.80; H, 5.98. Found: C, 51.29; H, 6.03. HRMS for $M^+ - Cl$: calcd 334.0744; found, 334.0743 ± 0.0013 amu.

In an NMR tube were combined 0.60 mL of $CDCl_3$, methyl isocyanide (0.007 mL, 0.15 mmol), and **1** (25 mg, 0.075 mmol), and the reaction was monitored by ^{1}H NMR at room temperature until reaction was complete. After 3 h, 60% **7** (^{1}H NMR (400 MHz) δ 1.32 (t, J = 7 Hz, 3 H), 1.44 (d, J = 7.5 Hz, 3 H), 3.25 (s, 3 H), 3.50 (m, 1 H), 3.69 (m, 1 H), 4.67 (q, J = 7.5 Hz, 1 H), 5.88 (s, 5 H), 5.89 (s, 5 H); ^{13}C{^{1}H} NMR (125.4 MHz, $CDCl_3$) δ 15.55, 17.19, 34.50, 64.45, 78.63, 108.85, 109.05, 236.45) had formed along with 31% **8** (^{1}H NMR (400 MHz) δ 1.15 (t, J = 7 Hz, 3 H), 1.36 (d, J = 7 Hz, 3 H), 3.34 (d, J = 2 Hz, 3 H), 3.78 (m, 1 H), 4.09 (m, 1 H), 4.89 (q of d, J = 7, 2 Hz, 1 H), 6.139 (s, 5 H), 6.143 (s, 5 H); ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$) δ 13.61, 17.68, 44.00, 62.99, 97.31, 110.48, 110.62 225.81). Signals were also observed for free methyl isocyanide (^{1}H NMR (400 MHz) δ 3.14 (t, J = 2.2 Hz); ^{13}C{^{1}H} NMR (125.6 MHz, $CDCl_3$) δ 26.85 (t, J = 8 Hz), 156.78 (t, J = 6 Hz)). Less than 5% of **1** remained. After 17 h, no **1** remained, but 9% of **8** was still present.

Crystallography. 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. Details of the data collection, reduction and refinement procedures were similar to those described elsewhere.[11] A total of 2514 reflections (+h,+k,±l) were collected in the range 3° < 2θ < 55° with the 1869 having $I_o > 2\sigma(I_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (154 variables) using SHELX-76. Final R_1 = 0.059 and R_2 = 0.068. Hydrogen atoms were ignored while all other atoms were refined anisotropically. The final difference Fourier map contained no chemically significant features.

Crystal data are a = 7.448 (4) Å, b = 13.379 (3) Å, c = 14.403 (2) Å, β = 90.31 (3)°, V = 1435.2 Å^3, space group $P2_1/n$, Z = 4, mol wt 330, ρ(calcd) = 1.527 g/cm^3, and μ = 8.3 cm^{-1}. A semiempirical absorption correction was applied.

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Registry No. 1, 116052-40-5; 3, 11087-28-8; 4, 12109-84-1; 5, 116025-27-5; 6, 116025-28-6; 7, 116025-29-7; Bu_3SnH, 688-73-3; $CH_3CH(Cl)OCH_2CH_3$, 7081-78-9; Cp_2ZrCl_2, 1291-32-3; $CH_2{=}C{-}HOCH_2CH_3$, 109-92-2; Cp_2ZrHCl, 37342-97-5; $Cp_2Zr(OCH_2CH_3)_2$, 11087-35-7; (1-ethoxyethyl)tri-*n*-butylstannane, 116005-05-1.

Supplementary Material Available: A table of final thermal parameters for 1 (1 page); a listing of final observed and calculated structure factors for 1 (8 pages). Ordering information is given on any current masthead page.

Pentadienyl–Metal–Phosphine Chemistry. 17.[1] Syntheses, Structures, and Spectroscopy of Pentadienyl–Ruthenium–Phosphine Complexes

J. R. Bleeke* and D. J. Rauscher

Department of Chemistry, Washington University, St. Louis, Missouri 63130

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The reaction of $RuCl_2(PPh_3)_3$ with pentadienyltributyltin produces (η^5-pentadienyl)$RuCl(PPh_3)_2$ (1), which serves as a convenient starting material for the synthesis of a large family of new pentadienyl–ruthenium–phosphine complexes. Treatment of 1 with 1 equiv of PMe_3, PMe_2Ph, PEt_3, or PEt_2Ph produces the mixed-phosphine complexes (η^5-pentadienyl)$RuCl(PR_3)(PPh_3)$ (**2a**, $PR_3 = PMe_3$; **2b**, $PR_3 = PMe_2Ph$; **2c**, $PR_3 = PEt_3$; **2d**, $PR_3 = PEt_2Ph$). Compound **2c** crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.435$ (2) Å, $b = 13.770$ (4) Å, $c = 18.237$ (5) Å, $\beta = 109.04$ (2)°, $V = 2715$ (1) Å^3, and $Z = 4$. This complex adopts a pseudooctahedral coordination geometry with the PEt_3 ligand residing under the open "mouth" of the pentadienyl ligand and the PPh_3 and Cl groups lying under the pentadienyl "edges". Treatment of 1 with 2 equiv of PEt_3, PEt_2Ph, or $PEtPh_2$ produces (η^5-pentadienyl)$RuCl(PR_3)_2$ (**3c**, $PR_3 = PEt_3$; **3d**, $PR_3 = PEt_2Ph$; **3e**, $PR_3 = PEtPh_2$). (η^5-Pentadienyl)$RuCl(PMe_2Ph)_2$ (**3b**) is obtained cleanly by reacting **2b** with one additional equivalent of PMe_2Ph. (η^5-Pentadienyl)$RuCl(PEt_3)_2$ (**3c**) [monoclinic, Cc, $a = 28.094$ (7) Å, $b = 10.003$ (2) Å, $c = 15.134$ (3) Å, $\beta = 98.54$ (2)°, $V = 4205$ (2) Å^3, $Z = 8$] and (η^5-pentadienyl)$RuCl(PEt_2Ph)_2$ (**3d**) [orthorhombic, $P2_12_12_1$, $a = 16.848$ (7) Å, $b = 19.409$ (4) Å, $c = 7.867$ (1) Å, $V = 2572$ (1) Å^3, $Z = 4$] have been structurally characterized. Both complexes adopt pseudooctahedral coordination geometries in which one phosphine resides under the pentadienyl "mouth" while the other phosphine and the chloro ligand lie under the pentadienyl "edges". Treatment of 1 with 3 equiv of PMe_3 produces (η^3-pentadienyl)$RuCl(PMe_3)_3$ (**4a**). (η^3-Pentadienyl)$RuCl(PMe_2Ph)_3$ (**4b**) is obtained upon treatment of **2b** with 2 equiv of PMe_2Ph. **4a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.628$ (3) Å, $b = 13.662$ (3) Å, $c = 15.667$ (4) Å, $\beta = 91.59°$, $V = 2060$ (1) Å^3, and $Z = 4$. **4a**'s coordination geometry is pseudooctahedral with C1 and C3 of the pentadienyl ligand, the three phosphorus atoms, and the chlorine atom occupying the six coordination sites. The η^3-pentadienyl ligand adopts a W-shaped syn geometry. Both **4a** and **4b** react with $Ag^+O_3SCF_3^-$ or $Me^+O_3SCF_3^-$ to yield [(η^5-pentadienyl)$Ru(PR_3)_3]^+O_3SCF_3^-$ (**5a**, $PR_3 = PMe_3$; **5b**, $PR_3 = PMe_2Ph$). **5a** crystallizes in the monoclinic space group $P2_1/m$ with $a = 8.622$ (2) Å, $b = 11.302$ (4) Å, $c = 12.676$ (2) Å, $\beta = 103.22$ (1)°, $V = 1202.6$ (6) Å^3, and $Z = 2$. It exhibits pseudooctahedral coordination geometry with one PMe_3 ligand under the open pentadienyl "mouth" and the other PMe_3 ligands under the pentadienyl "edges". Compounds 1, 3, and 5 undergo dynamic processes in solution involving rotation of their pentadienyl groups with respect to the metal–ligand framework. $\Delta G^{\ddagger}$'s for these processes have been determined from line-shape simulations of the variable-temperature ^{31}P NMR spectra.

Introduction

During the past several years, increased attention has been directed toward the synthesis and reactivity of transition-metal complexes containing the acyclic pentadienyl ligand.[2] Motivating this work has been the desire to exploit the unique features of the pentadienyl ligand, namely, (a) its ability to interconvert readily between η^5-, η^3-, and η^1-bonding modes and (b) its susceptibility to attack, both external nucleophilic attack and internal migratory attack.

Our own efforts in this area have focused on pentadienyl–metal–phosphine complexes of the late transition metals.[1] These electron-rich molecules may ultimately function as catalysts for the activation and functionalization of small molecules such as CH_4 and CO_2.[3] Further-

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