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Notes

Simple Functionalizations of Pentamethylcyclopentadienyl Ligands by Reactions of Decamethylzirconocene Complexes with Carbon Dioxide

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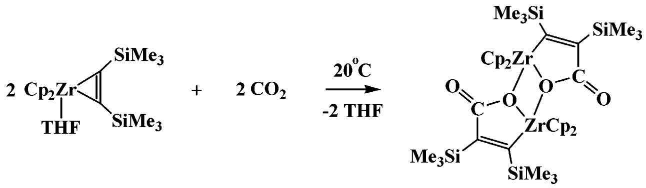
Summary: The well-known zirconafuranone, obtained by the reaction of the decamethylzirconocene bis(trimethylsilyl)acetylene complex $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ *with carbon dioxide, rearranges upon thermolysis to a complex with the* $[C_5Me_4-CH_2-CH(Me_3Si)C(=C=O)]^{2-}$ *ligand resulting from an electrophilic substitution of a hydrogen atom at one of the methyl groups of a Cp* ligand, a cleavage of the CO bond in the starting zirconafuranone, and a movement of the* Me_3Si *groups from β-carbon to oxygen. Another example of the functionalization of a pentamethylcyclopentadienyl ligand by carbon dioxide was found with a complex obtained by the reaction of* $Cp^*_2ZrCl_2$ *with magnesium in the presence of the butadiyne t-BuC≡CC≡Ct-Bu. This complex reacts by formally inserting 1 equiv of carbon dioxide into each of two ZrC bonds, but yields a dinuclear complex with twofold functionalized Cp* ligands acting as bridging dicarboxylato ligands,* $[O_2C-CH_2-C_5Me_3-CH_2-CH(t\text{-}Bu)C(=C=CH\text{-}t\text{-}Bu)-CO_2]^{3-}$*. Both complexes result from a simple method of functionalization of Cp* ligands of zirconocene complexes and were characterized by NMR and X-ray crystal structure analysis.*

Introduction

Coupling of unsaturated substrates with carbon dioxide in the coordination sphere of low-valent titanium and zirconium complexes is of interest for many synthetic applications.[1] We published such reactions for the metallocene alkyne complexes $Cp'_2M(\eta^2\text{-}RC_2R)$ (Cp′ = substituted or nonsubstituted cyclopentadienyl; M = Ti, Zr; R = alkyl, aryl, Me_3Si, etc.) with results strongly depending on the metals and ligands used in several reviews.[2] An example for a typical reaction was the coupling of the alkyne with carbon dioxide to zirconafuranones (alternatively, considered also as an insertion of carbon dioxide into the zirconacyclopropene), first described for the complex with nonsubstituted cyclopentadienyl ligands $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$. The obtained complex was stabilized by dimerization to a complex with ZrOZrO four-membered ring systems (Scheme 1).[3]

Scheme 1



We also published that the reaction of the permethyltitanocene bis(trimethylsilyl)acetylene complex $Cp^*_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with carbon dioxide was accompanied with full elimination of the alkyne ligand from the coordination sphere of titanium, and carbon dioxide disproportionated to form $Cp^*_2Ti(CO)_2$ and the titanium(III) carbonate complex $(Cp^*_2Ti)_2CO_3$.[4] The presence of two bulky trimethylsilyl groups together with $\eta^5\text{-}C_5Me_5$ ligands of titanocene did not allow the formation of a five-membered metallacycle, leading to the elimination of alkyne and the formation of carbonyl and carbonate complexes. Compared to titanium, we found that in the reaction of $Cp^*_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**)[5] with carbon dioxide the bigger decamethylzirconocene allows the coupling of bis(trimethylsilyl)acetylene with carbon dioxide and the formation of the monomeric zirconafuranone **2** (Scheme 2).[6] Here we publish the unexpected thermolysis of complex **2** giving complex **3**.

Results and Discussion

Complex **2** was found to be stable for a long time in solid state and in solution at rt.[6] However at elevated temperature

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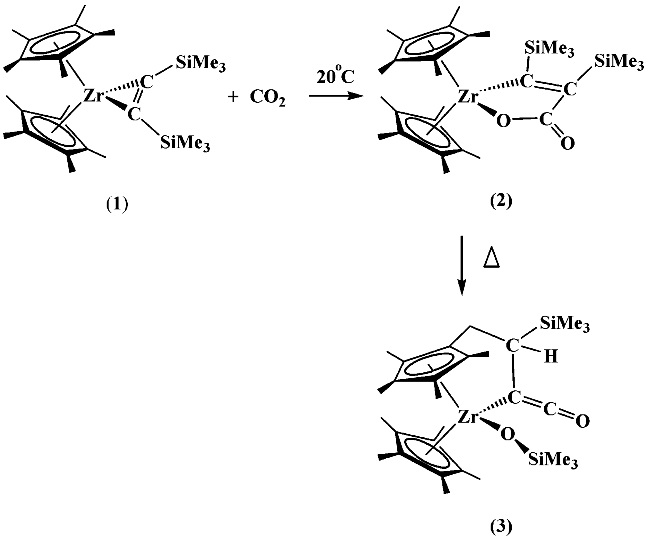
Scheme 2



(80 °C) the metallacycle of the zirconafuranone **2** decomposes to yield complex **3** (Scheme 2).

One can only speculate about mechanistic suggestions for the formation of complex **3**. The enlarged metallacycle is the result of an electrophilic substitution of a hydrogen atom at one of the methyl groups, a cleaveage of the CO bond, and the movement of the Me_3Si group from the β-carbon to oxygen. The new complex **3** contains trimethylsilanolate (zirconasiloxane) and ketenyl groups. The driving force for these processes is mostly a sterical problem in complex **2**. This was indicated before[6] by its NMR spectra, giving at room temperature only one sharp signal for one Me_3Si groups (δ: ^{1}H 0.19 and ^{13}C 3.2 ppm), whereas the other was detected only as a broad signal. After cooling in the ^{1}H NMR spectra the broad signal gave two absorptions in a 1 to 2 ratio (δ: 0.09 and 0.29 ppm), indicating a hindered rotation of one Me_3Si group.[6] Such an intramolecular interaction was observed in the X-ray molecular structure analysis, showing contacts between the carbonyl group and a hydrogen atom of a methyl group of the Me_3Si group attached to the β-carbon atom (H···O 2.490 Å).[6] These results could give an idea how overcrowded the coordination sphere in complex **2** is.

On the other side the formation of a Si−O bond in the ZrOSi system of complex **3** could also contribute to the thermodynamic stability. Nevertheless, differences in the stability of such complexes are obviously very small, because in the reaction of "Cp_2Zr" with the acetylenedicarboxylic diester $Me_3SiO(C{=}O)C{\equiv}C(C{=}O)OSiMe_3$ the opposite movement of the Me_3Si group from oxygen to carbon was observed.[7] In this case the driving force was the formation of a four-membered OZrOZr ring in a dinuclear complex. All these small effects lead to unexpected and unusual complexes.

Another unusual example of reactions of zirconocene complexes with carbon dioxide was found, if the product of the reaction of $Cp^*_2ZrCl_2$ with magnesium in the presence of the butadiyne t-BuC≡CC≡Ct-Bu, complex **4** [8] (Scheme 3), reacts with 2 equiv of carbon dioxide.

Carbon dioxide is inserted into both of the ZrC bonds, and complex **5** was formed, having bridging dicarboxylato ligands $[O_2C{-}CH_2{-}C_5Me_3{-}CH_2{-}CH(t\text{-Bu})C({=}C{=}CH\text{-}t\text{-Bu}){-}CO_2]^{3-}$, representing twofold functionalized Cp* ligands in the dinuclear complex (Scheme 3).

Structural Investigations

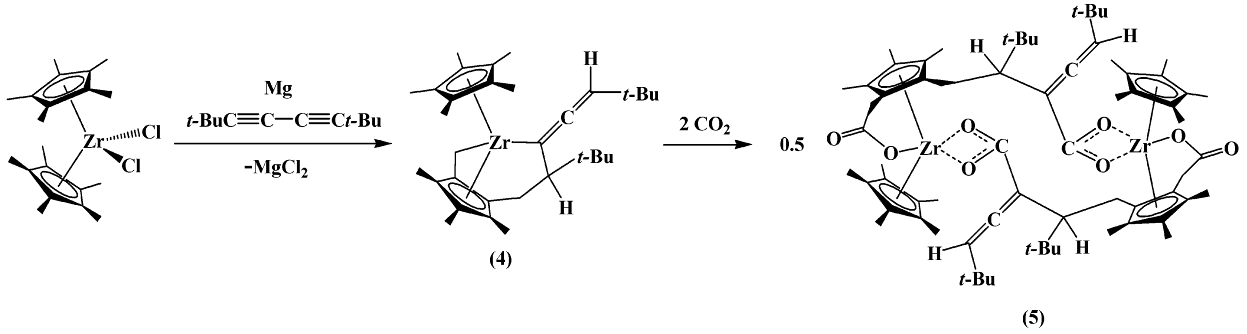
The IR spectra of complexes **3** and **5** (Nujol mull) give nice support for the structure of these complexes. For example, typical absorptions of cumulated double bonds in the area of 1900−2300 cm^{-1} were found for complex **3** at 2035 cm^{-1} (ν(C=C=O)) and for complex **5** at 1947 cm^{-1} (ν(C=C=C)). Additionally for complex **5** at 1655 and 1697 cm^{-1} the characteristic ν(C=O) vibrations were displayed.

The NMR signal patterns indicate the presence of an unchanged Cp* group (^{1}H singlets of relative intensity 15) besides a functionalized one by four additional methyl singlets (rel int 3) for **3** and three for **5**. The cumulenic systems are evident from their representative chemical shifts: the ketenyl unit in **3** with a significant high-field shift for its β carbon atom (C7, 35.3 ppm, a value that is otherwise unexpected for a sp^2 carbon adjacent to a transition metal) and a signal for the carbon atom in the carbonyl region (168.1 ppm), and the allene system in **5** with a deshielded central carbon (C24, 209.0 ppm) and two distinctly shielded terminal carbon atoms (C23, 109.2 ppm, and C25, 107.7 ppm). The observation of a 2 Hz coupling between 25-H and 47-H (over five bonds!) is also a typical feature for allenes. The carbonyl signals (C22, 168.9 ppm, and C28, 183.7 ppm) indicate the different binding mode of the two carboxylic functions. Only one set of signals is found for both "halves" of the dinuclear compound **5**, although they are distinguishable crystallographically.

Complexes **3** and **5** were investigated by X-ray crystallography. The crystallographic data are presented in Table 1, and the molecular structures are shown in Figures 1 and 2.

The X-ray crystal structure analysis of complex **3** shows the typical structural element resulting from an insertion into a *"tucked in"* zirconocene complex. The Cp* ligand is bonded in the typical manner. The bond distances and angles in the formed π,σ-bonded ligand $[C_5Me_4{-}CH_2{-}CH(Me_3Si)C({=}C{=}O)]^{2-}$ correspond to the expected data. Short distances C7−C22 (1.283(6) Å) and C22−O2 (1.191(5) Å) together with the almost linear arrangement of C7−C22−O2 (174.0(4)°) support the bonding description as a C=C=O unit. Angles Zr1−C7−C8, C7−C8−C9, and C8−C9−C10 (118.8(2)°, 107.3(3)°, and 110.0(3)°) reflect a relatively unstrained coordination of the

Scheme 3



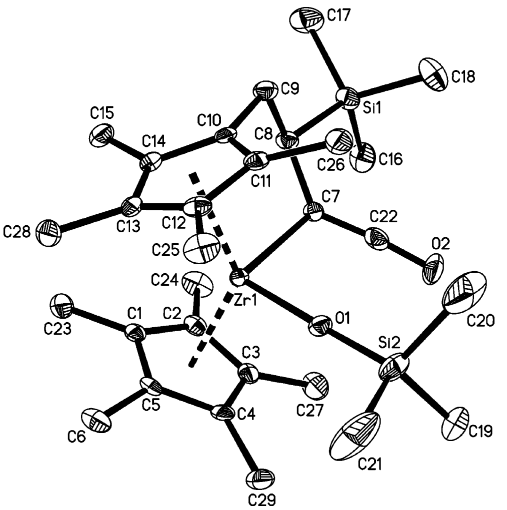


Figure 1. Crystal structure of complex **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: Zr1−C7 2.310(3), C7−C8 1.529(5), C8−C9 1.546(5), Zr1−O1 1.982(2), O1−Si2 1.634(3), C7−C22 1.283(6), C22−O2 1.191(5); Zr1−O1−Si2 177.8(2), O1−Zr1−C7 98.36(12), Zr1−C7−C8 118.8(2), Zr1−C7−C22 110.9(3), C7−C22−O2 174.0(4), C8−C7−C22 129.0(3), C7−C8−C9 107.3(3).

Table 1. Crystallographic Data

	3	5
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a [Å]	12.136(2)	13.363(3)
b [Å]	16.912(3)	24.786(5)
c [Å]	14.873(3)	21.233(4)
α [deg]	90	90
β [deg]	91.92(3)	93.21(3)
γ [deg]	90	90
V [Å^3]	3050.9(10)	7022(2)
Z	4	4
density [g·cm^{-3}]	1.254	1.196
μ(Mo Kα) [mm^{-1}]	0.461	0.347
T [K]	200	200
no. of rflns (measd)	8905	12 768
no. of rflns (indep)	4849	6783
no. of rflns (obsd)	3491	4275
no. of params	311	707
R1 ($I > 2\sigma(I)$)	0.039	0.059
wR2 (all data)	0.095	0.157

ligand. The silanolate ZrOSiMe$_3$ bond distances Zr1−O1 (1.982(2) Å) and O1−Si2 (1.634(3) Å) as well as the angle Zr1−O1−Si2 (177.8(2)°) correspond very well to those of similar complexes.[9]

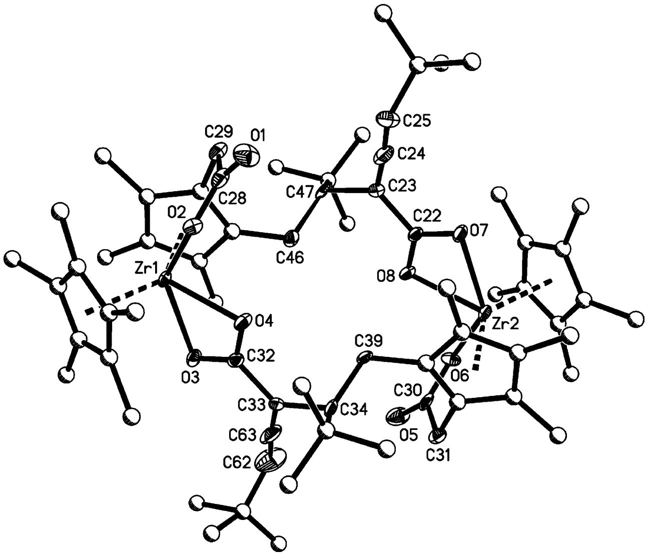


Figure 2. Crystal structure of complex **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths [Å] and angles [deg]: C28−O1 1.231(10), C30−O5 1.227(9), C32−O3 1.268(9), C32−O4 1.272(9), Zr1−O2 2.078(6), Zr1−O3 2.278(5), Zr1−O4 2.257(5), Zr2−O6 2.090(6), Zr2−O7 2.269(5), Zr2−O8 2.258(5), C28−C29 1.513(12), C32−C33 1.487(11), C22−C23 1.484(11), C30−C31 1.517(12), C62−C63 1.301(14), C33−C63 1.319(12), C62−C63 1.301(14), C23−C24 1.291(12), C24−C25 1.333(13); O1−C28−O2 123.9(9), O3−C32−O3 117.7(7), O5−C30−O6 123.8(9), O7−C22−O8 117.2(7).

The X-ray crystal structure analysis of complex **5** displays a dinuclear complex bridged by two dicarboxylato ligands [$O_2C-CH_2-C_5Me_3-CH_2-CH(t\text{-Bu})C(=C=CHt\text{-Bu})-CO_2$]$^{3-}$. There is no interaction of the two zirconium centers, and the two Cp* ligands remains in principle unchanged. Interestingly, the carboxylate group, connected directly to the Cp* ligands, coordinates with zirconium by one oxygen atom, whereas the other by both oxygen atoms. According to this behavior, slightly shorter C−O bonds were found for the uncoordinated groups C28−O1 (1.231(10) Å) and C30−O5 (1.227(9) Å) compared to the coordinated C32−O3 (1.268(9) Å) and C32−O4 (1.272(9) Å). This is connected with the expected consequences for all Zr−O bond distances (Zr1−O2 2.078(6), Zr1−O3 2.278(5), Zr1−O4 2.257(5), Zr2−O6 2.090(6), Zr2−O7 2.269(5), Zr2−O8 2.258(5) Å) and the angles in the carboxylate (O1−C28−O2 123.9(9)°, O3−C32−O4 117.7(7)°, O5−C30−O6 123.8(9)°, O7−C22−O8 117.2(7)°). The lengths of cumulated C═C═C bonds in complex **5**, C33−C63 (1.319(12) Å), C62−C63 (1.301(14) Å), C23−C24 (1.291(12) Å), and C24−C25 (1.333(13) Å) generally are in the range of allenes' double-bond length (1.307 Å).[10]

Conclusion

On the basis of reactions of decamethylzirconocene complexes a simple method of functionalization of Cp* ligands to the π,σ-bonded ligand [$C_5Me_4-CH_2-CH(Me_3Si)C(=C=O)$]$^{2-}$ of **3** and bridging dicarboxylato ligands [$O_2C-CH_2-C_5Me_3-CH_2-CH(t\text{-Bu})C(=C=CHt\text{-Bu})-CO_2$]$^{3-}$ of **5** exists. Both complexes **3** and **5** realize via *"tucked in complexes"* insertion reactions of carbon dioxide at the methyl groups of one Cp* ligand.

Experimental Section

General Procedures. All operations were carried out under argon with standard Schlenk techniques. Prior to use nonhalogenated solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvent (benzene-d_6) was treated with sodium tetraethylaluminate, distilled, and stored under argon.

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The following spectrometers were used. Mass spectra: AMD 402. NMR spectra: Bruker ARX 400. Chemical shifts (^{1}H, ^{13}C, ^{29}Si) are given relative to $SiMe_4$ and are referenced to signals of the used solvent (benzene-d_6, $\delta_H = 7.16$, $\delta_C = 128.0$); the spectra were assigned with the help of DEPT, NOE, and shift correlation experiments. This section gives only key data; full details can be found in the Supporting Information. Melting points: sealed capillaries, Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of Complex 3. Complex **2** (0.369 g, 0.64 mmol) was dissolved in 10 mL of *n*-heptane under Ar, and the mixture was warmed to 80 °C. After 3.5 h the resulting red-brown solution was evaporated to 3−4 mL and filtered. Upon cooling to −78 °C for 2 days, brownish-yellow crystals were formed, which were separated from the mother liquor by decanting, washed with a small amount of cold *n*-hexane, and dried in a vacuum. Yield of **3** was 0.169 g (46%), mp 206−207 °C under Ar. Anal. Calcd for $C_{29}H_{48}O_2Si_2Zr$: C, 60.46; H, 8.40. Found: C, 60.15; H 8.54. ^{1}H NMR (C_6D_6, 297 K): δ 0.28 (s, 9H, $SiMe_3$); 0.39 (s, 9H, $OSiMe_3$); 1.88 (s, 15H, Cp*); 1.71, 1.74, 1.86, 2.11 (4 s, 3H each, Me); 1.94 (dd, 1H, 8-H), 2.28 (dd, 1H, 9-H); 2.44 (t, 1H, 9-H). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): δ −2.4 ($SiMe_3$); 5.1 ($OSiMe_3$), 11.7 (Cp*), 10.7, 11.3, 11.8, 13.4 (4 Me); 27.5 (C9); 35.3 (C7); 39.7 (C8); 120.3 (Cp*); 114.9, 115.2, 118.2, 123.4, 142.1 (5 quart.); 168.1 (C22). ^{29}Si NMR (C_6D_6, 297 K): 2.1 ($SiMe_3$), 4.2 ($OSiMe_3$). IR (Nujol mull, cm^{-1}): 2035 (ν C═C═O). MS (70 eV, *m*/*z*): 574 [M]$^+$.

Preparation of Complex 5. Complex **4** (0.275 g, 0.525 mmol) was dissolved in 40 mL of *n*-hexane under Ar. The red solution was filtered, argon was carefully removed in a vacuum, and the flask with solution was filled with carbon dioxide at room temperature. Within a few hours the reaction mixture turned yellow, and light yellow crystals of **5** appeared. After 2 days the solution was decanted. Subsequent washing of the crystals with cold *n*-hexane and drying in a vacuum gave 0.229 g (71%) of **5**, mp 270−272 °C (dec) under Ar. Anal. Calcd for $C_{68}H_{96}O_8Zr_2$: C, 66.73; H, 7.91. Found: C, 66.76; H 8.11. ^{1}H NMR (C_6D_6, 297 K): δ 1.06, 1.17 (2 s, 9H each, *t*-Bu); 2.01 (s, 15H, Cp*); 1.92, 1.93, 2.23 (3 s, 3H each, Me); 1.91 (dd, 1H, 47-H); 2.30 (dd, 1H, 46-H); 2.88 (d, 1H, 46-H); 3.37, 3.50 (2 d, 1H each, 29-H); 5.47 (d, 1H, 25-H). ^{13}C{^{1}H} NMR (C_6D_6, 297 K): 11.0 (Cp*); 9.4, 11.2, 11.3 (3 Me), 28.3, 30.2 (2 *t*-Bu-Me); 30.6 (C46); 33.6 (C29); 34.1, 35.3 (2 *t*-Bu quart.); 50.9 (C47); 107.7 (C25); 109.2 (C23); 115.3, 120.2, 123.2, 124.4, 131.5 (5 quart.); 123.7 (Cp*); 168.9 (C22); 183.7 (C28); 209.0 (C24). IR (Nujol mull, cm^{-1}): 1655, 1697 (ν C═O), 1947 (ν C═C═C). MS (70 eV, *m*/*z*): 566 [1/2M − CO_2]$^+$, 509 [1/2M − CO_2 − *t*-Bu]$^+$.

X-ray Crystallographic Study of Complexes 3 and 5. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[11] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93, SHELXL-97).[12] XP (Bruker-AXS) was used for structure representations.

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Supporting Information Available: Tables of crystallographic data in cif format, including bond lengths and angles of compounds **3** and **5**. Full assignment of NMR signals for **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051063Z

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