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Metallacyclic Zirconoxycarbene Complexes from Metal Carbonyls and (η^2-Formaldehyde)zirconocene Dimer

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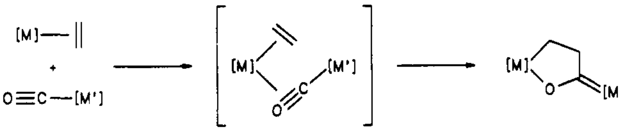
The metallatricyclic (η^2-formaldehyde)zirconocene dimer **10** reacts with metal carbonyl complexes $L_nM(CO)$ **4** [L_nM = $Mo(CO)_5$, $W(CO)_5$, $CpCo(CO)$, $CpRh(CO)$, $CpV(CO)_3$, $(C_6F_5)_2Pt(CO)$] to give the metallatricyclic zirconoxycarbene complexes $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}ML_n]O)$ **12a–f** in good yield. In each case, only one of the two Cp_2ZrOCH_2 metallaoxirane units of **10** can be reacted with the [M]–C≡O functionality. Under equilibrium conditions, the oxygen atom in the five-membered metallacycle adjacent to the CH_2 group bridges the zirconium center of the Cp_2ZrOCH_2 structural subunit. In the photochemical-assisted $W(CO)_6$ addition to $[Cp_2Zr(\mu\text{-}OCH_2)]_2$, a mixture of regioisomeric zirconoxycarbene complexes **12b** and **16** is formed under kinetic control. In **16**, an oxonium type oxygen atom is adjacent to the carbene carbon center. The metallatricyclic zirconoxycarbene rhodium complex $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)$ (**12d**) was characterized by X-ray diffraction. Complex **12d** crystallizes in space group $P2_1/n$ with cell parameter a = 11.537 (2) Å, b = 26.442 (5) Å, c = 12.249 (2) Å, β = 92.00 (2)°, Z = 4, $R(F_o^2)$ = 0.051, and $R_w(F_o^2)$ = 0.083. The Rh=C(carbene) bond is rather short at 1.930 (5) Å.

Introduction

Heteroatom-stabilized transition-metal carbene complexes have found many uses as stoichiometric reagents or as catalysts for the transformation of organic substrates.[1] Many of these electrophilic carbene complexes can easily be prepared from metal carbonyls by employing E. O. Fischer's synthesis, i.e., by adding a nucleophile to the carbonyl carbon atom of the [M]—C≡O moiety followed by electrophilic O-alkylation.[2] We have introduced an essentially nonnucleophilic alternative for the [M]—C≡O to [M]—carbene interconversion that is often applicable in cases where the conventional carbene complex synthesis meets its limits. Here, very reactive metal (η^2-olefin) type complexes, especially of the early transition-metal elements or actinides, add to the [M]—C≡O unit to give an unstable CO-bridged bimetallic intermediate (**1**), which rapidly undergoes electrocyclic ring closure to directly give a metallacyclic metal oxycarbene complex (**2**).[3]



1 **2**

We originally employed conjugated diene group 4 metallocene complexes as reagents for this nonnucleophilic carbene complex synthesis.[4] In addition, we have shown that thermally generated (η^2-aryne)titanocene or -zirconocene species as well as (η^4-butadiene)$ThCp^*_2$ can be used.[5] Mashima et al.[6] have reacted (η^2-ethylene)$TiCp^*_2$[7] with several metal carbonyls to synthesize metal carbene complexes. Thiele et al. have employed the related (η^2-$CH_2{=}CH_2$)- and (η^2-CH≡CH)MCp_2 (M = Ti, Zr, Hf) complexes for this purpose.[8] Up to now, neither E. O.

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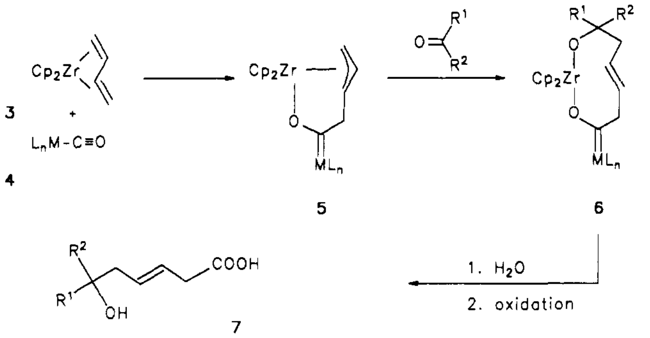
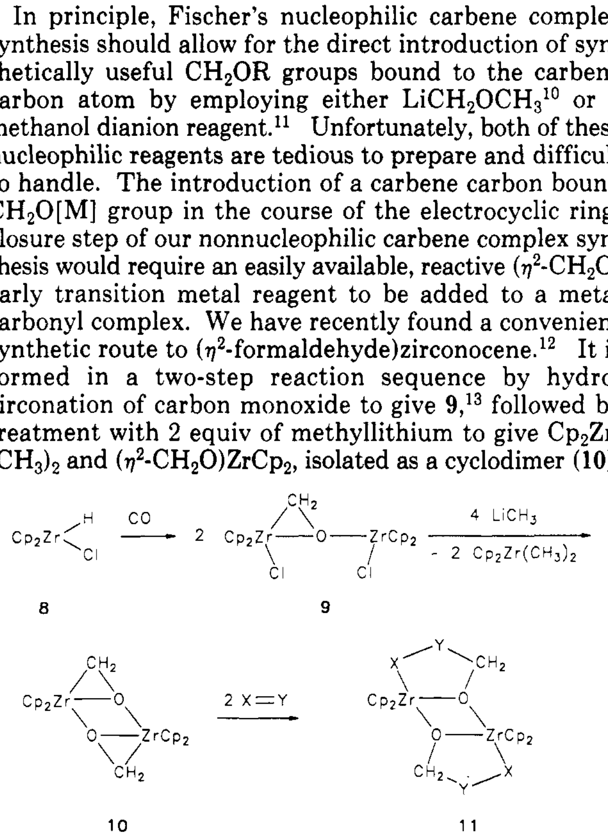
Fischer's nor our synthetic approach easily allows for the direct introduction of functional groups or suitable precursors thereof into the reaction step that generates the carbene complex. Chemically useful functionalities are usually attached in subsequent reactions, such as ketone or aldehyde addition to our metallacyclic (π-allyl)zirconoxycarbene complexes **5**, formed by (*s-trans*-η^4-butadiene)zirconocene addition to metal carbonyl complexes.[9]



In principle, Fischer's nucleophilic carbene complex synthesis should allow for the direct introduction of synthetically useful CH_2OR groups bound to the carbene carbon atom by employing either $LiCH_2OCH_3$[10] or a methanol dianion reagent.[11] Unfortunately, both of these nucleophilic reagents are tedious to prepare and difficult to handle. The introduction of a carbene carbon bound $CH_2O[M]$ group in the course of the electrocyclic ring-closure step of our nonnucleophilic carbene complex synthesis would require an easily available, reactive (η^2-CH_2O) early transition metal reagent to be added to a metal carbonyl complex. We have recently found a convenient synthetic route to (η^2-formaldehyde)zirconocene.[12] It is formed in a two-step reaction sequence by hydrozirconation of carbon monoxide to give **9**,[13] followed by treatment with 2 equiv of methyllithium to give $Cp_2Zr(CH_3)_2$ and (η^2-CH_2O)$ZrCp_2$, isolated as a cyclodimer (**10**).



Complex **10** has been found to exhibit a pronounced metallaoxirane character [X-ray crystallography $d(Zr–CH_2) = 2.243$ (3) Å; $d(Zr–O) = 2.103$ (2) Å; $d(O–CH_2) = 1.395$ (4) Å; angle Zr,C,O 65.9 (2)°; ^{13}C NMR $\delta = 64.0$, $^1J_{CH} = 153$ Hz (CH_2)]. With a variety of reagents, e.g., ketones, aldehydes, carbon dioxide, heterocumulenes, even with metal hydrides, complex **10** undergoes insertion into the zirconium–carbon bonds of the three-membered metallacycles to give ring-enlarged five-membered metallacyclic products.[14] We have now found that the carbonyl ligand of a variety of metal carbonyl complexes $L_nMC{\equiv}O$ reacts similarly with a $Cp_2\overline{ZrOCH_2}$ unit of **10** to give complexes containing the five-membered metallacyclic zirconoxycarbene complex with $Cp_2\overline{ZrOCH_2C[{=}ML_n]O}$ as a structural subunit. Several representative examples are described in this paper.

Experimental Section

All reactions were carried out in an argon atmosphere by using Schlenk type glassware or under purified nitrogen in a M. Braun glovebox. For other general conditions, including a list of spectrometers used, see ref 9. Dimeric (η^2-formaldehyde)zirconocene (**10**) was prepared as previously described.[12] The metal carbonyl complex *cis*-$(C_6F_5)_2Pt(CO)_2$ (**4f**) was synthesized according to a literature procedure.[15] For ^1H and ^{13}C NMR data of the products obtained, see Tables IV and V, respectively.

Reaction of 10 with $Mo(CO)_6$. A suspension containing 0.29 g (0.58 mmol) of bis[(η^2-formaldehyde)zirconocene] (**10**) and 0.15 g (0.58 mmol) of hexacarbonylmolybdenum in 30 mL of toluene is stirred at 40 °C for 4 days. The resulting yellow precipitate is collected by filtration, washed with pentane (10 mL), and dried in vacuo. From the filtrate, a second portion of product is obtained upon concentration in vacuo and cooling to -30 °C. The combined yield of the zirconoxycarbene complex **12a** is 0.40 g (90%), mp (DSC, exothermic) 134 °C dec. Anal. Calcd for $C_{28}H_{24}O_8MoZr_2$ (766.9): C, 43.85; H, 3.15. Found: C, 43.82; H, 3.03. IR (KBr): ν(CO) 2060, 1983, 1895 cm^{-1}.

Reaction of 10 with $CpCo(CO)_2$. (η^2-Formaldehyde)zirconocene dimer **10** (380 mg, 0.76 mmol) and $CpCo(CO)_2$ (360 mg, 2.0 mmol) are stirred for 3 days in toluene (10 mL) at 40 °C. The resulting clear red–brown solution is concentrated to a volume of ca. 2 mL. Upon cooling to -30 °C, red–brown crystals of **12c** are obtained: 370 mg (81%), mp 160 °C dec. Anal. Calcd for $C_{29}H_{29}O_4CoZr_2$ (682.6): C, 51.00; H, 4.28. Found: C, 51.24; H, 4.58. IR (KBr): ν(CO) 1905 cm^{-1}.

Reaction of 10 with $CpRh(CO)_2$. Cyclopentadienyldicarbonylrhodium (0.45 g, 2.01 mmol) is added dropwise to a suspension of 1.00 g (2.00 mmol) of **10** in 40 mL of toluene. Stirring is continued for 5 days at 50 °C. A small amount of an unidentified black precipitate is filtered off and the resulting clear filtrate concentrated to about 20 mL. The product **12d** is precipitated by adding 10 mL of pentane. The precipitate is collected by filtration, washed with pentane, and dried in vacuo. From the mother liquor, additional product is obtained upon cooling to -30 °C: combined yield 1.05 g (73%), mp 138 °C (DSC, exothermic) dec. Anal. Calcd for $C_{29}H_{29}O_4Zr_2Rh$ (726.9): C, 47.92; H, 4.02. Found: C, 47.84; H, 3.76. IR (KBr): ν(CO) 1917 cm^{-1}. Crystals suitable for an X-ray structure determination were obtained by recrystallization from benzene.

X-ray Data Collection and Structural Analysis of $Cp_2\overline{Zr(\mu\text{-}OCH_2)}ZrCp_2\overline{(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)}\cdot 2C_6H_6$ (12d). A rectangular red-orange crystal was sealed in a glass capillary tube under nitrogen. The sample was transferred to and then aligned optically on a Picker goniostat controlled by a Krisel Control diffractometer automation system. By use of a preliminary orientation matrix based upon an analysis of low-angle reflections, the orientation angles (ω, χ, and 2θ) for 20 higher order

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Table I. Crystallographic Data for the X-ray Diffraction Analysis of $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O) \bullet 2C_6H_6$

A. Crystal Data	
crystal system	monoclinic
space group	$P2_1/n$
a, Å	11.537 (2)
b, Å	26.442 (5)
c, Å	12.249 (2)
β, deg	92.00 (2)
V, Å^3	3734 (1)
fw, amu	883.12
d(calcd), g/cm^3	1.57
Z	4
μ, cm^{-1}	10.02
B. Data Collection and Structural Analysis	
crystal dimens, mm	0.275 × 0.225 × 0.500
reflns sampled	$\pm hkl$ ($5° \le 2\theta \le 50°$)
2θ range for centered reflns	$30° < 2\theta < 37°$
scan rate	2 deg/min
scan width	$1.1 + 0.9 \tan \theta$
no. std reflns	3
cryst decay	0
total no. of measd reflns	6932
no. of unique data used	5514 ($F_o^2 > \sigma(F_o^2)$)
agreement between equivalent data	
$R_{av}(F_o)$	0.016
$R_{av}(F_o^2)$	0.016
transmission coeffs	0.766–0.813
p	0.03
discrepancy indices ($F_o^2 > \sigma(F_o^2)$)	
$R(F_o)$	0.055
$R(F_o^2)$	0.051
$R_w(F_o^2)$	0.083
σ_1	1.57
no. of variables	549
data-to-parameter ratio	10.0:1

reflections were calculated. A least-squares fit of the optimized angles obtained by an automatic peak-centering routine provided the refined lattice parameters for the monoclinic unit cell (Table I). The systematic absences of $\{h0l\}$, $h + l = 2n+1$, and $\{0k0\}$, $k = 2n+1$, are consistent with the space group $P2_1/n$, a nonstandard setting of space group $P2_1/c$ (No. 14, C_{2h}^5).

Intensity data ($\pm hkl$) were measured with Zr-filtered Mo Kα X-ray radiation at a takeoff angle of 2°. Each diffraction peak was measured by using a θ–2θ scan. The intensities of three standard reflections were measured every 90 min. The integrated intensity and its standard deviation for each reflection were calculated from the corresponding relationships $I = \omega(S/t_s - B/t_b)$ and $\sigma_c(I) = \omega(S/t_s^2 + B/t_b^2)^{1/2}$, where S is the total scan count measured in time t_s and B is the combined background count in time t_b. The diffraction data were corrected for absorption and Lorentz–polarization effects. The standard deviation of F_o^2 was calculated from $\sigma(F_o^2) = [\sigma_c(F_o^2)^2 + (pF_o^2)]^{1/2}$. Duplicate reflections were averaged. Further information about the X-ray data collection procedure[16] is given in Table I.

Initial coordinates for the Rh and two Zr atoms were interpolated from the first E map calculated by using preliminary phases determined by MULTAN78.[17] Approximate coordinates for all of the remaining non-hydrogen atoms in this trinuclear complex were obtained from a Fourier synthesis based upon these three heavy atom positions. A subsequent difference Fourier summation further indicated the presence of two independent molecules of benzene in the crystallographic asymmetric unit. The hydrogens of the two oxymethylene groups were located on a difference Fourier map calculated by using low-angle data with $\sin \theta/\lambda <$ 0.40 A^{-1}, whereas coordinates for the idealized hydrogens of the five cyclopentadienyl and two benzene rings were calculated with the aid of MIRAGE.[18] Full-matrix refinement (based on F_o^2)[19–22] of the positional and anisotropic thermal parameters for the 48 non-hydrogen atoms and isotropic temperature factors for the 41 hydrogen atoms converged with final discrepancy indices of $R(F_o) = 0.055$, $R(F_o^2) = 0.051$, and $R_w(F_o^2) = 0.083$ with $\sigma_1 = 1.57$ for 5514 reflections with $F_o^2 > \sigma(F_o^2)$. A final difference map was essentially featureless.

The positional parameters from the final least-squares refinement cycle are given in Table II. Selected interatomic distances and bond angles and their esd's for the non-hydrogen atoms of $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)$ are provided in Table III. Tables of the thermal parameters, all of the bond distances and angles, the equations for pertinent least-squares planes and their dihedral angles, and the observed and calculated structure factors are available as supplementary material.[23]

Reaction of 10 with $CpV(CO)_4$. (η^2-Formaldehyde)zirconocene (**10**) (0.55 g, 1.09 mmol) and cyclopentadienyltetracarbonylvanadium (0.25 g, 1.09 mmol) are suspended in 50 mL of toluene. The reaction mixture is heated in the dark for 10 days at 60 °C (alternatively, the reaction mixture may be thermolyzed for 5 days at 50 °C with sunlight irradiation). The resulting red solution is concentrated until product begins to precipitate. Cooling to −30 °C yields **12e** as an orange–red solid, which is collected by filtration, washed with pentane, and dried: yield 0.49 g (80%), mp 198 °C (DSC, exothermic) dec. Anal. Calcd for $C_{31}H_{29}O_6VZr_2$ (731.0): C, 50.94; H, 4.00. Found: C, 51.02; H, 4.05. IR (KBr): ν(CO) 1934, 1809, 1806 cm^{-1}.

Reaction of 10 with $W(CO)_6$. (a) A mixture of 0.51 g (1.00 mmol) of **10** and 0.36 g (1.00 mmol) of hexacarbonyltungsten in 50 mL of toluene is stirred for 5 days at 40 °C. The resulting yellow–orange suspension is filtered. The obtained yellow solid is washed with pentane and dried in vacuo. After concentration of the mother liquor and cooling to −30 °C, a second fraction of the product **12b** is obtained: combined yield 0.70 g (81%), mp 136 °C (DSC, exothermic) dec. Anal. Calcd for $C_{28}H_{24}O_8WZr_2$ (854.8): C, 39.34; H, 2.83. Found: C, 39.06; H, 2.83. IR (KBr): ν(CO) 2059, 1976, 1917, 1889 cm^{-1}. (b) In 0.5 mL of tetrahydrofuran-d_8, one suspends 47 mg (93 μmol) of **10** and 33 mg (93 μmol) of $W(CO)_6$. The reaction mixture is sealed in an NMR tube and irradiated with a sunlight lamp (Osram Ultra-Vitalux) for 1 h at 60 °C. By $^1H/^{13}C$ NMR spectroscopy, one observes the signals of the isomeric zirconoxycarbene complexes **12b** and **16** in a 1:1 ratio. Upon thermolysis at 60 °C for 1 h, complex **16** completely rearranges to the thermodynamically favored isomer **12b**, as judged by ^1H NMR spectroscopy in tetrahydrofuran-d_8.

Reaction of 10 with $(C_6F_5)_2Pt(CO)_2$. A mixture of 0.20 g (0.40 mmol) of (η^2-formaldehyde)zirconocene (**10**) and 0.26 g (0.44 mmol) of bis(pentafluorophenyl)dicarbonylplatinum is dissolved in 40 mL of toluene and stirred for 30 min at room temperature. The volume of the resulting yellow solution is reduced in vacuo to ca. 20 mL, and then 10 mL of pentane is added. Cooling overnight at −30 °C produced **12f** as a yellow solid that was recovered by filtration: yield 0.28 g (64%), mp 174 °C dec. Anal. Calcd for $C_{36}H_{24}F_{10}O_4PtZr_2$ (1088.1): C, 39.74; H, 2.22. Found: C, 40.05; H, 2.52. IR (toluene): ν(CO) 2084 cm^{-1}. Irradiation of a sample of **12f** in toluene solution using a Pyrex-filtered HPK 125 lamp produces a photostationary equilibrium of the isomeric

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Table II. Positional Parameters for $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)\bullet 2C_6H_6$[a]

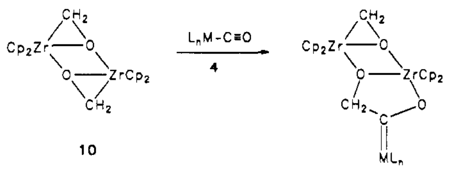
atom	*x*	*y*	*z*
Rh	−0.21602 (3)	0.34886 (1)	0.20414 (3)
Zr1	0.02299 (4)	0.12997 (2)	0.20023 (4)
Zr2	0.14706 (4)	0.25202 (2)	0.18742 (4)
O1	0.1756 (2)	0.1740 (1)	0.1847 (3)
O2	−0.0166 (2)	0.2122 (1)	0.1942 (2)
O3	0.0055 (3)	0.3051 (1)	0.2106 (3)
O4	−0.4124 (3)	0.2774 (2)	0.1674 (4)
C1	0.2165 (5)	0.1239 (2)	0.1973 (6)
C2	−0.1237 (4)	0.2388 (2)	0.1957 (5)
C3	−0.1031 (4)	0.2950 (2)	0.2039 (4)
C4	−0.3340 (5)	0.3047 (2)	0.1822 (5)
C5	−0.0983 (7)	0.4138 (3)	0.2443 (10)
C6	−0.1829 (8)	0.4175 (2)	0.3202 (7)
C7	−0.2842 (6)	0.4270 (2)	0.2628 (6)
C8	−0.2648 (8)	0.4314 (2)	0.1532 (6)
C9	−0.1474 (11)	0.4239 (3)	0.1375 (9)
C10	−0.1156 (5)	0.1267 (2)	0.3537 (5)
C11	−0.0910 (7)	0.0769 (3)	0.3305 (5)
C12	0.0247 (8)	0.0688 (3)	0.3581 (6)
C13	0.0708 (7)	0.1129 (3)	0.4020 (5)
C14	−0.0148 (6)	0.1488 (3)	0.3992 (4)
C15	0.0324 (6)	0.1196 (2)	−0.0053 (5)
C16	−0.0765 (6)	0.1370 (3)	0.0131 (5)
C17	−0.1347 (7)	0.1007 (3)	0.0704 (6)
C18	−0.0609 (8)	0.0593 (3)	0.0857 (6)
C19	0.0436 (8)	0.0713 (3)	0.0391 (5)
C20	0.2144 (7)	0.3148 (3)	0.3324 (6)
C21	0.3131 (6)	0.2976 (3)	0.2888 (6)
C22	0.3268 (6)	0.2479 (3)	0.3130 (6)
C23	0.2377 (7)	0.2338 (3)	0.3761 (6)
C24	0.1656 (7)	0.2749 (4)	0.3885 (6)
C25	0.1157 (8)	0.2494 (3)	−0.0221 (5)
C26	0.2274 (8)	0.2342 (4)	−0.0028 (6)
C27	0.2856 (9)	0.2746 (5)	0.0430 (7)
C28	0.2214 (10)	0.3147 (4)	0.0493 (6)
C29	0.1060 (9)	0.2989 (4)	0.0072 (6)
BC1	0.3496 (8)	0.4378 (3)	0.1229 (9)
BC2	0.2608 (9)	0.4640 (3)	0.0821 (6)
BC3	0.1882 (7)	0.4874 (3)	0.1484 (10)
BC4	0.2081 (9)	0.4846 (4)	0.2602 (9)
BC5	0.2986 (11)	0.4576 (4)	0.3004 (6)
BC6	0.3704 (7)	0.4344 (3)	0.2298 (11)
BC7	0.0634 (7)	0.3626 (4)	0.7324 (9)
BC8	0.0394 (7)	0.3553 (4)	0.6303 (10)
BC9	0.0353 (8)	0.3921 (7)	0.5600 (8)
BC10	0.0565 (11)	0.4413 (6)	0.5931 (15)
BC11	0.0823 (9)	0.4462 (4)	0.7064 (16)
BC12	0.0827 (7)	0.4073 (5)	0.7719 (8)
H1	0.259 (4)	0.119 (2)	0.267 (4)
H2	0.268 (4)	0.118 (2)	0.130 (4)
H3	−0.167 (5)	0.231 (2)	0.131 (4)
H4	−0.173 (4)	0.224 (2)	0.258 (4)
H5	−0.039 (6)	0.411 (3)	0.261 (6)
H6	−0.175 (6)	0.414 (3)	0.405 (6)
H7	−0.351 (6)	0.438 (3)	0.293 (6)
H8	−0.323 (6)	0.436 (2)	0.110 (5)
H9	−0.094 (5)	0.422 (2)	0.097 (5)
H10	−0.185 (5)	0.145 (2)	0.334 (4)
H11	−0.143 (5)	0.052 (2)	0.302 (5)
H12	0.057 (4)	0.044 (2)	0.352 (4)
H13	0.147 (6)	0.120 (2)	0.424 (5)
H14	−0.005 (5)	0.182 (2)	0.432 (5)
H15	0.096 (5)	0.134 (2)	−0.036 (4)
H16	−0.107 (5)	0.168 (2)	−0.013 (5)
H17	−0.200 (5)	0.104 (2)	0.090 (5)
H18	−0.073 (5)	0.032 (2)	0.117 (4)
H19	0.109 (5)	0.056 (2)	0.038 (5)
H20	0.180 (6)	0.350 (3)	0.322 (5)
H21	0.360 (5)	0.316 (2)	0.255 (5)
H22	0.372 (7)	0.226 (3)	0.301 (6)
H23	0.219 (5)	0.207 (2)	0.395 (5)
H24	0.103 (5)	0.272 (2)	0.418 (5)
H25	0.061 (5)	0.230 (2)	−0.051 (5)
H26	0.263 (7)	0.207 (3)	−0.016 (7)
H27	0.342 (5)	0.269 (2)	0.050 (5)
H28	0.217 (7)	0.343 (3)	0.072 (7)
H29	0.043 (5)	0.312 (3)	0.010 (5)
BH1	0.409	0.419	0.067
BH2	0.247	0.466	−0.003
BH3	0.117	0.508	0.120
BH4	0.149	0.504	0.314
BH5	0.311	0.456	0.384
BH6	0.441	0.414	0.261
BH7	0.065	0.330	0.790
BH8	0.022	0.316	0.600
BH9	0.016	0.387	0.476
BH10	0.054	0.471	0.542
BH11	0.097	0.484	0.732
BH12	0.103	0.414	0.856

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figures.

complexes **12f** and **17** in a 2:5 ratio. Complex **17** was identified by its characteristic ^1H and ^{13}C NMR spectra.

Results and Discussion

Thermally Induced Addition Reactions. Cyclodimeric (η^2-formaldehyde)zirconocene (**10**) reacts with hexacarbonylmolybdenum slowly at 40 °C in toluene solvent to give a single organometallic product that contains two zirconium atoms per molybdenum.



10

12 [ML_n = $Mo(CO)_5$ (a), $W(CO)_5$ (b), $CpCo(CO)$ (c), $CpRh(CO)$ (d), $CpV(CO)_3$ (e), $(C_6F_5)_2Pt(CO)$ (f)]

Increasing the $Mo(CO)_6/[Cp_2Zr(\mu\text{-}OCH_2)]_2$ ratio does not result in any more Mo being incorporated into the product. The product **12a** precipitates from the solution as the reaction proceeds. According to the NMR spectra (Tables IV and V), complex **12a** contains a metallacyclic three-membered ring system that exhibits similar spectroscopic features as **10** [$^1H/^{13}C$ NMR (CH_2): δ 2.53/66.8 (**12a**), 2.42/64.0 (**10**)]. A notable characteristic of this metalloxirane structure is the rather large $^1J_{CH}$ coupling constant of 154 Hz for the methylene unit (comparable to 153 Hz for **10**).[12,24] Also, a metal-bound CO ligand has been inserted into the Zr–CH_2 linkage of the second metallaoxirane ring of **10**. This is evident from the ^1H and ^{13}C resonances of this methylene group, which are shifted downfield (δ 4.65/100.9) relative to the CH_2 signals of the starting material **10**. The reduced $^1J_{CH}$ coupling constant of 141 Hz indicates that ring enlargement has taken place. This CH_2 group, however, remains bound to an oxygen atom. ^1H NMR integration shows four Cp groups to be present besides the two methylene groups. The observation of only two ^1H NMR singlets even at low temperature points to an overall C_s molecular geometry in solution. The IR spectrum of **12a** further indicates the presence of a $Mo(CO)_5$ unit. On the basis of these data, we conclude that complex **12a** contains a metallaoxirane subunit and a five-membered metallacyclic zirconoxycarbene unit, which

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[24] Erker, G.; Kropp, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447.

Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) for the Non-Hydrogen Atoms in $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)$[a,b]

A. Interatomic Distances			
Rh–C3	1.930 (5)	Rh–C4	1.807 (5)
Zr1–O1	2.125 (3)	Zr2–O1	2.089 (3)
Zr1–O2	2.222 (3)	Zr2–O2	2.167 (3)
Zr1–C1	2.240 (8)	Zr2–O3	2.181 (3)
C1–O1	1.413 (6)	C2–O2	1.424 (6)
C3–O3	1.281 (6)	C4–O4	1.166 (7)
Rh–Cp1	1.981 (8)	C2–C3	1.506 (7)
Zr1–Cp2	2.241 (8)	Zr2–Cp4	2.260 (8)
Zr1–Cp3	2.230 (7)	Zr2–Cp5	2.264 (8)
Zr1···Zr2	3.536 (1)		
range of Rh–C (Cp1) distances	2.234 (8)–2.333 (7)		
range of Zr–C (Cp2, Cp3) distances	2.497 (8)–2.553 (6)		
range of Zr–C (Cp4, Cp5) distances	2.498 (10)–2.582 (7)		
range of C–C (Cp1–Cp5) distances	1.354 (12)–1.431 (16)		
B. Bond Angles			
C3–Rh–C4	91.6 (2)	Rh–C4–O4	177.9 (5)
Cp1–Rh–C3	130.6 (3)	Cp1–Rh–C4	137.9 (3)
O1–Zr1–O2	68.3 (1)	O1–Zr2–O2	70.0 (1)
Cl–Zr1–O1	37.7 (2)	O2–Zr2–O3	69.5 (1)
Zr1–O1–Zr2	114.1 (1)	Zr1–O2–Zr2	107.4 (1)
Zr1–O1–C1	75.6 (3)	Zr2–O2–C2	121.2 (3)
Zr2–O1–C1	167.5 (3)	Zr1–O2–C2	131.4 (3)
Zr1–C1–O1	66.8 (2)	Zr2–O3–C3	126.3 (3)
O2–C2–C3	110.7 (4)	O3–C3–C2	111.3 (4)
C2–C3–Rh	128.5 (3)	O3–C3–Rh	120.2 (3)
Cp2–Zr1–Cp3	128.3 (3)	Cp4–Zr2–Cp5	125.3 (3)
range of C–C–C (Cp1–Cp5) angles	106.2 (8)–110.7 (7)		

[a] Cp*n* (*n* = 1–5) denotes the centroid of a cyclopentadienyl ring. The rings containing the centroids designated by Cp1, Cp2, Cp3, Cp4, and Cp5 contain carbon atoms C5–C9, C10–C14, C15–C19, C20–C24, and C25–C29, respectively. [b] The esd's for the interatomic distances and bond angles were calculated from the standard errors for the fractional atomic coordinates.

Table IV. ^1H NMR Data for the Metallacyclic Carbene Complexes $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}ML_n]O)$ (12)[a]

ML_n	compd	Cp	$ZrOCH_2$	$CH_2OC{=}[M]$
$Mo(CO)_5$	**12a**	5.40, 5.68	2.53	4.65
$W(CO)_5$[b]	**12b**	5.56, 5.96	2.62	4.97
	16	5.40, 5.66	2.53	4.55
CpCo(CO)[c]	**12c**	5.45, 5.81	2.58	4.34
CpRh(CO)[d]	**12d**	5.43, 5.77	2.56	4.40[e]
$CpV(CO)_3$[f]	**12e**	5.48, 5.75	2.58	4.88
$(C_6F_5)_2Pt(CO)$[b]	**12f**	5.36, 5.54	2.57	4.17[g]
	17	5.34, 5.56	2.54	4.37[h]

[a] In benzene-d_6 at ambient temperature. [b] Two isomers. [c] CpCo singlet (5 H) at δ 5.08. [d] CpRh signal (5 H) at δ 5.64 (J_{RhH} = 0.7 Hz). [e] J_{RhH} = 0.6 Hz. [f] CpV signal (br s, 5 H) at δ 5.04. [g] J_{PtH} = 7.5 Hz. [h] J_{PtH} = 10 Hz.

are connected by means of two zirconium–oxygen bridges, giving a four-membered Zr_2O_2 ring system. This type of structural arrangement is very common for electron-deficient chalcogen–$ZrCp_2$ containing metallacyclic three-, four-, and five-membered ring systems.[25] The analogous metallatricyclic zirconoxycarbene complexes containing the annulated three-, four-, and five-membered metallacyclic Cp_2ZrOCH_2, $(Cp_2ZrO)_2$, and $Cp_2ZrOCH_2C[{=}ML_n]O$ ring systems were formed from the reaction of $[Cp_2Zr(\mu\text{-}OCH_2)]_2$ (**10**) and a variety of other metal carbonyl complexes as well.

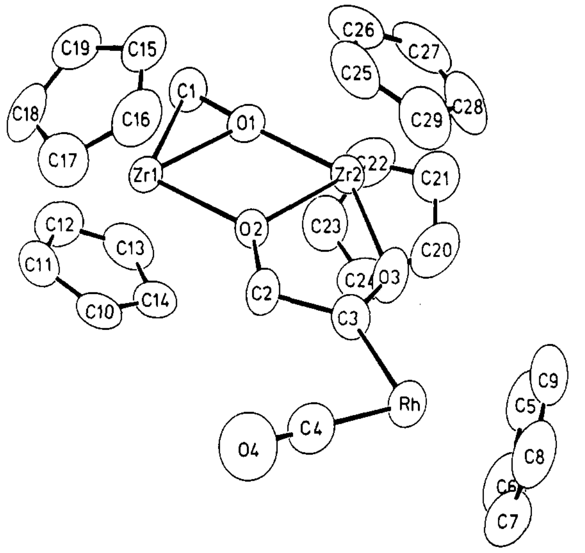

Figure 1. Perspective view of the molecular structure of $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)$ with atom numbering scheme. The thermal ellipsoids are scaled to 50% probability. The hydrogen atoms have been omitted for clarity.

As expected, the thermally induced reaction of (η^2-formaldehyde)zirconocene with $W(CO)_6$ at 40 °C produced a good yield (>70%) of $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}W(CO)_5]O)$ (**12b**). The reaction of **10** with $CpCo(CO)_2$ at 40 °C in toluene took 3 days to complete and gave an 80% yield of the corresponding zirconoxycarbene complex **12c**. $CpRh(CO)_2$ reacted similarly. The zirconoxycarbene rhodium complex **12d** [ν(CO) = 1917 cm^{-1}] was recovered in 73% yield.

Our method can also be used to prepare one of the rare examples of a heteroatom-stabilized vanadium carbene complex.[26] The reaction of **10** with $CpV(CO)_4$ requires more rigorous reaction conditions when conduced purely with thermal activation (10 days at 60 °C). The required reaction time is substantially shorter when the reaction mixture is irradiated with a sunlamp at elevated temperature. In each case, the zirconoxycarbene product $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}VCp(CO)_3]O)$ (**12e**) was isolated in good yield (ca. 80%). Even the platinum(II) carbonyl complex $(C_6F_5)_2Pt(CO)_2$ [ν(CO) = 2174, 2143 cm^{-1}] can cleanly be converted by reacting it with **10** to the zirconoxycarbene carbonylplatinum product **12f** [ν(CO) = 2084 cm^{-1}]. The metallacyclic (π-allyl)zirconoxycarbene platinum(II) complex $Cp_2ZrOC[{=}Pt(C_6F_5)_2CO]CH_2C_3H_4$, which we have recently prepared by reacting $(C_6F_5)_2Pt(CO)_2$ with (η^4-butadiene)zirconocene, exhibits a ν(CO) band at 2083 cm^{-1}.[27]

Description of the Molecular Structure of $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}RhCp(CO)]O)$. The zirconoxycarbene rhodium complex **12d** was characterized by X-ray diffraction methods. Each molecular unit of **12d** contains three metal atoms, two zirconiums and one rhodium, connected by carbon and oxygen atoms in a nearly planar metallatricyclic framework. A perspective view of

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Table V. Selected ^{13}C NMR Data for the Metallacyclic Zirconoxycarbene Complexes **12**[a]

ML_n	compd	Cp	$ZrOCH_2$	$[M]{=}COCH_2$	M—CO (trans/cis)
$Mo(CO)_5$	**12a**	107.9, 113.5	66.8 (154)	324.1, 100.9 (141)	214.8, 209.0
$W(CO)_5$[b,c]	**16**	108.6, 114.1	66.4 (155)	316.2, 100.6 (143)	216.5, 208.2
	12b	108.9, 114.4	67.5 (155)	308.6, 104.3 (143)	205.4, 200.5
CpCo(CO)	**12c**	107.8, 113.0	66.4 (154)	290.0, 95.4 (143)	*d*
CpRh(CO)[c]	**12d**	108.6, 113.8	67.0 (155)	279.0,[e] 96.4 (145)[f]	197.4[g]
$CpV(CO)_3$[c]	**12e**	108.7, 114.2	67.2 (155)	344.0,[h] 96.1	266.0[h,i]
$(C_6F_5)_2Pt(CO)$[b]	**12f**	108.1, 113.8	68.1	269.8,[k] 97.0[l]	175.6[m]
	17	*n*	67.9	266.6,[o] 93.9[p]	176.3[q]

[a] In benzene-d_6 at ambient temperature unless otherwise stated, $^1J_{CH}$ coupling constants in parentheses. [b] Two isomers. [c] In tetrahydrofuran-d_8. [d] Carbonyl C not observed, CpCo signal at 84.5 (174). [e] J_{RhC} = 56 Hz. [f] J_{RhC} = 11 Hz. [g] J_{RhC} = 103 Hz, CpRh signal at δ 87.8 (172). [h] At 243 K. [i] CpV signal at δ 93.8. [k] J_{PtC} = 825 Hz. [l] J_{PtC} = 210 Hz. [m] J_{PtC} = 1250 Hz, C_6H_5 signals at δ 151.0, 149.6, 146.7, 145.2, 141.2, 140.3, 136.2, 135.2. [n] Not distinguished between isomers. [o] J_{PtC} = 1070 Hz. [p] J_{PtC} = 270 Hz. [q] J_{PtC} = 970 Hz.

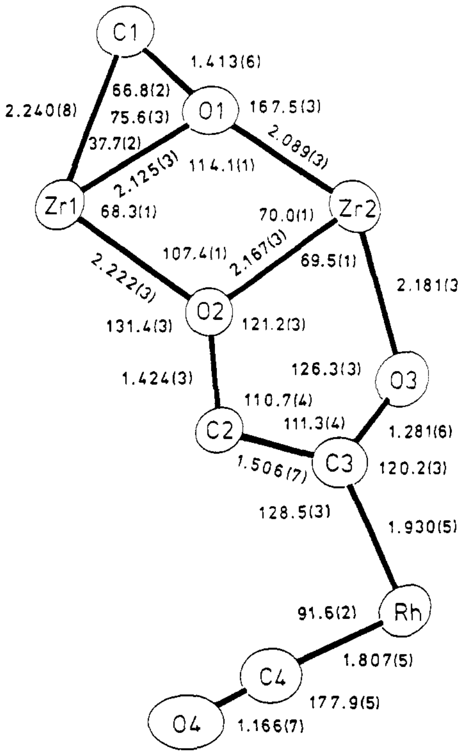
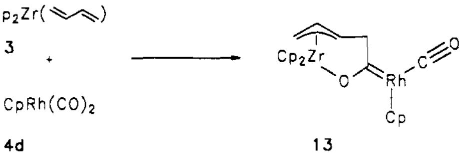


Figure 2. Pertinent interatomic distances (Å) and bond angles (deg) within the $RhZr_2C_4O_4$ core.

the molecular structure of **12d** with the atom-labeling scheme is depicted in Figure 1. Figure 2 provides a view of the central molecular framework and includes some pertinent bond distances and angles. The three metallacyclic rings are linearly annulated to form the central $RhZr_2C_4O_4$ core of **12d**. The Cp_2ZrOCH_2 ring possesses a pronounced metallaoxirane character as evidenced by the short Zr–C(1) bond (2.240 (8) Å) and a rather long C(1)–O(1) linkage (1.413 (6) Å). The average Zr–O bond length of the central Zr_2O_2 four-membered ring is 2.151 Å, which is at the low end of the range of zirconium–oxygen distances typically observed in a number of zirconaoxametallapolycyclic complexes containing this structural element [e.g., the mean Zr–O distance is 2.152 Å in $[Cp_2Zr(\mu\text{-}OCH_2)]_2$,[12] 2.152 Å in the $Cp_2Zr(\mu\text{-}H)B(C_8H_{14})CH_2O$ dimer,[14] 2.157 Å in $[Cp_2Zr(\mu\text{-}OCH_2)]_3$,[28] 2.164 Å in $[Cp_2Zr(\mu\text{-}OC{=}CPh_2)]_2$,[29] 2.190 Å in the $Cp_2ZrOCH_2C({=}NCMe_3)O$ dimer,[14] and 2.204 Å in $[Cp_2Zr(\mu\text{-}OCPh_2)]_2$[30]]. However, the Zr–O bond length distribution within the central Zr_2O_2 four-membered ring of **12d** varies over a wide range. The Zr–O(1) bonds are much shorter (2.089 (3), 2.125 (3) Å) than the Zr–O(2) bonds (2.167 (3), 2.222 (3) Å). Apparently, the bridging oxygen O(1) within the three-membered metallacyclic ring is a stronger donor ligand than oxygen atom O(2) for the lateral coordination to a Cp_2Zr unit. Both O(1) and O(2) are tricoordinated oxonium type oxygen atoms. The coordination geometry at O(2) is trigonal planar (the sum of bond angles at O(2) is 360°). The oxonium center O(1) is only marginally pyramidalized (357.2°).[31]

The five-membered metallacyclic ring in **12d** contains the zirconoxycarbene rhodium moiety. The bonding features around the carbene carbon atom C(3) are somewhat different from those of O-alkylated Fischer type carbene complexes of rhodium. The rather short carbene C to oxygen bond of 1.281 (6) Å in **12d** is typical for metallacyclic zirconoxycarbene metal complexes that exhibit significant metal acyl character.[3-5] For example, the corresponding O–C(carbene) distance in the metallacyclic (π-allyl)zirconoxycarbene rhodium complex **13**, which we prepared by reacting (η^4-butadiene)zirconocene with $CpRh(CO)_2$, is 1.278 (4) Å.[4a] The Rh–C(3) bond of 1.930 (5) Å in **12d** is among the shortest found for a rhodium–carbon bond[32] and is comparable to the Rh–C(carbene) bond of 1.925 (3) Å in **13**. This structural feature reflects the presence of a considerable metal to carbon multiple bond character. Consistent with the assumed Rh=C double-bond character in **12d** is the coplanar arrangement of the substituents C(2), O(3), C(4), and the centroid of the C(5)–C(9) Cp ring at the Rh=C moiety. Only one of the two possible isomers of such a bonding situation is observed for **12d** in the crystal, which is characterized by an entgegen (*E*) orientation of the substituents of highest



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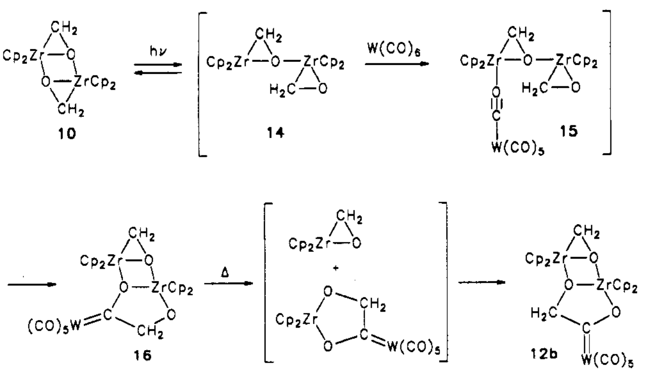
Scheme I

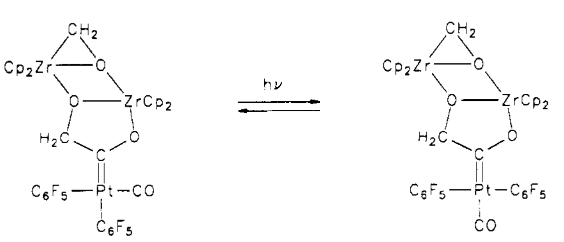


priority (O(3) at the carbene carbon and the C═O ligand at Rh). The (π-allyl)zirconoxycarbene rhodium complex **13** also exhibits an *E*-configurated Rh═C(carbene) unit,[4a] as do the analogous cobalt carbene complexes $Cp_2ZrOC[{=}Co(C_5H_4R)CO]CH_2C_3H_4$ (R = H, Cl).[4b]

Photochemically Assisted Reactions. It was already pointed out that the reaction between $CpV(CO)_4$ and the (η^2-formaldehyde)zirconocene dimer giving **12e** can be accelerated by sunlamp irradiation (vide supra). In this case, the reaction product remains the same whether the addition reaction is photochemically assisted or not. For the corresponding reaction of **10** with $W(CO)_6$, a different situation exists. When this reaction is carried out in a sealed tube at 60 °C with intensive irradiation from a sunlamp, a rapid consumption of the starting materials is observed with the formation of the carbene complex **12b** plus a new organometallic product (**16**). After 1 h, a maximum ratio of about 1:1 of the complexes **12b** and **16** was reached. Subsequent thermolysis at 60 °C led to a rapid rearrangement of **16** to **12b**. A comparison of the corresponding NMR data (Tables IV and V) reveals that **16** is an isomer of **12b**. Tentatively, we have assigned the structure of the regioisomer **16** to the newly observed complex that is formed from $W(CO)_6$ and **10** with the assistance of UV light (Scheme I).

The carbene complex **16**, however, is not formed from **12b** upon irradiation by the same UV light source. The appearance of **16** is strictly related to the reaction pathway involved in the formation of the carbene complexes. Subsequent attempts to establish a photostationary equilibrium between the isomers **12b** and **16** were unsuccessful.

A different type of photochemical reaction, which in this case can occur subsequent to the carbene complex formation, was observed for the zirconoxycarbene platinum complex **12f**. UV irradiation of **12f** (HPK 125 lamp, Pyrex filter) at ambient temperature produced an isomeric complex (**17**) which amounts to ca. 70% once the photostationary equilibrium is reached. In view of similar results obtained with the (π-allyl)zirconoxycarbene complex $Cp_2ZrOC[{=}Pt(C_6F_5)_2CO]CH_2C_3H_4$, prepared from Cp_2Zr(butadiene) (**4**) and $(C_6F_5)_2Pt(CO)_2$, we propose a cis/trans isomerization process taking place upon photolysis of **12f**. Probably a dissociative isomerization mechanism is operative similar to the recently reported example.[27]



12f 17

Conclusions

We have shown that a (η^2-formaldehyde)zirconocene unit of the metallaoxirane dimer **10** is able to add to a C═O ligand from a variety of metal carbonyl complexes to form O-metallated metallacyclic heteroatom-stabilized carbene complexes. Without exception, only one of the two available Cp_2ZrOCH_2 moieties of **10** is used in this transformation. Neither in the thermally nor in the photochemically induced reactions did we find any evidence that the remaining (η^2-formaldehyde)$ZrCp_2$ unit in $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OCH_2C[{=}ML_n]O)$ (**12**; $[ML_n = Mo(CO)_5, W(CO)_5, CpCo(CO), CpRh(CO), CpV(CO)_3$ or $(C_6F_5)_2Pt(CO)]$ reacts with additional amounts of L_nM-(CO). However, experimental evidence indicates that the reaction pathways for the thermally promoted and photochemically assisted reactions may be quite different.

The thermodynamically favored (η^2-formaldehyde)$ZrCp_2$ trimer $[Cp_2Zr(\mu\text{-}OCH_2)]_3$[28] can be formed from **10** by photolysis as well as thermolysis.[33] In either case, monomeric Cp_2ZrOCH_2 appears to be involved as a reactive intermediate. The regioisomeric carbene complex $Cp_2Zr(\mu\text{-}OCH_2)ZrCp_2(\mu\text{-}OC[{=}W(CO)_5]CH_2O)$ (**16**), formed during the photochemically assisted, kinetically controlled reaction of $W(CO)_6$ with **10**, leads us to assume that the photochemically induced dissociation of $[Cp_2Zr(\mu\text{-}OCH_2)]_2$ involves a two-step reaction proceeding via intermediate **14** as depicted in Scheme I. Tungsten hexacarbonyl traps the ring-opened dimetallic complex **14** to give **15**, which then reacts further to give the carbene complex **16**. Formation of the less stable isomer **16** thus appears to be an example of a bimetallic-induced CC-coupling process. According to this description, one electrophilic zirconium center activates the tungsten-bound carbonyl group, whereas the other zirconium center is used to provide the nucleophilic CH_2O group.

The formation of the mixed products **12**, each containing a Cp_2ZrOCH_2 metallaoxirane unit in addition to the five-membered metallacyclic zirconoxycarbene moiety $Cp_2Zr(OCH_2C[{=}ML_n]O)$, is probably thermodynamically controlled. We have recently shown that the metallatricyclic zirconocene(endiolato) dimers[34] **18** (R = H, CH_3) cleanly equilibrate with the (η^2-formaldehyde)zirconocene dimer **10** at 80 °C to give exclusively the "mixed dimers" **19** (R = H, CH_3).[33] This appears to be a general phenomenon. The equilibrium **20** + **10** $\rightleftharpoons$ 2 **21** also lies completely on the side of the unsymmetrical product at 80 °C.[33]

Therefore, we assume that the metallaoxirane-containing zirconoxycarbene complexes **12** represent the global minima in the systems studied to date. This remark is in accord with the observed structural features of the metallatricyclic zirconoxycarbene rhodium complex **12d**. The rather unsymmetrical arrangement of Zr–O bond lengths in the central four-membered Zr_2O_2 ring clearly shows that Cp_2ZrOCH_2 is both a better donor (at oxygen) and a better

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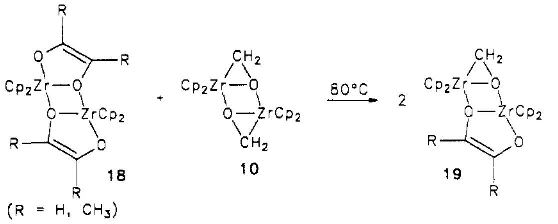

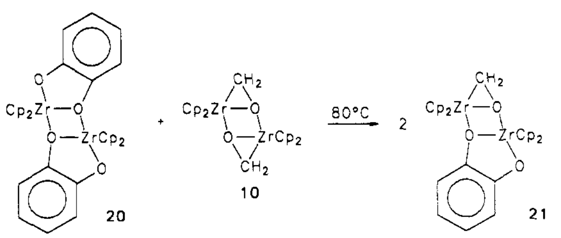

acceptor (at zirconium) compared to the five-membered metallacycle.

In the thermally induced reaction, the monomeric $Cp_2\overline{ZrOCH_2}$ intermediate most likely adds 1 equiv of the metal carbonyl. Carbon–carbon coupling then apparently occurs by means of a concerted electrocyclic ring closure reaction to give the five-membered metallacyclic zirconoxycarbene complex, which is then trapped by a second $Cp_2\overline{ZrOCH_2}$ species to give the observed stable product **12**. The addition of this molecular unit to $L_nM\text{-}C{\equiv}O$ thus represents another example of a nonnucleophilic route for the preparation of a heteroatom-stabilized carbene complex.

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Supplementary Material Available: Tables listing thermal parameters, interatomic distances and bond angles, and least-squares planes (15 pages); a table listing the observed and calculated structure factors of **12d** (20 pages). Ordering information is given on any current masthead page.

Oxidation of the Ruthenium Hydride Complex (η^5-C_5H_5)Ru(CO)(PPh_3)H: Generation of a Dihydrogen Complex by Oxidatively Induced Intermolecular Proton Transfer

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Ruthenium hydride (η^5-C_5H_5)Ru(CO)(PPh_3)H (**1**) undergoes a chemically irreversible oxidation at +0.39 V vs the ferrocene/ferrocenium couple. Oxidation of **1** with $(\eta^5\text{-}C_5H_5)_2Fe^+PF_6^-$ (**3**) in dichloromethane-d_2 yields the known dihydrogen complex $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^2\text{-}H_2)^+$ (**4**) as a primary decomposition product. Ferrocenium oxidation of **1** in acetonitrile-d_3 yielded $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(NCCD_3)^+$ (**2**-d_3), $HRu(CO)(PPh_3)(NCCD_3)_3^+$ (**5**-d_9), and cyclopentadiene. Cyclopentadiene and **5**-d_9 were generated via the prior formation of dihydrogen complex **4**. Solutions of independently prepared **4** in acetonitrile-d_3 were observed to decompose to yield some **2**-d_3, but mostly **5**-d_9 and cyclopentadiene. The results are discussed in terms of an initial proton transfer from cation radical $1^{\bullet+}$ to the Ru center of **1**, yielding **4**. It is proposed that a reversible, base-catalyzed deprotonation/protonation sequence generates an undetected cationic trans dihydride intermediate from which cyclopentadiene is eliminated.

Introduction

Transition-metal hydrides continually receive the attention of organometallic chemists because of their involvement in catalytic and stoichiometric processes.[2] The acidities of metal hydrides, in both the kinetic and the thermodynamic senses, in many cases have been systematically explored.[3] We recently reported the first estimates of metal hydride cation radical thermodynamic acidities in acetonitrile solution, noting that a number of group 6 hydride cation radicals were more acidic than their parent neutral hydrides by a relatively constant 20.6 ± 1.5 pK_a units.[4] All of the metal hydride cation radicals in that study were short-lived, their major mode of decomposition

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