$$f^0(\vec{r}) = [\partial\rho(\vec{r})/\partial N]_v^{\,0} \qquad (6)$$

The three cases have $\mu_S > \mu_R$, $\mu_S < \mu_R$, and $\mu_S \sim \mu_R$. A "frozen core" approximation now gives $d\rho = d\rho_{\text{valence}}$ in each case, and therefore, governing electrophilic attack,

$$f^-(\vec{r}) \approx \rho_{\text{HOMO}}(\vec{r}) \qquad (7)$$

governing nucleophilic attack,

$$f^+(\vec{r}) \approx \rho_{\text{LUMO}}(\vec{r}) \qquad (8)$$

and governing radical attack,

$$f^0(\vec{r}) \approx \tfrac{1}{2}[\rho_{\text{HOMO}}(\vec{r}) + \rho_{\text{LUMO}}(\vec{r})] \qquad (9)$$

These are the rules of classical frontier theory.[1] Errors in eq 7–9 should be small in the outer reaches of the species toward which the reagent approaches.

Frontier theory is equivalent, then, to the assumption that it is favorable for f to be big at a site, or that direction is preferred along which the incoming reagent will produce the biggest change in the system's electronic chemical potential.

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Trigonal-Bipyramidal Methyl Group Bridging Two Zirconocene–Ketene Centers

Robert M. Waymouth, Bernard D. Santarsiero, and Robert H. Grubbs*

*Contribution No. 6996, Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125*

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The role of methyl groups as bridging ligands has been a central topic in organometallic chemistry.[1] Although there was early controversy concerning the exact structure of such bridging groups,[2] it is well established that methyl bridges play a key role in alkylaluminum chemistry. In these cases and in most transition-metal analogues, the M–C–M angle is less than 90°. Only recently have complexes in which this angle approaches 180° been considered.[3-5] Calculations on $Li_2CH_3^+$ suggest that the linear M–C–M geometry is the most stable.[3] A neutron diffraction study of a B–CH_3Li complex indicated a linear structure in which the sp^3-methyl hydrogen atoms bridged to the lithium.[4] A linear methyl bridge has been reported for the dimer of a bis(pentamethylcyclopentadienyl)lutetium methyl complex.[5a] We report here the preparation of a complex in which a near-planar methyl group bridges two zirconium atoms.

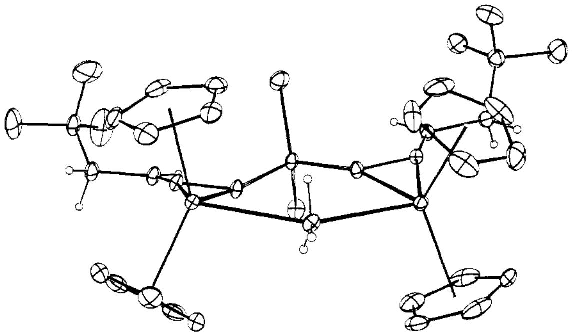
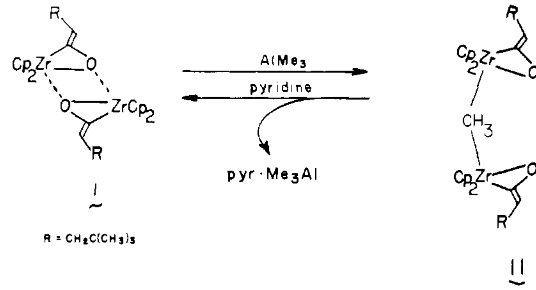


Figure 1. ORTEP diagram of II. Hydrogens on the cyclopentadienyl, *tert*-butyl, and aluminum methyl groups have been omitted for clarity.

Scheme I



In an attempt to activate zirconocene ketene complexes, a toluene solution of complex I[6] was treated with 1 equiv of trimethylaluminum. An intermediate forms and is observed to rearrange quantitatively to a symmetrical complex, II (Scheme I).[7] Colorless crystals of II suitable for an X-ray structure determination were obtained in 55% yield from a toluene–pentane solution.[8] The molecular structure of II is shown in Figure 1, and relevant bond angles and lengths are given in Figure 2. The bridging methyl hydrogens were located from a difference map and refined to a final $R = 0.081$ and a goodness-of-fit = 1.63 when averaged over 6573 reflections.

From the crystal structure, it is clear that the bridging methyl group is very nearly planar, approaching a trigonal-bipyramidal configuration. The carbon atom is displaced 0.08 Å out of the hydrogen atom plane; for a typical sp^3-hybridized methyl group, the carbon atom is displaced 0.3 Å out of the hydrogen atom plane. From Figure 2, it is also evident that the methyl bridge is not symmetrical but is 0.1 Å closer to Zr(2) than to Zr(1). This is

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(1) Holton, J.; Lappert, M. F.: Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

(2) Huffman, J. C.; Streib, W. E. *J. Chem. Soc. D* **1971**, 911.

(3) (a) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 527. (b) Schleyer, P. v. R.; Tidor, B.; Jemmis, E. D.; Chandrasekhar, J.; Wurthwein, E. U.; Kos, A. J.; Luke, B. T.; Pople, J. A. *Ibid.* **1983**, *105*, 484. (c) See also: Chinn, Jr., J. W.; Lagow, R. J. *Organometallics* **1984**, *3*, 75.

(4) (a) Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401. (b) Groves, D.; Rhine, W.; Stucky, G. D. *Ibid.* **1971**, *93*, 1553.

(5) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Forbus, T. R.; Martin, J. C. *Ibid.* **1979**, *101*, 5057. (c) Engelhardt, L. M.; Leung, W.; Raston, C. L.; Twiss, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 321. (d) Kaminsky, W.; Kopf, J.; Sinn, H.; Vollmer, H. J. *Angew. Chem., Intl. Ed. Engl.* **1976**, *15*, 629.

(6) (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (b) Straus, D. A. Ph.D. Thesis, California Institute of Technology, Pasadena, CA 1982. (c) Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *Ibid.* **1984**, *106*, 2210. (d) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *Ibid.* **1983**, *105*, 2068.

(7) II: ^{1}H NMR (benzene-d_6) δ 6.05 (t, $^3J_{HH} = 7.3$ Hz, 2H), 5.64 (s, 20 H), 2.14 (d, $^3J_{HH} = 7.3$ Hz, 4 H), 1.14 (s, 18 H), –0.19 (s, 3 H), –0.46 (s, 6 H); ^{13}C NMR (benzene-d_6) δ 178.3 (d, $^2J_{CH} = 7.3$ Hz, *C*O), 107.0 (d, $^1J_{CH} = 171.3$ Hz, C_5H_5), 102.1 (d, $^1J_{CH} = 147.9$ Hz, CH), 44.9 (t, $^1H_{CH} = 123.7$ Hz, CH_2), 31.6 [s, *C*$(CH_3)_3$], 30.0 [q, $^1J_{CH} = 124.5$ Hz, C(*C*$H_3)_3$], –9.24 (q, $^1J_{CH} = 136.2$ Hz, CH_3).

(8) II: crystal data, space group $P2_1/c$ ($0k0$ absent for k odd, $h0l$ absent for l odd); the unit cell parameters [$a = 10.2089$ (7) Å, $b = 20.214$ (3) Å, $c = 18.421$ (2) Å, $\beta = 94.375$ (8)°, $V = 3790.4$ (7) Å^3, $Z = 4$] were obtained by least-squares refinement of 25 2θ values. The data were collected at room temperature on a crystal mounted approximately along c in a glass capillary under N_2 with an Enraf-Nonius CAD4 diffractometer (graphite monochromator and Mo Kα radiation $\lambda = 0.71073$ Å). The total, 10114 ($+h$, $\pm k$, $\pm l$), yielded an averaged data set of 6573 reflections upon deletion of 87 for overlap; 5216 had $I > 0$ and 3380 had $I > 3\sigma(I)$. The four check reflections indicated no decomposition, and the intensity data were reduced to F^2. The positions of the two independent Zr atoms were derived from the Patterson map, and the subsequent Fourier map phased on these two atoms revealed the remainder of the structure. The bridging methyl hydrogen atoms and those on the *tert*-butyl groups were located from difference maps; all other hydrogen atoms were introduced into the model at idealized positions with isotropic $U = 0.101$ Å^2. Least-squares refinement of atomic coordinates and U's [anisotropic for all nonhydrogen atoms and isotropic for H(1), H(2), and H(3)] minimizing $\sum w\Delta^2$ with weights $w = \sigma^{-2}(F_o^{\,2})$ and $\Delta = F_o^{\,2} - (F_c/k)^0$ gave $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.0813$ [for $I > 0$, $R_F = 0.042$ for $I > 3\sigma(I)$] and S (goodness-of-fit) $= [\sum w\Delta^2/(n-p)]^{1/2} = 1.63$ ($p = 391$ parameters); the maximum shift/error ratio is 0.50, the average <0.10, and the maximum deviations in the $\Delta\rho$ map are close to the Zr atoms and are less than 1.1 e Å^{-3}. All calculations were carried out on a VAX 11/780 computer using the CRYRM system of programs. The form factors for all atoms were taken from: *Int. Tables X-Ray Crystallogr.* (**1974**), Table 2.2B. Those for Zr and Al were corrected for anomalous dispersion.

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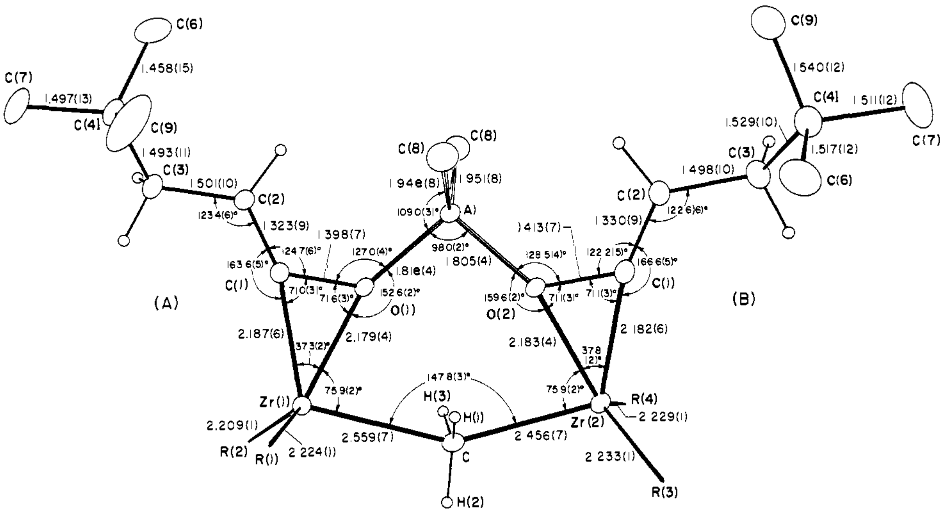

Figure 2. Additional bond lengths and angles: Al–C = 3.739 (8), C–H (1) = 0.94 (5), C–H(2) = 0.98 (5), C–H(3) = 0.86 (5) Å; H(1)–C–H(2) = 119 (4)°, H(1)–C–H(3) = 117 (4)°, H(2)–C–H(3) = 122 (4)°.

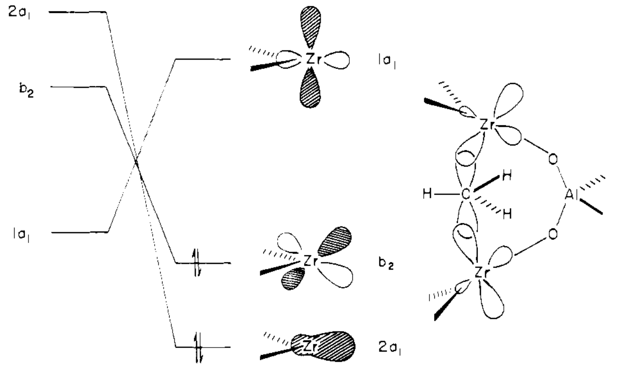

Figure 3.

consistent with the slight distortion of the methyl group from planarity. The bond distance Zr(2)–C of 2.456 (7) Å is comparable to the longest reported terminal Zr–C bond, 2.431 (5) Å, for the methyl group of $Cp_2Zr(\eta^2\text{-}C(NMe)CHPh_2)Me$.[9] The Zr(1)–C bond length of 2.559 (7) Å is not unreasonably long, since bridging metal–alkyl bonds are typically 0.1–0.2 Å longer than the corresponding terminal bond.[10]

The Zr–C–Zr angle is not 180° as might be expected for a trigonal-bipyramidal carbon atom but is 147.8 (3)°. We attribute this to the disposition of the zirconium bonding orbitals. According to Lauher and Hoffmann,[11] the zirconium orbitals available for bonding to the methyl group are derived from orbitals of a_1 symmetry. The orientation of the ketenes in II is such that these orbitals are directed away from the aluminum atom. Maximum overlap is achieved via a bent "banana" bond as illustrated in Figure 3.

The methyl group of II appears to be a pentacoordinate carbanion of approximate D_3h symmetry.[3,5b] The C–H coupling constant of 136.18 Hz is consistent with a large amount of sp^2 hybridization. The configuration of the methyl group is strikingly similar to that of Schleyer's $CH_3Li_2^+$, for which calculations indicate that the trigonal-bipyramidal geometry is energetically favored.[3] Our results, and those of Watson[5a] and Schleyer,[3] suggest that the trigonal-bipyramidal geometry is a stable configuration for carbanions in the coordination sphere of Lewis-acidic metals.

Complex II reacts with 1 equiv of pyridine in benzene (12 h, 25 °C) to afford the dimer I and the $Me_3Al\cdot py$ adduct, indicating that methyl transfer between the two metals is reversible.

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Supplementary Material Available: Summary of crystal data and intensity collection information (Table XI), atom coordinates (Tables X2 and X5), anisotropic Gaussian amplitudes (Table X4), bond lengths and angles (Table X3), structure factor amplitudes (Table X6), and labeling scheme (Figure 2) (43 pages). Ordering information is given on any current masthead page.

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[9] Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, *462*, ref 10.

[10] Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.

[11] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[12] Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

Relative Gas-Phase Acidities of the Alkanes

Charles H. DePuy* and Veronica M. Bierbaum*

Department of Chemistry
University of Colorado
Boulder, Colorado 80309

Robert Damrauer*

Department of Chemistry
University of Colorado at Denver
Denver, Colorado 80202

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Although the gas-phase acidities of a large number of organic molecules have been determined,[1] those of many of the simplest, namely, the alkanes, cycloalkanes, and substituted alkanes, remain to be established. This is so because these compounds are so weakly acidic that no way has yet been devised to generate the carbanions in the gas phase. The only exception is methane whose acidity (ΔH°_{acid} = 416.6 kcal/mol) can be calculated from thermochemical data which are unavailable for other alkanes.[2,3]

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[1] Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11. Bartmess, J. E., private communication. Boand, G.; Houriet, R.; Gäumann, T. *J. Am. Chem. Soc.* **1983**, *105*, 2203–2206.

[2] $\Delta H^\circ_{acid}(RH)$ is defined as the enthalpy of ionization to R^- and H^+; it can be computed from the bond-dissociation energy of R–H (McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532), the ionization potential of H· (Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables", NSRDS-NBS-37, 2nd ed.; National Bureau of Standards: Washington, D.C., 1971), and the electron affinity (EA) of R·.

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