oxidation of the alkyl-substituted carbyne complexes **3** and **4** is achieved at −95 °C. The initially dark red solutions turn orange brown upon warming to room temperature. The products are recrystallized[18] from CH_2Cl_2/pentane and obtained as dark green **7**[15] and dark turquoise **8**[16] microcrystals in 70% and 50% yield, respectively. The new alkylidyne complexes **5–8** are thermally stable but very sensitive toward the atmosphere.

With the oxidation reaction described in this paper and the methods developed earlier[9,10] thermally stable carbyne complexes of both known types of the group 6[17] transition metals are now easily accessible. The *trans*-halotetracarbonylmetal carbyne complexes, while rather thermally labile themselves,[7] prove to be the critical intermediates in these synthetic procedures.

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(14) **4**: Chromatography on silica at −40 °C, eluted with pentane/CH_2Cl_2, 5:2. ^{13}C NMR ($CDCl_3$, −40 °C) δ 293.9 (J_{CW} = 172.3 Hz, CCH_2CMe_3), 192.1 (J_{CW} = 129.1 Hz, CO).

(15) **7**: Anal. Calcd for $C_6H_{13}Br_3O_2W$: C, 13.33; H, 2.42; Br, 44.33. Found: C, 13.34; H, 2.33; Br, 45.99. ^1H NMR (CD_2Cl_2) δ 7.32 (s, 3, $^3J_{WH}$ = 9.8 Hz, CCH_3); ^{13}C NMR (CD_2Cl_2, −20 °C) δ 337.5 (J_{CW} = 219 Hz, CMe).

(16) **8**: Anal. Calcd for $C_{10}H_{21}Br_3O_2W$: C, 20.12; H, 3.55. Found: C, 20.14; H, 3.77. ^1H NMR (CD_2Cl_2) δ 7.41 (s, 2, $^3J_{WH}$ = 7 Hz, CCH_2CMe_3); ^{13}C NMR ($CDCl_3$, −20 °C) δ 345.4 (J_{CW} = 215 Hz, CCH_2CMe_3).

(17) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(18) After removal of the solvent from the reaction solution the dark orange-brown solid is taken up in a small amount of CH_2Cl_2 (typically 5 mL of CH_2Cl_2 per mmol of product) and precipitated with pentane (3× to 4× the volume of CH_2Cl_2 present). This precipitation procedure is repeated two or three times. The resulting solid (orange-brown, **5**; deep green, **6–8**) is taken up in a small amount of CH_2Cl_2, cooled to 0 °C, and filtered to remove any insolubles. Pentane is added to the resulting solution to precipitate the product as a microcrystalline powder. For R = alkyl the initial precipitate is removed as well by filtration when it is oily.

Zirconoxycarbene Complexes of Ruthenium—Reduction of Coordinated CO in the Reaction of a Zr–Ru Compound with H_2

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We have synthesized compounds with directly bonded early and late transition metals such as $Cp_2Zr[Ru(CO)_2Cp]_2$ (**1**) in the hope of cleaving the metal–metal bond with H_2.[1] The resulting mixture containing reactive hydridic M–H and acidic M–H units might be a powerful reducing system for polar molecules including CO. Here we present evidence for a circuitous stepwise conversion of **1** into Ru–H and Zr–H units and for the reduction of coordinated CO to a formyl or zirconoxy carbene group.

Previously, we reported that **1** reacts with ethylene or with CO to form the strained, reactive adducts **2** or **3** and to expel

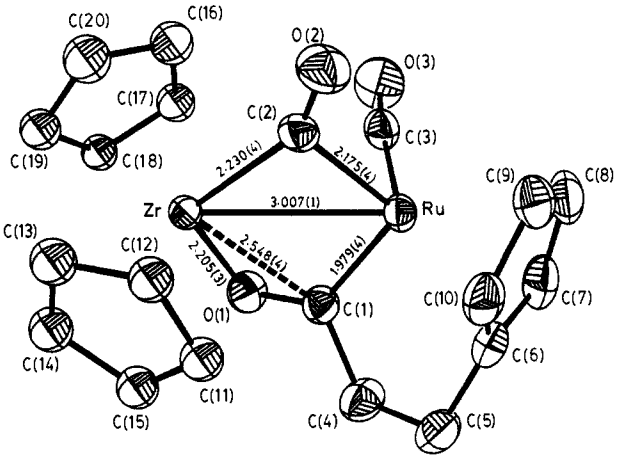
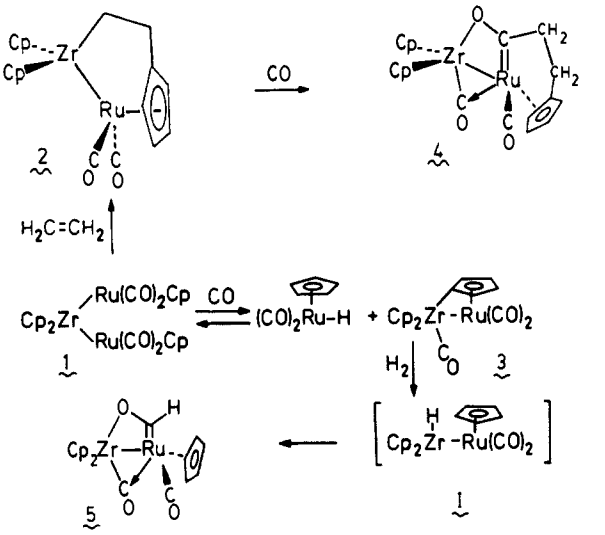


Figure 1. Molecular structure and labeling scheme for **4**.

$CpRu(CO)_2H$.[2] Here we report that the reaction of **2** with CO and the reaction of **3** with H_2 produce zirconoxycarbene complexes of ruthenium.



When an amber C_6D_6 solution of ethylene product **2** was treated with CO (700 mm), the solution slowly turned dark red. ^1H NMR demonstrated that **2** was converted to **4** without the intervention of a detectable intermediate ($t_{1/2} \simeq 15$ h). Crystalline **4** was isolated in 80% yield from the reaction of **2** with CO (760 mm) in toluene at 55 °C for 30 h. The structure of **4** was determined by single-crystal X-ray diffraction (Figure 1).[3]

The metals in **4** are linked by a direct Zr–Ru bond (3.007 Å), by a zirconoxycarbene bound to Ru (which can also be regarded as a Zr-complexed Ru–acyl), and by a semibridging carbonyl bound strongly to Zr. The metrical details of this semibridging carbonyl are similar to those in $Cp_2Zr(CO)(\mu\text{-}\eta^1(Zr),\eta^5\text{-}C_5H_4)\text{-}Ru(PMe_3)(CO)$.[2]

The key spectral features of **4** which characterize its structural type are the ^{13}C NMR and IR parameters associated with the carbonyl ligands and the zirconoxycarbene ligand.[4] In the ^{13}C NMR of **4**, the terminal ruthenium CO appears at δ 205, the semibridging CO appears at δ 316, and the carbene carbon appears at δ 279 as a peak significantly broadened by unresolved two-bond

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(3) See the supplementary material for details of X-ray crystallography.

(4) ^1H NMR (benzene-d_6) δ 5.71 (s, 5 H, CpZr), 5.62 (m, 1 H, C_5H_4), 5.06 (s, 5 H, CpZr), 4.94 (m, 1 H, C_5H_4), 4.81 (m, 1 H, C_5H_4) 4.35 (m, 1 H, C_5H_4), 3.62 (dt, J = 18, 8 Hz, 1 H, C(O)C*H*H), 2.92 (ddd, J = 18, 8, 4 Hz, 1 H, C(O)CH*H*), 1.75 (ddd, J = 14, 10, 4 Hz, 1 H, $C(O)CH_2CHH$), 1.42 (dt, J = 12, 9 Hz, 1 H, $C(O)CH_2CHH$). $^{13}C\{^1H\}$ NMR (THF-d_8, 26 °C) δ 316 (μ-CO), 279 (ZrOC=Ru), 205 (RuCO), 127 (C_1 of C_5H_4), 108 (CpZr), 105 (CpZr), 104 (CH_2), 92, 89, 84, 79 (C_5H_4), 22 (CH_2).

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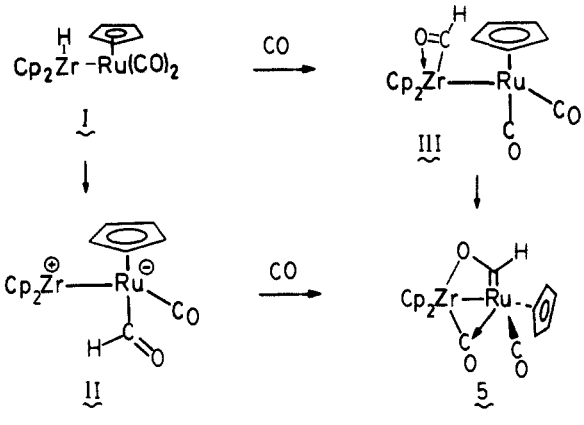
coupling to the α-methylene protons. In the IR spectrum of **4**, bands were observed at 1909 cm^{-1} for the terminal CO, at 1704 cm^{-1} for the semibridging CO, and at 1380 cm^{-1} for the C-O stretch of the zirconoxycarbene.

When the reaction of **2** with ^{13}CO was monitored by ^{13}C NMR, the isotopic label initially appeared only at the carbene carbon of **4**. This observation is consistent with initial insertion of CO into the Zr-CH_2 bond, to form an η^2-acyl zirconium intermediate, followed by rapid transfer of the very electrophilic η^2-acyl carbon to the electron-rich ruthenium. Such acyl transfers have been observed before in Zr/Mo systems[5] and may be a general phenomenon in early/late heterobimetallic compounds.

When the CO product **3** was reacted with H_2 (700 mm) at room temperature in THF, the hydrido-zirconoxycarbene complex **5** was obtained ($t_{1/2} \simeq 40$ min). No intermediates were observed by ^1H NMR in THF-d_8. The structure of **5** is very similar to that of **4** and was established by spectroscopy. **5** does not possess a plane of symmetry and consequently three Cp resonances are seen in the ^1H NMR at δ 5.78, 5.40, and 5.39. The ruthenium-bound Cp ligand arises from hydrogenolysis of the Zr-C_5H_4 bond. The hydrogen attached to the Ru-bound zirconoxycarbene carbon (or Zr complexed ruthenium formyl) appears at δ 14.05. The IR spectrum of **5** has bands at 1930 cm^{-1} for the terminal Ru-CO, at 1740 cm^{-1} for the semibridging Zr-CO, and at 1350 cm^{-1} for the C-O stretch of the zirconoxy carbene unit. The correspondence between the IR spectra of **4** and **5** indicates that these complexes have the same functional groups. **5** has only limited stability in solution and decomposes slowly at room temperature to a complex mixture of products. **5** was isolated as a slightly impure red solid that slowly decomposes at ambient temperature.

Earlier ^{13}CO exchange studies on **3** demonstrated that rapid CO dissociation from Zr occurs to generate a reactive intermediate[2] which has a Zr-based orbital available for interaction with H_2. We suggest that reaction of this intermediate with H_2 leads to hydrogenolysis of the strained Zr-C_5H_4 bond and formation of zirconium hydride intermediate I. This strained Zr-C_5H_4 bond is also cleaved by $Cp(CO)_2RuH$[2] and by *t*-BuOH;[6] hydrogenolysis of Zr-C bonds has been observed previously.[7] There are two plausible routes from I to **5**. First, addition of the Zr-H to a ruthenium carbonyl[8] could produce ruthenium formyl complex II which could readd CO to Zr to produce **5**. Alternatively, CO



could coordinate to I at Zr and insert into the Zr-H bond to produce the η^2-formyl zirconium complex III. Formyl migration to ruthenium as suggested for the formation of **4** could produce **5**. Studies utilizing selectively labeled **3** are in progress to distinguish these alternatives.

It should be noted that reaction of $Cp_2Zr[Ru(CO)_2Cp]_2$ (**1**) with CO and then with H_2 resulted in a net cleavage of a Zr-Ru bond by H_2 and in the formation of the late-transition-metal hydride $Cp(CO)_2RuH$ and of the early-transition-metal hydride intermediate $Cp_2Zr(H)Ru(CO)_2Cp$ (I).

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Supplementary Material Available: X-ray crystal data for **4** (28 pages). Ordering information is given on any current masthead page.

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Molecular Orbital Calculations on the Th-Ni Interaction in $Th(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PH_2)_2Ni(CO)_2$

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Organometallic chemists continue to search for new types of bonding and the relatively unexplored chemistry of the f-block elements[1] presents inviting possibilities. Stimulated by the recent observation[2] of a short Th-Ni separation in $Th(\eta^5\text{-}C_5(CH_3)_5)_2(\mu\text{-}PPh_2)_2Ni(CO)_2$, the following extended Hückel[3] calculations seek to clarify the nature of the proposed metal-metal interaction.

If one considers the central ThP_2Ni quadrilateral (Figure 1) with the average observed Th-P and Ni-P bond lengths, it is possible to vary the Th-Ni distance by changing the Th-P-Ni angle. (C_{2v} symmetry is maintained in these calculations on $Th(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PH_2)_2Ni(CO)_2$; the structures of the $(C_5H_5)_2Th$ and $Ni(CO)_2$ fragments are also held constant.) Two structural extremes are now defined. The first has the experimental Th-Ni separation of 3.206 Å while the second takes 3.70 Å for the same quantity. This latter figure arises from an ionic model assumption in which metal atom radii are summed.[2] Th-P-Ni angles range from 76° to 93° and the P-P distance from 3.84 to 3.41 Å as the Th-Ni separation is increased.

At first glance, the plot of reduced atomic overlap populations (see Figure 2) for this distortion seems disappointing, since the Th-Ni values are negative.[4] Yet the trend with respect to metal-metal separation is encouraging. Of all the interactions, this one changes the most. Note the relative passivity of Th-P overlap population; apparently there is some geometrical flexibility about the Th. Ni bonding with P is at a maximum when the P-Ni-P angle is near 110°. Of course, P-P overlap populations are indicative of lone pair repulsions and grow more negative as the P-P distance decreases.

Now let the molecule be divided into two fragments: $Cp_2Th(PH_2)_2$ and $Ni(CO)_2$. In terms of the molecular orbitals of these entities, two principal sources of Th-Ni interaction are discernible. First is the filled-filled repulsion between the d-levels of the Ni

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(4) Reduced atomic overlap populations are indices of the degree of bonding between two atoms. Negative values imply a net antibonding relationship.

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