is converse and quite unique. It was found that the Rh-Rh bond was re-formed together with the formation of the acyl group. It is to be noted that species **2** and **4** with no Rh-Rh bonding do not act as monomers, but the CO insertion reaction was assisted by dimer formation. The vacant site on Rh produced by insertion of CO into the Rh-ethyl bond is replaced by the Rh-Rh metal bond to stabilize the acyl group. Similar metal-promoted CO insertions have been observed in homogeneous systems.[7,8] In these homogeneous systems, however, neither the reverse decarbonylation of acyl (COR) nor the reaction of the acyl group with H_2 to form aldehyde has been observed. The CO insertion mechanism has been discussed in the context of reaction steps for mononuclear metal complexes in homogeneous systems. However, the present work implies that CO insertion on the metal dimers and the surface of metal particles could proceed by the promotion of metal-metal bonding. The metal-assisted mechanism discussed here would be an example to explain the role of metal ensembles for metal catalysts.

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Complexes Containing a C_2 Bridge between an Electron-Rich Metal and an Electron-Deficient Metal. An Agostic Interaction in a $RuCH_2CH_2Zr$ Moiety

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Complexes containing two metals of disparate electronic properties often exhibit unusual structural and reactivity features. Examples of such compounds include those in which early and late transition metals are joined by a direct metal-metal bond,[1] a bridging CH_2 ligand,[2] or a single carbon atom (μ_2-carbide).[3] Complexes in which two metals are linked by a C_2 bridge have been far less extensively studied than the well-known bridging methylene[4] (MCH_2M) compounds. Dimetalloethanes (MCH_2CH_2M)[5] and dimetalloalkenes ($MCH{=}CHM$)[6] reported to date have either identical or similar electronic environments of the two metals. We report here the preparation of compounds which contain $CH{=}CH$ and CH_2CH_2 bridges between an electron-rich $(C_5H_5)(PMe_3)_2Ru$ fragment and an electron-deficient $(C_5H_5)_2ZrCl$ moiety.

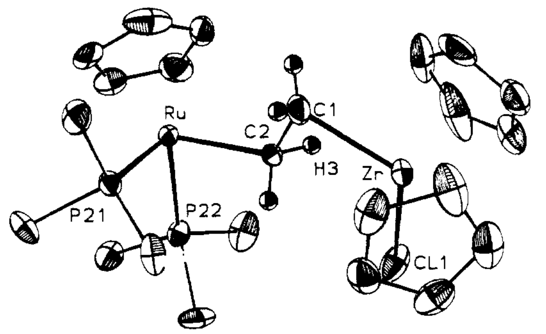

Figure 1. An ORTEP view of **3** (thermal ellipsoids at 50% probability level) with hydrogen atoms omitted except those on the bridging CH_2CH_2. The atoms Ru, C2, C1, Zr, and CL1 are approximately coplanar with the maximum deviation ±0.05 Å from the plane defined by these five atoms. The distance Zr–H3 is 2.19 (2) Å. Some other distances (Å) and angles (deg) are as follows: Zr–Cl, 2.276 (10); Zr–C2, 2.549 (9); Zr–CL1; 2.579 (3); Ru–C2, 2.186 (9); C1–C2, 1.485 (14); Zr–C1–C2, 82.5 (6); C1–C2–Ru, 118.2 (7); Cl–Zr–CL1; 117.4 (3); C2–H3–Zr, 100 (1).

Unsaturated carbon ligands bonded to late transition metals generally undergo β-attack by electrophiles and α-attack by nucleophiles.[7] We have shown[8] that relatively acidic transition metal hydrides such as $(C_5H_5)(CO)_3MoH$ protonate the β-carbon of the metal alkynyl complex $(C_5H_5)(PMe_3)_2RuC{\equiv}CCH_3$ to give the ionic product $[(C_5H_5)(PMe_3)_2Ru{=}C{=}C(H)CH_3]^+[(C_5H_5)(CO)_3Mo]^-$. Early transition metal hydrides typically exhibit hydridic rather than acidic reactivity.[9] Accordingly, the opposite regiochemistry is expected upon their reaction with ruthenium alkynyl complexes, with the H of the early-metal hydride being delivered to the α-carbon of the alkynyl ligand. The reaction of $(C_5H_5)(PMe_3)_2RuC{\equiv}CH$[10] with $(C_5H_5)_2ZrHCl$ in toluene leads to formation of the dimetalloalkene complex $(C_5H_5)(PMe_3)_2RuCH{=}CHZrCl(C_5H_5)_2$ (**1**) in 73–87% isolated yield[11] (Scheme I). Both of the vinyl protons of **1** appear as a doublet of triplets in the ^1H NMR spectrum, since they couple to each other (J_{HH} = 18.7 Hz) as well as to the two equivalent phosphorus atoms. In CD_2Cl_2, the RuCH appears at δ 9.46 ($^3J_{PH}$ = 4.3 Hz) while the ZrCH resonance appears at δ 8.38 ($^4J_{PH}$ = 0.8 Hz). A particularly intriguing feature of the ^{13}C NMR spectrum was the value of J_{CH} = 110 Hz observed for the carbon bonded to Ru (δ 114.7, $^2J_{PC}$ = 16 Hz in CD_2Cl_2). This low J_{CH} value suggests an agostic[12] interaction between the CH and the unsaturated Zr center. A broad band at 2590 cm^{-1} in the IR spectrum of **1** (which sharpened and shifted to 1900 cm^{-1} in $RuCD{=}CHZr$) is assigned to the agostic ν_{CH}. The NMR and IR data indicate that the agostic interaction is between Zr and the CH that is β to Zr. Erker and co-workers have found[13] an agostic interaction in a closely

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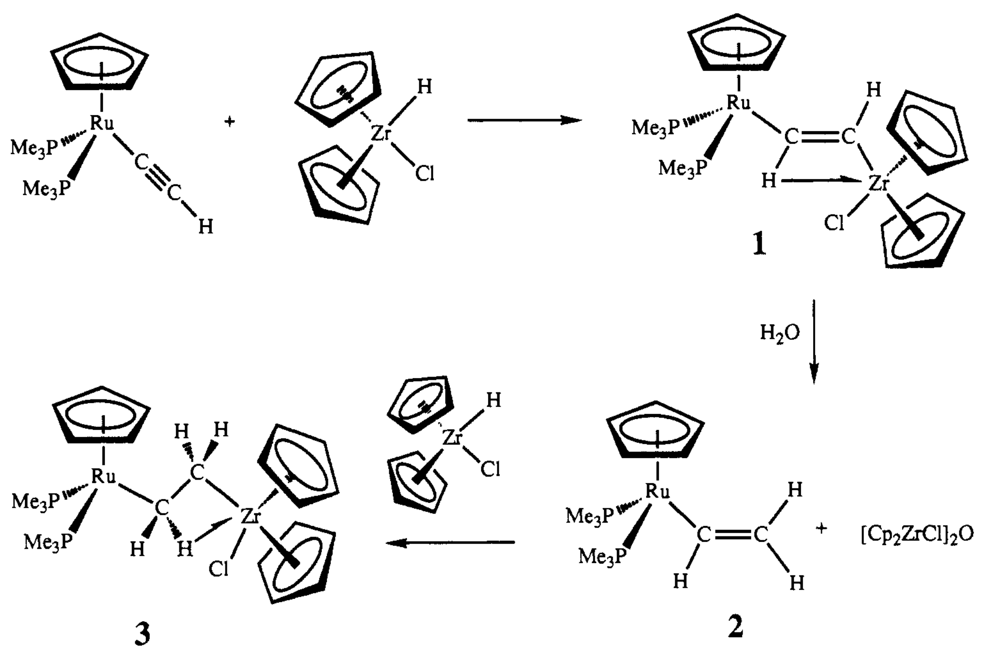
Scheme I



related homobimetallic complex, $(C_5H_4Me)_2ZrCl(CH{=}CMe)\text{-}ZrCl(C_5H_5)_2$.

Hydrolysis of the Zr–C bond of **1** by H_2O (0.5 equiv) in toluene results in the formation of ruthenium vinyl complex[11] $(C_5H_5)(PMe_3)_2RuCH{=}CH_2$ (**2**) (51–67% yield) and $[(C_5H_5)_2ZrCl]_2O$.[14] Reaction of **2** with $(C_5H_5)_2ZrHCl$ produces the dimetalloethane complex[11] $(C_5H_5)(PMe_3)_2RuCH_2CH_2ZrCl(C_5H_5)_2$ (**3**) (50–70% isolated yield). The resonance for the carbon bonded to Zr appears at δ 53.9 (J_{CH} = 145 Hz) in the ^{13}C NMR spectrum (toluene-d_8, 200 K) while the CH_2 bonded to Ru is observed at δ −34.4 (J_{CH} = 111 Hz). As in the case of **1**, the low J_{CH} value suggests the presence of an agostic interaction between one H of the $RuCH_2$ and the unsaturated Zr center. A low-frequency IR band at ν_{CH} = 2743 cm^{-1} (ν_{CD} = 2031 cm^{-1} in $RuCHDCH_2Zr$) gave further evidence for an agostic interaction.

Confirmation of the proposed structure came from a single-crystal X-ray diffraction study of **3**.[15] An ORTEP drawing of **3** is shown in Figure 1. The distance from one of the hydrogen atoms of the $RuCH_2$ group (H3) to Zr is only 2.19 Å. The agostic C–H in **3** is bonded to the central position of the $(C_5H_5)_2ZrCl(R)$ moiety, between the Cl and CH_2CH_2Ru ligands. This contrasts with the structure of a cationic mononuclear zirconium complex, $(C_5H_4CH_3)_2Zr(PMe_3)CH_2CH_3^+$, in which Jordan and co-workers found the agostic CH of the ethyl group to occupy a lateral site.[16]

Further support for the agostic bonding interaction in **3** is the small Zr–C(1)–C(2) angle of 82.5 (6)°. This is similar to the M–C–C angles found in mononuclear complexes containing agostic[12] ethyl groups: the Ti–C–C angle in $TiCl_3(dmpe)\text{-}CH_2CH_3$[17] is 86.3 (6)°, while the Co–C–C angle in $[(C_5Me_5)P(CH_3C_6H_4)_3CoCH_2CH_3]^+$[18] is 63.4 (2)°. Acute Zr–C–C angles have previously been found in $Zr_2(C_2H_4)$ complexes in which the CH_2CH_2 is perpendicular to the Zr–Zr axis. Cotton and Kibala[19] have studied $Zr_2X_2(PEt_3)_4(C_2H_4)$ (X = Cl, Br) and have designated the $M_2(\mu_2\text{-}\eta^4\text{-olefin})$ formulation on the basis of crystallographic data and molecular orbital calculations. An earlier report by Kaminsky and co-workers[20] reported a Zr–C–C angle of 75.9° for $Et_3Al{\leftarrow}Cl(C_5H_5)_2ZrCH_2CH_2Zr(C_5H_5)_2Cl{\rightarrow}AlEt_3$.

The C(2)–C(1) bond distance of 1.485 (14) Å in **3** is significantly shortened compared to a normal C–C single bond length of 1.54 Å, indicating some double-bond character. This, along with the agostic interaction noted above, suggests that the structure of **3** is a model for a complex along the reaction coordinate for β-hydride elimination (in which a Zr—H bond and the C=C double bond are fully formed). Indeed, we have found that when a C_6D_6 solution of **3** (0.035 M) and $^tBuC{\equiv}CH$ (0.076 M) is kept at room temperature for 45 h, **2** (83%) is formed by β-hydride elimination of $(C_5H_5)_2ZrHCl$ from **3**. The $(C_5H_5)_2ZrHCl$ is trapped by reaction with $^tBuC{\equiv}CH$ to give $(C_5H_5)_2ZrCl(CH{=}CH^tBu)$ (80%).[21]

We have found unusual structural features in complexes with a C_2 bridge between an electron-rich late transition metal and an electron-deficient early transition metal. Further synthetic and structural studies of these compounds and their acyl and iminoacyl derivatives are presently underway.

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Supplementary Material Available: Spectroscopic and analytical data for **1**, **1**-d_1, **2**, **3**, and **3**-d_1 and tables of positional parameters and bond angles and distances for **3** (9 pages). Ordering information is given for any current masthead page.

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(15) Crystal data for **3**: Orange rectangular prisms were grown from a saturated toluene solution at −20 °C. A crystal of dimensions 0.13 × 0.17 × 0.28 mm was coated with petroleum jelly and mounted in a thin-walled capillary tube. Crystal data at 200 K are as follows: $(C_5H_5)(PMe_3)_2RuCH_2CH_2ZrCl(C_5H_5)_2$; $P2_1/n$ (an alternate setting of $P2_1/c$) a = 11.906 (3) Å, b = 14.001 (5) Å, c = 15.203 (5) Å, β = 99.83 (2)°, V = 2497 (2) $Å^3$, Z = 4, ρ(calcd) = 1.604 g cm^{-3}. Enraf-Nonius CAD-4 diffractometer, μ = 12.4 cm^{-1} (Mo Kα), data absorption corrected by using ABSOR, an analytical absorption correction program based on the original program AGNOST by L. Templeton and D. Templeton (Abstract E10, Am. Cryst. Assoc., Storrs, CT, 1973), $2\theta_{max}$ = 55°, data collected $h,k,\pm l$, N_{refl} = 6241 with 2735 reflections with $F_o > 3\sigma(F_o)$ used in the refinement. R = 0.055, R_w = 0.067 with $w = 0.8937/\sigma(F_o)^2 + 0.003157F_o^2$. Heavy-atom solution, full-matrix least-squares refinement (SHELX-76), all non-hydrogen atoms anisotropic; hydrogen atoms were placed at calculated positions (except for the hydrogen atoms on the bridging C_2H_4 which were located on a ΔF map) and refined with a common isotropic thermal parameter. A complete report of the structure will be reported in a full paper.

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