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Synthesis and reactions of directly bonded zirconium–ruthenium heterobimetallic complexes

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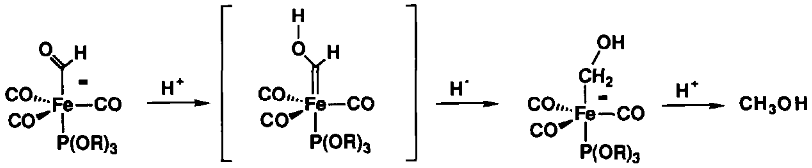
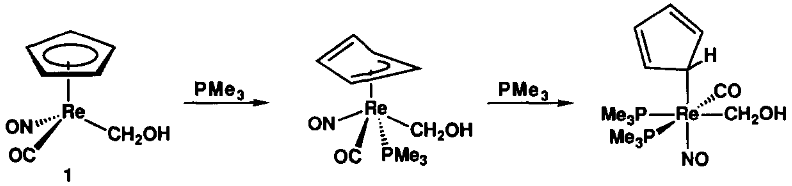
Abstract

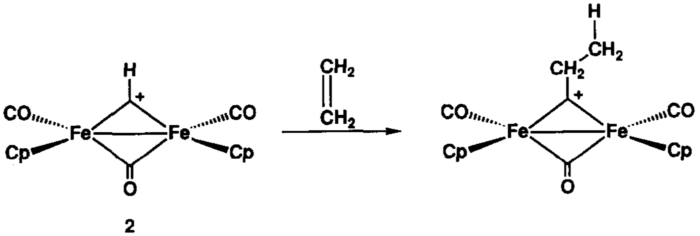
The directly bonded zirconium–ruthenium heterobimetallic compounds $Cp_2(X)ZrRu(CO)_2Cp$ (X = Cl, $OCMe_3$, CH_3, CH_2CH_3) were synthesized by reaction of $Cp_2(X)ZrCl$ with $K^+Cp(CO)_2Ru^-$. The zirconium–diruthenium compound $Cp_2Zr[Ru(CO)_2Cp]_2$ (**21**) was synthesized by reaction of Cp_2ZrI_2 with $K^+Cp(CO)_2Ru^-$. Reaction of **21** with a variety of ligands led to expulsion of $Cp(CO)_2RuH$ and formation of C_5H_4–Zr products or intermediates. Reaction of **21** with CO produced $Cp_2(CO)Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (**22**), with PMe_3 produced $Cp_2Zr(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)(PMe_3)$ (**23**), and with $CH_2{=}CH_2$ produced $Cp_2Zr(\mu\text{-}CH_2CH_2C_5H_4)Ru(CO)_2$ (**26**). All three of these reactions proceeded at the same rate which was independent of incoming ligand concentration. All three reactions are proposed to involve rate determining formation of the reactive intermediate $Cp_2Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (**I**). The reaction of the CO adduct **22** with H_2 led to hydrogenolysis of the Zr–C_5H_4 bond and to the formation of $Cp_2Zr(\mu\text{-}CO)(\mu\text{-}OCH)Ru(CO)Cp$ (**32**). Labelling studies demonstrated that reversible formation of both zirconium formyl and ruthenium formyl intermediates occurs during the reduction of **22** to **32**.

Introduction

The oil crisis in the mid-1970s induced a resurgence of interest in the Fischer–Tropsch process for converting coal via CO and H_2 into chemicals and hydrocarbon fuels. Organometallic chemists responded to this challenge by initiating fundamental studies of postulated intermediates in metal catalyzed CO reduction. In my group, Steve Neumann devised a new synthesis of metal formyl compounds from metal carbonyl complexes and borohydride reagents and we compared the structure, thermodynamic stability, and reactivity of closely related iron formyl and iron acetyl complexes [1]. Jim Rinz, a talented undergraduate, working with Mark Andrews, a postdoctoral research associate, synthesized the first hydroxymethyl metal complex $Cp(CO)(NO)ReCH_2OH$ (**1**) and studied its reactions [2]. In other work, we studied hydrogenation reactions of metal carbene complexes [3]. When the work of Pettit and others indicated that bridging methylene compounds might be key intermediates in CO reduction [4], Bill Miles and Paul Fagan in my group synthesized a diiron μ-methylene complex and converted it to $[Cp(CO)Fe]_2(\mu\text{-}$







CH)$^+$PF$_6^-$ (2) the first bridging methylidyne complex in which the μ-CH unit bridged two metals [5].

In the course of pursuing this work on model compounds related to CO reduction, we discovered, often by accident, some very interesting reactions. For example, when Bill Jones was trying to induce migration of the CH_2OH group of **1** to CO, he employed high concentrations of PMe_3 and discovered phosphine induced ring slippage reactions [6]. We then spent several years exploring $\eta^5 \Leftrightarrow [\eta^3] \Leftrightarrow \eta^1$ ring slippage of Cp complexes [7]. Paul Fagan was trying to insert ethylene into a carbon iron bond of the μ-CH ligand of **2** when he discovered the hydrocarbation reaction in which the μ-CH bond adds across the carbon–carbon double bond of alkenes [8]. For the next several years, our group worked on sorting out the mechanistic details of hydrocarbation and in devising other carbon–carbon bond forming reactions of diiron complexes [8].

Reinvestigations of heterogeneous and homogeneous CO hydrogenation catalysts provided improved understanding of the processes. Work at Union Carbide on rhodium catalyzed hydrogenation of CO to ethylene glycol appeared promising in the early 1980's, but the basic problem of finding a selective and active catalyst for CO reduction remained. It was becoming apparent that totally new kinds of catalyst systems would be required for a significant breakthrough. We thought that early–late heterobimetallic complexes held great promise as powerful new catalysts for CO reduction and we set out to study their chemistry. However, after nearly ten years of work by our group and many others, no new heterobimetallic catalysts for CO reduction have been made. Nevertheless, a great deal of fascinating new chemistry has been discovered and the hope of finding new catalysts remains.

Concept of an early–late heterobimetallic dihydride

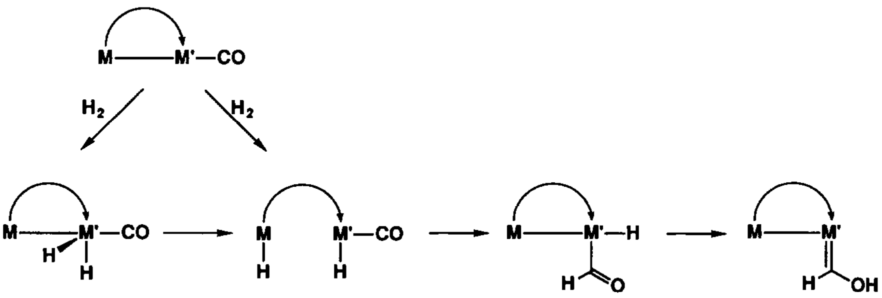
We set a long range goal of synthesizing a heterobimetallic dihydride having one hydridic M–H bond to a high oxidation state early transition metal (Ti, Zr, etc), one acidic M–H bond to a low oxidation state late transition metal (Co, Fe, Ru, Rh, etc.), and a heterodifunctional ligand joining the two metals. We believed such compounds would be powerful reducing agents for polar molecules including CO.

When we began our work, it was known that early transition metal hydrides were good donors of hydride to coordinated CO. Labinger had demonstrated that Cp_2NbH_3 reacted with $Fe(CO)_5$ to produce an unstable formyl species [9] and Bercaw had shown that $Cp^\star{}_2ZrH_2$ ($Cp^\star = C_5Me_5$) reacted with metal carbonyls such as $Cp_2W(CO)$ to produce a formyl species with zirconium bound to the formyl oxygen [10].

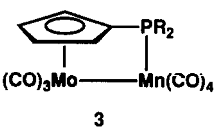
We had found that borohydrides would reduce metal carbonyls to formyl complexes, but the anionic formyl complexes were resistant to further reduction by hydride donors. However, further reduction of the anionic formyl $[(RO)_3P](CO)_3FeCHO^-$ to methanol occurred upon addition of acid [11]. Apparently, protonation of the formyl oxygen produced an intermediate neutral hydroxycarbene complex that was reduced by a less potent hydride source – a second molecule of the anionic formyl complex. We thought that a late transition metal hydride might be sufficiently acidic (for example, the pK_a of $(CO)_4CoH$ is 8.3 and of $(CO)_5MnH$ is 15.1 in acetonitrile [12]) to serve as a proton donor in CO reduction.

We thought a heterodifunctional ligand would serve to link the early and late transition metals and to maximize the opportunity for the two metal hydrides to act cooperatively to reduce CO.

Our initial plan was to synthesize a heterobimetallic dihydride by addition of H_2 to a metal-metal bonded system (Scheme 1). The obvious problem that a hydride and an acidic metal hydride might instantaneously react to form H_2 was optimistically viewed as the microscopic reverse of the desired reaction. We considered it more crucial to have rapid kinetic access to a heterobimetallic dihydride than to have the equilibrium lie far on the side of the heterobimetallic dihydride. We conceived of two possible routes to heterobimetallic dihydrides. First, direct cleavage of the metal–metal bond by H_2 might occur in a reaction that would now be termed a σ-bond metathesis. Second, oxidative addition to a late transition metal center might be followed by metal hydride elimination.



Scheme 1



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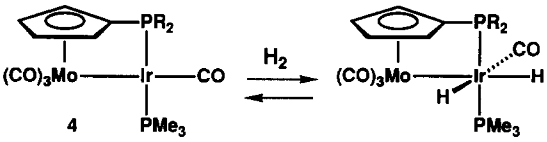

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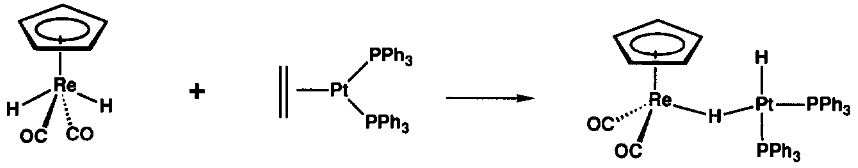

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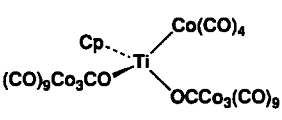
At the time we began this work, the problems of combining so many new features into a single system seemed monumental. We decided to take a deliberate systematic approach. Along one line of research, we synthesized bimetallic compounds linked by heterodifunctional ligands but employed metals with much smaller electronegativity differences than we ultimately would need [13]. Three milestones along this pathway will be mentioned. The first was Morris Bullock's synthesis of Mo–Mn compound **3** in which the two metals were linked by a heterodifunctional $C_5H_4PR_2$ ligand [14]. This coordinatively saturated compound failed to react with H_2 even under high pressure at 145° C. The second milestone was the synthesis of Mo–Ir compound **4** which added hydrogen reversibly to the iridium center at room temperature and under 1 atm pressure [15]. However, the molybdenum–iridium dihydride did not undergo metal hydride elimination to produce a heterobimetallic dihydride. The third milestone was Ed Rutter's synthesis of the rhenium platinum dihydride **5** from $Cp(CO)_2ReH_2$ and $(Ph_3P)_2Pt(CH_2{=}CH_2)$ which has one bridging and one terminal hydride [16]. Interestingly, **5** reduced alkynes to rhenium alkene complexes [17].

In this account, I will concentrate on our effort to synthesize heterobimetallic compounds with directly bonded early and late transition metals. Initially no effort was made to link the two metals by a heterodifunctional ligand. Since the emphasis in this account is on our own work and since a recent comprehensive review on early–late heterobimetallics has recently appeared [18], related work of other groups will be mentioned only peripherally.

Directly bonded zirconium–ruthenium compounds

When we initiated our efforts to make compounds with directly bonded early and late transition metals, the only known compound with a metal bound to a group 4 metal without a supporting carbonyl or other bridging ligand was Ti–Co compound **6** [19]. A major problem that we anticipated was that early and late transition metals can be joined by an isocarbonyl linkage as Stucky had found for Ti–Mo compound **7** [20] and Caulton and Norton had found for Zr–Mo compound **8** [21]. Fortunately, isocarbonyl linkages have a very low energy CO vibration that allows them to be easily distinguished from metal–metal bonded compounds.



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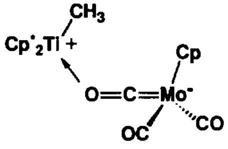

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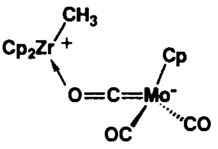

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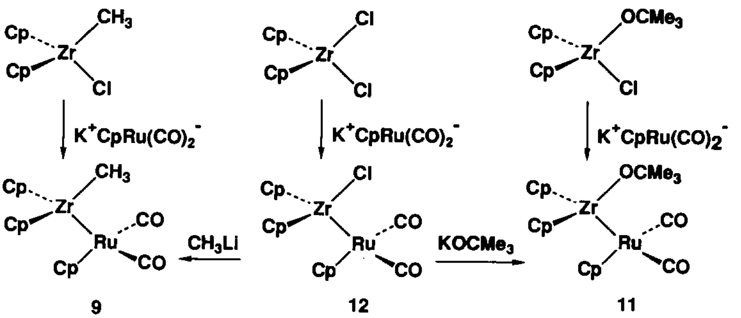
Rich Jordan initiated our work in this area by synthesizing a series of Zr–Ru and Zr–Fe compounds by reaction of zirconium halides with $Cp(CO)_2Ru^-$ and $Cp(CO)_2Fe^-$ [22]. Reaction of $Cp_2Zr(CH_3)Cl$ with $K^+CpRu(CO)_2^-$ in THF at room temperature produced the bright yellow metal–metal bonded compound $Cp_2(CH_3)ZrRu(CO)_2Cp$ (**9**) in 83% yield. The presence of two strong IR bands at 1950 and 1880 cm^{-1} indicated direct metal-metal bonding. These bands are shifted 45 and 120 cm^{-1} to higher energy from the corresponding bands of $K^+CpRu(CO)_2^-$ as expected for Zr–Ru bond formation; in contrast, an isocarbonyl linkage to Zr would have resulted in a shift of one of the carbonyl bands to much lower energy. **9** was thermally quite stable and underwent only about 40% decomposition after 3 hours at 90 °C. **9** was very water sensitive and rapidly hydrolyzed to give $[Cp_2(CH_3)Zr]_2O$ and $Cp(CO)_2RuH$ upon exposure to air. This indicated that the Zr–Ru bond was very polar and more easily hydrolyzed than the Zr–methyl bond. The related ethyl zirconium derivative $Cp_2(CH_3CH_2)ZrRu(CO)_2Cp$ (**10**) was similarly prepared from $Cp_2Zr(CH_2CH_3)Cl$ and $K^+CpRu(CO)_2^-$. It was somewhat less thermally stable than the methyl analog and underwent thermal decomposition at 50 °C as will be described in detail later.

The more hydrolytically stable t-butoxy zirconium compound $Cp_2(Me_3CO)ZrRu(CO)_2Cp$ (**11**) was prepared by reaction of $Cp_2Zr(OCMe_3)Cl$ with $K^+CpRu(CO)_2^-$ in 75% yield [22]. The Zr–Ru bond of **11** was cleaved slowly on treatment with Me_3COH. The corresponding chloro zirconium compound $Cp_2(Cl)ZrRu(CO)_2Cp$ (**12**) was prepared by careful addition of only one equivalent of $K^+CpRu(CO)_2^-$ to Cp_2ZrCl_2 [22]. Reaction of **12** with CH_3Li gave the methyl zirconium compound **9** and reaction with $KOCMe_3$ gave the t-butoxy compound **11**.

The X-ray crystal structure of t-butoxy zirconium compound **11** confirmed the presence of an unsupported Zr–Ru bond [22]. The Zr–Ru bond length of 2.910(1) Å is somewhat longer than the sum of covalent radii of about 2.70 Å as pointed out by



Scheme 2

Wolczanski [23] and is indicative of the crowded environment around the metal–metal bond. The wide 169° Zr–O–C angle indicated extensive π-donation from oxygen to zirconium.

The zirconium–iron compounds $Cp_2(CH_3)ZrFe(CO)_2Cp$ and $Cp_2(Me_3CO)ZrFe(CO)_2Cp$ were prepared in high yield by reaction of $K^+Cp(CO)_2Fe^-$ with the appropriate zirconium halide [22]. Because the Fe–Zr compounds were more sensitive than the corresponding Ru–Zr compounds, we concentrated our efforts on the more stable ruthenium compounds.

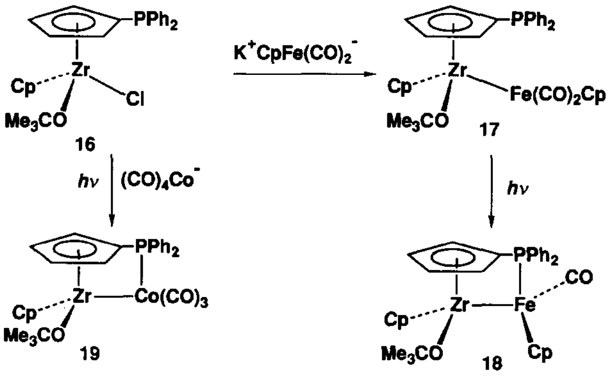
Reaction of $K^+Cp(CO)_2ReH^-$ with $Cp_2Zr(OCMe_3)Cl$ led to the isolation of the directly bonded zirconium–rhenium complex $Cp_2(Me_3CO)ZrRe(H)(CO)_2Cp$ (**13**) [24]. We have subsequently exploited the ability of $Cp(CO)_2ReH^-$ to form bonds to zirconium in a synthetic route to rhenium carbene complexes.

The tendency of Ti(IV) to be easily reduced to Ti(III) made it impossible to carry out analogous Ti–Ru chemistry. For example, reaction of Cp_2TiCl_2 with $K^+CpRu(CO)_2^-$ in THF led to oxidation of the ruthenium anion to $[Cp(CO)Ru]_2(\mu\text{-}CO)_2$ (**14**). The reaction of $Cp_2(Me_3CO)TiCl$ with $K^+CpRu(CO)_2^-$ was followed by ^1H NMR. Resonances due to ruthenium dimer **14** and resonances at δ 6.11 (Cp_2Ti), 5.09 (CpRu), and 1.15 ($TiOCMe_3$) attributed to $Cp_2(Me_3CO)TiRu(CO)_2Cp$ (**15**) were observed. Titanium–ruthenium compound **15** was stable at room temperature but could not be isolated as a pure material.

The tendency of $CpRu(CO)_2$ and $CpFe(CO)_2$ to form metal–metal bonds to Ti and Zr stands in stark contrast to the formation of isocarbonyl links between $CpMo(CO)_3$ and Ti or Zr. Selegue has observed a similar change in bonding mode between metal–metal bonding in $(Me_2N)_3TiM(CO)_2Cp$ (M = Fe, Ru) and isocarbonyl bridges for a related $CpMo(CO)_3$ analog [25]. Both steric and electronic factors favor metal–metal bonding for Zr–Ru compounds compared with Zr–Mo compounds. Thermodynamic protonation of mononuclear metal carbonyl anions invariably occurs at the metal center and, in the absence of overriding steric effects, metal carbonyl anions would be expected to add to the Lewis acidic Zr center and to form a metal–metal bond. Selegue has suggested that the site of binding of a Lewis acid to a metal carbonyl anion may be related to the nature of the HOMO of the metal carbonyl anion [25]. Bursten has done MO calculations on $CpCr(CO)_3^-$ that show a large 35% contribution of carbonyl oxygens to the HOMO while the HOMO of $CpFe(CO)_2^-$ has essentially no contribution from carbonyl oxygens [26]. The high thermodynamic stability of the d^6 electronic configuration may also be invoked to explain Zr–Ru bond formation. When the d^8 $CpRu(CO)_2^-$ forms a metal–metal bond to Zr, it attains a stable d^6 configuration whereas bonding via a carbonyl oxygen leaves Ru with a less stable d^8 configuration. In contrast, the d^6 $CpMo(CO)_3^-$ forms an isocarbonyl link to Zr and retains a d^6 configuration rather than forming a Mo–Zr bond and attaining a less stable d^4 configuration.

Early–late transition metal complexes linked by a metal–metal bond and a heterodifunctional ligand

Francois Nief in our group combined the use of the heterodifunctional $C_5H_4PPh_2$ ligand and the Zr–Fe bond-forming chemistry in the synthesis of Zr–Fe and Zr–Co compounds linked by a heterodifunctional ligand and by an early–late transition metal bond [27]. Reaction of $Cp(C_5H_4PPh_2)Zr(OCMe_3)Cl$ (**16**) with $K^+(C_5H_5)Fe$-



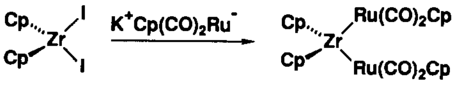
Scheme 3

$(CO)_2^-$ gave compound **17**, which has a Zr–Fe bond but no bond between the phosphine and Fe. Photolysis of **17** led to expulsion of one carbonyl and bonding of the phosphine to Fe in **18**. Both Zr and Fe are stereocenters in **18**, and separate resonances were seen for all four cyclopentadienyl protons on the $C_5H_4PPh_2$ ligand.

No reaction was observed between **16** and $Na^+Co(CO)_4^-$ until the solution was photolyzed; this led to loss of one CO from cobalt and formation of Zr–Co bonded compound **19**. Compounds **18** and **19** are the first examples of bimetallic compounds in which a group 4 metal and a late transition metal are joined by both a direct metal–metal bond and a heterodifunctional ligand.

$Cp_2Zr[Ru(CO)_2Cp]_2$—a trimetallic compound with two zirconium–ruthenium bonds

As an extension of our work with bimetallic zirconium–ruthenium complexes, Rich Jordan wanted to see if he could synthesize trimetallic compounds with two late transition metals bonded to zirconium. This seemed particularly interesting since the formation of an alternative isomeric structure related to Bercaw's zirconium–diiron complex **20** [28] seemed possible. Reaction of Cp_2ZrI_2 with two equivalents of $K^+CpRu(CO)_2^-$ in THF gave a 90% yield of orange crystalline $Cp_2Zr[Ru(CO)_2Cp]_2$ (**21**) [29]. The infrared spectra of **21** had two carbonyls at 1934 and 1882 cm^{-1} consistent with a metal–metal bonded structure. X-ray crystallography showed that **21** had two unsupported Zr–Ru bonds of 2.938(1) and 2.948(1) Å. These bonds are longer than the sum of covalent radii and indicate that **21** is a strained and crowded molecule. In the solid state, two sets of terminal CO ligands were seen: two CO's were in the plane defined by the three metals and two were nearly perpendicular to this plane. In the ^{13}C NMR of **21**, two CO signals were seen at δ 203.7 and 214.0 at $-60\,^\circ C$ and coalescence to a single peak at δ 207 occurred at $51^\circ C$. The barrier to the gear like rotation about the Zr–Ru bonds that interchanges carbonyl positions was found to be 13.5 kcal mol^{-1}. Reaction of $K^+CpFe(CO)_2^-$ with Cp_2ZrI_2 in THF at $-20\,^\circ C$ gave ^1H NMR evidence for formation of an unstable diiron compound $Cp_2Zr[Fe(CO)_2Cp]_2$ which decomposed upon warming above $-20\,^\circ C$.



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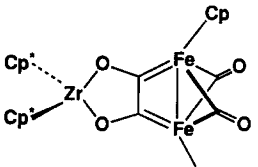

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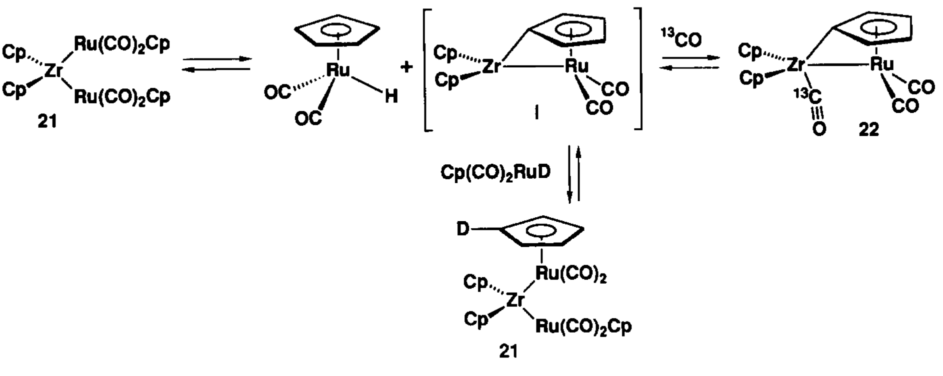
Bercaw has prepared $(C_5Me_5)_2ZrRu_2$ compounds similar to **20**. The difference between our compounds with direct Zr–Ru bonds and Bercaw's compounds are probably due to some combination of steric and electronic differences between C_5H_5 and C_5Me_5 ligands. Steric hinderance might prevent bonding of ruthenium to the more crowded $(C_5Me_5)_2Zr$ center, and the better electron donor properties of the C_5Me_5 ligand might enhance the reducing power of the $(C_5Me_5)_2Zr$ unit and lead to products similar to **20** in which the carbonyl units are reductively coupled and bonded to zirconium through oxygen.

Reversible elimination of $CpRu(CO)_2H$ from $Cp_2Zr[Ru(CO)_2Cp]_2$ (21)

The zirconium–diruthenium compound **21** was thermally stable in THF-d_8 to over 50 °C but reacted with a variety of ligands within several hours at room temperature. All of the reactions involved expulsion of $Cp(CO)_2RuH$ and formation of C_5H_4 products or intermediates.

Bob Palermo found that the reaction of **21** with 1 atm of CO in benzene occurred over several hours at room temperature to produce $Cp(CO)_2RuH$ and $Cp_2(CO)Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (**22**) [30]. Isolation of pure **22** required workup under a CO atmosphere. The structure of **22** was determined by X-ray crystallography and showed that the Zr and Ru centers are linked by a 3.064(1) Å metal–metal bond and by a bond from Zr to the η^5-C_5H_4 ligand on Ru. This Zr–C bond is bent 34° below the plane of the η^5-C_5H_4 ligand; the resulting angle strain is probably responsible for the unusually high reactivity of this Zr–C bond. The zirconium bound CO is bent slightly away from Ru (Zr–C–O, 167°) indicating a very weak interaction with the remote (2.70 Å) Ru. While the evidence for a Ru–CO interaction in **22** was not compelling, the observation of a much stronger Ru–CO



interaction in the related PMe_3 derivative **23** provided convincing evidence that the long range interaction in **22** was real.

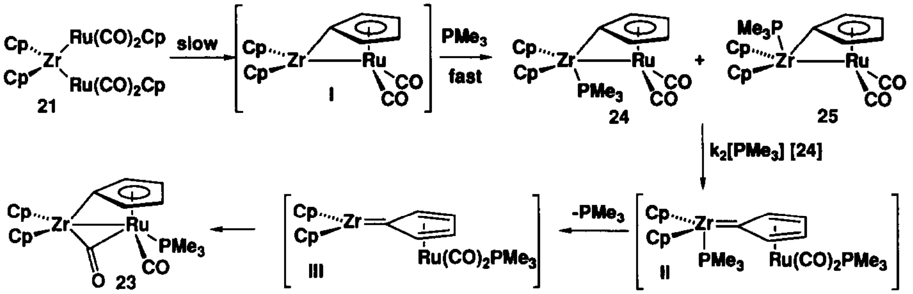
Our observation that pure **22** could only be isolated under a CO atmosphere led us to check for ^{13}CO exchange and for the reversibility of the formation of **22** [30]. When a THF-d_8 solution of **22** under 1 atm ^{13}CO at 0 °C was examined by ^{13}C NMR, instantaneous exchange of the Zr-bound carbonyl at δ 279 was seen; no exchange with the Ru-bound CO (δ 205) was observed over several days at room temperature. When the reaction of isolated **22** with $Cp(CO)_2RuH$ in toluene–THF was examined by ^1H NMR, we found that zirconium–diruthenium compound **21** was regenerated. These experiments are consistent with the hypothesis that **22** readily dissociates CO to form reactive intermediate **I** which then adds $Cp(CO)_2RuH$ across the strained $Zr–C_5H_4$ bond of **I** to reform **21**.

This hypothesis requires that intermediate **I** be formed reversibly from **21** in the absence of trapping ligands. To test this hypothesis, the reaction of **21** with 9.2 equiv of $Cp(CO)_2RuD$ in toluene was studied by ^2D NMR [31]. After 1.25 h, about 0.5 D was incorporated into the CpRu ring of **21**; and after 20 h, 3.4 D was incorporated into the CpRu ring of **21**. This provides strong evidence that reactive intermediate **I** is generated in the absence of a trapping ligand.

Our proposed mechanism requires that the rate of reaction of **21** with CO be independent of CO pressure. Indeed, Hideo Nagashima found that the initial rate of reaction of **21** with CO in THF-d_8 was pressure independent [32]. At 22 °C, the rates of reaction under 0.81 atm CO (2.78×10^{-4} s^{-1}) and under 0.47 atm CO (2.72×10^{-4} s^{-1}) were the same within experimental error.

Reaction of PMe_3 with zirconium–diruthenium compound **21** led to the formation of $Cp(CO)_2RuH$ and $Cp_2Zr(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)(PMe_3)$ (**23**) which was characterized by X-ray crystallography [30]. In **23**, the interaction of the more electron rich phosphine substituted ruthenium with the Zr-bound CO is substantially stronger than in **22**. The 2.21 Å Ru to bridging CO distance is 0.5 Å shorter than in CO product **22**. The wider Zr–C–O angle of 145° compared with the Ru–C–O angle of 127° is consistent with a semi-bridging interaction with Ru. The bridging carbonyl is bound tightly in **23** and did not exchange with ^{13}CO. The PMe_3 product **23** is qualitatively different from CO product **22** in that the new ligand is bound to Ru and not to Zr.

The kinetics of the reaction of **21** with varying concentrations of PMe_3 in THF-d_8 were followed by ^1H NMR. The rate of disappearance of **21** was first order in **21**



Scheme 4

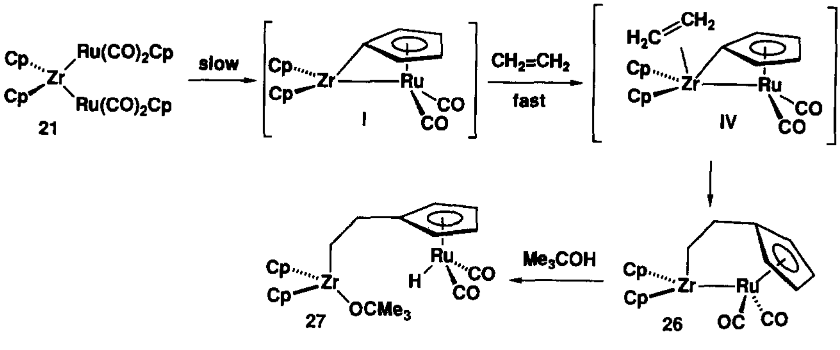
and independent of PMe_3 concentration within experimental error [31]. The first order rate constants at 26 °C were 3.2×10^{-4} s^{-1} at 0.21 M PMe_3 and 3.7×10^{-4} s^{-1} at 0.42 M PMe_3. These first order rate constants are similar to the rate constants for reaction of **21** with CO at 22° C, suggesting that both reactions involve rate determining formation of reactive intermediate **I**.

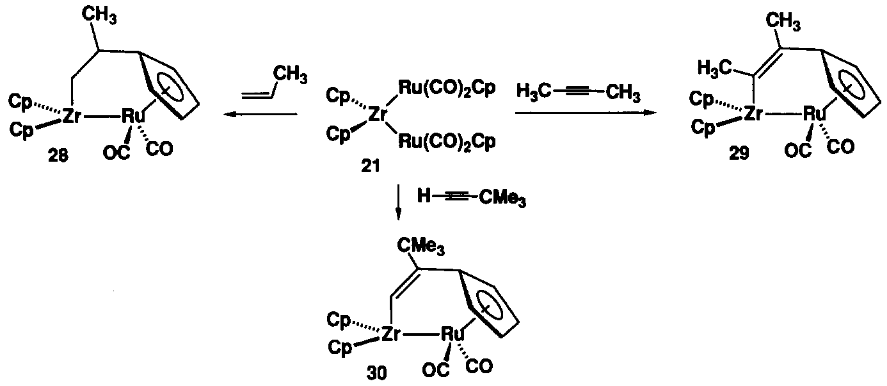
In the course of measuring the kinetics of the reaction of **21** with PMe_3, Bob Palermo observed the formation of two intermediates in a 2 : 1 ratio by ^1H NMR. The major intermediate (**24**) had a Cp_2Zr doublet at δ 5.85 with a 1.4 Hz coupling to phosphorus in addition to a doublet at δ 1.53 for the PMe_3 ligand and an AA′XX′pattern at δ 3.97 and 5.21 for a C_5H_4 fragment. The minor intermediate (**25**) had similar resonances at δ 5.80 (d, $J = 1.4$ Hz, Cp_2Zr), 2.60 (PMe_3), and 5.10 and 4.24 (C_5H_4). These spectra are consistent with intermediates formed by addition of PMe_3 to the two different faces of intermediate **I**. We are unable to assign the stereochemistry of **24** and **25**.

The build-up of intermediates **24** and **25** was greater at lower PMe_3 concentration. At 0.21 M PMe_3, the total concentration of intermediates peaked at 42%, while at 0.42 M PMe_3, the maximum concentration of intermediates was 30%. The rise and fall of the concentrations of the intermediates was fitted to a kinetic model involving first order conversion of **21** to intermediates **24** and **25**, followed by a second order reaction of **24** or **25** with a second equivalent of PMe_3 [31].

The mechanism we favor for generation of intermediates **24** and **25** and their conversion to **23** is shown in Scheme 4. The rate determining step is the expulsion of $Cp(CO)_2RuH$ from **21** as in the case of the reaction with CO. The reactive intermediate **I** is efficiently trapped by PMe_3 to generate the intermediates **24** and **25** which are close analogs of CO product **22**. The kinetics of the reaction demand that conversion of intermediates **24** and **25** to final product **23** involve attack by a second equivalent of PMe_3. We suggest that attack of PMe_3 on **24** and/or **25** occurs at Ru and breaks the Zr–Ru bond to form **II** which subsequently loses PMe_3 from zirconium to form **III** which then couples to form the Zr–Ru bridging carbonyl unit of **23**.

Bob Palermo also found that the reaction of alkenes and alkynes with zirconium-diruthenium compound **21** led to the expulsion of $Cp(CO)_2RuH$ and formation of a third type of adduct in which the alkene or alkyne inserted into the strained $Zr–C_5H_4$ bond of reactive intermediate **I**. For example, reaction of ethyl-

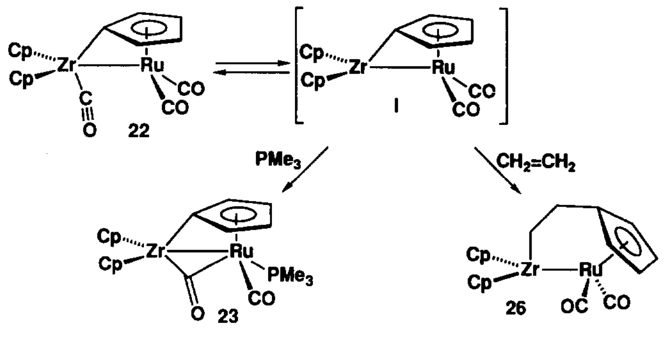




ene with **21** occurred at room temperature to produce $Cp_2Zr(\mu\text{-}CH_2CH_2C_5H_4)Ru(CO)_2$ (**26**), which was characterized by spectroscopy and derivatization with $(CH_3)_3COH$ [30]. The similarity of the IR carbonyl bands of **26** at 1948 and 1888 cm^{-1} to those seen for $Cp_2(CH_3)ZrRu(CO)_2Cp$ (**9**) suggested the presence of a Zr–Ru bond. In the ^1H NMR of **26**, the mirror symmetric bridging $CH_2CH_2C_5H_4$ ligand gave rise to one AA′XX′ pattern at δ 4.75 and 4.19 for the cyclopentadienyl protons and to a second AA′XX′ pattern at δ 2.18 and 0.28 for the CH_2CH_2 unit. Reaction of **26** with $(CH_3)_3COH$ resulted in cleavage of the Zr–Ru bond and formation of $Cp_2[(CH_3)_3CO]Zr(\mu\text{-}CH_2CH_2C_5H_4)Ru(CO)_2$ (**27**).

Reaction of propene with **21** led to regioselective formation of $Cp_2Zr[\mu\text{-}CH_2CH(CH_3)C_5H_4]Ru(CO)_2$ (**28**), in which propene inserted into the strained $Zr\text{–}C_5H_4$ bond of intermediate **I** to form the less substituted alkyl zirconium product [31]. 2-Butyne reacted with **21** to produce $Cp_2Zr[\mu\text{-}(CH_3)C{=}C(CH_3)C_5H_4]Ru(CO)_2$ (**29**) which was characterized by X-ray crystallography [31]. Reaction of t-butyl acetylene with **21** led to regioselective insertion of the alkyne into the $Zr\text{–}C_5H_4$ bond of reactive intermediate **I** and formation of the less substituted alkenyl zirconium product $Cp_2Zr[\mu\text{-}CH{=}C(CMe_3)C_5H_4]Ru(CO)_2$ (**30**).

The kinetics of the reaction of **21** with $CH_2{=}CH_2$ in THF-d_8 at 26 °C were studied by ^1H NMR. As in the cases of the reactions of **21** with CO and with PMe_3, the rate was independent of the concentration of the incoming group. The first



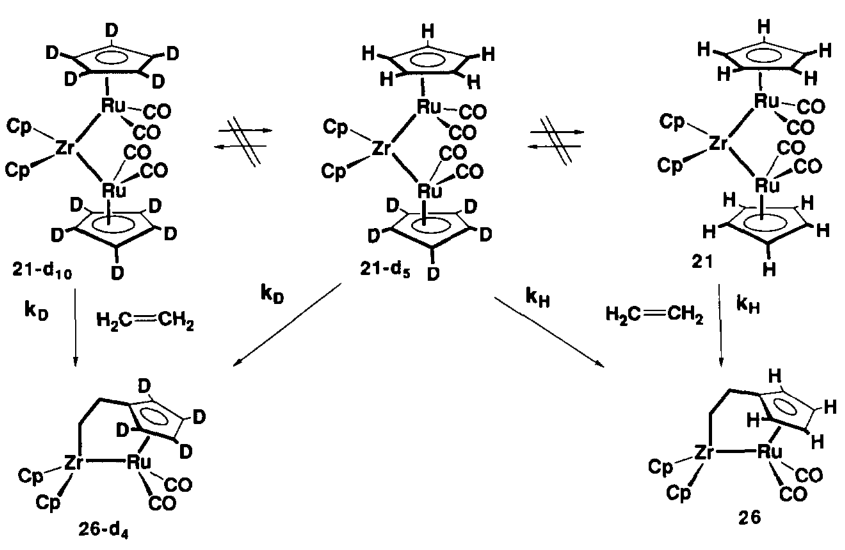
order rate constant for reaction of **21** with 0.12 *M* $CH_2{=}CH_2$ (3.3×10^{-4} s^{-1}) and with 0.23 *M* $CH_2{=}CH_2$ (3.7×10^{-4} s^{-1}) were the same within experimental error. The fact that the first order rate constants for the reactions of **21** with CO, PMe_3, and $CH_2{=}CH_2$ are all the same provides strong evidence that all three reactions involve rate determining formation of the same reactive intermediate **I**. Although no intermediates were observed in the reaction of **21** with $CH_2{=}CH_2$, we propose that ethylene coordinates to Zr to form adduct **IV** prior to insertion into the $Zr{-}C_5H_4$ bond.

In agreement with our proposal that **I** is the key intermediate in the reversible formation of CO adduct **22**, PMe_3 adduct **23**, and ethylene insertion product **26**, Bob Palermo found that **22** reacted with PMe_3 to produce **23** via intermediates **24** and **25**, and that **22** reacted with ethylene to produce **26** [31].

Mechanism of the formation of the reactive intermediate $Cp_2Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (I)

Fred Askham carried out more detailed mechanistic studies of the formation of the reactive intermediate $Cp_2Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (**I**) from zirconium-diruthenium compound **21** [33]. He prepared **21**-d_{10} in which the CpRu groups were nearly fully deuterated (94% d_{10}). The first order rate constants for reaction with ethylene in benzene-d_6 at 26 °C were $1.2 \pm 0.3 \times 10^{-4}$ s^{-1} for **21** and $2.8 \pm 0.3 \times 10^{-5}$ s^{-1} for **21**-d_{10}. After correcting for incomplete deuteration, this corresponds to a kinetic isotope effect $k_H/k_D = 4.5 \pm 1.0$. This large kinetic isotope effect indicates that the transition state for reaction of **21** involves extensive C–H bond breaking.

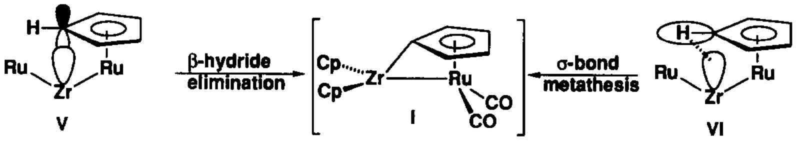
This large kinetic isotope effect allowed Fred Askham to carry out an unusual crossover experiment to determine whether the formation of reactive intermediate **I** occurred by an intra- or intermolecular pathway [33]. The nature of the crossover experiment can best be understood by examining Scheme 5. If the reaction is

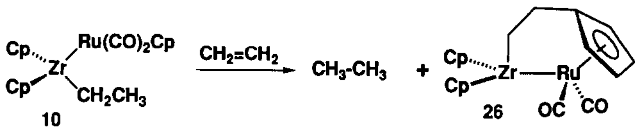


Scheme 5

intramolecular, then a mixture of **21** : **21**-d_{10} should produce the same ratio of products **26** : **26**-d_4 when both reactions have gone to completion. If the reaction is intermolecular or involves prior scrambling of $Cp(CO)_2Ru$ units to give a mixture of **21**, **21**-d_5, and **21**-d_{10}, then because of the kinetic isotope effect, **21**-d_5 would be selectively converted to a 4.5 : 1 mixture of **26** : **26**-d_4. The net effect is that an intermolecular mechanism would produce a higher ratio of protio : deuterio ethylene insertion products **26** : **26**-d_4 than the ratio of starting materials **21** : **21**-d_{10}.

Reaction of a benzene solution containing a 0.75 ± 0.03 ratio of **21** : **21**-d_{10} with excess ethylene produced a 0.70 ± 0.03 ratio of **26** : **26**-d_4. Since we know that **21** undergoes spontaneous reversible expulsion and readdition of $Cp(CO)_2RuH$ in the absence of added ligands, it was crucial to avoid having **21** and **21**-d_{10} together in the absence of a trapping ligand. The ratio of **21** : **21**-d_{10} was determined by ^1H NMR comparison of the Cp_2Zr and CpRu resonances of **21**, while the ratio of **26** : **26**-d_4 was determined by comparison of the Cp_2Zr and C_5H_4Zr resonances of **26**. The experimentally indistinguishable ratios of deuterated starting materials and products establishes the intramolecular nature of the elimination of $Cp(CO)_2RuH$ from **21** and excludes intermolecular mechanisms involving either homolytic or heterolytic cleavage of Zr–Ru bonds.

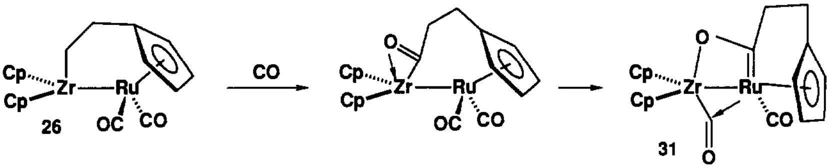




Two different explanations for the facile intramolecular elimination of $Cp(CO)_2RuH$ from **21** seemed plausible. First, interaction of an empty orbital on zirconium with a filled π-orbital of a Ru-bound Cp ligand as depicted in **V** sets up a β-relationship between the second Ru and a cyclopentadienyl hydrogen; β-hydride elimination would then produce $Cp(CO)_2RuH$ and intermediate **I**. Second, an agostic interaction between zirconium and a C–H bond of a Ru-bound Cp ligand as depicted in **VI** would enhance the acidity of the C–H bond; the second Ru center could then act as an intramolecular base to deprotonate the Cp group and produce $Cp(CO)_2RuH$ and intermediate **I**. This latter pathway is essentially a σ-bond metathesis reaction [34]. A possible distinction between these descriptions is that the β-hydride elimination requires two ruthenium atoms bonded to zirconium while the agostic interaction description requires one ruthenium atom and a basic group. Hideo Nagashima's observation that $Cp_2(CH_3CH_2)ZrRu(CO)_2Cp$ (**10**) reacted with ethylene at room temperature to produce **26** with a time for half reaction of 7 h suggests that a second metal center is not required for the generation of **I** from **21** and that the reaction is best viewed as a σ-bond metathesis reaction [32].

Zirconoxycarbene complexes of ruthenium

Reaction of ethylene insertion product **26** with 1 atm CO at room temperature produced the zirconoxycarbene complex **31** in high yield [35]. The structure of **31** was determined by X-ray crystallography. The two metals are linked by a direct Zr–Ru bond (3.007 Å), by a zirconoxycarbene bound to Ru, and by a semibridging carbonyl bound strongly to Zr. The ^{13}C NMR resonances at δ 205 for the terminal RuCO, at δ 316 for the semibridging CO, and at δ 279 for the carbene carbon and IR bands at 1909 cm^{-1} for the terminal RuCO, 1704 cm^{-1} for the semibridging CO, and 1380 cm^{-1} for the C–O stretch of the zirconoxycarbene were very useful in characterizing **31** and related compounds.



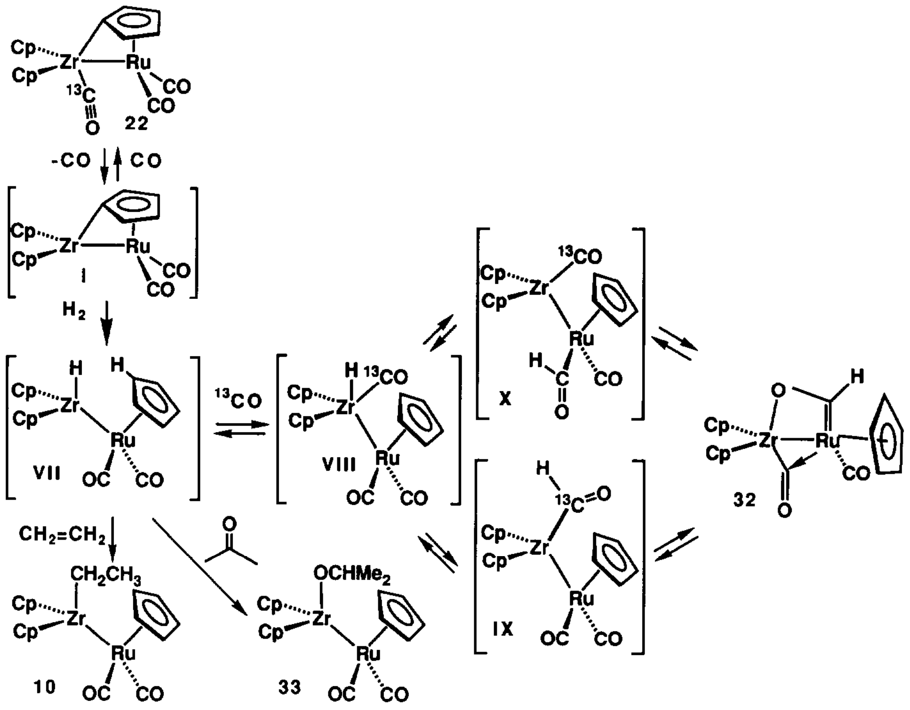
When the reaction of **26** with ^{31}CO was studied by ^{13}C NMR, the isotopic label initially appeared only at the carbonyl carbon of **31**. This observation is consistent with initial insertion of CO into the Zr–CH_2 bond to form an η^2-acyl intermediate, followed by rapid transfer of the very electrophilic η^2-acyl carbon to the electron rich ruthenium. Such acyl transfers have been observed before in Zr–Mo systems [21] and may be a general phenomenon for early–late heterobimetallic compounds.

Reaction of $Cp_2(CO)Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (22) with hydrogen-reduction of coordinated CO

When Bob Palermo reacted the CO adduct **22** with 1 atm H_2 at room temperature in THF for several hours, he obtained the zirconoxycarbene complex $Cp_2Zr(\mu\text{-}CO)(\mu\text{-}OCH)Ru(CO)Cp$ (**32**) [35]. No intermediates were observed by NMR. The structure of **32** was established by spectroscopic comparison with the closely related zirconoxycarbene complex **31**. The hydrogen attached to the carbene carbon appears far downfield at δ 14.05 in the ^{1}H NMR of **32**. The IR spectrum had bands for a terminal RuCO at 1930 cm^{-1}, for a semibridging ZrCO at 1740 cm^{-1}, and for the C–O stretch of the zirconoxycarbene at 1350 cm^{-1}. The ^{13}C NMR of **32** had resonances at δ 205 for the RuCO, at δ 306 for the semibridging ZrCO, and at δ 266 for the carbene carbon.

The proposed mechanism for the formation of **32** is shown in Scheme 6. We propose that dissociation of CO from **22** produces reactive intermediate **I** which was shown to be involved in other reactions of **22** including rapid ^{13}CO exchange. The 16e reactive intermediate **I** has a vacant Zr based orbital available for interaction with H_2. We suggest that a σ-bond metathesis reaction of H_2 with the strained Zr–C_5H_4 bond of **I** produces zirconium hydride intermediate **VII**. There are two plausible routes from **VII** to **32**. In the first route, coordination of CO to the Zr center of **VII** would produce zirconium carbonyl hydride complex **VIII**. Insertion of this carbonyl into the Zr–H bond of **VIII** would produce η^2-formyl zirconium complex **IX**. Formyl migration to Ru would then produce **32**. In the second route, addition of a Zr–H to a RuCO produces a ruthenium formyl complex **X** and eventually **32**.

We thought that these two alternatives could be readily distinguished by ^{13}CO labeling experiments using $Cp_2(^{13}CO)Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (**22**-^{13}CO). The zirconium formyl mechanism predicts ^{13}C label exclusively at the zirconoxycarbene

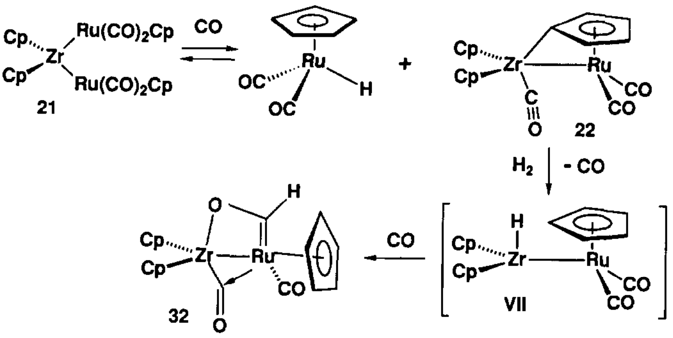


Scheme 6

carbon, while the ruthenium formyl mechanism predicts ^{13}C label exclusively at the semibridging CO bound to Zr. Surprisingly, when Hideo Nagashima studied the reaction of **22**-^{13}CO with H_2 by ^{13}C NMR, he found ^{13}C label equally distributed between three positions: the Zr–CO, the Ru–CO, and the carbene carbon of **32** [32]. Even at low conversion, the ^{13}C label was evenly distributed among these three centers in **32**. In a separate experiment, the exchange of ^{13}CO into unlabeled **32** was followed by ^{13}C NMR at room temperature. Exchange occurred with a time for half reaction of about 1 h and label entered all three sites at the same rate within experimental error. This data is consistent with rapid and reversible formation of **32** via *both* the zirconium formyl and the ruthenium formyl routes. It also suggests that CO dissociation from zirconium carbonyl hydride intermediate **VIII** can occur to regenerate zirconium hydride intermediate **VII**.

To test the hypothesis that zirconium hydride intermediate **VII** was accessible from zirconoxycarbene complex **32**, Hideo Nagashima reacted **32** with ethylene and trapped **VII** by hydrozirconation which produced ethyl zirconium compound $Cp_2(CH_3CH_2)ZrRu(CO)_2Cp$ (**10**) [32]. Similarly, reaction of **32** with acetone led to trapping of **VII** and formation of $Cp_2(Me_2CHO)ZrRu(CO)_2Cp$ (**33**).

It should be noted that reaction of $Cp_2Zr[Ru(CO)_2Cp]_2$ (**21**) 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 $Cp_2Zr(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ru(CO)_2$ (**I**). Thus, our initial goals of generating a hydridic M–H bond and an acidic M–H bond by reaction of H_2 with a heterobimetallic compound and of using these hydrides for CO reduction has in



some sense been formally achieved by this circuitous route. We are continuing to explore the area of heterobimetallic chemistry in the search for effective reducing agents.

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