

probably one of the alkene-chromium species described above. This argument suggests an intermediate chromium-hydrogen system possibly containing a π -allyl moiety. The activation of the C-H bond is apparently related to the resonance stabilization gained upon formation of the arene and the further stabilization from the tendency of chromium to form strong π bonds with arene ligands. This unusual nature of our chromium-cyclohexene reaction system is further demonstrated by the absence of the oligomerization products observed when 1-butene is cocondensed with chromium atoms as reported by Skell;⁵ the addition of D₂O is necessary to generate oligomeric products in the case of 1-propene, but we observed oligomerization in the absence of a proton source.

We are currently attempting to further elucidate the mechanistic details of the process involved in this reaction, as well as optimizing the process as a synthetic method for the convenient preparation of mixed, π -complexed arene chromium compounds.

Acknowledgment. We acknowledge our debt to the Robert A. Welch Foundation for its support of this work.

Reaction of Diene Group 4 Metallocene Complexes with Metal Carbonyls: A Novel Entry to Fischer-Type Carbene Complexes

Gerhard Erker,* Ulrich Dorf, Reinhard Benn, and Rolf-Dieter Reinhardt

Max-Planck-Institut für Kohlenforschung
D 4330 Mülheim a. d. Ruhr, Germany

Jeffrey L. Petersen

Department of Chemistry, West Virginia University
Morgantown, West Virginia 26506

Received July 2, 1984

Transition-metal carbene complexes are among the most important organometallic substrates involved in stoichiometric as well as catalytic reaction sequences for the transformation of organic compounds.¹ Surprisingly, most presently employed synthetic routes for the conversion of a metal carbonyl to a transition-metal carbene moiety are basically variations of E. O. Fischer's original method,² published back in 1964, which is characterized by a nucleophile initially attacking the carbonyl carbon atom. Limitations of this route³ have been circumvented by using carbene precursors other than coordinated carbon monoxide.¹ However, a general mechanistic alternative to Fischer's procedure for the $M\equiv C\text{O} \rightarrow M=\text{C}R(\text{OR}')$ conversion seems still to be lacking.

We have recently observed two competing reactions taking place upon exposure of the unique (*s-cis*-/*s-trans*- η^4 -conjugated diene)metallocene system **1** \rightleftharpoons **3**⁴ to ketones and aldehydes. Metallacyclic σ^2, π -type structured **3** reacts by a usual carbonyl addition reaction.^{5,6} Under equilibrium conditions, the reactivity of the *s-trans* isomer **1** is much higher, however. Its reactions with ketones is believed to proceed through a coordinatively unsaturated

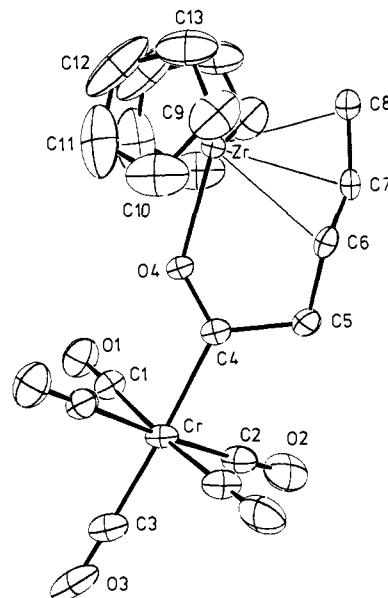
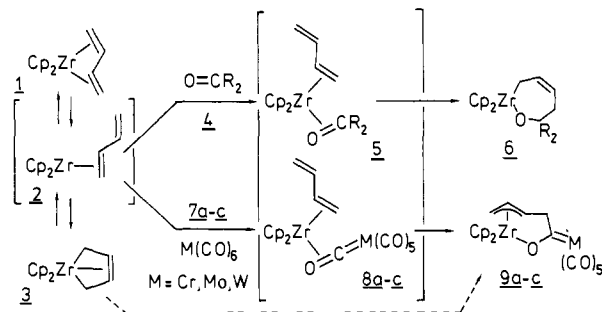


Figure 1. Perspective view of the molecular structure of **9a** with atom numbering scheme.

Scheme I



(η^2 -diene)MCP₂ intermediate **2**. It has been suggested that CC coupling takes place during a (probably concerted) electrocyclic ring-closure reaction of **5** to produce a metallacyclic σ -allyl complex **6**.^{6,7} Replacement of the organic carbonyl compound **4** in this reaction sequence (Scheme I) by its inorganic analogue, a transition-metal carbonyl, should lead to a Fischer-type carbene complex, formed from coordinated carbon monoxide by electrocyclic CC coupling.

In fact, the (*s-cis*-/*s-trans*- η^4 -butadiene)zirconocene equilibrium mixture (**1** \rightleftharpoons **3**)⁴ slowly reacts at room temperature with Cr(CO)₆ (equimolar, 2% in benzene, 12 h) to yield the (zirconoxycarbene)Cr(CO)₅ complex⁸ **9a**. (Yellow crystals from benzene, 51% isolated yield. Anal. Calcd for C₂₀H₁₆O₆CrZr: C, 48.47; H, 3.25. Found: C, 48.59; H, 3.13. IR⁹ (C₆D₆) ν_{CO} = 2048 (m), 1994 (s), 1920 (vs) cm⁻¹.) The NMR spectra of **9a** indicate the presence of a syn-substituted π -allyl unit^{7b,10} (C₆D₆ solution,

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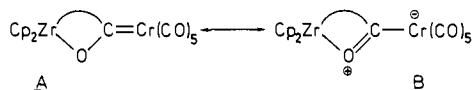
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ambient temperature).¹¹ (¹H NMR δ 1.49, 1.50 (H8s/a), 4.91 (H7), 4.53 (H6), 4.20, 2.66 (H5/5'); ²J_{HH} (Hz) = 4.0 (H8s/a), -17.4 (H5/5'); ³J_{HH} (Hz) = 8.4 (H8s/7), 13.5 (H8a/7), 15.9 (H7/6), 4.7, 9.8 (H6/5,5'); ¹³C NMR (¹J_{CH}, Hz) δ 44.4 (149) C8, 129.3 (146) C7, 112.3 (149) C6, 68.3 (129) C5.) This causes the zirconocene Cp ligands to be diastereotopic (¹H NMR δ 5.23, 5.26; ¹³C NMR δ 108.87, 109.02). A typical ¹³C chemical shift difference¹² is found between CO ligands trans (δ 225.0) and cis (δ 219.7) to the carbene unit. The observed ¹³C absorption of the carbene carbon atom itself (δ 363.7) is close to the low-field limit of the range characteristic of Fischer-type carbene complexes.¹²

The molecular structure of the metallacyclic zirconoxycarbene complex **9a** was determined by X-ray crystallography (Figure 1).¹³ The bent metallocene unit (Zr-C(Cp) = 2.486 (5) Å, Cp(C)-Zr-Cp'(C) = 129.2 (4)°) is connected to the chromium carbene moiety by a rigid framework, incorporating a substituted η^3 -allyl unit¹³ and the "carbene oxygen" O4. Structural features around chromium are in the expected range for a Fischer-type carbene complex¹ (Cr-C1 = 1.887(3), Cr-C2 = 1.882 (4), Cr-C3 = 1.879 (5), Cr-C4 = 2.063 (4) Å; C3-Cr-C4 = 177.0 (2)°). Quite remarkable is the short O4-C4 bond, with 1.254 (5) Å clearly among the shortest values so far observed for a Cr=C-OR moiety.^{1,14} In connection with the observed rather long Zr-O4 bond⁶ of 2.188 (3) Å this is an indication for a pronounced metal acyl character, emphasizing on the relative importance of resonance form **B** for describing the metal carbene moiety in **9a**.



This might well be the primary reason that a substantially decreased Zr-O4-C4 angle (136.1 (3)°) and a π -allyl ligand is favored around zirconium for **9a** as opposed to **6**.⁶

Reactions of butadiene zirconocene (**1** \rightleftharpoons **3**) with molybdenum and tungsten hexacarbonyl proceed exactly analogously. We obtained the bimetallic carbene complexes **9b** (M = Mo) and **9c** (W) in 61% and 72% isolated yield. Spectroscopic properties of these compounds are almost identical with those observed for the chromium complex **9a**.¹⁵

Unfortunately, the reaction of the M(CO)₆ complexes **7a-c** with the rapidly equilibrating (butadiene)ZrCp₂ isomer system is too slow for an experimental observation of differences in reaction rates between **1** and **3**. The much higher isomerization activation barrier of the (*s-trans*-/*s-cis*-butadiene)hafnocene system

($\Delta G^{\ddagger}_{60^\circ\text{C}}(\mathbf{1}' \rightarrow \mathbf{3}') = 24.7$ kcal/mol; equilibrium at 60 °C, $\mathbf{1}'/\mathbf{3}' < 1/99$)^{4b} compared to the zirconium analogue ($\Delta G^{\ddagger}_{10.5^\circ\text{C}}(\mathbf{1} \rightarrow \mathbf{3}) = 22.7$ kcal/mol; equilibrium 25 °C, $\mathbf{1}/\mathbf{3} = 45/55$)⁴ allows a clear mechanistic differentiation,^{6,7b} however. Reaction of a 80/20 mixture of the hafnium complexes **1'/3'** with 0.7 equiv of Cr(CO)₆ (**7a**) in benzene at room temperature results exclusively in the consumption of the (*s-trans*- η^4 -butadiene)HfCp₂ isomer **1'** to yield the Hf/Cr-carbene complex **9a'**.¹⁵ Under these conditions (*s-cis*-butadiene)hafnocene remains unaffected by the added metal carbonyl. Treatment of a **1'/3'** mixture with W(CO)₆ at ambient temperature furnishes a similar result. This is a strong indication that the reactions of the diene zirconocene and hafnocene systems with coordinated carbon monoxide indeed represent examples of a principally new synthetic entry to the class of Fischer-type carbene complexes, which is characterized by an electrocyclic ring-closure reaction of a (η^2 -olefin)(η^2 -carbonyl)metallocene-type intermediate (**8**).^{6,7} There is a good chance that a rapid expansion of the already extremely well-studied chemistry of Fischer-type carbene complexes will result from the discovery of this new reaction type.¹⁶

Acknowledgment. Financial aid from the Thyssen-Stiftung and the Fonds der Chemischen Industrie (grants to G.E.) is gratefully acknowledged.

Supplementary Material Available: Detailed description of the structural analysis of **9a**; includes tables of positional parameters and temperature factors, interatomic distances and bond angles for hydrogen and non-hydrogen atoms, least-squares planes, and calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

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Catalytic Methanol Synthesis from Carbon Monoxide and Water

Robert J. Klingler and Jerome W. Rathke*

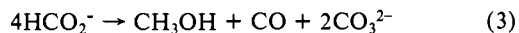
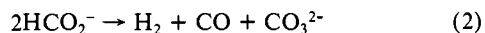
Chemical Technology Division
Argonne National Laboratory
Argonne, Illinois 60439
Received July 26, 1984

The chemistry of formate ion is an active area of current interest due to its importance in the catalysis of the water gas shift reaction¹ (WGS) in eq 1. The hydrogen produced by WGS is typically



used for catalytic methanol or Fischer-Tropsch synthesis in a second process. We report here the first catalytic reaction of formate ion to yield an organic product, methanol. This new formate ion chemistry is generally applicable to a range of metal oxide catalysts and allows the direct synthesis of methanol from carbon monoxide and water in a single process.

Addition of metal oxide catalysts to the molten lithium/potassium formate salts listed in Table I results in the smooth evolution of gaseous products containing hydrogen, methanol, and carbon monoxide as described by the limiting stoichiometries given in eq 2 and 3, respectively.² Significantly, only the lead-based



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(11) Atom numbering scheme as given in Figure 1.

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(13) **9a** crystallizes in the orthorhombic space group *Pnam*; lattice parameters $a = 22.398$ (5) Å, $b = 7.283$ (2) Å, $c = 12.302$ (2) Å; $V = 2006.7$ (8) Å³; $Z = 4$; 1857 unique data; $R(F_o) = 0.036$, $R(F_o)^2 = 0.048$, $R_w(F_o)^2 = 0.069$. Since the molecule lies on a crystallographic mirror plane (passing through Zr, Cr, C3, O3, C4, and O4), the four carbon atoms originating from the butadiene unit occupy twofold disorder positions on either side of the plane. The perpendicular displacements of these atoms from the plane are +0.24 (2), -0.36 (2), +0.49 (2), and +0.30 (2) Å for C5, C6, C7, and C8, respectively. Details of the X-ray data collection and structural analysis are given in the supplementary material.

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(15) **9b** (M = Mo): Anal. Calcd for C₂₀H₁₆O₆MoZr: C, 44.53; H, 2.99. Found: C, 43.97; H, 2.74. IR (C₆D₆) 2057, 1986, 1924 cm⁻¹. ¹H NMR δ 5.22, 5.26 (Cp), 1.49, 1.50, 4.94, 4.63, 4.08, 2.54 (H8-H5); ²J_{HH} (Hz) = 4.0 (H8s/a), -17.7 (H5/5'); ³J_{HH} (Hz) = 8.7 (H8s/7), 13.1 (H8a/7), 16.0 (H7/6), 4.8, 9.9 (H6/5,5'); ¹³C NMR: 108.91, 108.76 (Cp), 44.3, 129.3, 113.7, 70.0 (C8-C5), 359.7 (C4), 215.6 (C3), 208.8 (C2,C1). **9c** (M = W): Anal. Calcd for C₂₀H₁₆O₆WZr: C, 38.29; H, 2.57. Found: C, 38.29; H, 2.60. IR 2058, 1979, 1922 cm⁻¹. ¹H NMR: 5.20, 5.24, 1.48, 1.51, 4.94, 4.56, 4.01, 2.42; ²J_{HH} (Hz) = 4.0 (H8s/a), -17.7 (H5/5'); ³J_{HH} (Hz) = 8.0 (H8s/7), 14.0 (H8a/7), 16.0 (H7/6), 4.8, 9.9 (H6/5,5'); ¹³C NMR: 108.81, 108.93, 44.5, 129.3, 113.2, 71.7, 342.2, 205.7, 200.7. **9a'** (Hf, Cr): IR 2052, 1981, 1929 cm⁻¹; ¹H NMR: 5.196, 5.198 (Cp), 1.27, 1.31, 4.92, 4.50, 4.18, 2.63 (H8-H5); ²J_{HH} (Hz) = 4.9 (H8s/a), -17.5 (H5/5'); ³J_{HH} (Hz) = 7.7 (H8s/7), 14.1 (H8a/7), 16.1 (H7/6), 4.9, 9.6 (H6/5,5').