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Reactivity of Anionic Zirconaoxiranes toward Metal Carbonyls. Implications for the Mechanism of Homogeneously Catalyzed Carbon Monoxide Hydrogenation

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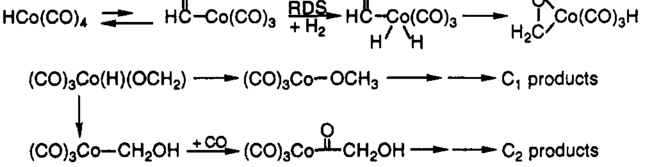
Summary: Reactions of anionic zirconocene η^2-aldehyde complexes with metal carbonyls lead to rapid and quantitative formation of heterobimetallic complexes containing a new carbon–carbon bond, thereby suggesting a modified mechanism for homogeneously catalyzed carbon monoxide hydrogenation. Nine new bimetallic complexes are reported, including the X-ray structure of $(\eta^5\text{-}C_5H_4Me)_2Zr(Me)\{OCH(C_6H_4Me)C(O)Fe(CO)_4\}Li(THF)_2$.

The homogeneous catalytic conversion of synthesis gas to polyols has been the subject of many investigations[1] and the mechanism(s) by which these transformations occur are still of considerable debate. Mechanisms involving metal clusters,[2] hydroxycarbyne ligands,[3] and intermediate formaldehyde complexes[4] are among those that have been postulated. With group 9 catalysts, the intermediacy of mononuclear formaldehyde–hydride complexes has been supported by kinetic observations during cobalt catalyzed CO hydrogenations.[5] This intermediate is postulated to serve as a common precursor to both C_1 and C_2 products, with subsequent branching into separate C_1 and C_2 manifolds occurring by a competition between intramolecular migration of the hydride ligand onto either the formaldehyde carbon or the oxygen atom.



While these proposed reaction sequences are based on established organometallic precedent and well characterized models for these reactions have been reported,[6] this mechanism fails to account for several important observations regarding C_2 selectivity as a function of reaction variables (vide infra).

Because of this mechanistic failure, we have considered the possibility that carbon–carbon bond formation during

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(1) An especially valuable, critical review of this area is found in: Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325–416.

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(3) Fachinetti, G.; Lazzaroni, R.; Puchi, S. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1063. Fachinetti, G.; Balocchi, L.; Secco, F.; Venturini, M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 204. Adams, H. N.; Fachinetti, G.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 125. Nicholas, K. M. *Organometallics* **1982**, *1*, 1713–15.

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(5) Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 3623.

(6) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353–362. Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410. Vaughin, G. D.; Gladysz, J. A. *Organometallics* **1984**, 3, 1596. Vaughin, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1473. Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505. Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335–360.

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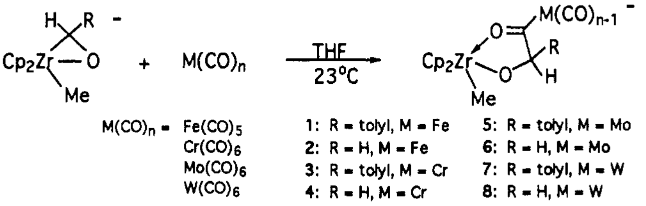
catalysis occurs in an *inter*molecular reaction by direct nucleophilic attack of the bound formaldehyde carbon on an electrophilic carbon monoxide ligand in another complex. We now report that reactions of metal carbonyls with coordinatively saturated anionic zirconocene aldehyde complexes provide the first model system for such a mechanistic step.

We have recently obtained general access to anionic zirconocene η^2-aldehyde complexes through a synthetic route involving transmetalation of zirconocene α-stannylalkoxide complexes with methyllithium.[7] We have also found that anionic zirconaoxiranes are available by reaction of neutral, dimeric zirconaoxiranes with methyllithium.

Reaction of the anionic formaldehyde or *p*-tolualdehyde complexes with 1 equiv of simple mononuclear metal carbonyls proceeds rapidly and quantitatively in room temperature tetrahydrofuran giving heterobimetallic complexes containing a new carbon–carbon bond.[8]



Initial support for formation of a new carbon–carbon bond was obtained by measurement of a 14-Hz C–C coupling constant in **4**. Measurement of $^1J_{CC}$ for $(CO)_5$-Cr(acetyl)Li, a closely related model complex in which a C–C bond is known to exist, also yields a value of 14 Hz. It should be noted that the magnitude of this one bond C–C coupling constant is very low compared to organic compounds such as acetone ($^1J_{CC}$ = 62 Hz).

Since X-ray quality crystals of **1** through **8** could not be obtained, the Cp′ (Cp′ = C_5H_4Me) analogue of **1** (**1′**) was synthesized and recrystallized from diethyl ether. The ORTEP diagram of **1′** (Figure 1) clearly shows that a new C–C bond has been formed.[9] Although the acyl oxygen is coordinated to the zirconium center, this complex should not be viewed as a zirconaoxycarbene since the IR stretching frequency (1498 cm^{-1}, KBr pellet) is more typical of an anionic acyl coordinated to a Lewis acid through a simple dative bond.[10] Since the zirconium atom in the anionic zirconaoxirane starting materials is coordinatively saturated, the mechanism of this reaction must involve direct attack of the aldehyde carbon on the late-metal-bound carbonyl without prior coordination to zirconium.

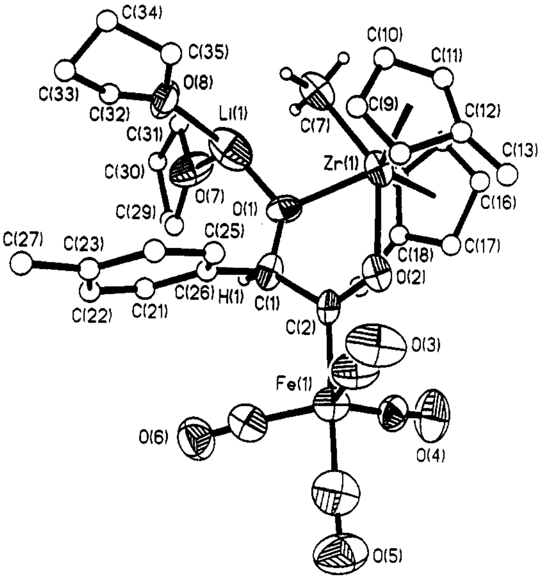


Figure 1. ORTEP drawing and labeling scheme for **1′** with selected bond distances (Å) and angles (deg): Zr(1)–O(1), 2.13(1); Zr(1)–O(2), 2.31(1); Zr(1)–C(7), 2.34(2); O(1)–C(1), 1.37(2); O(2)–C(2), 1.20(2); C(1)–C(2), 1.54(2); Fe(1)–C(2), 2.00(2); Zr(1)–O(1)–C(1), 124(1); O(1)–C(1)–C(2), 112(2); C(1)–C(2)–O(2), 111(2); C(2)–O(2)–Zr(1), 124(1); O(1)–Zr(1)–O(2), 68.6(5); C(7)–Zr(1)–O(1), 75.7(6); C(1)–C(2)–Fe(1), 127(1); O(2)–C(2)–Fe(1), 122(1).

With the establishment of this precedent, we now feel that it is necessary to reconsider the mechanism of carbon–carbon bond formation which has been proposed for the catalytic system. The most important conflicts between the current mechanism and experiments on functioning catalytic systems concern the effects of reaction variables on C_2 selectivity. Increased C_2 selectivity is observed when mixed-metal catalysts are employed,[11] when catalyst concentrations are increased,[12] or when Brønsted bases are present.[1,13]

Kaplan has postulated that the intermediacy of unspecified anionic complexes is necessary for formation of C_2 products in order to explain the beneficial effects of Brønsted bases on C_2 selectivity during rhodium catalyzed hydrogenations.[13] We now postulate that this intermediate is an anionic formaldehyde complex and that carbon–

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(7) Askham, F. R.; Carroll, K. M.; Alexander, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1993**, *12*, 4810.

(8) Under a nitrogen atmosphere, a solution of $Fe(CO)_5$ (0.196 g, 1 mmol, 5 mL of thf) was added rapidly to a room temperature solution of $Cp_2Zr(Me)(tol\text{-}CHO)Li(thf)_{0.5}$ (0.400 g, 1 mmol, 10 mL of thf). The reaction mixture was stirred for 30 min at room temperature, and then all volatiles were removed in vacuum. The product was suspended in 20 mL of hexane, filtered, and washed with 10 mL of additional hexane. After drying under vacuum, 0.591 g of $\mathbf{1}\cdot Li(thf)_2$ was obtained as a yellow solid (84%). When this reaction is conducted in an NMR tube (thf-d_8), **1** is the only product observed. Complexes derived from the anionic formaldehyde complex are unstable and decompose upon attempts at isolation. These complexes were observed to form cleanly in NMR tube reactions. NMR data for compounds **1**–**8** in thf-d_8: **1**: yield = 84%; ^{1}H NMR δ 7.10 (br s, 4H), 6.00 (s, 5H), 5.94 (s, 5H), 5.60 (s, 1H), 2.30 (s, 3H), −0.32 (s, 3H); $^{13}C\{^1H\}$ NMR δ 297.00, 219.49, 140.79, 137.14, 129.81, 129.45, 111.94, 111.65, 108.86, 21.22, 19.33. **1′**: yield = 79%; ^{1}H NMR δ 7.11 (AB, 4H), 5.85–5.61 (m, 8H), 5.73 (s, 1H), 2.29 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H), −0.32 (s, 3H); $^{13}C\{^1H\}$ NMR δ 289.54, 219.63, 141.02, 136.97, 129.65, 129.30, 114.32, 114.17, 114.02, 112.92, 111.64, 109.91, 109.40, 109.32, 108.24, 21.22, 20.27, 15.31, 14.96. **2**: ^{1}H NMR δ 5.86 (s, 10H), 4.92 (s, 2H), −0.25 (s, 3H); $^{13}C\{^1H\}$ NMR δ 293.32, 219.61, 111.66, 98.69, 21.83. **3**: yield = 75%; ^{1}H NMR δ 7.11 (AB, 4H), 5.96 (s, 5H), 5.91 (s, 5H), 5.32 (s, 1H), 2.31 (s, 3H), −0.42 (s, 3H); $^{13}C\{^1H\}$ NMR δ 320.85, 226.15, 220.75, 140.59, 137.80, 130.26, 130.07, 112.08, 111.97, 111.73, 21.21, 17.95. **4**: ^{1}H NMR δ 5.77 (s, 10H), 4.75 (s, 2H), −0.43 (s, 3H); $^{13}C\{^1H\}$ NMR δ 314.55, 226.58, 221.55, 111.34, 101.08, 21.52. **5**: yield = 69%; ^{1}H NMR δ 7.10 (AB, 4H), 5.94 (s, 5H), 5.88 (s, 5H), 5.15 (s, 1H), 2.30 (s, 3H), −0.42 (s, 3H); $^{13}C\{^1H\}$ NMR δ 316.08, 216.70, 209.56, 140.57, 137.67, 130.11, 129.99, 113.89, 111.95, 111.49, 21.21, 17.97. **6**: ^{1}H NMR δ 5.78 (s, 10H), 4.69 (s, 2H), −0.39 (s, 3H); $^{13}C\{^1H\}$ NMR δ 311.68, 216.55, 210.26, 111.44, 103.17, 20.43. **7**: yield = 78%; ^{1}H NMR δ 7.12 (AB, 4H), 5.96 (s, 5H), 5.90 (s, 5H), 5.16 (s, 1H), 2.30 (s, 3H), −0.41 (s, 3H); $^{13}C\{^1H\}$ NMR δ 303.52, 206.55, 201.23, 140.62, 137.71, 130.04, 115.07, 111.96, 111.52, 21.22, 18.08. **8**: ^{1}H NMR δ 5.75 (s, 10H), 4.62 (s, 2H), −0.42 (s, 3H); $^{13}C\{^1H\}$ NMR δ 297.83, 206.74, 201.63, 111.20, 106.16, 21.14.

(9) $C_{68}H_{82}Fe_2Li_2O_{16}Zr_2$; a = 25.093(5), b = 10.499(5), c = 26.833(7) Å; orthorhombic; $Pca2_1$; Z = 4; T = 299 K; full-matrix least-squares minimization of $\sum w(F_o - F_c)^2$; R = 6.77%.

(10) Fischer, E. O.; Kiener, V. *J. Organomet. Chem.* **1970**, *123*, 215. Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* 1981, 91. Arndt, L. W.; Bancroft, B. T.; Darensbourg, M. Y.; Janzen, C. P.; Kim, C. M.; Reibenspies, J.; Varner, K. E.; Youngdahl, K. A. *Organometallics* 1988, *7*, 1302–9.

(11) Dombek, B. D. *Organometallics* **1985**, *4*, 1707–12.

(12) Keim, W.; Berger, M.; Eisenbeis, A.; Kadelka, J.; Schlupp, J. *J. Mol. Catal.* **1981**, *13*, 95–106.

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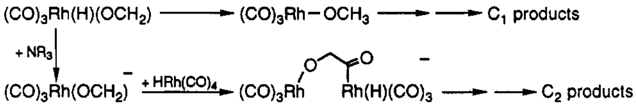
carbon bond formation is accomplished in an *inter*molecular reaction by nucleophilic attack of the aldehyde carbon on an electrophilic CO ligand in a different complex. A simple mechanism incorporating this type of step is shown below.



This scheme conserves the most well-supported aspects of the previous mechanism, namely, the intermediacy of a hydrido–formaldehyde complex, the route by which this intermediate is formed including its position relative to the catalyst resting state and the rate determining step, and the branching from this intermediate into C_1 and C_2 product manifolds. It also retains the proposition that C_1 products arise via methoxide complexes formed by intramolecular migration of the hydride ligand to the formaldehyde carbon.

It differs, however, in the way in which branching ocurs and in how the carbon–carbon bond is formed. We propose that the branching step involves a competition between formation of a methoxide complex by hydride migration (thereby entering the C_1 manifold) and formation of an anionic formaldehyde complex by deprotonation (thereby entering the C_2 manifold). This easily rationalizes the increase in C_2 selectivity observed upon addition of Brønsted bases to catalytic systems.

We then propose that the carbon–carbon bond is formed by direct nucleophilic attack of a coordinatively saturated, anionic formaldehyde complex upon an electrophilic carbon monoxide ligand in another complex. The reactivity of anionic zirconaoxiranes toward metal carbonyls reported in this work supplies the first model system for such a reaction step. Inclusion of such an intermolecular carbon–carbon bond forming reaction between two metal complexes in the C_2 manifold is supported experimentally in catalytic systems by the observation of increased C_2 selectivity upon an increase in catalyst concentration. It also explains the origin of mixed-metal synergism in the ruthenium–rhodium catalyst system, if it is assumed that the role of rhodium is to supply an electrophilic carbonyl complex which efficiently traps a ruthenium formaldehyde complex. Thus, C_2 selectivity would increase while the total primary product formation rate would remain unchanged.

The modified catalytic mechanism we have proposed suggests that if high concentrations of relatively inexpensive metal carbonyls were added to catalytic systems the intermediate formaldehyde complexes would be effectively diverted to the C_2 forming pathway, thereby giving improved C_2 selectivity without the prohibitive costs associated with using high concentrations of rhodium or ruthenium to accomplish this end.

We are currently investigating syntheses of anionic aldehyde complexes of the catalytically relevant metals (Co, Rh, and Ru) to determine directly whether late-transition-metal aldehyde complexes have access to this same reactivity manifold.

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Supplementary Material Available: Details of the X-ray crystal structure of 1′ including tables of crystallographic parameters, atomic coordinates, bond lengths, bond angles, and thermal parameters and figures of ^{1}H NMR spectra of complexes 1–8 (22 pages). Ordering information is given on any current masthead page.

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