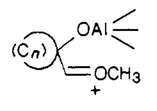
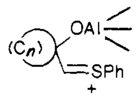
product **8**, only a single isomer also results; its stereochemistry is assigned by analogy.

This approach for ring expansion to α-methoxy ketones proceeds well for four- and five-membered rings. At present, larger rings do not succumb to ring expansion in contrast to the phenylthio reagent **1**. The reason for the difference may relate to the better ability of oxygen vs. sulfur to stabilize a positive charge. The higher stability associated with the presumed intermediate in the oxygen series, i.e., **9**, compared to the sulfur series, i.e., **10**, may provide a smaller driving force for rearrangement.



9



10

α-Thio- and α-alkoxy sulfones are excellent conjuctive reagents for ring expansion to α-heteroatom-substituted cycloalkanones. In contrast to reagents like diazo compounds, they are more available, simpler and safer to handle, and they offer greater structural flexibility. Analogues of the rearrangements reported herein are not known for the diazo series. The better anion-stabilizing abilities of a sulfone compared to a sulfide also make these reactions more general than the corresponding reactions using thio ethers.[12] The ability of sulfones to be chemical chameleons, i.e., to be nucleophiles in the presence of base and electrophiles in the presence of acid, appears to provide great opportunities for designing new reagents and reactions.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

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(12) In control experiments, we find that lithiated methoxymethyl phenyl sulfide[13] which we previously employed for ring expansions of lactones cannot be used for ring expansions of cycloalkanones. A ring expansion of a (butylthio)methylenecyclohexanone has been reported: Bosch, M. P.; Camps, F.; Coll, J.; Guerrero, A.; Tatsuoka, T.; Meinwald, J. *J. Org. Chem.* **1986**, *51*, 773.

(13) Trost, B. M.; Miller, C. H. *J. Am. Chem. Soc.* **1975**, *97*, 7182.

Models for Organometallic Molecule-Support Complexes. Synthesis and Properties of Cationic Organoactinides

Zerong Lin, Jean-Francois Le Marechal, Michal Sabat, and Tobin J. Marks*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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Chemical and ^{13}C CPMAS NMR data[1] suggest that cationic species play a major role in the surface and possibly catalytic chemistry of actinide alkyls (and by inference, of many other organometallics[2]) on electron-deficient metal oxide supports (e.g., γ-Al_2O_3). Straightforward solution routes to model cationic organoactinide alkyls and complexes free of coordinating[3] bases would be highly desirable, and we report here the first efficient synthetic approach as well as initial observations on the properties of the products. Base-coordinated $Cp_2Zr(Me)L^+$ complexes have recently been prepared via a completely different route.[4]

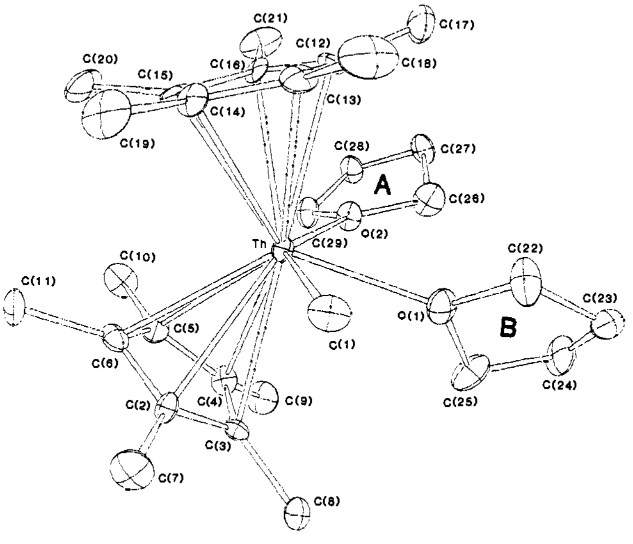

Figure 1. Molecular structure of the cation portion of $Cp'_2Th(Me)(THF)_2^+BPh_4^-$ (**7**). Important bond distances (Å) and angles (deg) are Th–C(1) = 2.49 (1), Th–O(1) = 2.531 (9), Th–O(2) = 2.628 (8), Th–C_{ring} = 2.80 (1,2,4,10),[12] C(1)–Th–O(1) = 72.9 (4), C(1)–Th–O(2) = 140.2 (4), and ring centroid–Th–ring centroid = 136.2. Thermal ellipsoids are at the 30% probability level.

Trialkylammonium tetraphenylborate reagents[5] effect quantitative (by NMR) protonolysis of actinide alkyls in *noncoordinating* solvents to yield cationic tetraphenylborates (eq 1–3). For

$$Cp'_2ThMe_2 + R_3N^+H\ BPh_4^- \xrightarrow[-MeH]{toluene} Cp'_2Th(Me)NR_3^+\ BPh_4^- \xrightarrow{-NR_3} Cp'_2Th(Me)^+\ BPh_4^- \quad (1)$$

1a, R = Me, 70% isolated, yield
1b, R = Et
2, 90% isolated yield

$$Cp'_2Th(o\text{-}C_6H_4CH_2NMe_2)Me + Et_3N^+H\ BPh_4^- \xrightarrow[-MeH,\ -NEt_3]{toluene} Cp'_2Th(o\text{-}C_6H_4CH_2NMe_2)^+BPh_4^- \quad (2)$$

3
4, 88% isolated yield

$$Cp^{\ddagger}_3ThMe + Et_3N^+H\ BPh_4^- \xrightarrow[-MeH,\ -NEt_3]{toluene} Cp_3^{\ddagger}Th^+BPh_4^- \quad (3)$$

5a, $Cp^{\ddagger} = CH_3C_5H_4$
5b, $Cp^{\ddagger} = Me_3SiC_5H_4$
6a, $Cp^{\ddagger} = CH_3C_5H_4$, 82% isolated yield
6b, $Cp^{\ddagger} = Me_3SiC_5H_4$, 70% isolated yield

Me_3N, intermediate amine complexes are sometimes isolated (**1a**), while bulkier Et_3N forms labile adducts that dissociate upon workup, yielding base-free cationic products. All new compounds

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(2) (a) *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: Amsterdam, 1986. (b) Hartley, F. R. *Supported Metal Complexes, a New Generation of Catalysts*; Reidel: Boston, 1985. (c) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302–308. (d) *Transition Metal Catalyzed Polymerization. Alkenes and Dienes*; Quirk, R. P., Hsieh, H. L., Klingensmith, G. C., Tait, P. J., Eds.; Harwood Publishers for MMI Press: New York, 1983. (e) Yermakov, Yu. I. *J. Mol. Catal.* **1983**, *21*, 35–55 and references therein. (f) Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981.

(3) (a) Takats, J. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I., Eds.; Reidel: Dordrecht, 1985; Chapter 5 and references therein. (b) Fischer, R. D.; Klähne, E.; Sienel, G. R. *J. Organomet. Chem.* **1982**, *238*, 99–111 and references therein.

(4) (a) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718–1719. (b) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410–7411. See also: (c) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J9; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219–7220. (d) Bochmann, M.; Wilson, L. *J. Chem. Soc., Chem. Commun.* **1986**, 1610–1611. (e) For Cp'_2ThMe_2, we find silver regents[4a] to be ineffective in inert, noncoordinating solvents and to give low yields in coordinating solvents.

(5) Barker, B. J.; Sears, P. J. *J. Phys. Chem.* **1974**, *78*, 2687–2688 and references therein.

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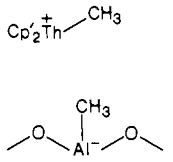
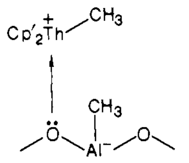
were characterized by standard spectroscopic[6]/analytical[7] techniques.

NMR spectroscopic data suggest a tightly ion-paired or nonrigid η^n-arene[8,9] structure for **2**. Thus, upon lowering the temperature, 400-MHz ^{1}H spectra in toluene-d_8/CF_2Cl_2 reveal broadening and collapse of the BPh_4^- resonances and emergence of a more complex aryl pattern by −80 °C (the Th–CH_3 and Cp′ signals broaden only slightly). In comparison to $NaBPh_4$, the 75-MHz ^{13}C CPMAS spectrum of **2** exhibits a complex pattern in the aryl region.[6]

Recrystallizing **2** from THF/pentane yields $Cp'_2Th(Me)(THF)_2^+BPh_4^-$ (**7**).[6,7] The resonance position of Th–$^{13}CH_3$, δ 69.3, the lowest yet observed for a $Cp'_2Th(CH_3)X$ complex in solution, can be qualitatively correlated with electron deficiency at thorium[1d] and is remarkably close to the δ 71.0 observed for $Cp'_2Th(^{13}CH_3)_2$ adsorbed on dehydroxylated alumina.[1c] Here, surface cationic structures such as A and B have been proposed.[1c] The diffraction-derived molecular structure of **7** (Figure 1)[10] consists of discrete $Cp'_2Th(Me)(THF)_2^+$ and unexceptional[11] BPh_4^- ions. The cation is a relatively rare[3a,12] "bent-sandwich" $Cp'_2An(X)Y_2$ complex with an unsymmetrical arrangement of X and Y groups in the equatorial girdle. The ring centroid–Th–ring centroid angle of 136.2° and the average Th–C(ring) distance of 2.80 (1, 2, 4, 10) Å[13] are not unusual for neutrally charged Cp'_2ThX_2 complexes.[3a,12,14] The maximum deviation of an atom (C(1)) from the Th,C(1),O(1),O(2) least-squares plane is 0.23 Å. The present Th–CH_3 distance of 2.49 (1) Å may be at the low end of the range for Th–C(alkyl) distances (c.f. 2.446 (4) and 2.543 (4) Å in $Cp'_2Th(neopentyl)_2$,[14c] 2.493 (11) Å in $Cp'_2\overline{ThCH_2Si(Me)_2\text{-}o\text{-}C_6H_4}$,[14c] 2.55 (3) Å in $Cp'_2Th(C_4H_6)$,[14b] 2.571 (9) Å in $Th(CH_3)_7^{3-}$ [15] but is not conspicuously short (c.f. 2.377 (8) Å in $Cp'_2Th(\mu\text{-}CH_2)(\mu\text{-}1\text{-}\eta^1{:}\eta^5\text{-}3,4\text{-}Me_2C_5H_2)Zr(1,2\text{-}Me_2C_5H_3)Me$[14a]). The distances Th–O(1) = 2.531 (9) and Th–O(2) = 2.628 (8) Å compare favorably with Th–O = 2.53 (1) to 2.59 (1) Å in $Th(C_8H_8)(THF)_2Cl_2$.[16] Dihedral angles between the Th,C(1),O(1),O(2) and THF C(α)OC(α′) planes, 29.5° (A) and 60.8° (B),[17] suggest that the differing Th–O distances may reflect, among other factors,[18] differing π donation to thorium frontier orbitals[19] in the equatorial girdle.



A



B

In regard to reactivity, **2** is far more active than Cp'_2ThMe_2 for ethylene polymerization ($N_t \approx 1$ min^{-1} vs. ≈0 min^{-1} at 25 °C, 1 atm C_2H_4).[20] Curiously, Th–CH_3 hydrogenolysis in **2** is very slow while that in **7** (yielding a hydride, δ 19.2) proceeds at ca. one-third the rate of that in Cp'_2ThMe_2 where $k = 3.3 \times 10^{-2}$ M^{-1} s^{-1} (30 °C).[21] It thus appears that ancillary ligands and

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(6) **1a**: ^{1}H NMR (room temperature, C_6D_6) δ 7.85 (br complex, 8 H, *o*-Ph), 7.25 (t, $^3J_{HH} = 6 \pm 1$ Hz, 8 H, *m*-Ph), 7.07 (t, $^3J_{HH} = 6 \pm 1$ Hz, 4 H, *p*-Ph), 2.05 (s, 9 H, NMe_3), 1.59 (s, 30 H, Cp′), 0.39 (s, 3 H, Th–Me). **2**: ^{1}H NMR (room temperature, C_6D_6) δ 7.85 (br complex, 8 H, *o*-Ph), 7.25 (t, $^3J_{HH} = 7.3$ Hz, 8 H, *m*-Ph), 7.10 (t, $^3J_{HH} = 7.3$ Hz, 4 H, *p*-Ph), 1.59 (s, 30 H, Cp′), 0.40 (s, 3 H, Th–Me); ^{13}C NMR (room temperature, C_6D_6) δ 138.1 (Ph), 124.3 (Ph), 64.8 (quart, $^1J_{CH} = 115.5$ Hz, Th–Me), 12.4 (quart, $^1J_{CH} = 126.6$ Hz, $C_5(\mathit{C}H_3)_5$); ^{13}C CPMAS 141–137 (br, Ph), 132 (Ph), 128.7 and 126.9 ($\mathit{C}_5(CH_3)_5$), 125 (Ph), 124 (Ph), 121 (Ph), 71.8 (Th–Me), 13.3 $C_5(\mathit{C}H_3)_5$). **3**: ^{1}H NMR (room temperature, C_6D_6) δ 7.80 (t, $^3J_{HH} = 5.5$ Hz, 1 H, Ph), 7.40 (t of d, $^3J_{HH} = 5.5$, $^4J_{HH} = 2$ Hz, 1 H, Ph), 7.20 (m, 1 H, Ph), 7.17 (d of d, $^3J_{HH} = 5.5$, $^4J_{HH} = 2$ Hz, 1 H, Ph), 3.38 (s, 2 H, $C\mathit{H}_2$), 2.01 (s, 6 H, NMe_2), 1.91 (s, 30 H, Cp′), −0.10 (s, 3 H, Th–Me). **4**: ^{1}H NMR (room temperature, CD_3CN) δ 7.5–6.9 (m, 24 H, Ph), 3.90 (s, 2 H, $C\mathit{H}_2$), 2.55 (s, 6 H, NMe_2), 2.10 (s, 30 H, Cp′); ^{13}C CPMAS (room temperature, neat solid) δ 140.1–119.0 (aromatics), 129.5 and 126.8 ($\mathit{C}_5(CH_3)_5$), 57.0 ($\mathit{C}H_2$), 45.5 and 40.1 ($N(\mathit{C}H_3)_2$), 10.7 and 10 ($C_5\mathit{C}H_3)_5$. **5a**: ^{1}H NMR (room temperature, C_6D_6) δ 5.85 and 5.65 (AA′BB′, 12 H, $C_5\mathit{H}_4Me$), 2.10 (s, 9 H, $C_5H_4\mathit{Me}$), 0.55 (s, 3 H, Th–Me). **5b**: ^{1}H NMR (room temperature, C_6D_6) δ 6.22 (s, 12 H, $C_5\mathit{H}_4SiMe_3$), 0.75 (s, 3 H, ThMe), 0.20 (s, 27 H, $SiMe_3$). **6a**: ^{1}H NMR (room temperature, THF-d_8) δ 7.32 (m, 8 H, *o*-Ph), 6.89 (t, $^3J_{HH} = 7$ Hz, 8 H, *m*-Ph), 6.74 (t of t, $^3J_{HH} = 7$, $^4J_{HH} = 1.2$ Hz, 4 H, *p*-Ph), 6.55 and 6.33 (AA′BB′, 12 H, $C_5\mathit{H}_4Me$), 2.4 (s, 9 H, $CpC\mathit{H}_3$). **6b**: ^{1}H NMR (room temperature, C_6D_6) δ 8.20 (m, 8 H, *o*-Ph), 7.35 (t, $^3J_{HH} =$ Hz, 8 H, *m*-Ph), 7.20 (t, $^3J_{HH} = 7$ Hz, 4 H, *p*-Ph), 6.50 and 6.40 (AA′BB′, 12 H, $C_5\mathit{H}_4SiMe_3$), 0.20 (s, 9 H, $CpSi\mathit{Me}_3$). **7**: ^{1}H NMR (room temperature, THF-d_8) δ 7.28 (br complex, 8 H, *o*-Ph), 6.87 (t, $^3J_{HH} = 7.4$ Hz, 8 H, *m*-Ph), 6.72 (t, $^3J_{HH} = 7.2$ Hz, 4 H, *p*-Ph), 3.62 (m, 8 H, THF), 2.05 (s, 30 H, Cp′), 1.78 (m, 8 H, THF), 0.25 (s, 3 H, Th–Me); ^{13}C NMR (room temperature, THF-d_8) δ 137.2 (d, $^1J_{CH} = 155.6$ Hz, Ph), 128.3 (s, $\mathit{C}_5(CH_3)_5$), 125.7 (d, $^1J_{CH} = 149.5$ Hz, Ph), 121.8 (d, $^1J_{CH} = 155.9$ Hz, Ph), 69.3 (quart, $^1J_{CH} = 112.6$ Hz, Th–Me), 11.8 (quart, $^1J_{CH} = 126.8$ Hz, $C_5(\mathit{C}H_3)_5$); ^{13}C CPMAS (room temperature, neat solid) δ 136 (Ph), 127.6 and 126.8 ($\mathit{C}_5(CH_3)_5$), 126 (Ph), 123 (Ph), 73 (110 Hz br, αC, THF), 68.8 (Th–Me), 25 (90 Hz br, βC, THF), 13.5 and 12.4 ($C_5(\mathit{C}H_3)_5$).

(7) All isolable compounds gave satisfactory analytical results except **7** (0.70% low in C), which slowly loses THF in vacuo; see the supplementary material for details.

(8) Actinide(IV) arene complexes: (a) Campbell, G. C.; Cotton, F. A.; Haw, J. F.; Schwotzer, W. *Organometallics* **1986**, *5*, 274–279. (b) Cotton, F. A.; Schwotzer, W.; Simpson, C. Q. *Angew. Chem., Int Ed. Engl.* **1986**, *25*, 637–639.

(9) BPh_4 π-complexes: (a) Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069–1072 and references therein. (b) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191–1197. (c) Kruger, G. J.; DuPreez, A. L.; Haines, R. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1302–1305.

(10) Crystal data: $C_{53}H_{69}BO_2Th$; $M_r = 980.98$; monoclinic, space group $P2_1/c$; $a = 10.523$ (2) Å, $b = 12.417$ (3) Å, $c = 34.534$ (7) Å, $\beta = 97.44$ (2)° at −120 °C; $V = 4482$ (3) Å^3; $Z = 4$; $d_{calcd} = 1.45$ g cm^{-3}. The structure was solved by Patterson and Fourier techniques and refined to $R(F)$ and $R_w(F)$ of 0.045 and 0.058, respectively, by using 3708 absorption-corrected reflections with $I > 3\sigma(I)$ measured on a CAD4 diffractometery (Mo Kα radiation, $\lambda = 0.71069$ Å, $2\theta_{max} = 45°$). A full description of the structure determination is included in the supplementary material.

(11) (a) Watkins, M. I.; Ip, W. M.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2365–2372. (b) Glidewell, C.; Holden, H. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *38B*, 667–669.

(12) (a) Marks, T. J.; Streitweiser, A., Jr. In *The Chemistry of the Actinide Elements*; 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Chapter 22. (b) Marks, T. J. *Ibid.* Chapter 23. (c) Marks, T. J.; Day, V. W. In ref 3a, Chapter 4. (d) $Cp_2'U(H)(dmpe)$: Duttera, M. R.; Fagan, P. J.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 865–866. (e) $Cp'_2U(pyrazole)Cl_2$: Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653–2660.

(13) The first number in parentheses following an averaged value of a bond length or angle is the estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

(14) (a) Smith, G. M; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 1854–1856. (b) Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549–551 and references therein. (c) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56 and references therein. (d) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237–246.

(15) Lauke, H.; Swepston, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 6841–6843.

(16) Zalkin, A.; Templeton, D. H.; LeVanda, C.; Streitwieser, A., Jr. *Inorg. Chem.* **1980**, *19*, 2560–2563.

(17) This angle is close to 90° in $Cp_2Zr(Me)(THF)^{+\,4b}$ and closer to 0° in similar lanthanide complexes: (a) Ni, C.; Zhang, Z.; Deng, D.; Qian, C. *J. Organomet. Chem.* **1986**, *306*, 209–214 ($Cp_2Lu(Cl)(THF)$, ca. 0°). (b) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263–270 ($Cp_2Yb(Me)(THF)$, 16.9°)

(18) Close intramolecular nonbonded interactions include C(8)–C(25) = 3.46 (2), C(9)–C(29) = 3.48 (2), C(17)–C(26) = 3.68 (2), C(21)–C(29) = 3.35 (2), and C(25)–C(26) = 3.29 (2) Å.

(19) (a) Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.*, in press. (b) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467–4476.

(20) (a) Cf. $N_t \approx 10^5$ min^{-1} for $(Cp'_2LaH)_2$: Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (b) Relatively high density, linear polyethylene[20c] is produced: mp 132 °C with <5CH_3/1000CH_2 (by ^{13}C NMR[20d]). (c) *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1986; Vol. 6, pp 386–465. (d) Koenig, J. L. *Chemical Microstructure of Polymer Chains*; Wiley: New York, 1980; pp 364–373.

(21) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.*, in press.

gegenion interactions significantly modulate the reactivity of these cationic species. Further studies of organo-f-element cations are under way.

Acknowledgment. This research was supported by the DOE under contract DE-FG02-86ER13511. The diffraction instrumentation was acquired under NSF Grant CHE-8300958 and NIH Grant 1-510-RR-01672-01. J.-F. Le Marechal thanks NATO for a postdoctoral fellowship.

Supplementary Material Available: Analytical data, X-ray experimental datails (including positional and anisotropic displacement parameters), and tables of bond lengths and angles (33 pages); tables of observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Synthesis and Crystal Structure of an Enantiomerically Pure, Internally Coordinated Alkylchloroborane. The Boron-Centered Anomeric Effect [*J. Am. Chem. Soc.* **1985**, *107*, 7167–7172]. CHRISTOPHER S. SHINER,* CHARLES M. GARNER, and R. CURTIS HALTIWANGER

The connectivity of the *gem*-dimethyl bridge is drawn incorrectly in structures **3** (p 7168, right column) and **4–7**, and should be as shown in **3** (p 7168, left column).

In the ^{1}H NMR data for **5** (p 7170), substitute 1.9–2.5 (m, 7 H) for 1.9–2.5 (m, 9 H), and add 3.39 (t, J = 6.8 Hz, 2 H).

Novel Peri-Condensed Weitz-Type Donors: Synthesis, Physical Properties, and Crystal Structures of 3,10-Dithiaperylene (DTPR), 1,6-Dithiapyrene (DTPY), and Some of Their CT Complexes [*J. Am. Chem. Soc.* **1986**, *108*, 3460–3466]. KAZUHIRO NAKASUJI,* HIROHISA KUBOTA, TOMOYUKI KOTANI, ICHIRO MURATA,* GUNZI SAITO, TOSHIAKI ENOKI, KENICHI IMAEDA, HIROO INOKUCHI, MASAKO HONDA, CHUJI KATAYAMA, and JIRO TANAKA

Page 3463, Table III: space group for $Ph_2DTPR{-}ClO_4$ should read *C*2/*c*.

Gas-Phase Acidities and Heats of Formation of 2,4- and 2,5-Cyclohexadien-1-one, the Keto Tautomers of Phenol [*J. Am. Chem. Soc.* **1986**, *108*, 5699–5701]. CHRISTOPHER S. SHINER,* PAUL E. VORNDAM, and STEVEN R. KASS

The protocol described in the Supplementary Material for the Diels–Alder step en route to **3** has been found to be unreliable. We recommend the following alternative: a 30-mL heavy-walled glass tube was charged with 15.0 mL (0.139 mol) of bicyclo[2.2.1]hepta-2,5-diene, 5.6 mL (28.8 mmol) of 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene, and 3.8 mL (54 mmol) of propylene oxide and was heated at 180 °C for 24 h.

The spectroscopic data for **4** presented as Supplementary Material are in fact those for the *endo* stereoisomer of **4**, which we prepared from the Diels–Alder adduct of cyclohex-2-en-1-one and cyclopentadiene. The correct data for **4** are as follows: ^{1}H NMR ($CDCl_3$) 1.14 (br m, 2 H), 2.05 (br m, 3 H), 2.32 (s, 1 H), 2.38 (dddd, 1 H, J = 1.9, 4.2, 4.8, 10.1 Hz), 3.07 (s, 1 H), 6.00 (dt, 1 H, J = 1.9, 10.1 Hz), 6.13 (dd, 2 H, J = 3.1, 4.8 Hz), 6.79 (dt, 1 H, J = 4.8, 10.1 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) 30.2, 34.0, 44.5, 48.1, 48.4, 51.9, 129.7, 136.7, 137.4, 148.5, 200.0; IR (film) 3000 (w), 2900 (s), 1650 (s); mass spectrum (70 eV), m/z (rel intensity) 160 (0.3%, M+), 95 (25%), 66 (100%), 39 (32%). Anal. ($C_{11}H_{12}O$) C, H.

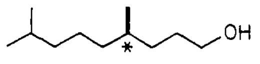
Catalysis of Electrochemical Reactions at Redox Polymer Coated Electrodes. Mediation of the Fe(III)/Fe(II) Oxido-Reduction by a Polyvinylpyridine Polymer Containing Coordinatively Attached Bisbipyridine Chlororuthenium Redox Centers [*J. Am. Chem. Soc.* **1986**, *108*, 8175–8182]. CLAUDE P. ANDRIEUX, OTTO HAAS, and JEAN-MICHEL SAVÉANT*

Page 8178, footnote 21: $C_P^\circ \simeq 10$ mol·L^{-1} should read $C_P^\circ \simeq 1$ mol·L^{-1}.

Page 8179, footnote 23: 1.3×10^{-10} cm^2 s^{-1} should read 1.3×10^{-7} cm^2 s^{-1}.

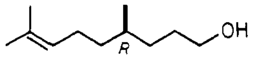
Enantioselective Hydrogenation of Allylic and Homoallylic Alcohols [*J. Am. Chem. Soc.* **1987**, *109*, 1596–1597]. HIDEMASA TAKAYA,* TETSUO OHTA, NOBORU SAYO, HIDENORI KUMOBAYASHI, SUSUMU AKUTAGAWA, SHIN-ICHI INOUE, ISAMU KASAHARA, and RYOJI NOYORI*

Page 1597: The structure of **7** was incorrectly drawn as



7

The proper structure is



7