Models for the Elusive $Cp_2Zr(R)(olefin)^+$. Characterization of the d^0 Metal Olefin Complex $Cp_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)^+$

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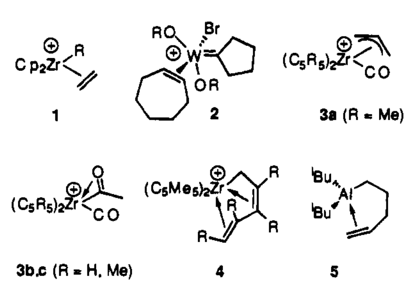
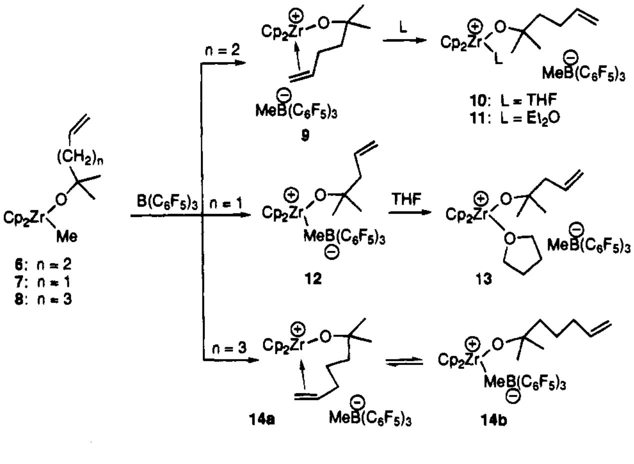
Zr(IV) olefin complexes of the type $Cp_2Zr(R)(olefin)^+$ (**1**, Chart 1) are presumed intermediates in $Cp_2Zr(R)^+$-catalyzed olefin polymerization, but have never been observed.[1,2] The characterization of **1**, or models thereof, is of interest for understanding how $Cp_2Zr(R)^+$ and related d^0 metal alkyls activate olefins for migratory insertion, how olefins and counterions compete for binding to $Cp_2Zr(R)^+$, and other issues relevant to olefin polymerization. Olefin complexes of d^0 metals are destabilized by the absence of conventional $d-\pi^*$ backbonding and, in many cases, by the availability of facile reaction pathways (e.g., insertion). The only known d^0 metal complex of a simple olefin is W^{VI} olefin alkylidene species **2**, which was observed spectroscopically at low temperature.[3,4] However, the recent characterization of Zr(IV) carbonyl complexes $(C_5Me_5)_2Zr(allyl)(CO)^+$ (**3a**) and $(C_5R_5)_2Zr\{\eta^2\text{-}C({=}O)Me\}(CO)^+$ (**3b,c** R = H, Me)[5] and of σ,π^2,π^2-pentadienyl complex **4**,[6] as well as earlier studies of Al alkyls containing pendant vinyl groups (e.g., **5**),[7] suggests that properly designed d^0 olefin complexes might be quite stable. Here were describe a simple strategy for the synthesis of $Cp_2Zr(X)(olefin)^+$ complexes.

As shown in Scheme 1, our strategy for promoting olefin binding to $Cp_2Zr(X)^+$ involves (i) attachment of the olefin to an alkoxide ligand to exploit the chelate effect, (ii) incorporation of substituents at the alkoxide carbon to disfavor alkoxide abstraction or μ-alkoxide dimer formation, and to promote ring closure, and (iii) the use of a weakly coordinating anion.

Chart 1



Scheme 1



Alkoxide complexes **6**–**8** are generated by alcoholysis of Cp_2ZrMe_2. The NMR parameters of the vinyl groups of **6**–**8** are unchanged from the free olefin values, indicating that the vinyl groups are not coordinated.[8]

The reaction of **6** with $B(C_6F_5)_3$ yields $[Cp_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)][MeB(C_6F_5)_3]$ (**9**), which can be isolated (94%) as an analytically pure yellow crystalline solid.[9] NMR data establish that the vinyl group in **9** coordinates to Zr in preference

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[8] Acceptable C, H analyses for **6** and **9** were obtained. The remaining new compounds were characterized by multinuclear NMR (see supplementary material). The following key data are not provided in the text. **6**: ^1H NMR (CD_2Cl_2) δ 5.86 (m, $=CH$, 1 H), 5.04 (dq, J = 17.1 Hz; J = 2 Hz, $CH_2CH{=}CH_2$ cis to CH_2, 1 H), 4.94 (dq, J = 10.1 Hz; J = 2 Hz, $CH_2CH{=}CH_2$ trans to CH_2, 1 H), −0.002 (s, $ZrCH_3$, 3 H); ^{13}C NMR (CD_2Cl_2) δ 140.0 ($=CH$, J_{C-H} = 151 Hz), 113.9 ($=CH_2$, J_{C-H} = 154 Hz), 17.4 ($ZrCH_3$, J_{C-H} = 119 Hz). **7**: ^1H NMR (CD_2Cl_2) δ 5.78 (m, $=CH$, 1 H), 5.02 (m, $=CH_2$, 2 H), −0.01 (s, $ZrCH_3$, 3 H); ^{13}C NMR (CD_2Cl_2 δ 136.3 ($=CH$), 116.7 ($=dCH_2$), 17.4 ($ZrCH_3$). **8**: ^1H NMR (CD_2Cl_2) δ 5.86 (m, $=CH$, 1 H), 4.99 (m, $=CH_2$, 2 H), −0.03 (s, $ZrCH_3$, 3 H); ^{13}C NMR (CD_2Cl_2) δ 139.7 ($=CH$), 114.3 ($=CH_2$), 17.2 ($ZrCH_3$). **9**: ^1H NMR (CD_2Cl_2, −80 °C) δ 7.50 (m, $=CH$, 1 H), 6.42 (s, C_5H_5, 5 H), 6.39 (s, C_5H_5, 5 H) 5.35 (d, J = 20.5 Hz, $CH_2CH{=}CH_2$ cis to CH_2, 1 H), 4.58 (d, CH_2, J = 8.6 Hz, $CH_2CH{=}CH_2$ trans to CH_2, 1 H), 0.39 (s, BCH_3, 3 H); ^{13}C NMR (CD_2Cl_2, −80 °C) δ 158.8 ($=CH$, J_{C-H} = 151 Hz), 114.6 (C_5H_5, J_{C-H} = 169 Hz), 114.2 (C_5H_5, J_{C-H} = 169 Hz), 94.3 ($=CH_2$, J_{C-H} = 157 Hz), 9.2 (BCH_3); ^1H NMR (CD_2Cl_2, 23 °C) δ 7.51 (br m, $=CH$, 1 H), 6.46 (s, C_5H_5, 10 H), 5.40 (br d, J = 17.9 Hz, $CH_2CH{=}CH_2$ cis to CH_2, 1 H), 4.62 (d, J = 8.8 Hz, $CH_2CH{=}CH_2$ trans to CH_2, 1 H), 0.50 (br s, BCH_3, 3 H); ^{13}C NMR (CD_2Cl_2, 23 °C) δ 159.2 ($=CH$, J_{C-H} = 150 Hz), 115.5 (C_5H_5, J_{C-H} = 175 Hz), 95.9 ($=CH_2$, J_{C-H} = 160 Hz), 10.1 (BCH_3). **10**: ^1H NMR (CD_2Cl_2) δ 6.47 (s, C_5H_5, 10 H), 5.84 (m, $=CH$, 1 H), 5.07 (d, J = 17.1 Hz, $CH_2CH{=}CH_2$ cis to CH_2, 1 H), 5.00 (d, J = 10.2 Hz, $CH_2CH{=}CH_2$ trans to CH_2, 1 H), 0.51 (br s, BCH_3, 3 H); ^{13}C NMR (CD_2Cl_2) δ 138.1 ($=CH$, J_{C-H} = 152 Hz), 115.1 ($=CH_2$, J_{C-H} = 156 Hz), 9.9 (BCH_3). **11**: ^1H NMR (CD_2Cl_2) δ 6.51 (s, C_5H_5, 10 H) 5.84 (m, $=CH$, 1 H), 5.08 (dq, J = 17.1 Hz; J = 1.6 Hz, $CH_2CH{=}CH_2$ cis to CH_2, 1 H), 5.02 (dq, J = 10.2 Hz; J = 1.5 Hz, $CH_2CH{=}CH_2$ trans to CH_2, 1 H), 0.49 (br s, BCH_3). **12**: ^1H NMR (CD_2Cl_2) δ 6.43 (s, C_5H_5, 10 H), 5.68 (m, $=CH$, 1 H), 5.07 (m, $=CH_2$, 2 H), 0.72 (br s, BCH_3, 3 H); ^{13}C NMR (CD_2Cl_2) δ 133.6 ($=CH$), 118.5 ($=CH_2$), 2.7 (br, BCH_3). **13**: ^1H NMR (CD_2Cl_2) δ 5.78 (m, $=CH$, 1 H), 5.17 (m, $=CH_2$, 2 H), 0.51 (br s, BCH_3, 3 H); ^{13}C NMR (CD_2Cl_2) δ 133.9 ($=CH$), 119.2 ($=CH_2$), 10.3 (br, BCH_3). **14a**: ^1H NMR (CD_2Cl_2, −80 °C) δ 7.40 (m, $=CH$, 1 H), 6.41 (s, C_5H_5, 5 H), 6.40 (s, C_5H_5, 5 H), 5.25 (d, J = 18.3 Hz, $=CH_2$, 1 H), 4.69 (d, J = 8.4 Hz, $=CH_2$, 1 H), 0.38 (br s, BCH_3, 3 H); ^{13}C NMR (CD_2Cl_2, −80 °C) δ 157.9 ($=CH$, J_{C-H} = 157 Hz), 114.3 (C_5H_5), 114.0 (C_5H_5), 92.6 ($=CH_2$), 9.1 (BCH_3). **14b**: ^1H NMR (CD_2Cl_2, −80 °C) δ 6.35 (s, C_5H_5, 10 H), 5.71 (m, $=CH$, 1 H), 4.92 (m, $=CH_2$, 2 H), 0.60 (br s, BCH_3, 3 H); ^{13}C NMR (CD_2Cl_2, −80 °C) δ 138.2 ($=CH$), 114.5 (C_5H_5), 114.2 ($=CH_2$), 1.9 (BCH_3).

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to the counterion in CD_2Cl_2. The terminal vinyl ^{13}C resonance shifts substantially upfield (δ 94.3), and the internal vinyl ^{13}C resonance shifts downfield (δ 158.8) from the corresponding resonances of the free olefin and **6** (δ 113.9, 140.4).[10] Similarly, the vinyl ^1H resonances are substantially shifted from those of the free olefin or **6**.[8] The $MeB(C_6F_5)_3^-$ NMR parameters are identical to those of the free anion (B*CH$_3$*, 23 °C, ^1H δ 0.5 br; ^{13}C δ 10.3 br).[4d,9] Variable temperature studies establish that **9** undergoes a dynamic process which renders the diastereotopic pairs of Cp and Me groups equivalent ($\Delta G^\ddagger = 10.7$ kcal/mol, CD_2Cl_2). This process most likely involves dissociation or displacement (by CD_2Cl_2 or $MeB(C_6F_5)_3^-$) of the olefin and recoordination through the opposite face. The vinyl and counterion resonances do not shift significantly over the range −80 to 25 °C, which indicates that the extent of olefin dissociation/displacement is minor.[8] IR spectra of **9** under a variety of conditions contain a $\nu_{C=C}$ band at 1641 cm^{-1} which is virtually unshifted from those in the free olefin and THF adduct **10** (Scheme 1, *vide infra*).

The molecular structure of **9** was determined by X-ray diffraction (Figure 1).[11] The precision of this study was limited by a two-site conformational disorder involving the alkoxide ligand but is sufficient to confirm that the vinyl group is coordinated. Complex **9** crystallizes as discrete ions. The coordinated olefin of the cation is tipped significantly from the O−Zr−olefin centroid plane[11b] and interacts with Zr primarily through the terminal carbon (Zr−C5) 2.68(2) Å, Zr−C(4) 2.89(2) Å). The Zr−C(5) distance is in the range observed for Zr−C_{sp2} distances in other Zr^{IV} complexes of unsaturated π systems, e.g., $Cp_2Zr(\eta^2\text{-benzyl})(L)^+$ (Zr−C_{ipso} 2.63−2.65 Å),[12] **4** (Zr−C_{sp2} 2.66−2.76 Å),[6] $Cp_2Zr(\sigma^2,\pi\text{-diene})$ (Zr−Cβ 2.55−2.71 Å),[13] and the Zr^{IV} arene species $CpZr(CH_2Ph)_2\{\eta^5\text{-PhCH}_2B(C_6F_5)_3\}$ (2.65−2.76 Å) and $Zr(CH_2Ph)_3\{\eta^6\text{-PhCH}_2B(C_6F_5)_3\}$ (2.65−2.76 Å).[4e,f] These Zr^{IV}−C_{sp2} distances are far longer than those in Zr(II) olefin complexes in which significant d−π* back-bonding is present, e.g., $Cp_2Zr(C_2H_4)(PMe_3)$ (2.36 Å).[14] The Zr−O distance (1.888(5) Å) and Zr−O−C angle (167.8(6)°) indicate the presence of significant O−Zr π-donation.[15] The X-ray structural data and the olefin carbon ^{13}C shifts for **9** may be rationalized collectively in terms of a weak electrostatic interaction between Zr and the (filled) p orbital on the terminal vinyl carbon or, alternatively, in terms of resonance structures **A** (major) and **B** (minor)[14b] in Chart 2.

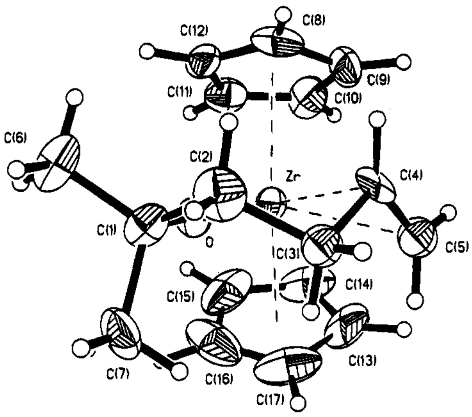
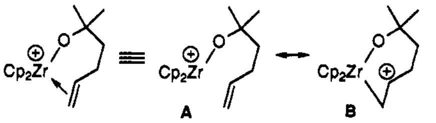


Figure 1. ORTEP view of the $Cp_2Zr(OCMe_2CH_2CH_2CH{=}CH_2)^+$ cation of **9**.

Chart 2



Addition of THF or Et_2O to a CD_2Cl_2 solution of **9** causes the vinyl ^1H and ^{13}C NMR resonances to shift to the free olefin positions, but does not influence the $MeB(C_6F_5)_3^-$ resonances. These observations are consistent with the formation of adducts **10** and **11** and confirm that the anion of **9** is not coordinated in CD_2Cl_2.[8] Addition of CO broadens but does not shift the resonances of **9**, suggesting that CO binds reversibly to a very small extent.[5] Addition of ethylene or 2-butyne has no effect on the NMR spectra of **9**.

The influence of chain length on olefin binding was probed by NMR studies of the reactions of **7** and **8** with $B(C_6F_5)_3$. Complex **7**, which contains a one-carbon spacer between the alkoxide and vinyl functions, reacts with $B(C_6F_5)_3$ to yield $Cp_2Zr^{(+)}(OCMe_2CH_2CH{=}CH_2)(\mu\text{-Me})B^{(-)}(C_6F_5)_3$ (**12**, >95% NMR), in which the counterion rather than the olefin coordinates to Zr. The NMR parameters of the vinyl group of **12** are almost unchanged from those of the free olefin and **7**; in contrast, the $BMe(C_6F_5)_3^-$ NMR parameters are significantly perturbed from the free anion values.[8] Addition of THF to a CD_2Cl_2 solution of **12** causes the $BMe(C_6F_5)_3^-$ resonances to shift to the free anion values, consistent with the formation of THF adduct **13**. In contrast, the reaction of $B(C_6F_5)_3$ with **8**, in which the alkoxide and vinyl functions are linked by a three-carbon tether, yields a mixture of olefin adduct **14a** and $BMe(C_6F_5)_3^-$ adduct **14b** (93%, NMR; **14a**/**14b** = 1.2/1 at −90 °C).[8] These species exchange rapidly on the NMR time scale at 23 °C.

The structural, spectroscopic, dynamic, and ligand exchange properties of **9** and the sensitivity of the structures of **9**, **12**, and **14** to the chain length indicate that the Zr−olefin bonds in these species are quite weak. This may be due to (i) the hard character and minimal back-bonding ability of the cationic Zr(IV) center, which disfavor coordination of the soft π-acidic olefin,[1,5] (ii) the tempering of the metal Lewis acidity of O−Zr π-donation, and/or (iii) the constraints imposed by the chelated structure. The strategy outlined here should provide access to other chelated olefin complexes of d^0 metals, which will allow more extensive study of their structures and properties.

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Supplementary Material Available: Experimental details and X−ray results for **9** (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(10) As expected, the vinyl J_{CH} values are insensitive to olefin coordination. See: Bender, B. R.; Norton, J. R.; Miller, M. M.; Anderson, O. P.; Rappé, A. K. *Organometallics* **1992**, *11*, 3427 and references therein.

(11) (a) X-ray data for **9**: space group $P\bar{1}$, $a = 9.762(2)$ Å, $b = 12.878(2)$ Å, $c = 14.531(2)$ Å, $\alpha = 76.13(1)°$, $\beta = 86.89(1)°$, $\gamma = 81.37(1)°$, $V = 1753.1(4)$ Å^3, $Z = 2$, R1 = 0.0651, wR2 = 0.722. The alkoxide ligand is disordered between two conformations which are very similar except for differing in the olefin face which is coordinated. The C2−C7 atoms and their H atoms in each disordered site were weighted equally and the C−C and C=C distances restrained to 1.54 ± 0.02 and 1.38 ± 0.02 Å, respectively. The C(3), C(5), C(3′), C(4′), and C(5′) atoms were refined isotropically; the other non-H atoms were refined anisotropically. H atom positions were idealized. The conformational disorder limited the precision of the experimentally determined C=C distance; as a result, detailed discussion of this structural feature is unwarranted at present. (b) Angle between planes Zr−C4−C5/O−Zr−olefin centroid: 39.5° site 1; 25.3° site 2.

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(15) For other $Cp_2Zr(OR)(L)^+$ species, see: (a) Jordan, R. F.; Dasher, W. D.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (b) Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092. (c) Hong, Y.; Kuntz, B. A.; Collins, S. *Organometallics* **1993**, 12, 964.