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Notes

Reactivity of Carbon Dioxide toward Zirconocene Cations

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*Summary: Cationic methyl- and phenylzirconocene species readily undergo insertion of CO_2 into the zirconium−carbon bond, giving the corresponding dimeric carboxylato complexes **12** and **13** in quantitative yield. **12** was structurally characterized, displaying a bridging acetate ligand.*

The insertion reaction of carbon dioxide into metal−carbon bonds is well-known and has been used successfully in the chemistry of non-transition-metal species such as Grignard reagents and alkyllithium compounds.[1] While reactions of CO_2 with such main-group species can readily lead to the desired products, the reactions are invariably stoichiometric with respect to the organometallic compounds.

Carbon dioxide insertion into a transition-metal−carbon bond is therefore of great interest, because it could lead to the possibility of introducing CO_2 into catalytic processes. Examples of CO_2 insertions into M−H and M−C bonds are numerous; in the case of CO_2 insertion into a transition-metal−carbon bond this generally transforms the coordinated alkyl or aryl group into a coordinated carboxylate via formation of a new C−C bond.[2] There are excellent reviews which encompass this area.[3]

The insertion of CO_2 into transition-metal−carbon σ bonds has been described for titanocene and zirconocene compounds. Some zirconocene imine,[4] (η^2-formaldehyde)zirconocene,[5] and zirconaazacyclopentene[6] complexes insert CO_2 into the zirconium−carbon bond. Moreover, insertion reactions of CO_2 have been found to occur with the titanium benzyne intermediate formed from the corresponding diphenyltitanocene by a thermal reaction.[7] Similarly, ethylene and acetylene zirconocene[8] and titanocene[9] complexes react readily with CO_2 under mild conditions to give the corresponding furanone metallacycles in good yields.

Whereas dimethyltitanocene gives the expected carboxylato-type complexes by both thermal[10] and photochemical[11] reaction in the presence of CO_2, the analogous reaction of carbon dioxide with dialkylzirconocene complexes, Cp_2ZrR_2 (R = Me, $PhCH_2$, Ph), does not occur under ambient conditions, while under more drastic conditions (50 atm of CO_2, 80 °C, 24 h) only the dimethylzirconocene complex was found to form an ill-defined product, giving acetic acid upon hydrolysis.[12] Addition of CO_2 to dimethylzirconocene under ambient conditions was described to proceed in the case of a *constrained geometry* analogue, with insertion into the two Zr−C(Me) bonds giving a dinuclear structure with chelating and bridging acetate ligands.[13]

Moreover, CO_2 is known as an extremely efficient catalyst poison for the Ziegler−Natta catalyst. Small

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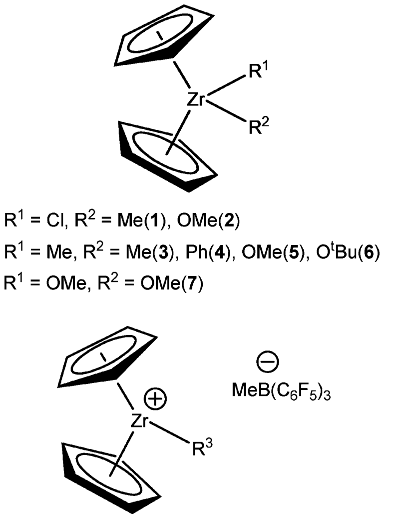
10.1021/om050741e CCC: $30.25

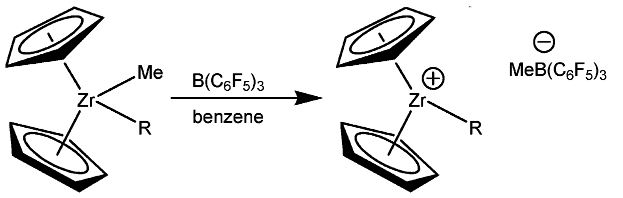
Chart 1



R^1 = Cl, R^2 = Me(**1**), OMe(**2**)
R^1 = Me, R^2 = Me(**3**), Ph(**4**), OMe(**5**), O^{t}Bu(**6**)
R^1 = OMe, R^2 = OMe(**7**)

R^3 = Me(**8**), Ph(**9**), OMe(**10**), O^{t}Bu(**11**)

Scheme 1



R = Me(**8**), Ph(**9**), OMe(**10**), O^{t}Bu(**11**)

amounts were enough for the total deactivation of these cationic catalyst systems, supposedly by coordination of CO_2 into the vacancy at the active site, thus restricting the coordination of monomer.[14]

Here we report on the interaction of CO_2 with several zirconocenes, $Cp_2Zr(Me)R$ (R = Cl, alkyl, aryl, O-alkyl),[15] and their corresponding cations, $[Cp_2ZrR]^+[MeB(C_6F_5)_3]^-$. We also report the structural characterization of a dinuclear acetate complex.

The investigated zirconocenes are shown in Chart 1. They were synthesized by literature methods, and the cations were obtained by abstraction of the zirconium-bound methyl group using tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, as abstractor[16] (Scheme 1), All of the neutral zirconocenes (**1**–**7**) were found to be unreactive toward carbon dioxide in both CD_2Cl_2 and C_6D_6, even at elevated temperatures. Similarly, the alkoxide cations **10** and **11** were found to be unreactive, but addition of CO_2 induces small shifts of the resonances in the ^1H NMR spectra. However, treating the cationic hydrocarbyl species **8** and **9** in C_6D_6 with CO_2 immediately resulted in precipitation of yellow oils (**12** and **13**, respectively) that solidified upon standing. These solids were not suitable for X-ray diffraction and are insoluble in hydrocarbon and chlorinated solvents but readily soluble in a donor solvent such as THF (Scheme 2). Elemental analysis indicated dimeric structures for **12** and **13**. This was confirmed by repeating the carboxylation of **8** in CD_2Cl_2, giving large amounts of white crystals that were subjected to an X-ray diffraction analysis, revealing the molecular structure shown in Figure 1, where selected distances and angles are also given. A packing diagram is given in Figure S1 (Supporting Information). Compound **12** is a dimeric zirconocene acetate system with two methyltris(pentafluorophenyl)borate counteranions that is stable under ambient conditions. It crystallizes in the triclinic space group $P\bar{1}$, displaying an inversion center between the two zirconium atoms. The most noteworthy struc-

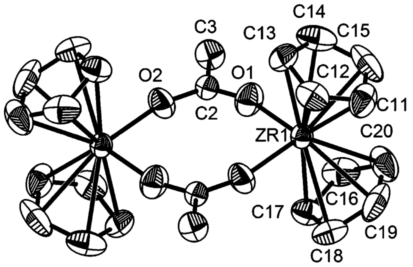
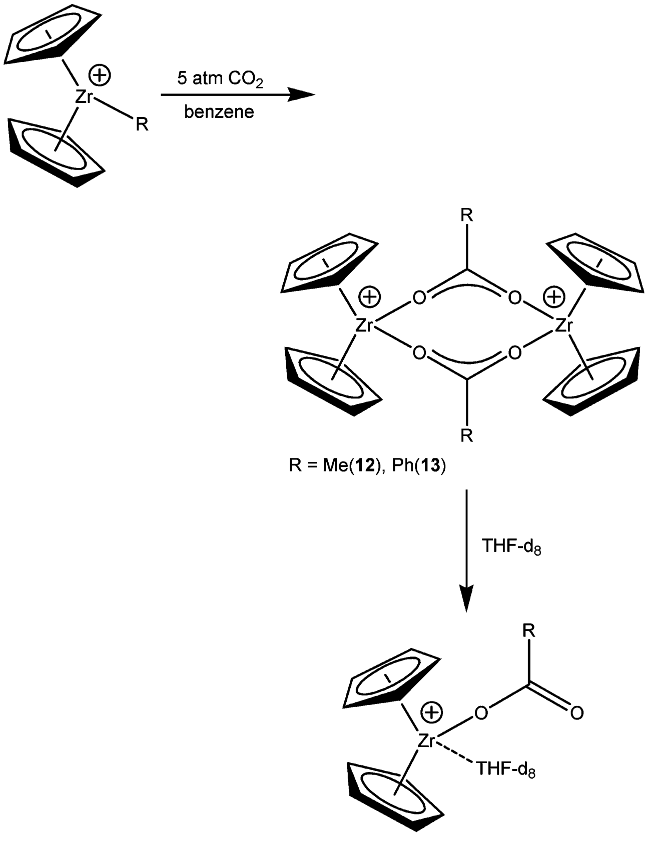


Figure 1. DIAMOND[25] drawing of **12**. For clarity hydrogen atoms and borate counteranions have been omitted. Selected bond distances (Å) and angles (deg) with estimated standard deviations: Zr–Cp1 = 2.197(16); Zr–Cp2 = 2.186(14); Zr–O1 = 2.084(6); Zr–O2 = 2.067(5); C2–O1 = 1.227(8); C2–O2 = 1.256(8); C2–C3 = 1.468(9); Cp1–Zr–Cp2 = 131.8(1); O2–Zr–O1 = 95.1(2); C2–O1–Zr = 160.6(6); C2–O2–Zr = 163.3(6); O1–C2–O2 = 120.1(7); O1–C2–C3 = 119.4(7); O2–C2–C3 = 120.5(7).

Scheme 2



R = Me(**14**), Ph(**15**)

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[15] The zirconocene complexes were prepared according to literature procedures. $Cp_2Zr(Me)(O\text{-alkyl})$: Nishihara, Y.; Aoyagi, K.; Hara, R.; Suzuki, N.; Takahashi, T. *Inorg. Chim. Acta* **1996**, *252*, 91 (but using 2 equiv of the corresponding alcohol). $Cp_2Zr(Me)Ph$: Cuny, G. D.; Gutierrez, A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 537. Ma, X.-B.; Regitz, M. *Synthesis* **1995**, *6*, 667 (but using diethyl ether as solvent).

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tural feature is the presence of two newly formed C(sp^2)−C(sp^3) bonds between the former zirconium-bound methyl groups and CO_2 (C2−C3 = 1.468(9) Å, O1−C2−C3 = 119.4(7)°, and O2−C2−C3 = 120.5(7)°). The methyl groups have become part of two bridging acetate groups. Most distances and angles are comparable to those reported for a similar μ-isobutyrate zirconocene dimer.[17] Dissolution of **12** and **13** in THF-d_8 results in cleavage of the dimers and formation of the adducts **14** and **15**. Upon standing these cations induce polymerization of the THF solvent,[18] but they were sufficiently stable in solution to be fully characterized by 1D and 2D ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR experiments. The ^{1}H NMR spectra of the compounds **14** and **15** each display one singlet for the Cp protons (δ 6.51, 6.60) and one broad high-field singlet (δ 0.60, 0.52), attributed to the methyl protons of the borate anions. Additionally a singlet at δ 2.09 (methyl protons) and three multiplets at δ 8.05, 7.73, 7.55 (ortho, para, and meta phenyl protons) are observed in the spectra, revealing the presence of acetate and benzoate, respectively. This assignment is supported in particular by 2D ^{1}H−^{13}C experiments; the key data include correlations in the gHMBC experiments between the high-field ^{1}H resonance (δ 2.09, CH_3CO_2) and a ^{13}C resonance (δ 188.8, CH_3CO_2) for the methyl derivative **14** and between the ^{1}H resonance of the ortho phenyl protons (δ 8.05) and a ^{13}C resonance at δ 180.5 ($PhCO_2$) for the phenyl derivative **15**.

The IR spectra for both compounds (THF solution and KBr) showed broad bands at 1640−1410 cm^{-1}, which can be assigned to symmetrically bonded carboxylato groups, either bridging or bidentate.[19]

With these group IV metal systems we observe a reactivity trend that is quite opposite to that observed for CO_2 insertion into late-metal−carbon bonds. In those latter cases an increased electron density on the metal center usually gives rise to a higher reactivity and there is no need for an open coordination site. This has been interpreted in terms of a mechanism involving direct insertion into the M−C bond.[2d,e,g] In our present systems the least Lewis acidic, neutral zirconocenes are completely unreactive, whereas the highly electrophilic hydrocarbyl cations react cleanly and instantaneously. The cations differ from the neutral systems not only in electrophilicity but also in their coordinating ability. The coordinating ability is obviously crucial, since these reactions proceed exclusively in noncoordinating and weakly coordinating solvents such as benzene and dichloromethane. We believe that these observations are best explained by a coordination of CO_2 prior to the actual insertion. This coordination results in a polarization that can sufficiently perturb the electron distribution to render the CO_2 reactive toward fairly weak nucleophiles such as Zr−C bonds, something that cannot happen in a direct insertion scenario. It also brings the CO_2 in a close geometrical proximity of the alkyl or aryl group. The coordination probably takes place in an η^2 fashion with a side-on C=O interaction, as observed for similar Nb(III) systems (where the reaction stops after coordination).[20] It should be noted that the coordination interaction of CO_2 is weak; in the absence of Lewis bases the carboxylate formed from the insertion dimerizes and precipitates out of solution, and the excess carbon dioxide is not sufficiently nucleophilic to neither prevent dimerization nor dissolve the precipitated dimer. The lack of reactivity of the alkoxide cations can be understood on the basis of this mechanism. The use of an alkoxide instead of an alkyl ligand is expected to decrease the metal Lewis acidity, so that CO_2 coordination in $Cp_2Zr(O\text{-alkyl})(CO_2)^+$ may be weaker than in $Cp_2ZrR(CO_2)^+$ species.[21] Additionally, the Zr−R bond strength is of course enhanced, making the actual insertion less favored.

In conclusion, cationic zirconocene alkyls and aryls readily insert carbon dioxide into the zirconium−carbon bond. The insertion is probably preceded by CO_2 coordination to the metal, resulting in an altered reactivity by enhancing the polarization of the heterocumulene. The zirconocene carboxylates are stable, dimeric species with low solubility, and this can explain the CO_2-induced deactivation of cationic metallocene systems that has been observed in olefin polymerization.

Experimental Section

General Procedures and Materials. All experiments were carried out using standard high-vacuum-line or Schlenk techniques or in a glovebox under nitrogen. Solvents were dried over and distilled from Na/benzophenone prior to use. If nothing else is stated, all commercially available reagents were used as received from Aldrich. Dry carbon dioxide was obtained by passing it through a −78 °C trap at the high-vacuum line. The complexes $Cp_2Zr(Me)(O\text{-alkyl})$[15] and $Cp_2Zr(Me)Ph$[15] were prepared with slight modifications of literature procedures. The NMR spectroscopic measurements were performed in THF-d_8 unless otherwise stated. ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer operating at 499.77 MHz (^{1}H). The assignment of the atoms is supported by 2D ^{1}H−^{13}C experiments. Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H and ^{13}C NMR) or BF_3−etherate and (trifluoromethyl)benzene as reference. Infrared spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer (4000−200 cm^{-1}).

General Preparation of CO_2-Activated Complexes (14, 15). The reactions of $B(C_6F_5)_3$ with the methyl complexes $Cp_2Zr(Me)R$ were conducted according to literature procedures in benzene and transferred to a J. Young NMR tube.[16] This solution or a C_6D_6 solution of the neutral zirconocenes was degassed via three freeze−pump−thaw cycles and dry carbon dioxide, which was obtained by passing it through a −78 °C trap on the vacuum line and was then condensed in at −196 °C to give a pressure of 5 atm. The tube was thawed and any reaction allowed to evolve. In the case of **8** and **9** the instantaneously formed oil was allowed to solidify and dissolved in THF-d_8, giving the mononuclear THF adducts **14** and **15**.

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14: ^{1}H NMR (THF-d_8) δ 6.51 (s, 10H, Cp H), 2.09 (s, 3H, O_2CMe), 0.60 (broad, 3H, BMe); $^{13}C\{^{1}H\}$ NMR (THF-d_8) δ 188.8 (O_2CMe), 117.4 (Cp C), 70.4 (α-C of coord THF), 26.5 (β-C of coord THF), 22.7 (O_2C*Me*), 10.9 (broad, BMe), 149.4 ($^{1}J_{CF}$ = 237.6 Hz, *o*-C of C_6F_5), 138.4 ($^{1}J_{CF}$ = 243.4 Hz, *p*-C of C_6F_5), 137.3 ($^{1}J_{CF}$ = 247.4 Hz, *m*-C of C_6F_5), 130.6 (broad, ipso-C of C_6F_5); $^{11}B\{^{1}H\}$ NMR (THF-d_8) δ −14.8 ($\nu_{1/2}$ = 82 Hz); ^{19}F NMR (THF-d_8) δ −133.3 (m, 6F, *o*-F of C_6F_5), −166.8 (m, 3F, *p*-F of C_6F_5), −169.0 (m, 6F, *m*-F of C_6F_5); IR (KBr) $\tilde{\nu}$ 3120 (w), 2949 (w), 1642 (m), 1561 (s), 1510 (s), 1459 (s), 1447 (s), 1372 (m), 1364 (m), 1356 (m), 1261 (s) cm^{-1}; IR (THF) $\tilde{\nu}$ 3104 (w), 3092 (w), 2948 (w), 1639 (m), 1549 (m), 1509 (s), 1479 (m), 1459 (s), 1447 (s), 1384 (w), 1368 (w), 1358 (w), 1298 (w), 1268 (m) cm^{-1}. Anal. Calcd for $C_{62}H_{32}B_2F_{30}O_4Zr_2$ (1614.95): C, 46.11; H, 2.00. Found: C, 46.20; H, 2.10.

15: ^{1}H NMR (THF-d_8) δ 8.05, 7.73, 7.55 (each m, 5H, *o*-, *p*-, *m*-H of Ph), 6.60 (s, 10H, Cp H), 0.52 (broad, 3H, BMe); $^{13}C\{^{1}H\}$ NMR (THF-d_8) δ 180.5 (O_2CPh), 136.0 (p−C), 130.4 (*o*-C), 129.6 (*m*-C), 128.7 (ipso-C), 116.7 (Cp C), 70.3 (α-C of coord THF), 26.4 (β-C of coord THF), 10.7 (broad, BMe); 149.3 ($^{1}J_{CF}$ = 239.8 Hz, *o*-C of C_6F_5), 138.3 ($^{1}J_{CF}$ = 242.7 Hz, *p*-C of C_6F_5), 137.1 ($^{1}J_{CF}$ = 247.0 Hz, *m*-C of C_6F_5), 130.3 (broad, ipso-C of C_6F_5); $^{11}B\{^{1}H\}$ NMR (THF-d_8) δ −14.8 ($\nu_{1/2}$ = 48 Hz); ^{19}F NMR (THF-d_8) δ −132.8 (m, 6F, *o*-F of C_6F_5), −166.2 (m, 3F, *p*-F of C_6F_5), −168.4 (m, 6F, *m*-F of C_6F_5); IR (KBr) $\tilde{\nu}$ 3120 (w), 3095 (w), 3038 (w), 2977 (w), 2945 (w), 2911 (w), 2847 (w), 1643 (m), 1592 (m), 1523 (s), 1510 (s), 1459 (s), 1446 (s), 1411 (s), 1313 (m), 1299 (m), 1265 (m), 1184 (m) cm^{-1}; IR (THF) $\tilde{\nu}$ 3102 (w), 3092 (w), 3072 (w), 3036 (w), 2948 (w), 2916 (w), 2850 (w), 1639 (m), 1601 (m), 1592 (w), 1509 (s), 1480 (m), 1458 (s), 1449 (s), 1437 (s), 1419 (m), 1384 (w), 1368 (w), 1299 (w), 1269 (m) cm^{-1}. Anal. Calcd for $C_{72}H_{36}B_2F_{30}O_4Zr_2$ (1739.10): C, 49.73; H, 2.09. Found: C, 49.68; H, 2.11.

Crystallography. Performing the reaction of **8** with CO_2 in dichloromethane gave prisms of compound **12** suitable for X-ray diffraction. Intensity data were collected at 293 K with an Oxford Diffraction Xcalibur 3 system using ω scans and Mo Kα (λ = 0.710 73 Å) radiation.[22] CCD data were extracted and integrated using Crysalis RED.[23] The structure was solved by Patterson methods and refined by full-matrix least-squares calculations on F^2 using SHELXTL 5.1.[24] Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. All crystallographic data are available in CIF format in the Supporting Information. CCDC reference number: 282560.

Crystal data: $C_{62}H_{32}B_2F_{30}O_4Zr_2$, M_r = 1614.95, triclinic, a = 11.9868(16) Å, b = 12.3812(17) Å, c = 12.543(2) Å, α = 90.053(17)°, β = 118.416(13)°, γ = 108.960(12)°, V = 1521.1(4) Å^3, space group $P\bar{1}$, Z = 1, D_{calcd} = 1.763 g cm^{-3}, μ = 0.484 mm^{-1}, θ range 2.33−26.37°, 10 136 reflections measured, 5166 unique (R_{int} = 0.0422), which were used in all calculations. The final $R_w(F^2)$ value was 0.2346 (all data), and the $R(F)$ value was 0.0772 ($I > 2\sigma(I)$) using 452 parameters. S = 1.042.

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Supporting Information Available: Full crystallographic data in CIF format and a figure giving a packing diagram of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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