Fischer-Tropsch Intermediates: Tris[(η^2-formaldehyde)zirconocene] from the Carbonylation of a Zirconium Hydride

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The formation of free formaldehyde as an intermediate in Fischer-Tropsch-type chemistry is questionable in view of its unfavorable thermodynamics with regard to the synthesis gas components.[1] However, it is still a matter of controversy whether CH_2O bound to a transition metal center might play an important role in the transformation of carbon monoxide/hydrogen mixtures.[2] We have recently been able to establish the key function of a (η^2-formaldehyde)zirconocene complex in the course of the stoichiometric reductive coupling of two carbon monoxide molecules to form a bridging enediolate ligand starting from a dinuclear zirconocene hydride.[3] To our knowledge an η^2-formaldehyde complex (**2**) derived from the carbonylation of a transition-metal hydride has been characterized for the first time and its structure determined by X-ray diffraction.[4]

The formation of **2** was observed upon prolonged carbonylation of the oligomeric zirconocene $[Cp_2ZrH_2]_x$ (**1**).[5] In a typical experiment of 10-g sample of **1** suspended in toluene (100 mL) was converted to a complex mixture of organometallic products upon treatment with carbon monoxide (150 bar) for 1 week at room temperature. Zirconocene dicarbonyl (~30%) was separated by extraction with pentane; repeated fractional crystallization from toluene and then benzene yielded pure **4** (~5%) and the trimeric (η^2-formaldehyde)zirconocene complex **2** (14%).[6,7] The IR spectrum of **2** ($CDCl_3$, compensated) shows characteristic absorptions of the bent metallocene units at ν 3100, 1438, and 1012 cm^{-1}. In the mass spectrum (70 eV) features[8] at m/e 500, 470, (100%), 455, 404, and 389 exhibit isotopic distribution patterns typical for the presence of two zirconium atoms per ion. The ^1H NMR spectrum of **2** is very simple, comprising only two singlets at δ 5.77 (Cp) and 2.70 (CH_2) in a 5:1 ratio ($CDCl_3$ solvent). The spectrum remains practically unchanged upon cooling to -145 °C ($CD_2Cl_2/CHFCL_2$, 1:9). In the ^{13}C NMR spectrum a single Cp absorption is observed at δ 107.4 ("gated decoupled", d, $^1J_{CH} = 171$ Hz). The "aldehyde" carbon atom resonance appears at δ 69.2 (t, $J_{CH} = 151$ Hz).

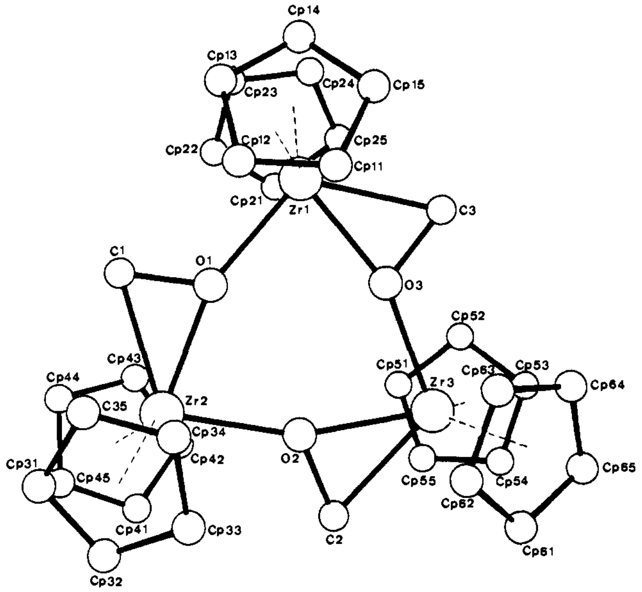

Figure 1. Molecular structure of **2**. Bond distances (Å): Zr1–O1 2.178 (5), Zr1–O3 2.133 (5), Zr1–C3 2.275 (10), Zr1–Cp1 2.263, Zr1–Cp2 2.269, Zr3–O3 2.183 (5), Zr3–O2 2.142 (5), Zr3–C2 2.270 (10), Zr3–Cp5 2.263, Zr3–Cp6 2.257, Zr2–O2 2.175 (5), Zr2–O1 2.129 (5), Zr2–C1 2.278 (10), Zr2–Cp3 2.265, Zr2–Cp4 2.270, O1–C1 1.411 (10), O2–C2 1.415 (11), O3–C3 1.454 (13). Bond angles (deg): O3–Zr1–O1 79.1 (2), O2–Zr2–O1 79.4 (2), O3–Zr3–O2 78.8 (2), O3–Zr1–C3 38.3 (4), O1–Zr2–C1 37.1 (3), O2–Zr3–C2 37.3 (3), Zr2–O1–Zr1 160.7 (2), Zr3–O2–Zr2 160.7 (3), Zr3–O3–Zr1 160.8 (2), Zr2–O1–C1 77.2 (4), Zr3–O2–C2 76.3 (4), Zr1–O3–C3 76.2 (5).

Repeated recrystallization of **2** from benzene yielded crystals suitable for an X-ray structure determination. The crystal structure of **2** has been elucidated from 7264 diffractometer-collected reflections[9] (of which 2959 were considered unobserved) and refined to a final R value of 0.055 (R_w 0.06), including one molecule of solvent (benzene) located on an inversion center. Molecules of **2** each consist of three structurally equivalent Zr-(η^2-CH_2-O-) subunits (**5**), exhibiting (averaged) bond lengths [2.275 (Zr-C), 2.135 (Zr-O), and 1.427 Å (C-O)] and angles [37.6 (O-Zr-C) and 76.6° (Zr-O-C)] as expected for a metallacyclic σ structure. A slightly longer bond [2.179 Å (Zr-O (av)] extending from each ligand oxygen to the remaining vacant coordination site of an adjacent unit **5** completes an almost planar hexangular arrangement of alternating metal and oxygen centers [Zr-O-Zr: 160.7°] to make up the framework of **2** (Figure 1).

Our findings demonstrate that an η^2-formaldehyde complex of an early transition metal can indeed be obtained from the reaction of carbon monoxide with a metal hydride. **2** appears to represent the first unequivocally characterized example of a η^2-formaldehyde transition-metal complex obtained by this route.[10] In addition to the structural features spectroscopic properties indicate an appreciable σ complex character in the $Cp_2Zr(CH_2O)$ fragments found in **2**. The description of these units as being metallaoxiranes rather than (formaldehyde)zirconocene π complexes finds precedence in the chemistry of (η^2-ketone and -aldehyde)zirconocene complexes.[11]

It is therefore not surprising that **2** is readily hydrolyzed (ambient temperature, aqueous HCl) to give Cp_2ZrCl_2 and methanol almost quantitatively. (η^2-Formaldehyde)zirconocene, **2**, like other (η^2-ketone and -aldehyde)zirconocene complexes[3,11] does react with

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(4) To our knowledge, X-ray structures of only three η^2-formaldehyde transition metal complexes have been reported so far. They have apparently all been obtained from reactions of suitable metal complex precursors with formaldehyde solutions (C–O bond lengths of the CH_2O ligand are given in parentheses). (a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ (1.59 Å): Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505. (b) $Fe(\eta^2\text{-}CH_2O)(CO)_2[P(OCH_3)_3]_2$ (1.32 Å): Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353–362. (c) $Cp_2V(\eta^2\text{-}CH_2O)$ (1.353 Å): Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019–2020.

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(6) The C and H elemental analyses corresponding to a $Cp_2Zr(CH_2O)$ oligomer were obtained only after residual solvent had been pumped off (0.005 torr, room temperature, 12 h). Anal. Calcd for $(C_{11}H_{12}OZr)_n$: C, 52.55; H, 4.81. Found: C, 52.53; H, 4.86.

(7) The composition of the complex residual organometallic mixture has not been clarified yet unequivocally.

(8) m/e values corresponding to naturally most abundant isotopes, i.e., ^{90}Zr (51.5%)

(9) Space group $P2_1/c$, $z = 4$; $a = 8.562$ (1), $b = 15.581$ (3), $c = 24.348$ (3) Å; $\beta = 95.679$ (9)°.

(10) From NMR data an analogous structure has to be suggested for $(Cp_2ZrCl)_2(CH_2O)$ obtained from the carbonylation of $[Cp_2Zr(H)Cl]_x$. Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269–270. Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437–2446.

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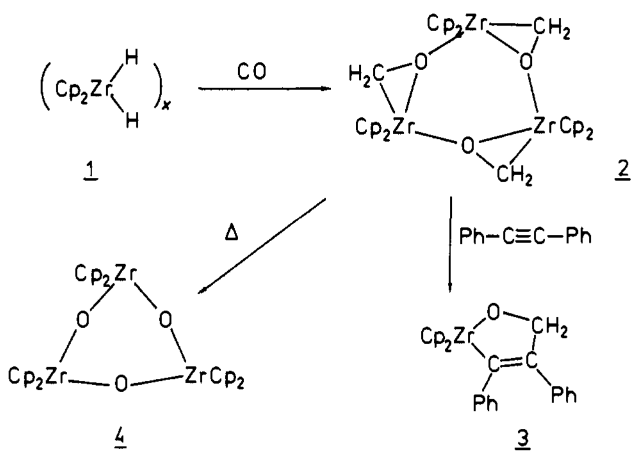
Scheme I



many unsaturated organic substrates under C–C bond formation. In contrast to the examples described previously, here such reactions are characterized by substantial activation barriers. Slow conversions of **2** take place above 180 °C with a variety of alkenes and alkynes forming complex mixtures of as yet unidentified organometallic compounds. Treatment of **2** with excess tolane at 200 °C is an exception and a 1:1 adduct [**3**: ^{1}H NMR (C_6D_6) δ 7.5 (m, 10 H, Ph), 5.9 (s, 10 H, Cp), 4.6 (s, 2 H, CH_2)] of (η^2-formaldehyde)zirconocene and diphenylacetylene is formed.[12,13] At that temperature the cyclotrimer **2** itself is thermally labile. The favorable alternation of oxygen atoms and zirconium metal centers in the ring system of **2** is retained on thermolysis: at 200 °C the trimeric (η^2-formaldehyde)zirconium complex is slowly converted ($\tau_{1/2} \sim 3$ h) to the known $Cp_2Zr{=}O$ trimer **4** (Scheme I).[14] The formation of the major reaction product **4** (≥80% yield) is accompanied by the appearance of a complex mixture of different organometallic components. These exhibit ^{1}H NMR features similar to the complex reaction mixtures obtained upon thermolysis of **2** in the presence of alkenes (see above). As the composition of these minor products has not yet been established, the fate of CH_2 groups "lost" in the thermolysis of **2** remains obscure at present. The unexpected loss of all three carbon monoxide derived methylene groups[15] from **2** by simply heating the complex may eventually lead to a new understanding of the factors controlling Fischer–Tropsch-type processes on a well-defined molecular level.[16] At present this is being actively pursued in our laboratory.

Registry No. 1, 85442-81-5; **2**, 85442-82-6; **3**, 85442-83-7; **4**, 70693-90-2.

Supplementary Material Available: Tables of positional and thermal parameters for **2** and a list of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(12) ≥80%, accompanied by ca. 20% of **4** as judged by ^{1}H NMR. Hydrolysis (aqueous NH_4Cl) of the mixture yields (*E*)-2,3-diphenylpropenol (63% isolated yield based on consumed starting material **2**): ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.74 (s, OH), 4.46 (d, 2 H, CH_2, $^4J_{HH}$ = 1.5 Hz), 6.69 (t, 1 H, =CH—), 6.93–7.46 (m, 10 H, Ph).

(13) We have recently shown that bis[(η^2-benzophenone)zirconocene] at 70 °C rapidly dissociates to give a monomeric (η^2-ketone)zirconocene species.[11] Here the isolation of oligomer **2** derived from an odd number of $Cp_2Zr(CH_2O)$–units (**5**) could indicate as well the presence of monomeric (η^2-formaldehyde)zirconocene as a reactive intermediate at some stage of the reaction. The formation of **3** by trapping thermally generated **5** with the added scavenger tolane would be in accord with this supposition.

(14) Average Zr–O bond length 1.959 Å; Zr–O–Zr angle (mean value) for **4**: Fachinetti, C.; Floriani, C.; Chiese-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767–1775.

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Observation of Coordinatively Unsaturated Intermediates following the Pulsed UV Photolysis of $Fe(CO)_5$

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Organometallic photochemistry is currently an area of vigorous investigation. One reason for this interest is the catalytic activity of photogenerated coordinatively unsaturated species.[1] A great deal of effort has gone into characterizing the nascent photoproducts, including elegant studies involving photochemically generated coordinatively unsaturated organometallics trapped in low-temperature inert-gas matrices.[2] Experiments have also been performed in the gas and liquid phases in an attempt to record the transient spectrum of photolytically generated coordinatively unsaturated species. Despite early problems of impurities coordinating with the photofragment(s), a few reports now exist where transient photofragments have been spectroscopically observed.[3] Other experiments have been successful in chemically trapping coordinatively unsaturated species following gas-phase pulsed UV photolysis of $Fe(CO)_5$ and $Cr(CO)_6$.[4]

In this communication we report the first gas-phase infrared spectrum of the carbonyl-stretch region of coordinatively unsaturated iron carbonyls generated via pulsed UV photolysis of $Fe(CO)_5$. The apparatus used in this study is schematically depicted in Figure 1. The basic experimental configuration is that of a pulsed UV–continuous-wave (CW) infrared double-resonance apparatus. UV pulses of a few millijoules per square centimeter are produced via an excimer laser. Almost collinear with the excimer beam is the output of a line-tunable liquid-N_2-cooled CW CO laser. The output of this laser is uniformly attenuated and diffused to produce a beam of ~10 mW/cm^2, which after passing through the flow cell is incident on an InSb detector. The detector and amplifier combination were carefully chosen to provide rapid response ($\tau \simeq 35$ ns) and linearity over a large dynamic range of incident power. A mixture of 3–30 mtorr of $Fe(CO)_5$ in Ar and/or CO is photolyzed in the 10-cm Teflon flow cell. A change of approximately 10^{11} $Fe(CO)_5$ or coordinatively unsaturated iron carbonyl molecules are necessary to produce a single-pulse transient with a signal to noise ratio of unity.

The transient absorption spectrum generated as a consequence of photolysis of $Fe(CO)_5$ with 248-nm light is displayed in Figure 2. The spectrum is produced by recording transient absorptions as a function of frequency as the CO laser is scanned over a portion of its wavelength range. Four spectral features are apparent and can be assigned by reference to matrix and chemical trapping data.[2,4,6] Feature 1 is the parent absorption. As the parent is

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