(μ-PhC(O)SCS)(μ-Me$_3$CS)Fe$_2$(CO)$_6$, 118378-36-2; [CH$_3$]$_3$CSH, 75-66-1; CH$_2$-CHCH$_2$Cl, 107-05-1; (η^5-C$_5$H$_5$)Fe(CO)$_2$I, 12078-28-3; (diphos)NiCl$_2$, 14647-23-5; *cis*-(Ph$_3$P)$_2$PdCl$_2$, 15604-37-2; *cis*-(Ph$_3$P)$_2$PtCl$_2$, 15604-36-1; (μ-MeS)(μ-EtS)Fe$_2$(CO)$_6$, 69480-75-7; (μ-EtS)$_2$Fe$_2$(CO)$_6$, 15634-62-5; (μ-EtS)(μ-(CH$_3$)$_3$CS)Fe$_2$(CO)$_6$, 118378-43-1; benzyl chloride, 100-44-7; ethanethiol, 75-08-1; iodoethane, 75-03-6; benzoyl chloride, 98-88-4; methyl isothiocyanate, 556-61-6; ethyl isothiocyanate, 542-85-8; phenyl isothiocyanate, 103-72-0; methyl isocyanate, 624-83-9; ethanesulfenyl chloride, 1496-75-9.

Supplementary Material Available: Tables of crystal data and anisotropic thermal parameters (2 pages); a listing of observed and calculated structure factors for [Et$_3$NH][(μ-SO$_2$)(μ-*t*-BuS)-Fe$_2$(CO)$_6$ (10 pages). Ordering information is given on any current masthead page.

Nine-Membered Metallacyclic Metaloxycarbene Complexes by Means of Sequential Coupling of Butadiene with a Ketone and a Metal Carbonyl at Bis(cyclopentadienyl)zirconium

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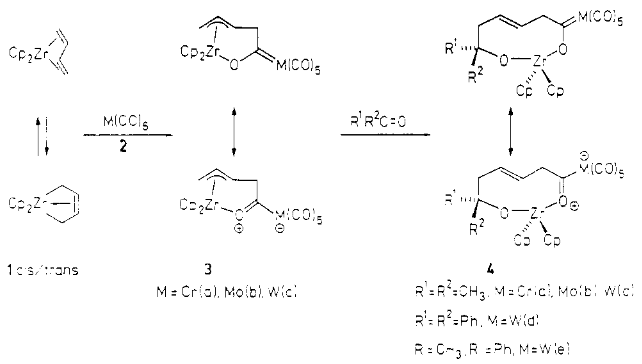
The metallacyclic zirconoxycarbene complexes $Cp_2\overline{Zr(\eta^3\text{-}C_3H_4)CH_2C[=M(CO)_5]O}$ (**3**) (M = Cr, Mo, W) were prepared by reacting M(CO)$_6$ with (butadiene)ZrCp$_2$. The (π-allyl)Zr functional group of complexes **3** was added to acetone, benzophenone, or acetophenone to regioselectively yield the nine-membered metallacyclic metaloxycarbene complexes $Cp_2\overline{ZrOC(R^1R^2)CH_2CH{=}CHCH_2C[=M(CO)_5]O}$ (**4a–e**), exhibiting a trans carbon–carbon double bond. The (MeCp)$_2$Zr analogue **4c′** (R^1 = R^2 = CH$_3$; M = W) was characterized by X-ray diffraction (space group $P2_1/n$, a = 15.623 (2) Å, b = 8.008 (1) Å, c = 21.672 (5) Å, β = 99.65 (1)°, Z = 4, R = 0.036, R_w = 0.034). Gibbs activation energies of topomerization, $\Delta G^{\ddagger}_{ent}$ between 16.6 and 17.0 kcal/mol, were estimated from the dynamic NMR spectra of the nine-membered metallacycles **4**.

Introduction

The medium-ring-sized *trans*-cycloalkenes are extraordinary olefins with regard to their reactivity and stereochemical features. In the sequence of *trans*-cyclodecene, *trans*-cyclononene, and *trans*-cyclooctene increasing ring strain and decreasing ring perimeter make the conformational equilibration more difficult. These *trans*-cycloalkenes exhibit chiral ground-state geometries. Racemization requires at least one olefinic hydrogen substituent to be moved through the inside of the circular framework. Rapidly increasing activation energies of enantiomerization are therefore observed on going from *trans*-C$_{10}$H$_{18}$ ($\Delta G^{\ddagger}_{ent}$(276 K) ≈ 12 kcal/mol) through *trans*-C$_9$H$_{16}$ ($\Delta G^{\ddagger}_{ent}$(263 K) ≈ 19 kcal/mol) to the *trans*-C$_8$H$_{14}$ system ($\Delta G^{\ddagger}_{ent}$(428 K) ≈ 35 kcal/mol).[1] We have prepared a group of organometallic compounds exhibiting very similar stereochemical features (with regard to their structural characteristics as well as their dynamic properties) although their composition is quite different from that of the *trans*-cycloalkenes.

Results and Discussion

Scheme I



Preparation of the Metallacyclic Carbene Complexes. Nine-membered metallacyclic organometallic systems were constructed by coupling 1,3-butadiene, a (CO)$_5$M-bound carbonyl ligand (M = Cr, Mo, W), and the C=O functionality of a ketone at the bis(cyclopentadienyl)zirconium bent metallocene unit. Reaction of the (butadiene)zirconocene system with the group 6 metal carbonyls yielded the metallacyclic (π-allyl)-zirconoxycarbene complexes **3a–c**, as described previously.[2] Complexes **3** contain a zirconium-bound allyl ligand which

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(1) *trans*-Cycloalkenes. (a) Ten-membered ring: Binsch, G.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 5157. Noe, E. A.; Wheland, R. C.; Glazer, E. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3488. (b) Nine-membered ring: Cope, A. C.; Banholzer, K.; Keller, H.; Pawson, B. A.; Whang, J. J.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3644. (c) Eight-membered ring: Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc.* **1965**, *87*, 3649. (d) See also: Marshall, J. A. *Acc. Chem. Res.* **1980**, *13*, 213.

(2) (a) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R. D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. Erker, G.; Mühlenbernd, T.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 402. Erker, G.; Lecht, R. *J. Organomet. Chem.* **1986**, *311*, 45. Reviews: Erker, G. In *Organometallics in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer-Verlag: Heidelberg, 1987, 143. Erker, G. *Polyhedron*, **1988**, in press. (b) See also: Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 572; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 584. Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145.

0276-7333/89/2308-0450$01.50/0

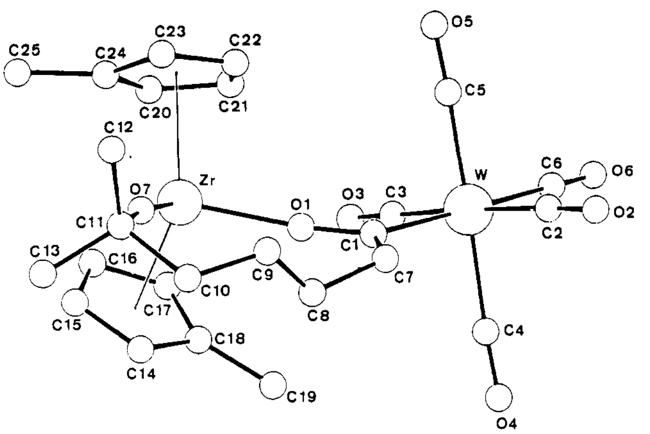

Figure 1. A view of the molecular geometry of the metallacyclic zirconoxycarbene complex **4c′** in the crystal.

can undergo nucleophilic addition reactions to organic carbonyl compounds.[3] Reaction of **3c** with 1 equiv of acetone thus led to the formation of the metallacyclic carbene complex **4c**. Similarly, benzophenone added cleanly to the π-allyl function of **3c** with carbon–carbon and metal–oxygen bond formation to give **4d**. The molybdenum- or chromium-containing carbene complex **4b** or **4a**, respectively, was analogously derived from the reaction of **3b**/**3a** with acetone. Finally, coupling **3c** with acetophenone produced the nine-membered metallacyclic carbene complex **4e**.

Experimental Section

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk type glassware. Solvents were dried and freshly distilled from potassium/benzophenone, lithium aluminum hydride, or P_4O_{10} under argon prior to use. Deuteriated solvents benzene-d_6, toluene-d_8, and *o*-xylene-d_{10} were treated with sodium/potassium alloy and $CDCl_3$ with P_4O_{10} (Sicapent, Merck), then distilled, and stored under argon. The following spectrometers were used: NMR, Bruker WP 200 SY (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz), Bruker AC 200 (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz, variable temperature), and Bruker WM 400 (^{13}C, 100.6 MHz); IR, Nicolet 5DXC FT IR spectrometer. Elemental analyses were carried out at the Mikroanalytisches Laboratorium des Instituts für Anorganische Chemie der Universität Würzburg. Melting points are uncorrected. Petroleum ether mentioned in the text refers to the 30–50 °C boiling range fraction. (Butadiene)bis(cyclopentadienyl)zirconium (**1**),[5] (butadiene)bis(methylcyclopentadienyl)zirconium (**1′**),[6] and the (π-allyl)zirconoxycarbene complexes **3a–c** were prepared according to literature procedures.[2]

Reaction of (Butadiene)Zr(CpCH$_3$)$_2$ (1′) with W(CO)$_6$. A mixture of 2.07 g (5.88 mmol) of hexacarbonyltungsten and 1.97 g (6.49 mmol, 1.1 equiv) of (butadiene)bis(methylcyclopentadienyl)zirconium **1′** in 150 mL of toluene was stirred for 20 h at room temperature. Solvent was then removed in vacuo. The residue was suspended in 30 mL of petroleum ether and filtered. The solid was washed twice with 30 mL of petroleum ether and dried in vacuo for 10 h to give 2.94 g (76%) of **3c′** as a pale yellow powder, mp 121 °C dec. Anal. Calcd for $C_{22}H_{20}O_6WZr$ (655.5): C, 40.32; H, 3.08. Found: C, 39.99; H, 2.95. ^{1}H NMR (C_6D_6, 200 MHz, numbering scheme analogous to that used in Figure 1): δ 5.30–4.85 (m, 9 H, MeCp-H and H9), 4.55 (m, 1 H, H8), 4.03 (dd, 1 H, H7′), 2.49 (dd, 1 H, H7), 1.70/1.68 (each s, 3 H, Me), 1.60 (m, 2 H, H10$_{syn,anti}$). Coupling constants: ^2J (Hz), H7/H7′ 17.8; ^3J (Hz), H7/H8 10.1, H7′/H8 4.8. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 342.3 (C–carbene), 205.5 (C–CO$_{trans}$), 200.7 (C–CO$_{cis}$), 130.3 (C9), 125.8/122.1 (C$_{ipso}$), 112.7, 112.3, 110.6, 110.3, 108.9, 106.7, 105.6, 105.3 (C–Cp), 112.7 (C8 under C–Cp signal), 71.9 (C7), 45.8 (C10), 15.2/14.9 (C–Me). Coupling constants: ^1J (Hz), C7/H7 125, C10/H10 146, C(Me)/H(Me) 128, C–CO$_{cis}$/^{183}W 127. IR (C_6D_6): ν(CO) 2057, 1963, 1917 cm^{-1}.

Reaction of the Zirconoxycarbene Complex 3c with Acetone. A sample of 570 mg (0.87 mmol) of **3c′** was dissolved in 10 mL of toluene. One molar equivalent of acetone (64 μL) was added. The solution was stirred at room temperature for 3 h. The solution was filtered and evaporated to dryness. The residue was triturated twice with 10 mL of petroleum ether. The solvent was decanted and the residue dried in vacuo for 3 h to give 450 mg (72%) of **4c′** as a yellow powder, which was recrystallized from toluene/heptane (4:1), mp 145 °C. Anal. Calcd for $C_{25}H_{26}O_7WZr$ (713.6): C, 42.08; H, 3.67. Found: C, 42.05; H, 3.70. ^{1}H NMR ($CDCl_3$, 200 MHz, numbering scheme see Figure 1): δ 6.41–5.80 (m, 8 H, MeCp-H), 5.10 (m, 1 H, H9), 4.87 (m, 1 H, H8), 4.53 (dd, 1 H, H7′), 3.19 (dd, 1 H, H7), 2.13/2.06 (each s, 3 H, *Me*-Cp), 2.1 (under *Me*-Cp signals, H10′), 1.87 (br t, 1 H, H10), 1.27/1.21 (each s, 3 H, H12 and H13). Coupling constants: ^2J (Hz), H7/H7′ 18.6; ^3J (Hz), H7/H8 10.0, H7′/H8 3.7, H8/H9 14.5, H9/H10 10.5, H9/H10′ 4.3. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 331.6 (C–carbene), 204.6 (C–CO$_{trans}$), 199.7 (C–CO$_{cis}$), 132.4 (C9), 128.0 (C8), 129.1/123.5 (C$_{ipso}$), 117.5, 115.0, 114.9, 113.7, 113.0, 112.1, 109.8, 106.5 (C-Cp), 83.2 (C11), 71.7 (C7), 48.6 (C10), 32.2/28.8 (C12, C13), 15.6/15.0 (*Me*–Cp). Coupling constants: ^1J (Hz), C7/H7 129, C8/H8 153, C9/H9 152, C10/H10 123, C12/H12 and C13/H13 124 and 126, C(*Me*–Cp)/H(*Me*–Cp) 126; C–CO$_{cis}$/^{183}W 127. IR (KBr): ν(CO) 2059, 1975, 1911 cm^{-1}.

X-ray diffraction data for $C_{25}H_{26}O_7WZr$ (4c′): crystal size 0.20 × 0.28 × 0.44 mm; monoclinic; space group $P2_1/n$; $a = 15.623$ (2) Å, $b = 8.008$ (1) Å, $c = 21.672$ (5) Å; $\beta = 99.65$ (1)°; $V = 2673.0$ Å^3; $Z = 4$; $d_{calcd} = 1.77$ g/cm^3; μ(Mo) = 48.13 cm^{-1}; $F(000) = 1384$ e; scan mode Ω–2θ; $T = 20$ °C; $(\sin\theta)/\lambda_{max} = 0.70$ Å; analytical absorption correction min 0.57, max 0.74; 8469 measured reflections ($\pm h,+k,+l$); 7695 unique reflections; 4703 observed reflections ($I > 2.0\sigma(I)$); parameter varied 307; max shift/esd 0.03; $R = 0.036$, $R_w = 0.034$; ρ(max) = 0.87 e/Å^3.[7]

Reaction of 3a with Acetone. A sample of 480 mg (0.97 mmol) of **3a** was suspended in 15 mL of toluene. One equivalent of acetone (72 μL) was added and the mixture stirred for 2 h at room temperature. The suspension slowly dissolved. The resulting slightly turbid solution was filtered. Cooling to −30 °C gave 300 mg (56%) of **4a** as yellow crystals, mp 152 °C dec. Anal. Calcd for $C_{23}H_{22}O_7CrZr$ (553.6): C, 49.90; H, 4.01. Found: C, 50.03; H, 4.09. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.32/6.25 (each s, 5 H, Cp-H), 5.07 (ddd, 1 H, H9), 4.87 (ddd, 1 H, H8), 4.65 (dd, 1 H, H7′), 3.28 (dd, 1 H, H7), 2.17 (dd, 1 H, H10′), 1.81 (br t, 1 H, H10), 1.24/1.19 (each s, 3 H, Me). Coupling constants: ^2J (Hz), H7/H7′ 18.3, H10/H10′ 12.7; ^3J (Hz), H7/H8 9.9, H7′/H8 3.5, H8/H9 14.3, H9/H10 11.3, H9/H10′ 3.4. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 355.2 (C–carbene), 224.4 (C–CO$_{trans}$), 218.6 (C–CO$_{cis}$), 132.1 (C9), 127.4 (C8), 113.4/113.1 (Cp), 83.6 (C11), 68.8 (C7), 48.4 (C10), 32.0/28.0 (Me). IR (KBr): ν(CO) 2050, 1970, 1911 cm^{-1}.

Reaction of 3b with Acetone. In a similar manner 240 mg (0.44 mmol) of **3b** in 5 mL of toluene was reacted with 1 equiv of acetone (33 μL) to give, after filtration and crystallization at −78 °C, 230 mg (87%) of **4b** as fine yellow crystals, mp 137 °C dec. Anal. Calcd for $C_{23}H_{22}O_7MoZr$ (597.6): C, 46.23; H, 3.71. Found: C, 46.46; H, 3.80. ^{1}H NMR (toluene-d_8, 200 MHz): δ 5.87/5.78 (each s, 5 H, Cp–H), 4.67–4.31 (m, 3 H, H7′, H8, H9), 2.90 (dd, 1 H, H7), 1.79 (dd, 1 H, H10′), 1.42 (br t, 1 H, H10),

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(3) (a) Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (b) See also: Kobayashi, Y.; Umejama, K.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1984**, 621. Sato, F.; Iijima, S.; Sato, M. *Tetrahedron Lett.* **1981**, *22*, 243.

(4) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

(5) Erker, G.; Engel, K.; Sarter, C. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Academic Press: New York, 1986; Vol. 3, p 29.

(6) Frömberg, W., Dissertation, Bochum, 1986. Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem.* **1986**, *98*, 456; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463. *s-cis*/*s-trans* ratio: 60:40. See for comparison: Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

(7) For further details concerning the methods and programs used see: Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *3*, 215.

0.87/0.78 (each s, 3 H, Me). Coupling constants: ^2J (Hz), H7/H7′ 17.9, H10/H10′ 14.7; ^3J (Hz), H7/H8 9.7, H9/H10′ 3.5. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 350.4 (C–carbene), 214.9 (C–CO$_{trans}$), 208.3 (C–CO$_{cis}$), 131.9 (C9), 127.3 (C8), 113.4/113.0 (Cp), 83.3 (C11), 70.3 (C7), 48.5 (C10), 31.7/27.8 (Me). IR (C_6D_6): ν(CO) 2059, 1970, 1928 cm^{-1}.

Reaction of 3c with Acetone. By the same route 1.03 g (1.64 mmol) of **3c** in 15 mL of toluene was reacted with 1 equiv of acetone (121 μL). After filtration, crystallization at -30 °C, concentration of the mother liquor to half volume, and a second crystallization at -30 °C, a total of 590 mg (52%) of **4c** was obtained as yellow crystals, mp 160 °C dec. Anal. Calcd for $C_{23}H_{22}O_7WZr$ (686.5): C, 40.30; H, 3.23. Found: C, 39.67; H, 3.06. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.31/6.25 (each s, 5 H, Cp-H), 5.11 (ddd, 1 H, H9), 4.88 (ddd, 1 H, H8), 4.55 (dd, 1 H, H7′), 3.04 (dd, 1 H, H7), 2.19 (dd, 1 H, H10′), 1.83 (br t, 1 H, H10), 1.25/1.20 (each s, 3 H, Me). Coupling constants: ^2J (Hz), H7/H7′ 18.3, H10/H10′ 12.5; ^3J (Hz), H7/H8 9.9, H7′/H8 4.2, H8/H9 14.9, H9/H10 10.8, H9/H10′ 4.0. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 332.5 (C–carbene), 204.9 (C–CO$_{trans}$), 200.2 (C–CO$_{cis}$), 132.1 (C9), 127.8 (C8, δ 128.4 in THF-d_8), 113.4/113.1 (Cp), 83.3 (C11), 72.0 (C7), 48.7 (C10), 31.8/27.7 (Me). Coupling constants: ^1J (Hz), C7/H7 122, C8/H8 149, C9/H9 152, C10/H10 128, C(Me)/H(Me) 122, C(Cp)/H(Cp) 173, C–CO$_{cis}$/^{183}W 125. IR (KBr): ν(CO) 2059, 1968, 1913 cm^{-1}.

Reaction of 3c with Benzophenone. A sample of 850 mg (1.36 mmol) of **3c** and 247 mg (1 equiv) of benzophenone were suspended in 15 mL of diethyl ether and stirred at room temperature for 3 days. During this period the suspension slowly dissolved. The remaining fine precipitate was allowed to settle. The resulting clear yellow solution was carefully decanted and evaporated to dryness. The oily residue was stirred with petroleum ether at -78 °C for 30 min. The solvent was then removed in vacuo at this temperature. The resulting solid was washed with 30 mL of petroleum ether and dried in vacuo for 4 h to give 820 mg (74%) of **4d** as a fine crystalline material, mp 120 °C dec. Anal. Calcd for $C_{33}H_{26}O_7WZr$ (809.6): C, 48.96; H, 3.24. Found: C, 49.30; H, 3.19. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.27–6.96 (m, 10 H, Ph), 6.05/5.62 (each s, 5 H, Cp), 4.88 (m, 1 H, H9), 4.67 (m, 1 H, H8), 4.52 (br dd, 1 H, H7′), 2.82 (br dd, 1 H, H10′), 2.65 (dd, 1 H, H7), 2.48 (dd, 1 H, H10). Coupling constants: ^2J (Hz), H7/H7′ 18.1, H10/H10′ 13.1; ^3J (Hz), H7/H8 9.9, H7′/H8 4.0, H9/H10 10.4. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 333.6 (C–carbene), 204.8 (C–CO$_{trans}$), 199.5 (C–CO$_{cis}$), 149.0/147.8 (C$_{ipso}$), 132.2 (C9), 130.0, 128.2, 127.8, 127.2, 126.6, 126.4, 126.2, (C8, C-Ph), 113.8/113.7 (C-Cp), 89.7 (C11), 71.7 (C7), 47.1 (C10); coupling constant ^1J-(C–CO$_{cis}$/^{183}W) = 127 Hz. IR (C_6D_6): ν(CO) 2059, 1971, 1925 cm^{-1}.

Reaction of 3c with Acetophenone. A sample of 560 mg (0.89 mmol) of **3c** was suspended in 15 mL of toluene. One equivalent of acetophenone (104 μL) was added and the resulting mixture stirred at room temperature for 4 h. After the suspension had dissolved, the solution was filtered. The filtrate was evaporated to dryness. The viscous residue was triturated with 10 mL of petroleum ether in an ultrasonic bath for 30 min. The resulting suspension was filtered. The solid was washed with petroleum ether and dried in vacuo for several hours to give 330 mg (50%) of **4e**/**4e′** as a yellow powder, mp 145 °C dec. Anal. Calcd for $C_{28}H_{24}O_7WZr$ (747.6): C, 44.99; H, 3.24. Found: C, 44.68; H, 2.94. ^{1}H NMR ($CDCl_3$, 200 MHz) for **4e**: δ 7.47–7.22 (m, 5 H, Ph), 6.42/6.17 (each s, 5 H, Cp), 5.27 (ddd, 1 H, H9), 4.98 (ddd, 1 H, H8), 4.56 (dd, 1 H, H7′), 3.15 (dd, 1 H, H7), 2.73 (br dd, 1 H, H10′), 2.19 (br t, 1 H, H10), 1.47 (br s, 3 H, Me). Coupling constants: ^2J (Hz), H7/H7′ 18.6, H10/H10′ 12.5; ^3J (Hz), H7/H8 9.4, H7′/H8 4.4, H8/H9 15.9, H9/H10 11.9, H9/H10′ 3.9. ^{1}H NMR ($CDCl_3$, 200 MHz) for **4e**: δ 6.26/6.22 (each s, Cp), 1.65 (br s, Me). ^{13}C NMR ($CDCl_3$, 50.3 MHz) for **4e**: δ 332.4 (C–carbene), 204.7 (C–CO$_{trans}$), 199.6 (C–CO$_{cis}$), 149.5 (C$_{ipso}$), 132.2 (C9), 128.3, 128.1, 126.8, 124.2 (C8, C-Ph), 113.8/133.3 (Cp), 86.6 (C11), 71.6 (C7), 47.1 (C10), 30.0 (Me); coupling constant ^1J(C–CO$_{cis}$/^{183}W) = 127 Hz. IR (**4e**/**4e′** mixture, C_6D_6): ν(CO) 2059, 1978, 1924 cm^{-1}.

Results

Table I. X-ray Crystal Structure Analysis of 4c′: Selected Bond Lengths (Å) and Angles (deg)

Bond Distances			
W–C1	2.206 (5)	O5–C5	1.140 (8)
W–C2	2.038 (6)	O6–C6	1.141 (8)
W–C3	2.041 (6)	O7–C11	1.417 (6)
W–C4	2.041 (7)	C1–C7	1.530 (7)
W–C5	2.044 (6)	C7–C8	1.499 (8)
W–C6	2.017 (6)	C8–C9	1.310 (7)
Zr–O1	2.093 (3)	C9–C10	1.492 (7)
Zr–O7	1.920 (3)	C10–C11	1.553 (8)
Zr–C14	2.557 (5)	C11–C12	1.527 (8)
Zr–C15	2.500 (6)	C11–C13	1.539 (8)
Zr–C16	2.487 (5)	C14–C15	1.410 (8)
Zr–C17	2.543 (6)	C14–C18	1.429 (7)
Zr–C18	2.614 (5)	C15–C16	1.395 (8)
Zr–C20	2.524 (5)	C16–C17	1.409 (9)
Zr–C21	2.520 (5)	C17–C18	1.416 (8)
Zr–C22	2.542 (6)	C18–C19	1.499 (8)
Zr–C23	2.585 (6)	C20–C21	1.388 (9)
Zr–C24	2.537 (5)	C20–C24	1.408 (9)
O1–C1	1.278 (6)	C21–C22	1.390 (9)
O2–C2	1.140 (8)	C22–C23	1.39 (1)
O3–C3	1.139 (8)	C23–C24	1.419 (9)
O4–C4	1.144 (9)	C24–C25	1.50 (1)
Bond Angles			
C6–W–C5	89.8 (3)	C7–C1–O1	112.7 (4)
C6–W–C4	92.7 (3)	C7–C1–W	123.8 (3)
C6–W–C3	87.5 (2)	O1–C1–W	123.5 (3)
C6–W–C2	91.1 (2)	O2–C2–W	176.2 (5)
C6–W–C1	176.7 (2)	O3–C3–W	177.8 (5)
C5–W–C4	177.2 (2)	O4–C4–W	177.7 (6)
C5–W–C3	88.9 (2)	O5–C5–W	178.3 (5)
C5–W–C2	93.5 (2)	O6–C6–W	175.0 (6)
C5–W–C1	89.6 (2)	C8–C7–C1	114.8 (4)
C4–W–C3	92.3 (2)	C9–C8–C7	126.1 (5)
C4–W–C2	85.4 (2)	C10–C9–C8	124.5 (5)
C4–W–C1	88.0 (2)	C11–C10–C9	112.7 (4)
C3–W–C2	177.3 (2)	C13–C11–C12	109.9 (4)
C3–W–C1	89.3 (2)	C13–C11–C10	110.2 (5)
C2–W–Cl	92.1 (2)	C13–C11–O7	109.4 (4)
O7–Zr–O1	106.1 (1)	C12–C11–C10	111.3 (5)
C1–O1–Zr	168.6 (3)	C12–C11–O7	108.4 (4)
C11–O7–Zr	171.7 (3)	C10–C11–O7	107.6 (4)

X-ray Crystal Structure Analysis of a Typical Example. Starting from the methyl–Cp-substituted conjugated diene complex (butadiene)Zr(CpMe)$_2$ (1′),[6] we have obtained the carbene complex (MeCp)$_2$ZrOC(Me$_2$)-CH$_2$CH=CHCH$_2$C[=W(CO)$_5$]O (**4c′**) by the route indicated. This typical example of the carbene complexes **4** was characterized by X-ray diffraction. The bent metallocene unit [angles D(1),Zr,D(2) = 129.4° (D(1) and D(2) denote the centroids of the cyclopentadienyl rings made up by carbon atoms C(14)–C(18) and C(20)–C(24), respectively); O(1),Zr,O(7) = 106.1 (1)°] is part of a rather rigid metallacyclic framework.[3a] The zirconium to oxygen bonds are both very short [Zr–O(1) = 2.093 (3) Å; Zr–O(7) = 1.920 (3) Å]. Bonding angles at both zirconium bound oxygens are rather large, deviating not very much from the linear M–O–C arrangements [angles Zr,O(1),C(1) = 168.6 (3)°; Zr,O(7),C(11) = 171.7 (3)°]. These structural features indicate considerable ligand to metal π-interaction of both zirconium–oxygen linkages,[8] although being quite different in strength. The Zr–O(7) π-conjugation is more pronounced, as becomes evident from the substantially shorter bond distance and the slightly larger bond angle at oxygen.[9] Of the two oxygen centers, O(1) appears to be the

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(8) Erker, G.; Dorf, U.; Krüger, C.; Tsay, Y.-H. *Organometallics* **1987**, *6*, 680. Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179. Clarke, J. F.; Drew, M. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2267. Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

Table II. Positional Parameters of the Non-Hydrogen Atoms of 4c′

atom	*x*	*y*	*z*
W	0.3190 (1)	0.2306 (1)	0.0362 (1)
Zr	0.5237 (1)	0.2745 (1)	0.2417 (1)
O1	0.4210 (2)	0.3145 (4)	0.1678 (1)
O2	0.1175 (3)	0.3081 (7)	0.0239 (2)
O3	0.5200 (3)	0.1653 (6)	0.0375 (2)
O4	0.3279 (4)	0.5996 (6)	−0.0170 (2)
O5	0.3065 (3)	−0.1290 (6)	0.0966 (2)
O6	0.2935 (4)	0.0697 (8)	−0.0985 (2)
O7	0.4861 (2)	0.3615 (4)	0.3152 (1)
C1	0.3490 (3)	0.3374 (6)	0.1312 (2)
C2	0.1898 (4)	0.2788 (8)	0.0305 (3)
C3	0.4484 (4)	0.1895 (8)	0.0383 (2)
C4	0.3265 (4)	0.4666 (9)	0.0020 (3)
C5	0.3098 (4)	−0.0008 (8)	0.0744 (3)
C6	0.2986 (4)	0.1285 (9)	−0.0501 (3)
C7	0.2851 (3)	0.4425 (7)	0.1610 (2)
C8	0.3247 (3)	0.5356 (6)	0.2187 (3)
C9	0.3242 (3)	0.4887 (7)	0.2766 (2)
C10	0.3794 (3)	0.5638 (7)	0.3325 (2)
C11	0.4521 (3)	0.4439 (7)	0.3637 (2)
C12	0.4164 (4)	0.3123 (9)	0.4035 (3)
C13	0.5250 (4)	0.5435 (8)	0.4042 (3)
C14	0.5902 (4)	0.5643 (6)	0.2347 (2)
C15	0.6515 (3)	0.4624 (7)	0.2723 (3)
C16	0.6779 (3)	0.3368 (8)	0.2350 (3)
C17	0.6338 (3)	0.3596 (7)	0.1734 (3)
C18	0.5801 (3)	0.5025 (6)	0.1721 (2)
C19	0.5266 (4)	0.5837 (7)	0.1163 (2)
C20	0.5929 (4)	−0.0079 (7)	0.2341 (3)
C21	0.5126 (5)	−0.0151 (7)	0.1956 (3)
C22	0.4492 (4)	−0.0087 (7)	0.2334 (4)
C23	0.4891 (4)	0.0008 (7)	0.2957 (3)
C24	0.5800 (4)	0.0069 (7)	0.2966 (3)
C25	0.6475 (5)	0.0111 (9)	0.3544 (4)

less favorable π-donor to zirconium because of competing delocalization of its electron density by effective conjugation with the adjacent metal carbene functionality.[2,10] This is evident from the bonding parameters around C(1) [O(1)–C(1) = 1.278 (6) Å; C(1)–W = 2.206 (5) Å; C(1)–C(7) = 1.530 (7) Å, indicating a pronounced acyl metalate character of this Fischer-type carbene complex.[4,11]

Complex **4c′** exhibits an endocyclic trans-disubstituted carbon–carbon double bond [C(8)–C(9) = 1.310 (7) Å]. Together with the almost linear zirconium–oxygen linkages, the trans configurated $-CH_2CH{=}CHCH_2-$ unit [C(7)–C(8) = 1.499 (8) Å; C(9)–C(10) = 1.492 (7) Å] leaves very little conformational flexibility in the metallacyclic ring system. Therefore, in the solid state the methyl substituents at C(11) (the former acetone carbonyl carbon atom) adopt two distinctly different positions, C(12) being oriented approximately axial and C(13) equatorial relative to the ring plane. Methyl groups at the η-cyclopentadienyl rings [C(25), C(19)] avoid interaction with the methyl substituents at C(11). The C(24)–C(25) and C(18)–C(19) vectors are arranged almost trans to each other.[12] They are pointing to the lateral sectors of the bent metallocene unit.[13]

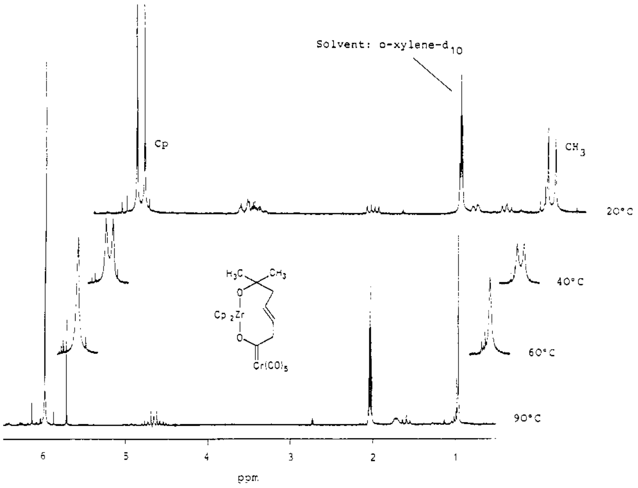

Figure 2. Dynamic ^1H NMR spectra of the metallacyclic zirconoxycarbene complex **4a** (in *o*-xylene-d_{10}, 200 MHz).

The incorporation of the *trans*-$CH_2CH{=}CHCH_2-$ moiety of local C_2 symmetry in the rigid nine-membered ring makes **4c′** chiral. Therefore, the methyl groups at C(11) should become diastereotopic, as should the pairs of hydrogens at C(10) and C(7), respectively, as well as the Zr-bound Cp ligands.

Dynamic NMR Spectra. In solution, complexes **4a–d** exhibit low-temperature-limiting ^1H and ^{13}C NMR spectra (see Experimental Section), indicating chiral metallacyclic ground-state conformations as observed for **4c′** in the crystal. As a typical example, in the ^1H NMR spectrum (200 MHz) at 20 °C the metallacyclic zirconoxycarbene chromium complex **4a** exhibits two Cp resonances at δ 6.25 and 6.32 and two AB(X)-type patterns due to four different $-CH_2CH{=}CHCH_2-$ methylene hydrogens at δ 1.81, 2.17, 3.28, and 4.65 (in $CDCl_3$ separated from the $-CH{=}CH-$ signals), plus two singlets at δ 1.19 and 1.24 originating from the acetone derived methyl groups (see Figure 2). When the temperature is increased, one observes pairwise coalescence of diastereotopic methylene hydrogens, Cp singlets, and CH_3 signals of **4a**. The spectrum obtained at 90 °C shows only one Cp resonance, one averaged CH_3 singlet, and a broad signal at δ 1.75 for one of the two methylene groups. The signals of the equilibrating diastereotopic methylene hydrogens adjacent to the metal carbene functional group are still too broad to be monitored at this temperature.

Analogous dynamic NMR behavior was observed for complexes **4b–d** as well. From the dynamic ^1H NMR spectra an activation energy of $\Delta G^{\ddagger}_{ent}(323\ K) = 16.6 \pm 0.4$ kcal/mol has been estimated for the conformational equilibration (topomerization)[14] of the metallacycle **4a**.

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(9) See for a comparison: Erker, G.; Czisch, P.; Mynott, R. *J. Organomet. Chem.* **1987**, *334*, 91. Erker, G.; Frömberg, W.; Krüger, C.; Raabe, E. *J. Am. Chem. Soc.* **1988**, *110*, 2400 and references cited therein.

(10) Fischer, E. O.; Fontana, S. *J. Organomet. Chem.* **1972**, *40*, 159; **1975**, *91*, 23. Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. Ferguson, G. S.; Wolczanski, P. T. *Ibid.* **1986**, *108*, 8293.

(11) Mills, O. S.; Redhouse, A. D. *Angew. Chem.* **1965**, *77*, 1142; *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1142. Fischer, E. O.; Gammel, F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261.

(12) This is rather unusual for $(\eta-C_5H_4CH_3)_2MX_2$-type complexes: Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422. Dusausoy, J.; Protas, J.; Renaut, P.; Gautheron, B.; Tainturier, G. *J. Organomet. Chem.* **1978**, *157*, 167. Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *388*, C4. See, however: Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *J. Organomet. Chem.* **1984**, *268*, 149. Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2347. Stahl, K.-P.; Boche, G.; Massa, W. *J. Organomet. Chem.* **1984**, *277*, 113. Thompson, D. W.; Lock, G. A. *Ibid.* **1986**, *303*, 213. Antinolo, A.; Lappert, M. F.; Singh, A.; Winterborn, D. J. W.; Engelhardt, L. M.; Raston, C. L.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1463. Erker, G.; Mühlenbernd, T.; Rufinska, A.; Benn, R. *Chem. Ber.* **1987**, *120*, 507. Erker, G.; Lecht, R.; Sosna, F.; Uhl, S.; Tsay, Y.-H.; Krüger, C.; Grondey, H.; Benn, R. *Chem. Ber.* **1988**, *121*, 1069. Benn, R.; Grondey, H.; Nolte, R.; Erker, G. *Organometallics* **1988**, *7*, 777.

(13) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

Complexes **4b** and **4c** exhibit identical "racemization" activation barriers as judged from the coalescence of the Cp resonances. For **4d**, $\Delta G^{\ddagger}_{\mathrm{ent}}(350\ \mathrm{K}) = 17.0 \pm 0.4$ kcal/mol has been obtained.

Complex **4e**, derived from coupling **3c** with a prochiral ketone, contains two chirality elements within the metallacyclic ring structure. Two diastereomers (85:15) are observed according to NMR spectroscopy at low temperature. Each of these exhibits a 1:1 pair of Cp resonances. The thermally induced topomerization process leaves the chirality center of **4e** unaffected. Pairwise exchange of Cp resonances is observed on increasing the temperature to give one averaged set of signals, still showing a pair of Cp singlets in the ^{1}H NMR spectrum. This observation shows beyond doubt that the metallacyclic ring system remains intact throughout the equilibration process. Carbon–carbon cleavage, which has been observed at higher temperatures,[15] is of no importance for the observed exchange phenomena.

It is quite remarkable that the topomerization barriers of the nine-membered metallacycles **4** are rather close to the $\Delta G^{\ddagger}_{\mathrm{ent}}$ value of *trans*-cyclononene. The rigidity introduced by the conjugatively interacting COZrOC moiety seems to compensate well for the much larger perimeter of the organometallic ring system.

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Registry No. **1′**, 101518-70-1; **3a**, 93403-13-5; **3b**, 93403-15-7; **3c**, 93403-16-8; **3c′**, 117754-11-7; **4a**, 117754-13-9; **4b**, 117754-14-0; **4c**, 117754-15-1; **4c′**, 117754-12-8; **4d**, 117754-16-2; **4e** (diastereomer 1), 117754-17-3; **4e** (diastereomer 2), 117858-26-1; **4e′** (diastereomer 1), 117754-18-4; **4e′** (diastereomer 2), 117858-27-2; $W(CO)_6$, 14040-11-0; $(CH_3)_2C{=}O$, 67-64-1; $Ph_2C{=}O$, 119-61-9; $(CH_3)PhC{=}O$, 98-86-2.

Supplementary Material Available: Listings of atomic fractional coordinates, atomic thermal parameters, and interatomic distances and angles for **4c′** (9 pages); a listing of observed and calculated structure factors for **4c′** (24 pages). Ordering information is given on any current masthead page.

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(14) Kessler, H. *Angew. Chem.* **1970**, *82*, 237; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

(15) At 70 °C complexes **4a** and **4b** cleanly loose 1 equiv of $M(CO)_6$ each to produce the seven-membered metallacyclic σ-allyl complex $\overline{Cp_2ZrOC(CH_3)_2CH_2CH{=}CHCH_2}$ which had been independently prepared previously from (η^4-*s-trans*-butadiene)$ZrCp_2$ and acetone: Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 494.

Hindered η-Cyclopentadienyl–Metal Rotation Caused by Lateral Interaction of Cp-Bonded Substituents at Chalcogen-Bridged Binuclear Bent Metallocene Complexes $[(RCp)_2ZrX]_2$

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(η-Butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium reacts with elemental tellurium to give $[(Me_3CCp)_2Zr(\mu\text{-Te})]_2$ (**6**). Upon controlled hydrolysis, one bridging tellurium is exchanged for oxygen to give the metallacyclic complex $[(Me_3CCp)_2Zr]_2(\mu\text{-O})(\mu\text{-Te})$ (**7**). The analogous oxygen/selenium-bridged bimetallic zirconium complex $[(Me_3CCp)_2Zr]_2(\mu\text{-O})(\mu\text{-Se})$ (**8**) is formed upon photolysis of the μ-oxo precursor $(Me_3CCp)_2Zr(CH_3)OZr(CH_3)(CpCMe_3)$ in the presence of a suspension of elemental selenium. Complex **6** exhibits a nearly square-planar array of alternating zirconium and tellurium atoms. In contrast, the planar ZrTeZrO framework of **7** is characterized by very different bond angles at tellurium (average 72.1 (1)°) and oxygen (average 119.2 (2)°), bringing the zirconium atoms (average Zr···Zr = 3.390 (1) Å) more closely together than in **6** (Zr···Zr = 4.067 (1) Å). In the crystal each $(Me_3CCp)_2Zr$ subunit is chiral, favoring a nearly C_2-symmetric conformation. The bulky *tert*-butyl groups are oriented trans to each other in the lateral sectors of the Cp-substituted bent metallocene unit. Combination of the two chiral $(Me_3CCp)_2Zr$ moieties can give rise to the formation of two diastereomeric bis(metallocene) complexes. For the bis(tellurium)-bridged compound **6** an achiral C_{2h}-symmetric meso form is favored, while the oxygen, tellurium-bridged analogue **7** adopts a chiral nearly C_2-symmetric conformation in the solid state. Complex **7** crystallizes in the monoclinic space group *Cc* with cell constants $a = 18.231$ (5) Å, $b = 18.186$ (6) Å, $c = 22.563$ (6) Å, $\beta = 107.57$ (2)°, $V = 7132$ (3) Å^3, $Z = 8$, and $R(F) = 4.08\%$. The $[(Me_3CCp)_2Zr](\mu\text{-X})(\mu\text{-Y})$ complexes feature hindered (Me_3CCp)–metal rotation in solution. Activation barriers $\Delta G^{\ddagger}_{\mathrm{rot}} \approx 9.6 \pm 0.4$ kcal/mol (for **7** at 206 K) and 11.0 ± 0.4 kcal/mol (for **8** at 222 K) have been estimated by dynamic ^{1}H NMR spectroscopy. Complexes **7** and **8** appear to be the first examples where hindered (RCp)–M rotation is induced by a lateral (RCp)···(RCp) interaction across a rigid metal complex framework.

Introduction

Rotational activation barriers in conformationally equilibrating systems have great informational value for estimating interactive forces between groups or substituents brought into close proximity.[1] In alkanes the interaction of groups attached to adjacent carbon atoms

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[1] Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley: New York, 1965. Kagan, H. B. *Organische Stereochemie*; Thieme: Stuttgart, 1977. Dale, J. *Stereochemie und Konformationsanalyse*; Verlag Chemie: Weinheim, 1978. See also: Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.

0276-7333/89/2308-0454$01.50/0