Organometallics 1992, 11, 4261-4267

Insertion and β-Hydride Elimination Reactions of Ruthenium/Zirconium Complexes Containing C_2 Bridges with Bond Orders of 1, 2, and 3

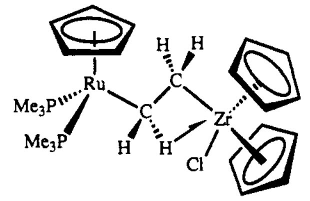
Frederick R. Lemke[†] and R. Morris Bullock*

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

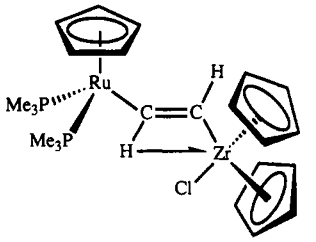
Received May 26, 1992

Carbon dioxide inserts into the Zr–C bond of $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$, producing the carboxylate complex $Cp(PMe_3)_2RuCH{=}CHCO_2ZrClCp_2$. An η^2-iminoacyl insertion product, $Cp(PMe_3)_2Ru{-}C{\equiv}C{-}C(N^tBu)ZrClCp_2$, results from insertion of ${}^tBuNC$ into the Zr–C bond of the dimetalloalkyne complex $Cp(PMe_3)_2Ru{-}C{\equiv}C{-}ZrClCp_2$. The reaction of $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$ with high concentrations of ${}^tBuNC$ also produces an η^2-iminoacyl insertion product, $Cp(PMe_3)_2RuCH_2CH_2C(N^tBu)ZrClCp_2$. At low concentrations of ${}^tBuNC$, a competing reaction is β-hydride elimination from $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$ to give $Cp(PMe_3)_2RuCH{=}CH_2$ and $Cp_2Zr(H)Cl$, which is trapped by ${}^tBuNC$ under these conditions to give $Cp_2ZrCl(\eta^2\text{-}{}^tBuN{=}CH)$. The reaction of benzophenone with $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$ gives the insertion product $Cp(PMe_3)_2RuCH_2CH_2CPh_2OZrClCp_2$. β-Hydride elimination is also observed from $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$; in the presence of excess ${}^nBuC{\equiv}CH$, the products are $Cp(PMe_3)_2Ru{-}C{\equiv}C{-}H$ and the zirconium vinyl complex $Cp_2Zr(Cl)CH{=}CH^nBu$.

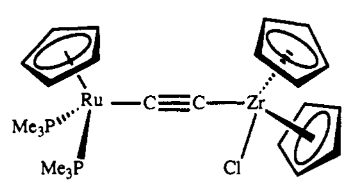
Organometallic complexes bridged by hydrocarbon ligands[1] are of interest since they provide useful models for species thought to be present in heterogeneous catalytic reactions or on metal surfaces. Our research in this area has focused on bimetallic complexes linked by C_2 bridges, and we recently reported[2] the synthesis, spectra, and crystallographic characterization of the homologous series of complexes (shown in 1–3) in which an electron-rich ruthenium center $[Cp(PMe_3)_2Ru]$ and an electron-deficient zirconium center $[Cp_2ZrCl]$ are linked by C_2 bridges of bond orders of 1, 2, and 3.



1

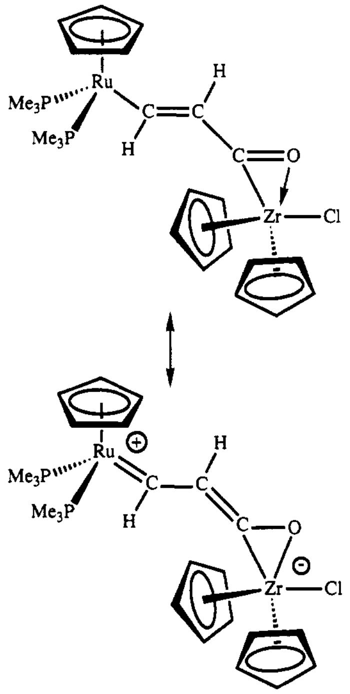


2



3

The formation of metal acyl complexes by insertion of CO into a metal–carbon bond is of fundamental importance to many catalytic processes. We found that carbonylation of the dimetalloalkene complex 2 proceeds cleanly under mild conditions (1 atm of CO, room temperature) to give the η^2-acyl complex 2-CO in which CO has inserted into the Zr–C bond.[2] Spectroscopic and crystallographic data indicated that the zwitterionic resonance form shown above was a substantial contributor to the electronic structure of the η^2-acyl complex 2-CO.



2-CO

In this paper, we report additional reactions in which metal–carbon and carbon–carbon bonds are made or broken, including insertion reactions of 1, 2, and 3 with unsaturated organic compounds. Under some conditions, the insertions occur cleanly, but in cases where insertion is less favorable, β-hydride elimination from 1 or 2 occurs.

[†] Present address: Department of Chemistry, Ohio University, Athens, OH 45701-2979.

(1) For reviews of organometallic hydrocarbon-bridged complexes, see: (a) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339–352. (b) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135–201. (c) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171–190.

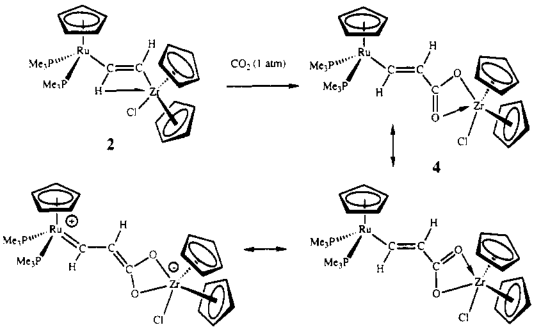
(2) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466–8477.

0276-7333/92/2311-4261$03.00/0

These β-hydride elimination reactions are the reverse of the synthetic reactions used to prepare 1 and 2 (e.g., 1 was prepared from the reaction of $Cp(PMe_3)_2RuCH{=}CH_2$ with $[Cp_2Zr(H)Cl]_n$).

Results and Discussion

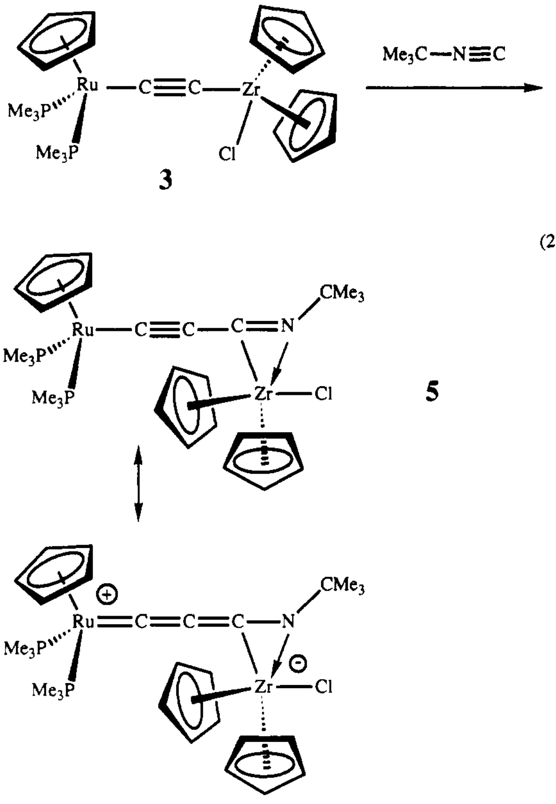
Insertion of CO_2 into Zr–C Bond of $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$. Although formation of metal carboxylates by insertion of CO_2 into a metal–carbon bond is commonly observed for many transition metals,[3] the zirconium complex $Cp_2(Cl)Zr(n\text{-hexyl})$ is reported[4] to be unreactive toward CO_2 (6 atm) at 50 °C. This lack of reactivity for a $Cp_2(Cl)ZrR$ complex containing a saturated alkyl group contrasts with the facile insertion of CO_2 into the Zr–C bond of the dimetalloalkene complex 2 (eq 1),



(1)

which occurs within 30 min at room temperature when a THF solution of 2 is stirred at room temperature under CO_2 (1 atm). Although insertion of CO_2 does not occur for $Cp_2(Cl)ZrR$ (R = alkyl), Cutler and co-workers[5] have reported other routes for the preparation of the alkyl and aryl carboyxlate complexes $Cp_2(Cl)Zr(\eta^2\text{-}O_2CR)$ (R = Me, Ph, etc). The ^{13}C NMR resonance (δ 175.7) that we assign to the CO_2 of $Cp(PMe_3)_2RuCH{=}CHCO_2ZrClCp_2$ (4) appears at a position similar to resonances reported by Cutler and co-workers for $Cp_2(Cl)Zr(\eta^2\text{-}O_2CPh)$ (δ 171.9) and $Cp_2(Cl)Zr(\eta^2\text{-}O_2CCH_3)$ (δ 187.1). Similarly, the IR bands (1415, 1441 sh, and 1491 cm^{-1}) which we observe for carboxylate complex 4 are similar to those assigned by Cutler to the symmetric and asymmetric $\nu(CO_2)$ stretches of the bidentate (η^2) carboxylate ligand. Spectra of $Cp_2(Cl)Zr(\eta^2\text{-}O_2CR)$ in THF exhibited intense bands at >1700 cm^{-1} which were assigned to the THF adduct of η^1-carboxylates, $Cp_2(Cl)Zr[\eta^1\text{-}OC({=}O)R](THF)$. In contrast, IR spectra of the bimetallic carboxylate complex 4 in THF solution are very similar to those obtained from KBr pellets, suggesting that the carboxylate ligand of 4 remains η^2-bonded in THF solution. The downfield chemical shifts of the Ru*CH* moiety of 4 in the ^1H NMR (δ 10.64) and ^{13}C NMR (δ 208.7) are suggestive of a modest contribution from a zwitterionic resonance form which exhibits ruthenium carbene character, as shown in eq 1. It is possible that the partial zwitterionic character of 4 is responsible for stabilizing the η^2 form and inhibiting the $\eta^2 \rightarrow \eta^1$ dissociation that would have enabled the ligation of THF. Solutions of 4 which were kept at room temperature for several days showed slow decomposition to unidentified products (in the presence or absence of 1 atm of CO_2 over the solution), and crystals suitable for a crystal structure determination were not obtained.

Reaction of $Cp(PMe_3)_2Ru{-}C{\equiv}C{-}ZrClCp_2$ with ^tBuNC. The reaction of $Cp(PMe_3)_2Ru{-}C{\equiv}C{-}ZrClCp_2$ (3) with ^tBuNC produced the η^2-iminoacyl complex $Cp(PMe_3)_2RuC{\equiv}CC(N^tBu)ZrClCp_2$ (5, eq 2). This insertion reaction is noteworthy since insertions of CO or isocyanides into the M–C bond of metal alkynyl complexes are rarely observed. Other than the preparation of 5 described here, the only other cases of insertion into the M–C bond of a dimetalloalkyne of which we are aware are isocyanide insertions into the Pd–C bonds of a series of $Pd{-}C{\equiv}C{-}Pd$ complexes studied by Takahashi and co-workers.[6] A particularly interesting result of their work is the double insertion of PhNC into a Pd–C bond, giving $Cl(PEt_3)_2PdC{\equiv}CC({=}NPh)C({=}NPh)Pd(PEt_3)_2Cl$, which was crystallographically characterized.



(2)

The characteristic ^{13}C NMR resonance of the iminoacyl carbon of the Ru/Zr η^2-iminoacyl complex 5 was observed at δ 217.5, which is similar to resonances found in other η^2-iminoacyl complexes of early transition metals.[7] The $\nu(C{\equiv}C)$ stretching frequency of 2003 cm^{-1} in the IR spectrum of 5 appears at a lower energy than typically found for metal alkynyl complexes (~2100 cm^{-1}).[8] On the other hand, the $\nu(C{\equiv}C)$ stretching frequency of this iminoacyl complex appears at a significantly higher frequency than that of dimetalloalkyne 3 (1868 cm^{-1}), which was suggested[2] to have a moderate contribution from the

---

(3) For reviews of the transition metal chemistry of CO_2, see: (a) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129–168. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747–764. (c) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661–678. (d) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135–174. (e) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651–731. (f) Ayers, W. M., Ed. *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988.

(4) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.

(5) Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877–2881.

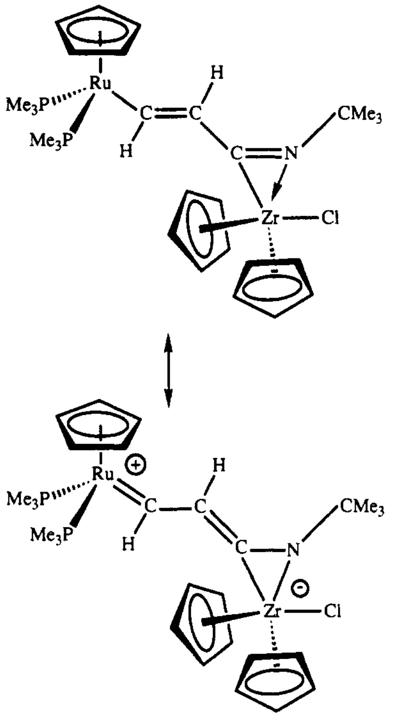
(6) (a) Ogawa, H.; Joh, T.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1988**, 561–562. (b) Onitsuka, K.; Ogawa, H.; Joh, T.; Takahashi, S.; Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Daltons Trans.* **1991**, 1531–1536.

(7) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079.

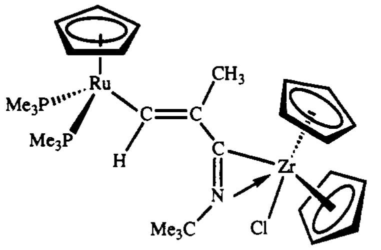
(8) For example, the $\nu(C{\equiv}C)$ stretching frequency of $Cp(PMe_3)_2RuC{\equiv}CCH_3$ appears at 2098 cm^{-1}. Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203–2207.

zwitterionic resonance form. In the ^{13}C NMR, the RuC resonance at δ 188.0 (t, $^2J_{PC}$ = 24 Hz) for **5** is suggestive of some Ru carbene character, since it appears significantly farther downfield than normal for metal alkynyl complexes [cf. δ 91.5 (t, $^2J_{PC}$ = 26 Hz) for the Ru*C* of Cp$(PMe_3)_2RuC{\equiv}C(CMe_3)$].[9] The spectroscopic data are thus consistent with a small contribution from the zwitterionic resonance form shown in eq 2.

A relevant comparison may be made between **5** and **6H**, the product resulting[10] from insertion of ^tBuNC into the Zr–C bond of **2**, the C=C double bond analog of **3**. As in the case of the η^2-acyl complex **2-CO**, structural and spectroscopic data for **6H** suggested the viability of a contribution from the zwitterionic resonance form. In contrast, structural and spectroscopic data indicated[10] a negligible contribution of the zwitterionic resonance form for the η^2-iminoacyl complex with a methyl group (**6Me**),



6H



6Me

due to steric inhibition of resonance caused by an unfavorable steric interaction of this methyl group with the ^tBu group in a conformation that would have enabled the requisite coplanarity of the metals and bridging organic ligand. Although attempts to grow crystals of **5** suitable for X-ray diffraction have been unsuccessful, the contribution from the zwitterionic resonance form that was deduced from an interpretation of the spectroscopic data for **5** does not appear to be precluded on steric grounds, as there are no obvious steric constraints preventing coplanarity of the bridging ligand and the metals.

Reaction of ^tBuNC with Cp$(PMe_3)_2RuCH_2CH_2ZrClCp_2$. When C–C single-bond compound **1** was dissolved in neat ^tBuNC, a yellow solution resulted, and a yellow precipitate formed after about 30 min. The η^2-iminoacyl complex Cp$(PMe_3)_2RuCH_2CH_2C(N^tBu)ZrClCp_2$ (**7**) was isolated in 77% yield from this reaction (Scheme I). Although ^tBuNC is certainly an unconventional solvent, it is useful for this (and other)[10] insertion reactions, and it is sufficiently volatile that the unreacted solvent can be readily recovered by vacuum transfer on a vacuum line for later use. In contrast, when the reaction of **1** (~0.03 M) was carried out with only a slight excess of ^tBuNC (~1.2 equiv) in C_6D_6, the ruthenium-containing products consisted of the η^2-iminoacyl complex **7** and the ruthenium vinyl complex Cp$(PMe_3)_2RuCH{=}CH_2$ in a ~3:1 ratio. The other product observed was the η^2-iminoformyl complex $Cp_2ZrCl(\eta^2\text{-}^tBuN{=}CH)$, which results from insertion of ^tBuNC into the Zr–H bond of $Cp_2Zr(H)Cl$. A sample of $Cp_2ZrCl(\eta^2\text{-}^tBuN{=}CH)$ was independently synthesized from the reaction of ^tBuNC with $[Cp_2Zr(H)Cl]_n$. These observations indicate competing pathways for the reaction of **1** with ^tBuNC, as shown in Scheme I. At high concentrations of the isocyanide, the insertion product forms cleanly, whereas at lower concentrations, when insertion of ^tBuNC into the Zr–C bond is slower, β-hydride elimination from **1** competes to give Cp$(PMe_3)_2RuCH{=}CH_2$ and $Cp_2Zr(H)Cl$. This mononuclear zirconium hydride is then rapidly converted to $Cp_2ZrCl(\eta^2\text{-}^tBuN{=}CH)$ by reaction with ^tBuNC.

The formation of η^2-iminoacyl complexes has been previously reported from reactions of isocyanides with mononuclear $Cp_2Zr(R)Cl$ complexes. Lappert and coworkers[11] found that (*p*-tolyl)NC inserts into the Zr–C bond of with $Cp_2Zr(Cl)CH(SiMe_3)_2$, and Tilley and coworkers[12] reported the formation of an η^2-iminoacyl complex from the reaction of $Cp_2Zr(Cl)SiMe_3$ with 2,6-$Me_2C_6H_3NC$.

The β-hydride elimination from **1**, which produces Cp$(PMe_3)_2RuCH{=}CH_2$ and $Cp_2Zr(H)Cl$, is the reverse of the reaction used to synthesize this compound.[2] These observations demonstrate the reversible nature of the insertion/β-hydride elimination reaction in this system. The equilibrium clearly favors the bimetallic product **1**, but the equilibrium can be driven to the side of the mononuclear products by trapping of the zirconium hydride by ^tBuNC (or other reagents, as discussed below).

Reaction of Benzophenone with Cp$(PMe_3)_2RuCH_2CH_2ZrClCp_2$. A similar competition between β-hydride elimination and insertion was observed in the reaction of **1** with benzophenone. Reaction of a C_6D_6 solution of **1** (0.024 M) with $Ph_2C{=}O$ (0.040 M) at room temperature gave about a 5:2 ratio of Cp$(PMe_3)_2RuCH_2CH_2CPh_2OZrClCp_2$ (**8**) and Cp$(PMe_3)_2RuCH{=}CH_2$. The heterobimetallic product **8** results from insertion of the C=O bond of benzophenone into the Zr–C bond of the dimetalloalkene (eq 3). The zirconium hydride resulting from β-hydride elimination was trapped to form $Cp_2Zr(Cl)(OCHPh_2)$, which was independently prepared from the reaction of $[Cp_2Zr(H)Cl]_n$ with $Ph_2C{=}O$. The formation of insertion product **8** is favored at high concentrations of benzophenone, but use of excess benzophenone results in problems in separating it from the organometallic product. We have prepared **8**

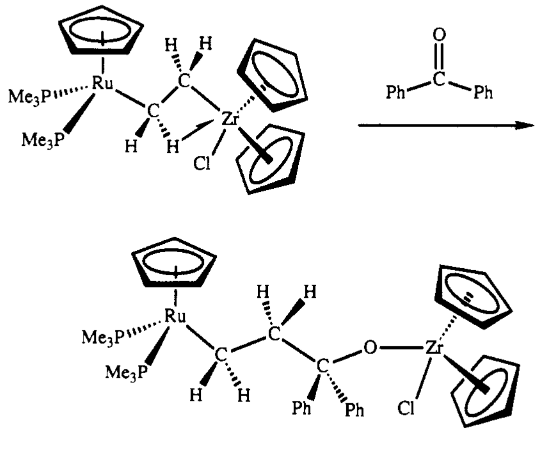
---

[9] Bullock, R. M., unpublished results.

[10] Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *Organometallics* **1992**, *11*, 876–884.

[11] Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. C. *J. Organomet. Chem.* **1979**, *174*, C35–C37.

[12] Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049–2056.



(3)

8

from the reaction between 1 and $Ph_2C{=}O$ (1.1 equiv) using a minimal amount of solvent, thereby attempting to maximize the concentration of benzophenone without using a large molar excess. This led to the isolation of 8 in 34% yield and ~90% purity. The ^1H and ^{13}C NMR spectra are fully in accord with the assignment of the product, but a pure sample for elemental analysis has not been obtained.

Ketones readily insert into the Zr–C bond of some mononuclear zirconium species such as $CH_3Zr(OC_4H_9)_3$, and these reactions are useful in organic synthetic reactions.[13] In contrast, aldehydes and ketones are reported[14] to be inert toward zirconocene complexes $Cp_2Zr(Cl)R$ (R = saturated alkyl group). Indeed, we observed no reaction when a C_6D_6 solution of $Cp_2Zr(Cl)CH_3$ (0.098 M) and $Ph_2C{=}O$ (0.20 M) was heated at 100 °C for 3 h. Several studies of CO insertion reactions[15] have shown that migratory aptitudes increase with steric bulk of the alkyl group, so an experiment with a larger alkyl group on Zr was carried out in order to see whether the same effect might be observed for insertion of benzophenone. However, the reaction of $Cp_2Zr(Cl)CH_2CH_2C(CH_3)_3$[16a] (0.12 M) and $Ph_2C{=}O$ (0.32 M) at 100 °C led to $Cp_2Zr(Cl)(OCHPh_2)$ and $CH_2{=}CHC(CH_3)_3$, indicating that β-hydride elimination rather than benzophenone insertion occurred. Jordan and co-workers found[17] that the formation of $Cp_2Zr(CH_3)(OCPh_2CH_3)$ from reaction of $Cp_2Zr(CH_3)_2$ with benzophenone was extremely slow at 100 °C, but the cationic zirconium alkyl complex $[Cp_2Zr(CH_3)(CH_3CN)]^+$ inserted benzophenone into the Zr–C bond at room temperature. The insertion of benzophenone into the Zr–C bond of 1 was, therefore, unexpected and apparently is not characteristic of neutral zirconocene alkyl complexes. Speculation about the details of the steric and/or electronic effects causing this unusual reactivity of 1 with benzophenone is probably not warranted in the absence of additional data on this reaction or related examples for comparison.

β-Hydride Elimination from $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$. The β-hydride elimination reaction becomes the predominant pathway observed in reactions of the dimetalloalkane complex 1 with unsaturated organic substrates that do not undergo competing insertion into the Zr–C bond. The reaction of a C_6D_6 solution of 1 (~0.025 M) with $^nBuC{\equiv}CH$ (~2.2 equiv) was about 75% complete after 2.5 h at room temperature and was complete in <18 h. The resulting products were the ruthenium vinyl complex $Cp(PMe_3)_2RuCH{=}CH_2$ and the zirconium vinyl complex $Cp_2Zr(Cl)CH{=}CH^nBu$. In principle, it should be possible to determine the rate constant for the β-hydride elimination reaction[18] (k_1 in Scheme II) if the reaction can be carried out at a sufficiently high concentration of $RC{\equiv}CH$ (or other organic trapping reagent) such that the monomeric $Cp_2Zr(H)Cl$ is trapped essentially every time it forms (rather than reinserting the C=C of $Cp(PMe_3)_2RuCH{=}CH_2$, or oligomerizing to form $[Cp_2Zr(H)Cl]_n$). At low $[RC{\equiv}CH]$, the observed rate constant (k_{obs}) should increase with increasing $[RC{\equiv}CH]$. At some higher $[RC{\equiv}CH]$, a plot of k_{obs} vs $[RC{\equiv}CH]$ should exhibit saturation kinetics. We carried out a number of kinetics experiments in which toluene solutions of 1 (~0.015 mM) were reacted with excess $^nBuC{\equiv}CH$, and the rate of disappearance of 1 was monitored by UV–vis spectroscopy. Many of these individual experiments gave clean first-order kinetics for disappearance of 1. For example, an approximate value of $k_{obs} = 3.7 \times 10^{-4}\ s^{-1}$ was obtained for the rate of disappearance of 1 in toluene at 20 °C with $[^nBuC{\equiv}CH] = 0.5$ M. Despite some encouraging results, however, we were ultimately not successful at obtaining data that would have enabled the accurate determination of k_1, the rate constant for β-hydride elimination from 1. We were not able to carry out the reaction at a sufficiently high $[^nBuC{\equiv}CH]$ to reach saturation (even at $[^nBuC{\equiv}CH] = 2$ M). Furthermore, the available data were not sufficiently precise to detect curvature in the plot of k_{obs} vs $[RC{\equiv}CH]$, in order to attempt to extrapolate a value of k_1 using curve-fitting methods.

Other reagents can also be used to trap the zirconium hydride resulting from β-hydride elimination from 1. The formation of $Cp(PMe_3)_2RuC{=}CH_2$ and the zirconium alkoxide complex $Cp_2Zr(Cl)(OCHMe_2)$[16] was about 60% complete in 1.5 h when a C_6D_6 solution of 1 (0.021 M) was treated with acetone (0.036 M). The reaction between 1 (0.036 M) and acetophenone (~2 equiv) produced the ruthenium vinyl complex and $Cp_2Zr(Cl)(OCPhHMe)$[19] (~50% completion after 1 h and >95% complete after 4.5 h at room temperature). A faster rate of β-hydride elimination was observed when 1 was dissolved in CD_3CN. This reaction was over half completed in 20 min and gave $Cp_2Zr(Cl)(N{=}CHCD_3)$[20] along with $Cp(PMe_3)_2RuCH{=}CH_2$. In contrast to the clean formation of η^2-acyl complex 2-CO from the reaction of CO with the dimetalloalkene 2, β-hydride elimination reaction appeared to be the main reaction when a C_6D_6 solution of dimetalloalkane 1 was placed under 1 atm of CO. The ruthenium vinyl complex $Cp(PMe_3)_2RuCH{=}CH_2$ was the predominant Ru species formed in this reaction; other resonances were also ob-

---

[13] Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31–45.

[14] Negishi, E.; Takahashi, T. *Aldrichchim. Acta* **1985**, *18*, 31–47.

[15] For reviews of the CO insertion reaction, see: (a) Alexander, J. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley and Sons: New York, 1985; Vol. 2, pp 339–400. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311. (c) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145. (d) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195–225.

[16] (a) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521–3531. (b) $Cp_2ZrCl(OCHMe_2)$ has also been prepared by the reaction of $LiOCHMe_2$ with Cp_2ZrCl_2, and by reaction of isopropyl alcohol with $[Cp_2Zr(H)Cl]_n$: Femec, D. A.; Silver, M. E.; Fay, R. C. *Inorg. Chem.* **1989**, *28*, 2789–2796.

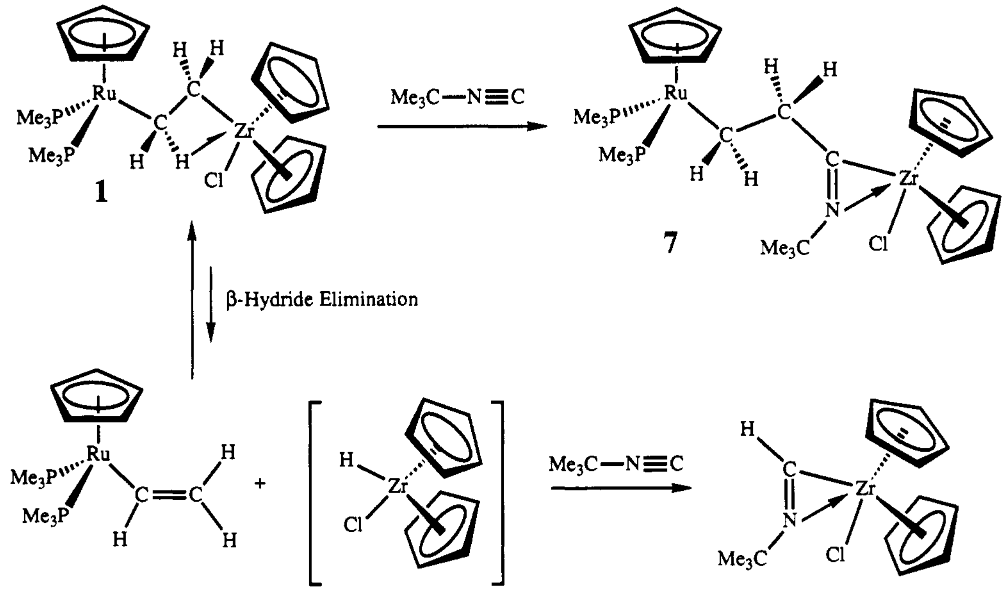
[17] Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718–1719.

[18] Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577.

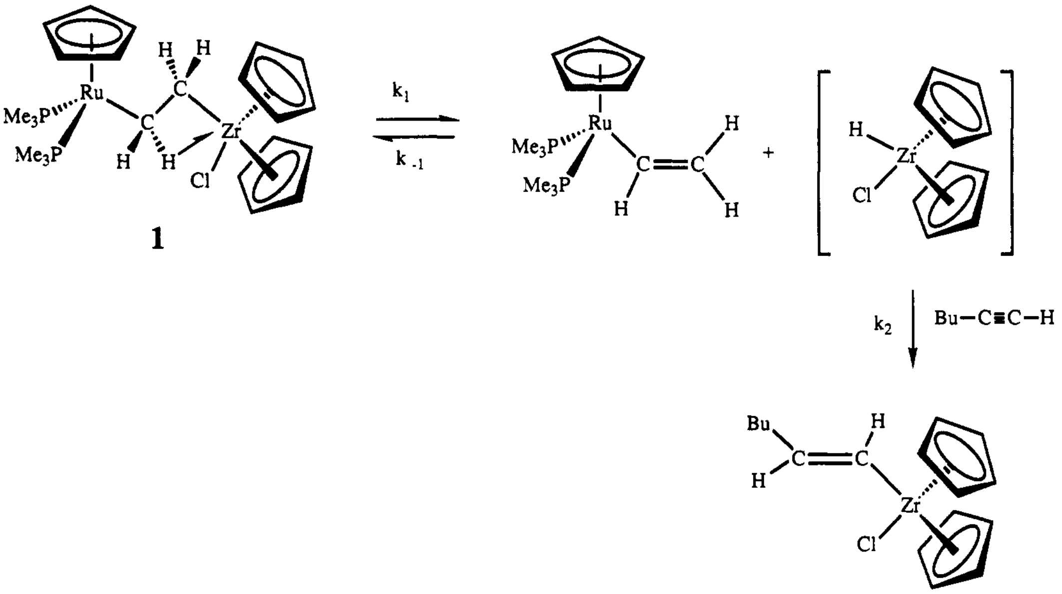
[19] Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349–2355.

[20] For the preparation of $Cp_2Zr(Cl)(N{=}CHCH_3)$ from the reaction of CH_3CN with $[Cp_2Zr(H)Cl]_n$, see: Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343–354.

Scheme I



Scheme II



served that may be due to competing formation of an η^2-acyl complex, but a detailed study of this reaction was not carried out.

β-Hydride Elimination from $Cp(PMe_3)_2RuCH{=}CHZrClCp_2$ (2) and $Cp(PMe_3)_2RuCH{=}C(CH_3)ZrClCp_2$. Although there have been numerous studies of β-hydride eliminations from metal alkyls, only a few examples[21,22] of β-hydride eliminations from metal vinyl complexes have been previously reported. The β-hydride elimination reaction involving the vinyl proton of 2 is noticeably slower than that observed for the saturated analog 1, which has aliphatic protons on the carbon that is β to Zr. The reaction of 2 (0.024 M) with $^nBuC{\equiv}CH$ (~10 equiv) in C_6D_6 was about 65% complete in 1 day at room temperature and was >90% complete after 4 days. The products were the ruthenium alkynyl complex $Cp(PMe_3)_2Ru{-}C{\equiv}C{-}H$ and the zirconium vinyl complex $Cp_2Zr(Cl)CH{=}CH^nBu$ (~75% yield). In contrast to this room-temperature reaction for β-hydride elimination from 2, the analogous reaction for the methyl-substituted dimetalloalkene $Cp(PMe_3)_2RuCH{=}C(CH_3)ZrClCp_2$ was significantly slower. No reaction was observed when a C_6D_6 solution of $Cp(PMe_3)_2RuCH{=}C(CH_3)ZrClCp_2$ (0.024 M) and $^nBuC{\equiv}CH$ (~10 equiv) was kept at room temperature for 4.5 days. The reaction was about 25% complete after 7.5 h at 60 °C, and an 86% yield of $Cp(PMe_3)_2Ru{-}C{\equiv}C{-}CH_3$ was observed after heating at 60 °C for 70 h. ^1H NMR resonances for several unidentified zirconium complexes were observed along with those for the zirconium vinyl complex $Cp_2Zr(Cl)CH{=}CH^nBu$, suggesting further reaction of this zirconium vinyl complex under the reaction conditions.

The observed rate of formation of β-hydride elimination products under our conditions is influenced by the competitive reaction of $Cp_2Zr(H)Cl$ with the trapping substrate ($^nBuC{\equiv}CH$, k_2 in Scheme II) and readdition to the eliminated ruthenium species ($Cp(PMe_3)_2RuCH{=}CH_2$, k_{-1}). Hence the slower overall rate of formation of β-hydride elimination products from 2 compared to 1 does not nec-

---

[21] Schwartz, J.; Hart, D. W.; McGiffert, B. *J. Am. Chem. Soc.* 1974, *96*, 5613–5614.

[22] McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* 1985, *279*, 281–315.

essarily reflect their relative rate constants (k_1) for the β-hydride elimination step, since it is quite possible that the relatively small differences in observed overall rates are overwhelmed by large differences in k_{-1} (i.e., a substantially faster reinsertion of the C≡C bond of Cp(PMe$_3$)$_2$RuC≡CH into the Zr–H bond of Cp$_2$Zr(H)Cl, compared to the analogous reaction of Cp(PMe$_3$)$_2$RuCH=CH$_2$ with Cp$_2$Zr(H)Cl).

Conclusions

The two predominant classes of reaction observed for Cp(PMe$_3$)$_2$RuCH$_2$CH$_2$ZrClCp$_2$ (1) and Cp(PMe$_3$)$_2$RuCH=CHZrClCp$_2$ (2) are insertions of unsaturated organic molecules into the Zr–C bond and β-hydride elimination. These reactions are competitive with each other under some conditions, but by proper choice of reagents and conditions it is possible to observe either of these reactions essentially exclusively. An insertion into the M–C bond of a dimetalloalkyne (3) is observed from the reaction of ^{t}BuNC with Cp(PMe$_3$)$_2$Ru—C≡C—ZrClCp$_2$. A Ru/Zr carboxylate complex results from insertion of CO$_2$ into the Zr–C bond of **2**. Since both **2** and **1** were prepared by insertion of an unsaturated Ru—C≡C—H or Ru—CH=CH$_2$ moiety into a Zr–H bond, the β-hydride elimination reaction which regenerates the Zr–H bond is the reverse of the reaction used in the synthesis of these compounds. The β-agostic interactions found in both **1** and **2** are suggestive of a developing Zr···H interaction, and it is thought that the structures found for these compounds[2] represent a point on the reaction coordinate for β-hydride elimination. The β-hydride elimination reaction from **1** regenerates the ruthenium vinyl complex Cp(PMe$_3$)$_2$RuCH=CH$_2$ and Cp$_2$Zr(H)Cl, which is trapped by unsaturated organic substrates (alkynes, ketones, etc.) to form stable zirconium complexes.

Experimental Section

General Techniques. All manipulations of oxygen- or water-sensitive compounds were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. Glassware was dried in a 120 °C oven for several hours or was flame-dried and cooled under vacuum immediately prior to use. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. ^{13}C NMR spectra were recorded in the presence of Cr(acac)$_3$ (0.04–0.07 M). $^1J_{CH}$ coupling constants were obtained from ^{13}C NMR spectra using gated decoupling. The PMe$_3$ resonances in these compounds do not appear as a simple first-order pattern in the NMR. In the ^{1}H NMR, the PMe$_3$ resonances appear as a A$_9$XX′A′$_9$ pattern; the appearance of these resonances in the ^{1}H NMR is a "filled-in-doublet", with the separation of the outer lines being equal to $^2J_{PH} + {}^4J_{PH}$.[23] In the ^{13}C{^{1}H} NMR, the PMe$_3$ resonance appears as a virtual triplet (designated as vt in the spectral assignments below), the observed coupling constant J is equal to $^1J_{PC} + {}^3J_{PC}$.[23] The ^{1}H chemical shifts were referenced to the residual proton peak of the solvent: C$_6$D$_5$H, δ 7.15; CHDCl$_2$, δ 5.32; CHD$_2$CN, δ 1.93. The ^{13}C chemical shifts were referenced to the central peak of CD$_2$Cl$_2$ (δ 53.8) or C$_6$D$_5$CD$_3$ (CD$_3$ at δ 20.4). IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory or by Galbraith Laboratory.

Materials. **1**–**3** were prepared as previously described.[2] THF was distilled from Na/benzophenone. Toluene and hexanes were stirred over concentrated H$_2$SO$_4$ until the H$_2$SO$_4$ remained colorless; these solvents were then distilled from Na/benzophenone and stored over [Cp$_2$TiCl]$_2$ZnCl$_2$.[24] Dichloromethane was distilled from P$_2$O$_5$. Anhydrous diethyl ether was stored over [Cp$_2$TiCl]$_2$ZnCl$_2$ and vacuum transferred immediately prior to use. Benzene-d_6 was dried over NaK and stored over [Cp$_2$TiCl]$_2$ZnCl$_2$. Dichloromethane-d_2 was dried over P$_2$O$_5$ and stored over CaH$_2$. THF-d_8 was dried and stored over NaK. Acetonitrile-d_3 was dried over activated 3-Å sieves and stored over Cp$_2$Zr(Me)Cl.[25] *tert*-Butyl isocyanide (Aldrich) and ^{n}BuC≡CH (Farchan) were stored over activated 3-Å molecular sieves and handled using calibrated gas bulbs on a vacuum line. Carbon dioxide (Airco) was used as received.

Cp(PMe$_3$)$_2$RuCH=CHCO$_2$ZrClCp$_2$ (4). THF (15 mL) was added by vacuum transfer to a flask containing **2** (249 mg, 0.41 mmol). CO$_2$ (1 atm) was added, and the dark orange solution had turned yellow after stirring for 0.5 h. The solution was filtered and concentrated, and the product was precipitated by addition of Et$_2$O. The solid was collected by filtration, washed with Et$_2$O, and dried under vacuum to give a yellow solid (121 mg). A second crop from THF/hexanes yielded 97 mg (81% total yield, ~80% purity by ^{1}H NMR). Attempts to obtain analytically pure material by vapor diffusion of Et$_2$O into THF solutions of **4** at room temperature resulted in precipitation of decomposition products after a few days. In an effort to obtain a pure sample of this complex by crystallization at low temperature, CO$_2$ (1 atm) was added to **2** (129 mg) in toluene (5 mL) to give a yellow solution. A layer of hexane (10 mL) was added, and yellow crystals formed after slow diffusive mixing of the layers at −20 °C. The yellow crystals of **4** contained ~0.8 molecule of toluene as determined by NMR in CD$_2$Cl$_2$: δ 7.2 (m, toluene solvate aromatic protons), 2.34 (s, toluene solvate CH$_3$ protons). The toluene was not removed by heating the solid sample of **4**·0.8 C$_7$H$_8$ overnight at 45 °C under vacuum (<10^{-4} Torr). ^{1}H NMR (CD$_2$Cl$_2$): δ 10.64 (dt, $^3J_{HH}$ = 16.7 Hz, $^3J_{PH}$ = 6.9 Hz, 1 H, RuCH), 6.18 (s, 10 H, ZrCp), 6.07 (dt, $^3J_{HH}$ = 16.7 Hz, $^4J_{PH}$ = 1.0 Hz, 1 H, RuC=CH), 4.73 (s, 5 H, RuCp), 1.39 ("filled-in-doublet", $^2J_{PH} + {}^4J_{PH}$ = 8.7 Hz, 18 H, PMe$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 0.05 M Cr(acac)$_3$): δ 208.7 (dt, $^1J_{CH}$ = 129 Hz, $^2J_{PC}$ = 17 Hz, RuCH), 175.7 (s, CO$_2$), 127.7 (dt, $^1J_{CH}$ = 157 Hz, $^3J_{PC}$ = 4 Hz, RuC=CH), 114.3 (d, $^1J_{CH}$ = 174 Hz, ZrCp), 83.8 (d, $^1J_{CH}$ = 175 Hz, RuCp), 22.8 (q of vt, $^1J_{CH}$ = 131 Hz, $^1J_{PC} + {}^3J_{PC}$ = 30 Hz, PMe$_3$). IR (KBr): ν(CO$_2$) 1491, 1441 (sh), 1415 cm^{-1}. IR (THF): ν(CO$_2$) 1507, 1440 sh, 1413 cm^{-1}. Anal. Calcd for C$_{29.6}$H$_{41.4}$ClO$_2$P$_2$RuZr (0.8 C$_7$H$_8$ per RuZr): C, 49.44; H, 5.81. Found: C, 49.73; H, 5.92.

Cp(PMe$_3$)$_2$RuC≡CC(NBu^t)ZrClCp$_2$ (5). Dimetalloalkyne complex **3** (106 mg, 0.18 mmol) was dissolved in neat ^{t}BuNC at room temperature to give a yellow solution which formed a yellow precipitate within a few seconds. After 0.5 h, the excess ^{t}BuNC was recovered by vacuum transfer, and the yellow residue was dissolved in THF. The THF solution was filtered, and the filtrate was concentrated. Et$_2$O was added to initiate precipitation. The resulting solid was isolated, washed with hexanes, and dried under vacuum to give an orange-yellow solid (73 mg, 59% yield, >98% pure by ^{1}H NMR). A second crop from THF/hexanes produced 27 mg (22%, ~80% purity by ^{1}H NMR). Crystals of **5** were obtained from slow diffusion of Et$_2$O into a THF solution at −20 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.77 (s, 10 H, ZrCp), 4.79 (s, 5 H, RuCp), 1.54 ("filled-in-doublet", $^2J_{PH} + {}^4J_{PH}$ = 9.1 Hz, 18 H, PMe$_3$), 1.36 (s, 9 H, CMe$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 0.04 M Cr(acac)$_3$): δ 217.5 (s, CN), 188.0 (t, $^2J_{PC}$ = 24 Hz, RuC), 109.0 (d, $^1J_{CH}$ = 172 Hz, ZrCp), 107.3 (s, RuC–*C*), 82.3 (d, $^1J_{CH}$ = 175 Hz, RuCp), 61.3 (s, *C*Me$_3$), 29.1 (q, $^1J_{CH}$ = 126 Hz, C*Me*$_3$), 23.3 (q of vt, $^1J_{CH}$ = 125 Hz, $^1J_{PC} + {}^3J_{PC}$ = 31 Hz, PMe$_3$). IR (KBr): ν(C≡C) 2003 cm^{-1}; ν(C=N) 1576, 1554 cm^{-1}. Anal. Calcd for C$_{28}$H$_{42}$ClNP$_2$RuZr: C, 49.28; H, 6.22; N, 2.05. Found: C, 49.84; H, 6.22; N, 2.21.

Cp(PMe$_3$)$_2$RuCH$_2$CH$_2$C(N^{t}Bu)ZrClCp$_2$ (7). Dimetalloalkane complex **1** (161 mg, 0.27 mmol) was dissolved in neat ^{t}BuNC to give a yellow solution, from which a yellow precipitate formed in ~0.5 h. The excess ^{t}BuNC was recovered by vacuum transfer, and the yellow residue was dissolved in THF. The THF solution was concentrated, and the product was precipitated with Et$_2$O. The precipitate was collected by filtration, washed with Et$_2$O and hexanes, and dried under vacuum to give **7** as a light yellow solid (121 mg). A second crop from THF/hexanes produced 22 mg of

---

(23) (a) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50–59. (b) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727–733.

(24) Sekutowski, D. G.; Stucky, G. D. *Inorg. Chem.* **1975**, *14*, 2192–2199.

(25) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *33*, 181–188.

yellow solid (total yield 77%, >95% purity by ^{1}H NMR). ^{1}H NMR (CD_2Cl_2): δ 5.80 (s, 10 H, ZrCp), 4.52 (s, 5 H, RuCp), 3.09 (m, 2 H, $RuCH_2C\mathit{H}_2$), 1.40 ("filled-in-doublet", $^2J_{PH} + {}^4J_{PH} = 8.1$ Hz, 18 H, PMe_3), 1.36 (s, 9 H, CMe_3), 1.13 (m, 2 H, $RuCH_2$). ^{13}C NMR (CD_2Cl_2, 0.05 M $Cr(acac)_3$): δ 235.6 (s, CN), 108.5 (d, $^1J_{CH}$ = 172 Hz, ZrCp), 80.5 (dt, $^1J_{CH}$ = 173 Hz, $^2J_{PC}$ = 1.7 Hz, RuCp), 61.9 (s, $\mathit{C}Me_3$), 47.2 (tt, $^1J_{CH}$ = 128 Hz, $^3J_{PC}$ = 5.0 Hz, $RuCH_2\mathit{C}H_2$), 29.7 (q, $^1J_{CH}$ = 127 Hz, $C\mathit{Me}_3$), 22.9 (q of vt, $^1J_{CH}$ = 126 Hz, $^1J_{PC} + {}^3J_{PC}$ = 26 Hz, PMe_3), −4.3 (tt, $^1J_{CH}$ = 124 Hz, $^2J_{PC}$ = 13 Hz, $RuCH_2$). IR (KBr): ν(CN) 1629, 1607 cm^{-1}. Anal. Calcd for $C_{28}H_{46}ClNP_2RuZr$: C, 48.99; H, 6.77; N, 2.04. Found: C, 48.96; H, 6.60; N, 1.89.

$Cp(PMe_3)_2RuCH_2CH_2CPh_2OZrClCp_2$ (8). Toluene (~2 mL) was added to a flask containing 1 (91 mg, 0.15 mmol) and $Ph_2C{=}O$ (29 mg, 0.16 mmol). The reaction was stirred for 2 h to give an orange homogeneous solution that was evaporated to dryness. The orange residue was washed with hexanes (2 × 5 mL) to give 8 as an off-white solid (40 mg, 34% yield, 89% pure by ^{1}H NMR). (Washing of the crude product led to a lower yield, since the product has some solubility in hexane, but was necessary in order to remove most of the remaining $Cp(PMe_3)_2RuCH{=}CH_2$, $Cp_2Zr(Cl)(OCHPh_2)$, and unreacted $Ph_2C{=}O$.) Attempts to obtain analytically pure 8 by recrystallization from toluene/hexane were not successful. ^{1}H NMR (CD_2Cl_2): δ 7.15–7.30 (m, Ph), 6.13 (s, CpZr), 4.52 (s, CpRu), 2.39 (m, $RuCH_2C\mathit{H}_2$), 1.18 ("filled-in-doublet", $^2J_{PH} + {}^4J_{PH}$ = 9 Hz, PMe_3), 0.43 (m, $RuCH_2$). ^{13}C NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$): δ 148.7 (s, ipso Ph), 127.6, 127.2 (d, $^1J_{CH}$ = 158 Hz, ortho and meta Ph), 126.0 (d, $^1J_{CH}$ = 159 Hz, para Ph), 113.5 (d, $^1J_{CH}$ = 173 Hz, CpZr), 92.5 (s, $Ph_2\mathit{C}$), 80.1 (d, $^1J_{CH}$ = 172 Hz, CpRu), 22.7 (q of vt, $^1J_{CH}$ = 125 Hz, $^1J_{PC} + {}^3J_{PC}$ = 34 Hz, PMe_3), −9.3 (tt, $^1J_{CH}$ = 126 Hz, $^2J_{PC}$ = 13 Hz, $RuCH_2$), $RuCH_2\mathit{C}H_2$ obscured by solvent; ^{13}C NMR (C_6D_6, 0.07 M $Cr(acac)_3$): δ 149.1 (s, ipso Ph), 113.6 (d, $^1J_{CH}$ = 173 Hz, CpZr), 92.8 (s, $Ph_2\mathit{C}$), 80.5 (d, $^1J_{CH}$ = 172 Hz, CpRu), 53.9 (tt, $^1J_{CH}$ = 126 Hz, $^3J_{PC}$ = 4 Hz, $RuCH_2\mathit{C}H_2$), 22.9 (q of vt, $^1J_{CH}$ = 128 Hz, $^1J_{PC} + {}^3J_{PC}$ = 26 Hz, PMe_3), −8.7 (tt, $^1J_{CH}$ = 122 Hz, $^2J_{PC}$ = 13 Hz, $RuCH_2$), ortho, meta, and para Ph carbons obscured by C_6D_6 solvent.

Preparation of $Cp_2Zr(Cl)(OCHPh_2)$. In a drybox, a solution of $Ph_2C{=}O$ (0.314 g, 1.72 mmol) in toluene (10 mL) was added dropwise to a suspension of $[Cp_2Zr(H)Cl]_n$ (0.508 g, 1.97 mmol) in toluene (10 mL). After stirring for 1 h at 22 °C, the pale yellow solution was filtered. Concentration of the toluene solution and addition of hexane resulted in the precipitation of a white precipitate, which was washed with hexane (3 × 5 mL) and dried under vacuum to give $Cp_2Zr(Cl)(OCHPh_2)$ (454 mg, 60%). ^{1}H NMR (CD_2Cl_2): δ 7.36–7.26 (m, 10 H, Ph), 6.24 (s, CpZr), 6.08 (s, 1 H, OCH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$): δ 145.3 (s, ipso Ph), 128.3, 126.4 (s, ortho and meta Ph), 127.1 (s, para Ph), 113.7 (s, Cp), 87.9 (s, $O\mathit{C}HPh_2$).

Reaction of $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$ with $^nBuC{\equiv}CH$. The reaction of 1 (0.025 M) with $^nBuC{\equiv}CH$ (0.055 M) in C_6D_6 was complete in 18 h and gave $Cp(PMe_3)_2RuCH{=}CH_2$ and $Cp_2ClZrCH{=}CH^nBu$ in high yield. The Zr vinyl complex was independently prepared by reaction of $^nBuC{\equiv}CH$ with $[Cp_2Zr(H)Cl]_n$. ^{1}H NMR of $Cp_2Zr(Cl)(CH{=}CH^nBu)$ in C_6D_6: δ 6.87 (dt, $^3J_{HH}$ = 18 Hz, $^4J_{HH}$ = 1 Hz, 1 H, ZrCH), 5.83 (s, 10 H, CpZr), 2.11 (q, J_{HH} = 6 Hz, 2 H, $ZrCH{=}CHC\mathit{H}_2$), 1.40 (m, 4 H, CH_2CH_2), 0.94 (t, J_{HH} = 7 Hz, 3 H, CH_3), $ZrCH{=}C\mathit{H}$ resonance at about δ 5.9 partially obscured by ZrCp resonance.

Reaction of $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$ with Acetone. The reaction of 1 (21 mM) with acetone (36 mM) in C_6D_6 gave $Cp(PMe_3)_2RuCH{=}CH_2$ and $Cp_2ZrCl(OCHMe_2)$.[16] This zirconium alkoxide complex was independently prepared from the reaction of $[Cp_2Zr(H)Cl]_n$ with acetone. ^{1}H NMR of $Cp_2ZrCl(OCHMe_2)$ in C_6D_6: δ 5.94 (s, 10 H, Cp), 4.02 (septet, J_{HH} = 6 Hz, 1 H, CH), 0.99 (d, J_{HH} = 6 Hz, 6 H, CH_3).

Reaction of $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$ with $Ph(C{=}O)CH_3$. The reaction of 1 (36 mM) with $Ph(C{=}O)Me$ (73 mM) gave $Cp(PMe_3)_2RuCH{=}CH_2$ (~95% yield) and $Cp_2ZrCl(OCPhHMe)$[19] (~85% yield) after 4.5 h at room temperature. This Zr complex was independently prepared from the reaction of $[Cp_2Zr(H)Cl]_n$ with $Ph(C{=}O)CH_3$. ^{1}H NMR of $Cp_2Zr(Cl)(OCPhHMe)$ in C_6D_6: δ 7.8–7.7, 7.4–6.9 (m, 5 H, Ph), 5.92 (s, 5 H, Cp), 5.89 (s, 5 H, Cp), 4.94 (q, $^3J_{HH}$ = 6 Hz, 1 H, CH), 1.32 (d, $^3J_{HH}$ = 6 Hz, CH_3).

Reaction of $Cp(PMe_3)_2RuCH_2CH_2ZrClCp_2$ with CD_3CN. The reaction of 1 (~8 mM) with neat CD_3CN gave nearly quantitative yields of $Cp(PMe_3)_2RuCH{=}CH_2$ and $Cp_2Zr(Cl)(N{=}CHCD_3)$[20] after 1 h at room temperature. $Cp_2Zr(Cl)(N{=}CHCD_3)$ was independently prepared from the reaction of $[Cp_2Zr(H)Cl]_n$ with CD_3CN. ^{1}H NMR of $Cp_2Zr(Cl)(N{=}CHCD_3)$ in CD_3CN: δ 6.11 (s, 10 H, Cp), 8.44 (s, 1 H, CH). ^{1}H NMR of $Cp(PMe_3)_2RuCH{=}CH_2$ in CD_3CN: δ 7.47 (ddt, $^3J_{H_aH_c}$ = 18.6 Hz, $^3J_{H_aH_b}$ = 11 Hz, $^3J_{PH}$ = 8.0 Hz, 1 H, H_a), 5.75 (ddt, $^3J_{H_aH_b}$ = 11 Hz, $^2J_{H_bH_c}$ = 4.4 Hz, $^4J_{PH}$ = 2.4 Hz, 1 H, H_b), 5.15 (dd, $^3J_{H_aH_c}$ = 18.6 Hz, $^2J_{H_bH_c}$ = 4.4 Hz, $^4J_{PH}$ unresolved, 1 H, H_c), 4.51 (s, 5 H, Cp), 1.32 ("filled-in-doublet", $^2J_{PH} + {}^4J_{PH}$ = 8.6 Hz, 18 H, PMe_3).

Acknowledgment. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

OM920295S