σ-bond, which eventually is split homolytically:

$$CH_3ReO_3 \rightarrow CH_3 + ReO_3$$

The fate of the primary radical pair depends on the medium. The strong interaction of CH_3ReO_3 with water may facilitate an aquation of the ReO_3 fragment. Since the coupling of two methyl radicals is apparently not favored,[20] product formation occurs only by back electron transfer:

$$CH_3 + H_2OReO_3 \rightarrow CH_4 + H^+ReO_4^-$$

Such an outer-sphere electron transfer applies also to the oxidation of certain Co(II) complexes by methyl radicals.[22] While at low complex concentrations the photolysis of CH_3ReO_3 in water proceeds only by this mechanism, another process competes at higher concentrations. Methyl radicals have an extremely strong tendency to abstract hydrogen atoms.[21] Suitable hydrogen donors apparently include CH_3ReO_3.[23] Among other products, methane and ReO_3, which is insoluble and not very reactive,[11] are formed by irradiation of CH_3ReO_3 at higher concentrations.

In nonaqueous solvents the methyl radicals prefer to attack the solvent[3] and ReO_3 is formed upon photolysis of CH_3ReO_3 at any concentration. Acetonitrile is a very efficient hydrogen donor for methyl radicals, while chlorine atoms are easily abstracted from CCl_4.[22] Accordingly, the formation of methane was observed if CH_3ReO_3 was photolyzed in CH_3CN, while CH_3Cl was released when the irradiation was carried out in CCl_4.

It is quite interesting that a related Re(VII) complex apparently also undergoes a homolytic Re–C bond splitting in the primary photochemical step. The photolysis of $(Me_3SiCH_2)_3ReO_2$ yields $(Me_3SiCH_2)_4Re_2O_4$,[24] which should arise from dimerization of $(Me_3SiCH_2)_2ReO_2$ radicals. The product formation certainly depends on the reactivity of the Me_3SiCH_2 radical, which may abstract a hydrogen atom from the solvent or another complex molecule. Finally, thermolytic scission of the carbon–rhenium bonds even *in the dark* is a major decomposition route of higher alkylrhenium oxides of formula $RReO_3$. Thus, the instability of $(^tC_4H_9)ReO_3$ and $(Me_3CCH_2)ReO_3$ are due to the radical stability of *tert*-butyl and neopentyl, respectively, while $C_2H_5ReO_3$ can be isolated in a pure state.[25] On the basis of our present findings, both thermal and photolytic reactions, including radical pathways, are expected to yield catalytically active species resulting from compounds $RReO_3$.[26] Photochemical activation of this class of compounds should therefore be exploited in future catalytic applications.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[20] Although the coupling of methyl radicals is a rapid process,[21] their stationary concentration is apparently too small for an efficient dimerization.

[21] Lazár, M.; Rychlý, J.; Klimo, V.; Pelikán, P.; Valko, L. *Free Radicals in Chemistry and Biology*; CRC Press: Boca Raton, FL, 1989.

[22] Roche, T. S.; Endicott, J. F. *Inorg. Chem.* 1974, *13*, 1575.

[23] Generally, the photochemical dealkylation of methyl complexes almost exclusively yields methane.[3]

[24] Cai, S.; Hoffmann, D. M.; Lappas, D.; Woo, H.-G. *Organometallics* 1987, *6*, 2273.

[25] Herrmann, W. A.; de Meric de Bellefon, C.; Fischer, R. W.; Kiprof, P.; Romao, C. C. *Angew. Chem., Int. Ed. Engl.*, in press.

[26] For an updated review, cf.: Herrmann, W. A. *J. Organomet. Chem.* 1990, *382*, 1.

Preparation, Reactivity, and X-ray Structure of a Cationic Alkoxyzirconocene Complex

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Summary: **The tetrahydrofuran adduct of bis(cyclopentadienyl)-*tert*-butoxyzirconium(1+) tetraphenylborate (2) was prepared, in high yield, by reaction of *tert*-butanol with bis(cyclopentadienyl)(methyl)zirconium(1+) tetraphenylborate (1). Analogous reactions of compound 1 with less hindered alcohols were complicated by the formation of several compounds of undetermined structure. The structure of compound 2 was determined by X-ray diffraction: triclinic, space group $P\bar{1}$, a = 15.564 (2) Å, b = 17.253 (4) Å, c = 21.647 (3) Å, α = 106.12 (1)°, β = 94.71 (1)°, γ = 101.76 (1)°, V = 5407.3 (17) Å^3, Z = 6 with three independent molecules of 2 in the asymmetric unit, R = 0.0483, and R_w = 0.0652, for 9608 observed reflections with $F > 6\sigma(F)$. In this structure, the lone pairs on the oxygen atom of the *tert*-butoxy ligand are involved in significant back-donation to the electron deficient metal center, as revealed by the short Zr–O bonds and near-linear angles at oxygen in the three independent molecules. The exchange of bound and free THF is a higher energy process in solution as compared to that observed for compound 1. Complex 2 catalyzes the Diels–Alder reaction between methyl acrylate and dienes in CH_2Cl_2 solution under mild conditions.**

Introduction. There is considerable interest in the structure and chemistry of cationic zirconocene compounds of the group 4 transition elements; in particular, alkyl derivatives 1 serve as useful models for the catalytic intermediates implicated in olefin polymerization and hydrogenation processes.[1] Moreover, these compounds are active in a number of other catalytic and stoichiometric processes that should prove useful in organic chemistry.[2]

Quite surprisingly, very little attention has been devoted to the preparation and chemistry of heteroatom derivatives of these d^0, 14e$^-$ zirconocene compounds.[3] We report here

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[1] For leading references see: (a) Jordan, R. F.; Bajgur, C. S. *J. Am. Chem. Soc.* 1986, *108*, 7410. (b) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* 1986, 1610. (c) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* 1987, *109*, 4111. (d) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* 1987, *6*, 2556. (e) Jordan, R. F. *J. Chem. Educ.* 1988, *65*, 285. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* 1989, *111*, 2728. (g) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* 1989, *8*, 2892. (h) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Ibid.* 1990, *9*, 1539. (i) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Ibid.* 1990, *9*, 1650.

[2] (a) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* 1990, *9*, 1546 and references cited therein. (b) Jordan, R. F. Personal communication.

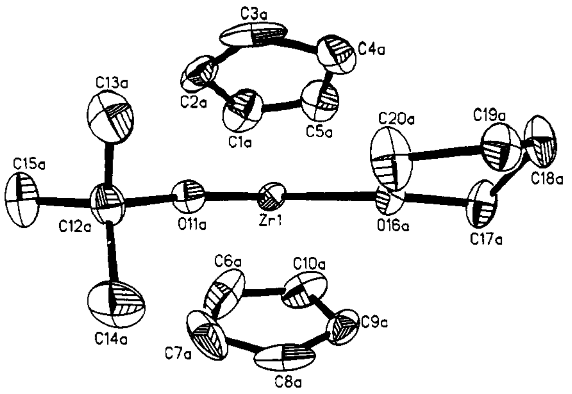
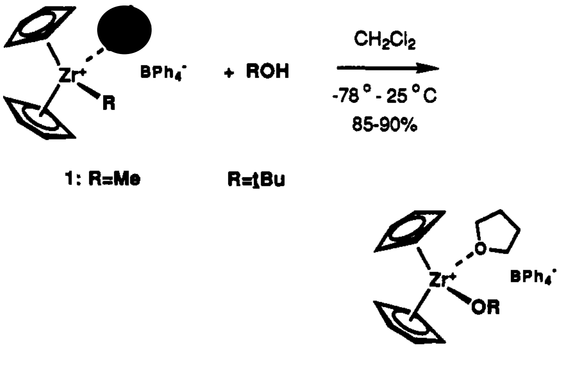


Figure 1. Molecular structure of one of the three independent cations of compound 2 in the unit cell with 30% thermal probability ellipsoids depicted and H atoms removed for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses [X(1a) and X(2a) are the centroids of the two cyclopentadienyl rings]: Zr(1)–O(11a) 1.899 (3), Zr(1)–O(16a) 2.200 (4), Zr(1)–X(1a) 2.221 (11), Zr(1)–X(2a) 2.217 (13), O(11a)–C(12a) 1.450 (6); O(11a)–Zn(1)–O(16a) 93.7 (1), X(1a)–Zr(1)–X(2a) 126.8 (5), Zr(1)–O(11a)–C(12a) 171.0 (4).

the preparation of a discrete derivative of this type (i.e. compound 2, R = *tert*-butyl, eq 1), the X-ray structure of this compound, which possesses some unusual features as compared with the alkyl derivatives 1, and some preliminary results concerning the use of such compounds as Lewis acid catalysts in organic synthesis.

Results and Discussion. The preparation of cationic compound 2 was readily achieved by the reaction of equimolar amounts of the known, cationic methylzirconocene complex 1 (R = Me)[1a] with *tert*-butanol in dichloromethane solution (eq 1). The spectral data[4] were



(1)

consistent with the monomeric structure indicated; the coordinated THF molecule (vide infra) could not be removed by, e.g., placing the complex prepared under high vacuum (10^{-5} mmHg). In contrast, the reaction of compound 1 with less sterically hindered alcohols (i.e. methanol, ethanol, or 2-propanol) led to the formation of a mixture of several unidentified products, none of which appear to be analogous to that of compound 2.

The molecular structure of one of the three independent molecules of complex 2 in the asymmetric unit (molecule 1) is depicted in Figure 1.[5] A packing diagram of the unit cell (along *c*) is included in the supplementary material. The cell is characterized by well-separated cationic units and tetraphenylborate counterions. The geometries of the latter show angular deviation from tetrahedral symmetry about the central boron atom (i.e. approximate D_{2d} symmetry) but are otherwise unexceptional and will not be discussed further.

The structures of the three independent cationic units are also rather similar, differing mainly in the relative orientation of the cyclopentadienyl (Cp) rings bound to the metal, the degree of thermal motion of the carbon atoms in the Cp rings, and/or the conformation adopted by the five-membered ring of the ligated THF molecule.

As can be seen from Figure 1 the *tert*-butoxide ligand is strongly bound to the metal—the Zr(1)–O(11a) distance of 1.899 (3) Å is very short compared with the sum of the covalent radii (~2.11 Å).[6] Furthermore, the alkoxide oxygen is approximately sp-hybridized with a Zr(1)–O(11a)–C(12a) angle of 171.0 (4)°. The other two independent molecules also have very short Zr–O bonds and near-linear angles at oxygen [Zr(2)–O(11b) = 1.880 (4) Å, Zr(3)–O(11c) = 1.892 (4) Å; Zr(2)–O(11b)–C(12b) = 175.6 (5)°, Zr(3)–O(11c)–C(12c) = 170.5 (4)°]. The closest neutral structural analogue of compound 2 that has been structurally characterized is $(\eta^8\text{-COT})(\eta^3\text{-C}_3\text{H}_5)\text{ZrO}^t\text{Bu}$.[7] In this structure the average Zr–O bond length in the two independent molecules [1.910 (2) Å] is similar to that observed here [1.890 (4) Å] and the average Zr–O–C^{t}Bu angle [169.8 (2)°] is somewhat less obtuse than is the average angle observed here [172.3 (5)°]. Other related compounds are the well-characterized μ-oxo dimers, $[\text{Cp}_2\text{ZrX}]_2\text{–O}$, in which the Zr–O distances are typically 1.95 Å and the Zr–O–Zr angles are ~165–170°.[8] Thus, in the structure of 2, the oxygen atom of the *tert*-butoxide ligand is undoubtedly engaged in significant pπ–dπ back-donation to the electron deficient metal center.

The structure of an analogous cationic titanium compound, $[\text{Cp*}_2\text{Ti}^+(\text{OH})(\text{H}_2\text{O})\cdot2\text{THF}][\text{BPh}_4^-]$, has been reported recently.[9] In this structure the Ti–OH bond is 1.853 (5) Å and the Ti–O–H angle is 125.7 (23)°. A neutral analogue of this compound, $\text{Cp}_2\text{Ti(OEt)Cl}$, has been structurally characterized, and the Ti–O bond is 1.855 (2) Å and the Ti–O–C angle is 133.2 (2)°.[10] The Cp* ligands in the former structure may sufficiently stabilize the cationic center so that strong back-donation to Ti by oxygen is not as pronouned as in the structure reported here.

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(3) The preparation, by a different route, and spectral characterization of a complex analogous to compound 2 with R = $\text{OC(CH}_3)\text{Ph}_2$ has been reported.[1a] See also ref 9 for some cationic titanium systems where R = H and the ligand is water.

(4) Compound 2: ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C) δ 7.46 (br m, 8 H), 7.15 (t, J = 7.0 Hz, 8 H) 7.00 (t, J = 7.0 Hz, 4 H), 6.32 (s, 10 H), 3.23 (m, 4 H), 1.82 (m, 4 H) 1.32 (s, 9 H) ppm; ^{13}C NMR (50 MHz, CD_2Cl_2, 25 °C) δ 162.6 (four lines, $^1J_{\text{CB}}$ = 49.2 Hz), 135.4 (meta carbons), 125.7 (four lines, $^2J_{\text{CB}}$ = 2.4 Hz), 121.7 (para carbons), 114.6 (C_5H_5), 82.95 $[\text{OC(CH}_3)_3]$, 77.96 $[\text{O(CH}_2\text{CH}_2)_2]$, 31.35 $[\text{OC(CH}_3)_3]$ 25.69 $[\text{O(CH}_2\text{CH}_2)_2]$ ppm; IR (Nujol) 1480, 1427, 1365, 1174, 1002, 843, 820, 811, 741, 735, 707 cm^{-1}. Anal. Calcd for $\text{C}_{42}\text{H}_{47}\text{BO}_2\text{Zr}$: C, 73.55; H, 6.91. Found: C, 73.37; H, 7.12.

(5) Compound 2: Triclinic, space group $P\bar{1}$, a = 15.564 (2) Å, b = 17.253 (4) Å, c = 21.647 (3) Å, α = 106.12 (1)°, β = 94.71 (1)°, γ = 101.76 (1)°, V = 5407.3 (17) Å^3, Z = 6 with three independent molecules of 2 in the asymmetric unit, R = 0.0483, R_w = 0.0652, for 9608 observed reflections with $F > 6\sigma(F)$.

(6) (a) *The Chemical Bond*; Pauling, L. Cornell University Press: Ithaca, NY, 1967; pp 148–150. See also: (b) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo Zirconium and -Hafnium Compounds*; Ellis Horwood Ltd.: West Sussex, U.K., 1986; Chapters 4 and 5.

(7) Brauer, D. J.; Kruger, C. *Organometallics* **1982**, *1*, 204.

(8) For typical examples see: (a) Clarke, J. C.; Drew, M. G. B. *Acta Crystallogr.* 1974, *B30*, 2267. (b) Petersen, J. L. *J. Organomet. Chem.* 1979, *166*, 179. (c) Fronczek, F. R.; Baker, E. C.; Sharp, P. R.; Raymond, K. N.; Alt, K. G.; Rausch, M. D. *Inorg. Chem.* 1976, *15*, 2284. (d) Hunter, W. E.; Hrncir, R. V.; Bynum, R. V.; Pentilla, R. E.; Atwood, J. L. *Ibid.* 1983, *2*, 750.

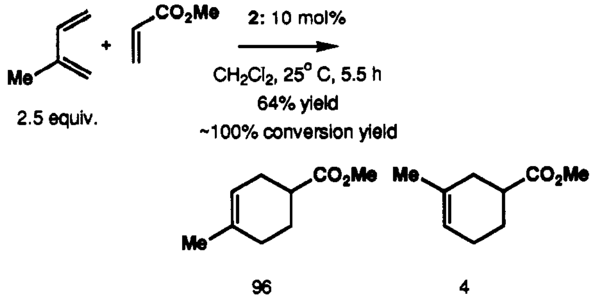
(9) (a) Bochmann, M.; Jaggar, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838. See also: (b) Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1988**, *348*, 291.

(10) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

Additional indirect evidence for back-donation by the *tert*-butoxide ligand is found by examining the geometry adopted by the ligated THF molecule. The THF molecule adopts an "in plane" conformation, as opposed to a perpendicular bonding mode in which the remaining lone pair on oxygen can back-donate into an empty d_{y^2} orbital on the metal.[11] The Zr(1)–O(16a) distance of 2.200 (4) Å is significantly longer than that observed in compound 1 itself [2.122 (14) Å].[1a] The "in-plane" coordination mode has been observed before where steric interaction of the THF molecule with the Cp ligands precludes perpendicular ligation in the solid state (e.g. in $[Cp^*_2Ti^+CH_3{\cdot}THF][BPh_4^-]$).[9a] Also, in the structure of $Cp'_2Zr^+\{(Z)\text{-}C(Me){=}C(Me)(^nPr)\}^*(THF)BPh_4^-$ ($Cp' = \eta\text{-}MeC_5H_4$), the coordinated THF molecule is rotated 50° out of the perpendicular orientation and the Zr–O bond length is 2.289 (6) Å.[1g] The conformation adopted by the ligated THF in this structure was attributed to the steric and/or electronic properties of the Cp′ and the alkenyl ligands. In the structure reported here, however, perpendicular coordination is not precluded by steric effects. The alkoxide ligand apparently stabilizes the metal center, so that additional back-donation from ligated THF is unnecessary.

At room temperature, the rate of exchange of free and bound THF in a mixture of compound 2 (0.190 M in CD_2Cl_2) and THF (1.0 equiv) is *slower* on the ^{13}C NMR (and ^1H NMR) time scale in CD_2Cl_2 solution than in the case of compound 1 (R = Me). At −40 °C, separate and sharp signals are observed at δ 77.97 and 25.70 and 67.72 and 25.41 for **2***THF and free THF, respectively. A value for the apparent second-order rate constant for an associative ligand-exchange process[12] at the temperature of coalescence (249 ± 2 K) of the signals at 25.70 and 25.41 ppm is $(2.37 \pm 0.05) \times 10^2\ M^{-1}\ s^{-1}$ ([Zr] = 0.190 M). The slower rate of exchange of free and bound THF observed for compound 2 (compared with compound 1[12]) is consistent with an increase in electron density at the metal center in compound 2 as a result of back-donation from the oxygen atom of the *tert*-butoxide ligand.

We have briefly examined the utility of complex 2 as a Lewis acid catalyst for the Diels–Alder reaction. For example, methyl acrylate and excess isoprene were converted to methyl 4-methylcyclohex-3-enecarboxylate (64% yield, 100% conversion yield) in the presence of 10 mol % of compound 2 in methylene chloride solution at room temperature over a period of 6 h (eq 2).[13] Very little of the "meta" regioisomer was produced under these conditions (para:meta 96.2:3.8). The regioselectivity of this process compares favorably with that obtained by using traditional Lewis acid catalysts (e.g. $AlCl_3$, C_6H_6; para:meta = 95:5 at 25 °C),[14] although the catalytic efficiency is somewhat reduced (e.g. $AlCl_3$ (10 mol %); 50% yield after 3 h at 25 °C).[14] The cycloaddition of methyl acrylate to cyclopentadiene was also catalyzed by compound 2; in this case complete conversion was observed after 1 h at room temperature (eq 3). Enhanced endo selectivity was observed (endo:exo = 11:1) compared with the uncatalyzed reaction (endo:exo ~4:1).[15]



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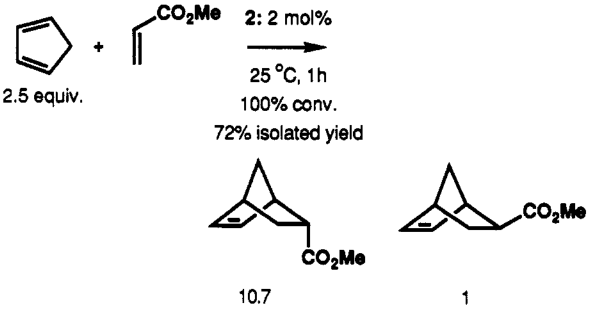

(3)

We are continuing to explore the reactivity and utility of these sterically demanding Lewis acids and will report on our results in due course.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supplementary Material Available: Textual presentation of the experimental details for the preparation of compound 2 and for the Diels–Alder reactions, low-temperature ^{13}C NMR spectra of compound 2 and low-temperature ^1H NMR spectra of compound 1, ORTEP diagrams and a packing diagram, tables of crystal, collection, and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters (33 pages); a listing of structure factors for compound 2 (51 pages). Ordering information is given on any current masthead page.

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

[12] As expected for an associative process, the *rate* of exchange is sensitive to both THF concentration and that of compound 2. An overall reaction order of 2.0 ● 0.2 was determined by VT-NMR experiments at two different concentrations of compound 2 at 249 K ([Zr]:[THF] = 1.0; $[Zr]_1 = 0.190$ M; $k_1 = 45\ s^{-1}$ $[Zr]_2 = 0.135$ M; $k_2 = 32\ s^{-1}$). The very low solubility of compound 1 in CD_2Cl_2 solution at low temperatures precluded determination of the exchange rates by ^{13}C NMR spectroscopy; a rough estimate for the apparent second-order constant for exchange of free and bound THF in compound 1 was determined by ^1H NMR spectroscopy to be $(2.81 \pm 0.05) \times 10^4\ M^{-1}\ s^{-1}$ at the temperature of coalescence (*T* = 188 ● 2 K at 200 MHz, [Zr] = 0.016M). See also ref 1g.

[13] In contrast, complex 1 did not catalyze the Diels–Alder reaction of methyl acrylate and isoprene. S. Collins, unpublished result.

[14] Inukai, T.; Kojima, T. *J. Org. Chem.* **1966**, *31*, 1121 and references therein.

[15] At 0 °C the reported selectivity is 4.5:1 endo:exo: Sauer, J.; Kredel, J. *Tetrahedron Lett.* **1966**, 731.