Studies on Hydrometalation Reactions: An Improved Hydrozirconation Reagent and the Structure of a $(MeCp)_2ZrCl$(alkenyl) Carbonylation Product

Gerhard Erker,*[†] Rüger Schlund,[†] and Carl Krüger[‡]

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG, and Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a. d. Ruhr, FRG

Received February 23, 1989

Mixing $(MeCp)_2ZrCl_2$ (2) and $[(MeCp)_2Zr(H)_2]_2$ (3) in tetrahydrofuran or toluene at ambient temperature apparently generates a small quantity of $(MeCp)_2Zr(H)Cl$ (4) in equilibrium which can be used very efficiently for hydrozirconation reactions of alkenes, alkynes, ketones, nitriles, or carbon monoxide. The MeCP reagent 4 reacts about 6–7 times faster with 1-hexene or acetophenone than the commonly used $Cp_2Zr(H)Cl$ (1) hydrozirconation reagent. Reaction of 4 with (trimethylsilyl)acetylene followed by carbonylation yields the α,β-unsaturated (η^2-acyl)metallocene complex $(MeCp)_2\overline{Zr(Cl)O{=}C}CH{=}CHSiMe_3$ (24). Complex 24 crystallizes in space group $P2_1/c$ with cell parameters $a = 12.321$ (2) Å, $b = 12.553$ (3) Å, $c = 13.367$ (1) Å, $\beta = 105.77$ (1)°, $Z = 4$, $R = 0.033$, and $R_w = 0.045$. The η^2-acyl ligand exhibits C=C (1.342 (5) Å), C—C (1.468 (4) Å), and C=O (1.226 (3) Å) bond lengths which are not significantly different from those of ordinary organic α,β-unsaturated carbonyl compounds.

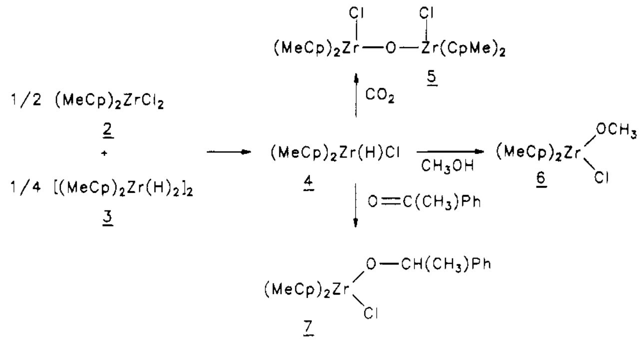
Introduction

The hydrozirconation reaction has been developed into a useful synthetic method for preparing organic as well as organometallic substrates.[1] Almost exclusively oligomeric $[Cp_2Zr(H)Cl]_x$ (1), first described in 1969 by Wailes and Weigold,[2] has been used as the hydrozirconation reagent. Reports of Cp-substituted analogues, e.g. $[(Me_2Si)(C_5H_4)_2Zr(H)Cl]$ or $[(Me_5C_5)_2Zr(H)Cl]$, are rare.[3] Using the parent compound instead of the more soluble derivatives bearing substituents on the Cp rings is probably due to the fact that 1 has been, thus far, more readily obtained. Upon treatment of Cp_2ZrCl_2 with hydridic reagents the oligomeric bis(η-cyclopentadienyl)hydridozirconium chloride rapidly precipitates and is thereby protected from further reaction giving undesired dihydridozirconocene. In contrast, the $(RCp)_2Zr$-derived systems tend to remain in solution until the $(RCp)_2Zr(H)_2$ species, usually subsequently isolated as a bis(μ-H)-bridged dimer, is formed.[4] We have now observed that a Cp-substituted hydrozirconation reagent can nevertheless quite easily be generated from the readily available $(RCp)_2ZrCl_2$ precursor and hydride. Using, e.g., $[(H_3C\text{-}C_5H_4)_2Zr(H)Cl]$ instead of the more common $[Cp_2Zr(H)Cl]$ hydrozirconation reagent seems to be advantageous in many cases.

Results and Discussion

Hydrozirconation with "$(H_3C\text{-}C_5H_4)_2Zr(H)Cl$". Bis($\eta$-methylcyclopentadienyl)zirconium dichloride (2) was treated with 0.25 equiv of lithium aluminum hydride in tetrahydrofuran. A sparingly soluble precipitate was obtained that gave a CH elemental analysis in agreement with an overall composition of $[(H_3C\text{-}C_5H_4)_2Zr(H)Cl]$. A small amount of this material was redissolved in tetrahydrofuran-d_8. The ^1H NMR spectrum[5] revealed only the presence of $(H_3C\text{-}C_5H_4)_2ZrCl_2$ and the dimeric metallocene dihydride $[(H_3C\text{-}C_5H_4)_2ZrH(\mu\text{-}H)]_2$ (3), in addition to some hydrolysis product $[(H_3C\text{-}C_5H_4)_2Zr(Cl)]_2O$ (ca. 15%). Mixing $[(H_3C\text{-}C_5H_4)_2ZrCl_2]$ and $[(H_3C\text{-}C_5H_4)_2ZrH(\mu\text{-}H)]_2$ (showing ^1H NMR hydride resonances at δ −3.00 and 3.76 with $^2J_{HH} = 7$ Hz) produced a virtually identical mixture, as judged by ^1H NMR.

Scheme I



Although the presence of bis(η-methylcyclopentadienyl)hydridozirconium chloride, being in equilibrium with $[(H_3C\text{-}C_5H_4)_2ZrCl_2]$ (2) and $[(H_3C\text{-}C_5H_4)_2ZrH(\mu\text{-}H)]_2$ (3), could not be seen in the ^1H NMR spectrum,

---

[†] Universität Würzburg.

[‡] MPI Mülheim.

(1) (a) Reviews: Schwartz, J.; Labinger, J. A. *Angew. Chem.* **1976**, *88*, 402. Negishi, E. *Pure Appl. Chem.* **1981**, *53*, 2333. (b) For some recent examples see: Kunieda, T.; Mori, T.; Higuchi, T.; Hirobe, M. *Tetrahedron Lett.* **1985**, *26*, 1977. Gambarotta, S.; Strogolo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278. Männig, D.; Nöth, H.; Schwarz, M.; Weber, S.; Wietelmann, U. *Angew. Chem.* **1985**, *97*, 979. Kochetkov, N. K.; Sviridov, A. F.; Yashunskii, D. V.; Ermolenko, M. S.; Borodkin, V. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 441; *Chem. Abstr.* **1987**, *106*, 120150c. Jacobsen, E. N.; Trost, M. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 8092. Gibson, T. *Organometallics* **1987**, *6*, 918. Hartner, F. M., Jr.; Clift, S. M.; Schwartz, J.; Tulip, T. H. *Ibid.* **1987**, *6*, 1346.

(2) (a) Kautzner, B.; Wailes, P. C.; Weigold, H. *J. Chem. Soc., Chem. Commun.* **1969**, 1105. Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405. Wailes, P. C.; Weigold, H.; Bell, A. P. *Ibid.* **1972**, *43*, C32. (b) For an improved synthesis of the original hydrozirconation reagent see: Buchwald, S. L.; La Maire, S. J.; Nielson, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

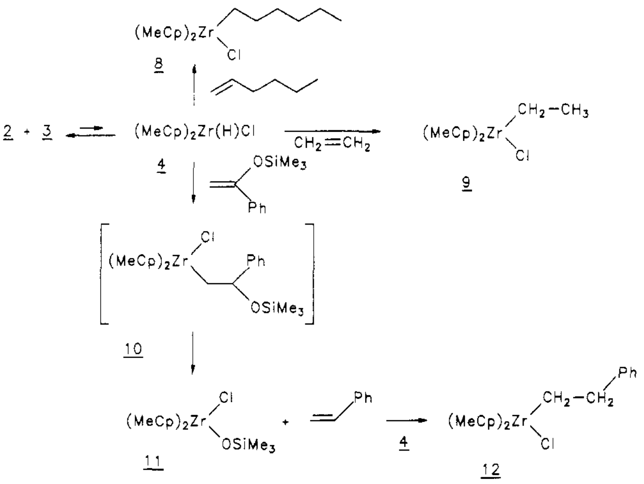
(3) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470. Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.

(4) Aitken, C.; Harrod, J. F.; Samuel, E. *Can J. Chem.* **1986**, *64*, 1677. Kot, W. K.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1987**, *26*, 1339. Jarrett, W. L.; Farlee, R. D.; Butler, L. G. *Inorg. Chem.* **1987**, *26*, 1381. Laarif, A.; Theobald, F.; Gautheron, B.; Tainturier, G. *J. Appl. Cryst.* **1983**, *16*, 277.

(5) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889. See for a comparison: Bickley, D. G.; Hao, N.; Bougeard, P.; Sayer, B. G.; Burns, R. C.; McGlinchey, M. J. *J. Organomet. Chem.* **1983**, *246*, 257.

0276-7333/89/2308-2349$01.50/0

Scheme II

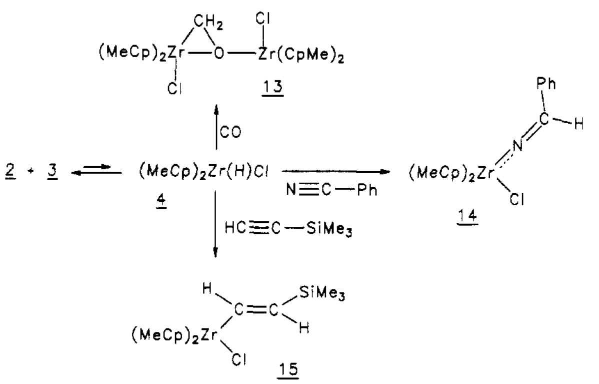


the **2**/**3** mixture can very effectively be used for carrying out hydrozirconation reactions via the "$(H_3C\text{-}C_5H_4)_2Zr(H)Cl$" species. Thus, a suspension of **2**/**3** in toluene reacts cleanly with methanol to give bis(η-methylcyclopentadienyl)methoxyzirconocene chloride (**6**). This product is the only organometallic compound found in this reaction. It was synthesized on a preparative scale and isolated in 70% yield.[6]

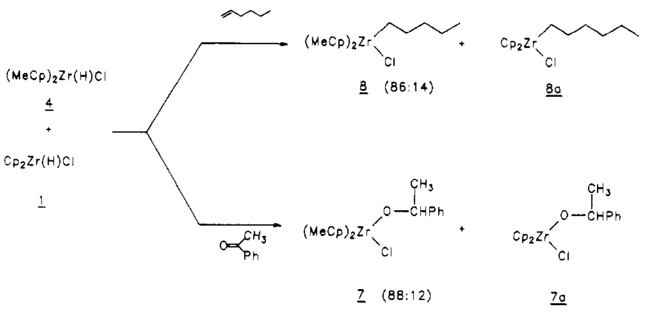
The **2**/**3** mixture reacts with CO_2 to form (μ-oxo)-zirconocene chloride (**5**) (73%).[7] Acetophenone consumed the **2**/**3** mixture (suspended in toluene) within ca. 20 s at ambient temperature to give $[(H_3C\text{-}C_5H_4)_2ZrCl(OCHMePh)]$ (**7**) (92% isolated). Hydrozirconation of 1-hexene or ethylene using the $(MeCp)_2ZrCl_2$/"$(MeCp)_2ZrH_2$" reagent proceeded rapidly to give the alkylmetallocene chlorides **8** or **9**, respectively, both in high yield. Alkenyl enol ethers can be employed as substrates as well. 1-Phenyl-1-(trimethylsiloxy)ethene was treated with 1 molar equiv of the **2**/**3** reagent at ambient temperature in benzene-d_6. Under these conditions only half of the olefin was used. Two products, $[(H_3C\text{-}C_5H_4)_2ZrCl(OSiMe_3)]$ (**11**) and $[(H_3C\text{-}C_5H_4)_2ZrCl(CH_2CH_2Ph)]$ (**12**), were formed in equal amounts. Apparently, the intermediately formed hydrozirconation product $(MeCp)_2ZrCl[CH_2CH(Ph)OSiMe_3]$ (**10**) undergoes a β-$OSiMe_3$ elimination to give **11** and styrene, which then adds another equivalent of "$(MeCp)_2Zr(H)Cl$" (more rapidly than the silyl enol ether) to produce the final product **12**.

Bis(η-methylcyclopentadienyl)hydridozirconium chloride (**4**) reacts with carbon monoxide at ambient conditions to form the binuclear (μ-O-η^1:C,O-η^2-formaldehyde)-metallocene complex **13**.[8a] Ordinary C≡C and C≡X triple bonds can be hydrozirconated as well by using the **2**/**3** mixture. With benzonitrile we have obtained the (phenylmethanimido)$ZrCl(CpMe)_2$ complex (**14**) ($\nu_{(C=N)}$ = 1671 cm^{-1}; $^1H/^{13}C$ NMR (ZrNC*H*Ph) δ 9.06/165.8). Probably complex **14** exhibits a near to linear heteroallene type $[Zr]\text{⁻⁻}N{=}CHPh$ unit.[8b] (Trimethylsilyl)acetylene is hydrozirconated by **2**/**3** to yield $(MeCp)_2ZrCl(CH{=}CHSiMe_3)$ (**15**) within minutes at room temperature in toluene [89% yield; trans product, $^1H/^{13}C$ NMR of the *trans*-[Zr]CH=CH[Si] unit: δ 6.59, 7.90 ($^3J_{HH}$ = 22.7 Hz)/δ 143.9 ($^1J_{CH}$ = 141 Hz), 205.4 (141 Hz)].

Scheme III



Scheme IV



These experiments show that a very reactive "$(H_3C\text{-}C_5H_4)_2Zr(H)Cl$" species is formed in equilibrium with $(H_3C\text{-}C_5H_4)_2ZrCl_2$ and $[(H_3C\text{-}C_5H_4)_2ZrH(\mu\text{-}H)]_2$. The modified Cp-substituted reagent can be used to prepare the typical hydrozirconation products quite analogously to the widely used $[Cp_2Zr(H)Cl]_x$ (**1**). However, the methylcyclopentadienyl-containing hydrozirconation reagent (**4**) seems to exhibit a rather enhanced reactivity compared to the parent compound. We carried out a few competition experiments to get a qualitative estimate as to how much faster the modified hydrozirconation reagent reacts with typical organic π-systems.

Competition Experiments. Relative rates of the hydrozirconation reactions were estimated by employing the reagents $Cp_2Zr(H)Cl$ (**1**) and $(H_3C\text{-}C_5H_4)_2Zr(H)Cl$ (**4**) and the substrates 1-hexene and acetophenone. In a first experiment, a 1:1 mixture of the reagents **1** and **4** was suspended in benzene-d_6. Then about $^1/_3$ molar equiv of 1-hexene was added and the mixture allowed to react for 10 min. A sample of the supernatant solution was analyzed by ^1H NMR. It revealed that the methyl-substituted hydrozirconation reagent had reacted predominantly. The reaction mixture contained the alkylmetallocene chloride products (1-hexyl)$ZrCl(\eta\text{-}C_5H_4CH_3)_2$ (**8**) and (1-hexyl)-$ZrClCp_2$ (**8a**) in a 86:14 ratio. Under the reaction conditions applied this serves as a measure of the relative observed reaction rates of the two hydrozirconation reagents. The modified hydrozirconation reagent $(H_3C\text{-}C_5H_4)_2Zr(H)Cl$ (**4**) reacts with 1-hexane about 6 times faster than $Cp_2Zr(H)Cl$ (**1**).

An analogous competition experiment between **1** and **4** was carried out by employing acetophenone. This furnished a similar result. Bis(η-methylcyclopentadienyl)-hydridozirconium chloride (**4**) reacts faster than $Cp_2Zr(H)Cl$ (**1**) with this ketone by a factor of about 7.

To further evaluate the outcome of these two experiments, we have reacted the $(MeCp)_2Zr(H)Cl$ hydrozirconation reagent **4** with an excess of various aceto-

---

[6] Erker, G.; Schlund, R.; Albrecht, M.; Sarter, C. *J. Organomet. Chem.* **1988**, *353*, C27.

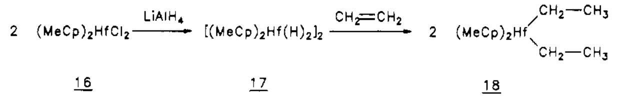
[7] Gambarotta, S.; Strogolo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278.

[8] For the analogous Cp_2Zr systems see: (a) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (b) Erker, G.; Frömberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1984**, *96*, 72.

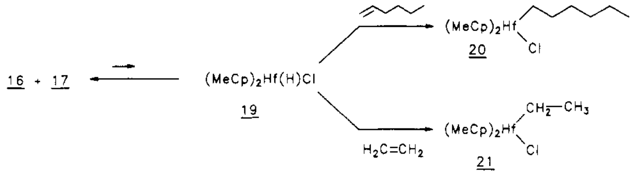
phenone/1-hexene mixtures. Even using an about 50-fold excess of the alkene did not result in formation of a measurable amount of (1-hexyl)ZrCl(CpMe)$_2$ (**8**). The reaction between (MeCp)$_2$Zr(H)Cl (**4**), acetophenone, and 1-hexene in a 1:1:48 molar ratio gave only (MeCp)$_2$ZrCl(OCHMePh) (**7**).

Although acetophenone is more quickly hydrozirconated than 1-hexene, it gives about the same competition ratio as 1-hexene when reacted with the mixture of hydrozirconation reagents (see above). This probably means that an enhanced solubility of the (H$_3$C-C$_5$H$_4$)$_2$Zr(H)Cl reagent and not its increased intrinsic reactivity is causing the pronouncedly faster product formation compared to that of the Cp$_2$Zr(H)Cl reagent.

Hydrohafnation. The hydridohafnocene chloride reagents Cp$_2$Hf(H)Cl and (Me$_5$C$_5$)$_2$Hf(H)Cl have been reported.[9] We have reacted (H$_3$C-C$_5$H$_4$)$_2$HfCl$_2$ (**16**) with lithium aluminum hydride and obtained bis(methyl-Cp) dihydridohafnium (**17**) as a μ-H-bridged dimer [(H$_3$C-C$_5$H$_4$)$_2$Hf(H)(μ-H)]$_2$.[10]



The dihydridohafnium complex **17** reacts with ethylene at room temperature in tetrahydrofuran with a near to quantitative formation of the diethylhafnocene **18**.[11] However, a mixture of (H$_3$C-C$_5$H$_4$)$_2$HfCl$_2$ and 0.5 equiv of [(H$_3$C-C$_5$H$_4$)$_2$HfH$_2$]$_2$, prepared either by mixing the two separately prepared components in tetrahydrofuran or by reacting (MeCp)$_2$HfCl$_2$ with 0.5 molar equiv of hydride (from LiAlH$_4$), reacted with 1-hexene quite differently, giving the hydrohafnation product 1-hexylbis(methylcyclopentadienyl)hafnium chloride (**20**) in high yield.



The reaction of the (MeCp)$_2$HfCl$_2$/(MeCp)$_2$HfH$_2$ $\rightleftharpoons$ 2 "(MeCp)$_2$Hf(H)Cl" equilibrium system with ethylene is more complicated. The major product is (MeCp)$_2$HfCl(ethyl) (**21**). However, we have also obtained appreciable amounts of (MeCp)$_2$Hf(ethyl)$_2$ (**18**) in addition to unreacted (MeCp)$_2$HfCl$_2$ starting material. The hydrohafnation products **21** and **18** are formed under the applied conditions in about a 2:1 ratio. Ethylene can apparently compete successfully with hafnocene dichloride for dihydridohafnocene which serves as a precursor of the hydrohafnation reagent **19**.

Carbonylation Reactions. Insertion of carbon monoxide into the newly formed metal to carbon bond is often applied for utilizing organometallic hydrometalation products. We have, therefore, reacted several σ-hydrocarbyl metallocenes, prepared from the (H$_3$C-C$_5$H$_4$)$_2$M(H)X reagents as described above, with CO.

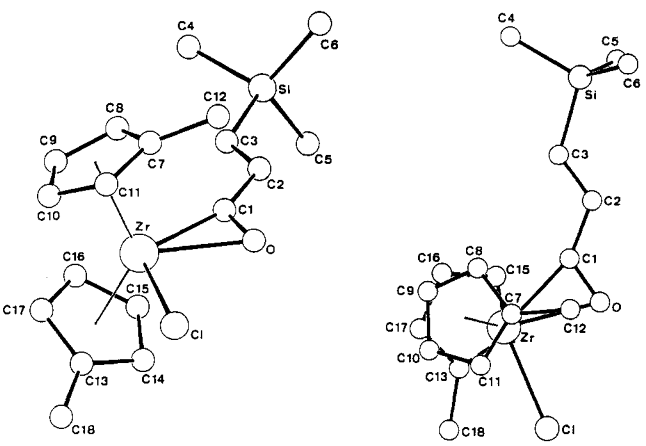
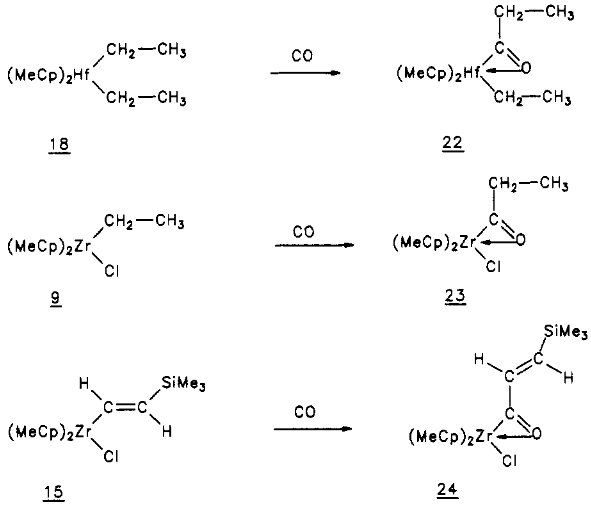


Figure 1. Two Projections of the molecular geometry of **24**.

Scheme V



The diethylhafnocene complex **18** consumes 1 equiv of CO at ambient temperature and pressure[12] to give **22** (94% isolated yield). The insertion of CO leads to a lowering of the overall molecular symmetry, as indicated by the increase in the observed ^{13}C NMR resonances for the distal and proximal carbons of the MeCp ligands from two for **18** (C_{2v} symmetry) at δ 108.4 and 111.2 to four for **22** (C_s symmetry) at δ 101.1, 101.5, 105.5, and 112.6. Complex **22** is characterized by exhibiting an acyl carbon ^{13}C NMR resonance at δ 331.6 (CDCl$_3$). The IR ν(C=O) absorption is observed at 1523 cm^{-1}. Both features are very typical for (η^2-acyl) group 4 metallocene complexes.[13]

Ethylbis(methylcyclopentadienyl)zirconium chloride (**9**) reacts equally facile with carbon monoxide in toluene at room temperature and ambient pressure to give (η^2-propionyl)ZrCl(CpMe)$_2$ (**23**) [^{13}C NMR (benzene-d_6) δ 316.3 (acyl C); IR ν(C=O) 1546 cm^{-1}].

The carbonylation of (σ-alkenyl)zirconocene complexes produces (α,β-unsaturated η^2-acyl)metallocene derivatives.[14] We have carried out the CO insertion into the Zr–C(sp^2) σ-bond of (H$_3$C-C$_5$H$_4$)$_2$ZrCl(CH=CHSiMe$_3$) (**15**) at ambient conditions in toluene. The (η^2-acyl)metallocene complex **24** was obtained in >90% yield. Complex **24** is

---

[9] Tolstokov, G. A.; Miftakov, M. S.; Valeev, F. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2576 *Chem. Abstr.* *92*:146863e. Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.

[10] Couturier, S.; Gautheron, B. *J. Organomet. Chem.* **1978**, 157, C61. See for a comparison: Couturier, S.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1980**, *195*, 291.

[11] In contrast, dialkylzirconocene complexes Cp$_2$Zr(–CH$_2$CH$_2$R)$_2$ rapidly decompose via β-hydride elimination/reductive elimination pathways. See, e.g.: Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

[12] Compare, e.g., with: Fachinetti, G.; Fochi, G.; Floriani, C.; *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

[13] Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. Erker, G.; Korek, U.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1989**, *364*, 133.

[14] Negishi, E.; Swanson, D. R.; Miller, S. R. *Tetrahedron Lett.* **1988**, *29*, 1631 (loc. cit.). See also: McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

Table I. Bond Distances (Å) and Angles (deg) for 24

Bond Distances

Zr–Cl	2.528 (1)	C(1)–C(2)	1.468 (4)
Zr–O	2.306 (2)	C(2)–C(3)	1.342 (5)
Zr–C(1)	2.189 (3)	C(7)–C(8)	1.414 (5)
Zr–C(7)	2.565 (3)	C(7)–C(11)	1.398 (5)
Zr–C(8)	2.526 (3)	C(7)–C(12)	1.510 (5)
Zr–C(9)	2.480 (3)	C(8)–C(9)	1.388 (5)
Zr–C(10)	2.474 (4)	C(9)–C(10)	1.368 (6)
Zr–C(11)	2.543 (3)	C(10)–C(11)	1.407 (6)
Zr–C(13)	2.570 (3)	C(13)–C(14)	1.419 (5)
Zr–C(14)	2.536 (3)	C(13)–C(17)	1.424 (5)
Zr–C(15)	2.518 (3)	C(13)–C(18)	1.475 (5)
Zr–C(16)	2.490 (3)	C(14)–C(15)	1.407 (5)
Zr–C(17)	2.513 (3)	C(15)–C(16)	1.396 (5)
Si–C(3)	1.877 (3)	C(16)–C(17)	1.379 (5)
Si–C(4)	1.870 (4)		
Si–C(5)	1.849 (4)		
Si–C(6)	1.849 (4)		
O–C(1)	1.226 (3)		

Bond Angles

C(1)–Zr–O	31.5 (1)	C(12)–C(7)–C(11)	126.4 (3)
C(1)–Zr–Cl	113.3 (1)	C(12)–C(7)–C(8)	126.7 (3)
O–Zr–Cl	81.8 (1)	C(11)–C(7)–C(8)	106.9 (3)
C(6)–Si–C(5)	110.6 (2)	C(9)–C(8)–C(7)	108.1 (3)
C(6)–Si–C(4)	112.0 (2)	C(10)–C(9)–C(8)	108.6 (3)
C(6)–Si–C(3)	108.9 (1)	C(11)–C(10)–C(9)	108.6 (3)
C(5)–Si–C(4)	111.0 (2)	C(10)–C(11)–C(7)	107.7 (3)
C(5)–Si–C(3)	109.2 (1)	C(18)–C(13)–C(17)	126.6 (3)
C(4)–Si–C(3)	105.0 (2)	C(18)–C(13)–C(14)	127.2 (3)
C(1)–O–Zr	69.0 (2)	C(17)–C(13)–C(14)	105.9 (3)
C(2)–C(1)–O	122.9 (3)	C(15)–C(14)–C(13)	108.1 (3)
C(2)–C(1)–Zr	157.5 (2)	C(16)–C(15)–C(14)	108.4 (3)
O–C(1)–Zr	79.5 (2)	C(17)–C(16)–C(15)	108.1 (3)
C(3)–C(2)–C(1)	121.4 (3)	C(16)–C(17)–C(13)	109.4 (3)
C(2)–C(3)–Si	127.6 (2)		

Table II. Positional Parameters for 24

atom	*x*	*y*	*z*
Zr	0.6926 (1)	0.2466 (1)	0.1720 (1)
Cl	0.8396 (1)	0.2294 (1)	0.3448 (1)
Si	0.1833 (1)	0.2558 (1)	−0.0079 (1)
O	0.5726 (2)	0.2216 (2)	0.2757 (1)
C(1)	0.5196 (2)	0.2342 (2)	0.1846 (2)
C(2)	0.3961 (2)	0.2294 (2)	0.1489 (2)
C(3)	0.3400 (2)	0.2549 (2)	0.0511 (2)
C(4)	0.1642 (3)	0.2615 (3)	−0.1514 (3)
C(5)	0.1225 (3)	0.3750 (3)	0.0377 (3)
C(6)	0.1228 (3)	0.1330 (3)	0.0312 (3)
C(7)	0.6644 (3)	0.0452 (2)	0.1454 (3)
C(8)	0.6082 (3)	0.0956 (2)	0.0510 (2)
C(9)	0.6885 (4)	0.1453 (3)	0.0118 (2)
C(10)	0.7926 (3)	0.1280 (3)	0.0789 (3)
C(11)	0.7796 (3)	0.0647 (3)	0.1617 (3)
C(12)	0.6109 (4)	−0.0199 (3)	0.2142 (3)
C(13)	0.7998 (2)	0.4227 (2)	0.1755 (3)
C(14)	0.7020 (3)	0.4451 (2)	0.2084 (3)
C(15)	0.6071 (3)	0.4279 (3)	0.1237 (3)
C(16)	0.6440 (3)	0.3912 (3)	0.0399 (2)
C(17)	0.7602 (3)	0.3881 (2)	0.0704 (3)
C(18)	0.9181 (3)	0.4426 (3)	0.2336 (3)
H(2)	0.3529	0.2033	0.1985
H(3)	0.3883	0.2796	0.0064
H(4a)	0.2005	0.3288	−0.1693
H(4b)	0.2016	0.1989	−0.1744
H(4c)	0.0825	0.2624	−0.1893
H(5a)	0.1399	0.3730	0.1167
H(5b)	0.1569	0.4412	0.0180
H(5c)	0.0393	0.3768	0.0081
H(6a)	0.1590	0.0694	0.0075
H(6b)	0.1412	0.1308	0.1096
H(6c)	0.0408	0.1314	0.0009
H(8)	0.5214	0.0970	0.0198
H(9)	0.6732	0.1879	−0.0551
H(10)	0.8670	0.1576	0.0716
H(11)	0.8425	0.0372	0.2250
H(12a)	0.5563	0.0281	0.2411
H(12b)	0.5639	−0.0800	0.1755
H(12c)	0.6678	−0.0479	0.2758
H(14)	0.7044	0.4685	0.2842
H(15)	0.5243	0.4419	0.1215
H(16)	0.5936	0.3706	−0.0316
H(17)	0.8126	0.3636	0.0256
H(18a)	0.9314	0.5208	0.2505
H(18b)	0.9390	0.4024	0.3026
H(18c)	0.9724	0.4194	0.1935

characterized by ν(C=O) = 1511 cm^{-1}. A ^{13}C NMR signal of the carbonyl carbon atom at δ 305.0 indicates the presence of η^2-acyl coordination in solution. The *E* configuration of the CH=CHSiMe$_3$ double bond is retained in the carbonylation reaction [**24**: ^{1}H NMR δ 7.05, 7.62 ($^3J_{HH}$ = 18.4 Hz)]. Complex **24** was characterized by an X-ray crystal structure analysis.

X-ray Crystal Structure Analysis of 24. The zirconium atom in **24** is pseudotetrahedrally coordinated by two η-methylcyclopentadienyl rings, a η^2-acyl ligand, and chloride. The Zr–Cl bond length is 2.528 (1) Å. The average RCp ring carbon zirconium distance is 2.52 (3) Å. The bent metallocene "wedge" shows a typical angle of 127.1° between the normals to the Cp ring planes.[15] The relative orientation of the Cp-methyl substituents is unusual.[16] One methyl group [C(12)] is pointing toward the central position at the open side of the bent metallocene wedge, whereas the other [C(18)] is oriented in the lateral position toward the chloride ligand. The C(12)–C(7) and C(18)–C(13) vectors comprize a dihedral angle of about 103°.

The C(1)–Zr–Cl angle is large (113.3 (1)°). The centers C(1) and Cl are separated by the η^2-acyl oxygen atom, binding to zirconium in the central position in the major plane of the bent metallocene unit; i.e., the η^2-acyl group is "η^2-O-inside" bound.[17] The η^2-acyl Zr–C(1) bond is quite short (2.189 (3) Å) while the Zr–O distance is much larger (2.306 (2) Å). However, both values are clearly within the limits typical for η^2-acyl coordination at zirconium, as is the rather short C(1)–O distance (1.226 (3) Å).[13,15] The η^2-acyl ligand is planar. The deviation of the acyl oxygen atom from the calculated plane going through Zr, Cl, Si, C(1), C(2), and C(3) is only 0.01 Å. Complex **24** exhibits a C(2)–C(3) trans double bond [angles O–C(1)–C(2) = 122.9 (3)°, C(1)–C(2)–C(3) = 121.4 (3)°, Si–C(3)–C(2) = 127.6 (2)°; torsion angles O–C(1)–C(2)–C(3) = 172.6°, Zr–C(1)–C(2)–C(3) = −12.7°; the angle between the Zr–C(1)–O and O–C(1)–C(2) planes is 2.2°]. The α,β-unsaturated carbonyl unit exhibits a pronounced short–long–short bond lengths sequence [C(1)–O = 1.226 (3) Å, C(1)–C(2) = 1.468 (4) Å, C(2)–C(3) = 1.342 (5) Å]. A comparison with typical averaged bond lengths (Å) of α,β-unsaturated ketones [O=CRC$^\alpha$=C$^\beta$ = 1.222 (C=O), 1.465 (acyl C–C$^\alpha$), 1.340 (C$^\alpha$=C$^\beta$)][18] reveals that the internal coordination of the acyl oxygen atom using its *n*-electron pair in this (η^2-acyl)zirconocene complex has only a marginal influence on the structural properties of the α,β-unsaturated car-

---

[15] Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986; loc. cit.

[16] Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422. Dusasoy, J.; Protas, J.; Renaut, P.; Gautheron, B.; Tainturier, G. *J. Organomet. Chem.* **1978**, *157*, 167. Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *338*, C4.

[17] Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. Erker, G.; Rosenfeldt, F. *Angew. Chem.* **1978**, *90*, 640. Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* **1980**, *188*, C1. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

[18] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, S1.

bonyl π-system that is oriented perpendicular to the plane of the Zr,C(1),O σ-bonds. Complex **24** seems to be the first α,β-unsaturated (η^2-acyl)zirconocene complex characterized by X-ray diffraction thus far.

Experimental Section

Reactions with organometallic compounds were carried out in an argon atmosphere by using Schlenk type glassware. Solvents were dried and freshly distilled from potassium/benzophenone, lithium aluminum hydride, or P_4O_{10} under argon prior to use. Deuterated solvents were treated with sodium/potassium alloy (benzene-d_6, toluene-d_8, tetrahydrofuran-d_8) or Sicapent (Merck) (chloroform-*d*), distilled, and stored under argon. The following spectrometers were used: NMR, Bruker WP 200 SY (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz); IR, Nicolet 5-DXC FT. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr. Melting points are uncorrected. The complexes $Cp_2Zr(H)Cl$ (**1**), $(MeCp)_2ZrCl_2$ (**2**), and $(MeCp)_2HfCl_2$ (**16**) were prepared following literature procedures (see text for references).

Generation of Bis(η^5-methylcyclopentadienyl)chlorohydridozirconium (**4**). To a suspension of 41.8 g (130 mmol) of $(MeCp)_2ZrCl_2$ (**2**) in 150 mL of tetrahydrofuran was added 33.0 mL (31.7 mmol) of a 0.96 M solution of $LiAlH_4$ in THF at ambient temperature during 1 h with stirring. The resulting amber suspension was stirred for an additional 2 h in the dark at room temperature and then filtered. The slightly pink solid was washed twice with 30 mL of THF and then with 30 mL of pentane to give 24.4 g (65%), mp 120–125 °C dec. Anal. Calcd for $C_{12}H_{15}ClZr$ (285.9): C, 50.40; H, 5.29. Found: C, 50.58; H, 5.27. The ^{1}H NMR spectrum (THF-d_8) shows only signals of a mixture of **4** and **2**. **4**: δ −3.00 (t, *J* = 7.1 Hz, 2 H, Zr(μ-H)), 2.15 (s, $CpCH_3$), 3.76 (t, *J* = 7.1 Hz, 2 H, ZrH), 5.43, 5.49, 5.69, 5.88 (m, 4 H each, $C_5H_4CH_3$). **2**: δ 2.22 (s, $CpCH_3$), 6.17, 6.35 (m, 4 H each, $C_5H_4CH_3$).

Bis(η^5-methylcyclopentadienyl)chloromethoxyzirconium (6). A solution of 1.20 mL (30.0 mmol) of methanol in 10 mL of toluene was added dropwise to a suspension of 8.58 g (30.0 mmol) of $(MeCp)_2Zr(H)Cl$ (**4**) at −78 °C in 50 mL of toluene. The reaction mixture was warmed to room temperature during 20 h. The solvent was removed in vacuo from the gold-yellow solution. The residue was suspended in 20 mL of pentane. Filtration yielded 6.62 g (70%) of **6**: mp 160–164 °C dec. Anal. Calcd for $C_{13}H_{17}ClOZr$ (316.0): C, 49.41; H, 5.42. Found: C, 48.64; H, 5.18. ^{1}H NMR (benzene-d_6): δ 2.04 (s, 6 H, $CpCH_3$), 3.71 (s, 3 H, OCH_3), 5.71 (m, 4 H), 5.80 (m, 4 H) (MeCp). ^{13}C NMR (benzene-d_6): δ 14.9 ($CpCH_3$), 62.4 (OCH_3), 110.7, 111.0, 112.8, 115.0 (CpC), 128.3 (CpC_{ipso}).

(μ-Oxo)bis[bis(η^5-methylcyclopentadienyl)chlorozirconium] (5). A 30-mL Schlenk tube was charged with 1.26 g (4.41 mmol) of **4** in 20 mL of toluene. The flask was evacuated. Dry carbon dioxide gas (50.0 mL, 2.20 mmol) was introduced. The precipitate dissolved during 2 min. The solvent was removed in vacuo to give 940 mg (73%) of **5**, mp 165 °C. Anal. Calcd for $C_{24}H_{28}Cl_2OZr_2$ (585.8): C, 49.21; H, 4.82. Found: C, 49.58; H, 5.13. ^{1}H NMR (benzene-d_6): δ 2.17 (s, 12 H, $CpCH_3$), 5.60 (m, 4 H), 5.77 (m, 4 H), 5.97 (m, 4 H), 6.06 (m, 4 H) (MeCp). ^{13}C NMR (benzene-d_6): δ 15.4 ($CpCH_3$), 109.5, 112.9, 113.5, 117.3 (MeCpC), 126.9 ($MeCpC_{ipso}$).

***rac*-Bis(η^5-methylcyclopentadienyl)chloro(1-phenylethoxy)zirconium (7).** Acetophenone (0.31 mL, 2.69 mmol) was added dropwise with stirring to a suspension of 770 mg (2.69 mmol) of **4** in 20 mL of toluene at room temperature. The precipitate dissolved instantaneously. The resulting slightly yellow solution was stripped to give an amber, waxlike substance from which residual solvent was removed in vacuo (10^{-3} bar, 3 h): yield 1.00 g (92%). Anal. Calcd for $C_{20}H_{23}ClOZr$ (406.1): C, 59.15; H, 5.71. Found: C, 59.16; H, 5.63. ^{1}H NMR (benzene-d_6): δ 1.34 (d, *J* = 7.1 Hz, 3 H, CH_3), 2.03, 2.10 (2 s, 6 H, $CpCH_3$), 5.04 (q, *J* = 7.1 Hz, 1 H, C–H), 5.70–5.82 (m, 8 H, MeCp), 7.05–7.31 (m, 5 H, Ph). ^{13}C NMR (benzene-d_6): δ 15.2, 15.3 ($CpCH_3$), 26.5 (CCH_3), 81.6 (OC), 110.3, 110.5, 110.6, 110.8, 114.7, 114.8, 115.1 (MeCpC), 125.8, 128.5 (Ph), 127.2 ($MeCpC_{ipso}$), 147.3 (PhC_{ipso}). ^{17}O NMR (toluene): δ 261.0.

Bis(η^5-methylcyclopentadienyl)chloroethylzirconium (9). Ethylene (44 mL, 2.0 mmol) was introduced to the suspension of 570 mg (1.99 mmol) in **4** in 20 mL of toluene at ambient temperature. Within 2.5 min a clear yellow solution was formed. The solvent was removed in vacuo to give a brightly yellow oil: 618 mg. The product was only characterized by NMR spectroscopy. ^{1}H (benzene-d_6): δ 1.06 (q, 2 H, CH_2CH_3), 1.43 (t, 3 H, CH_2CH_3), 2.06 (s, 6 H, $CpCH_3$), 5.32 (m, 2 H), 5.49 (m, 2 H), 5.64 (m, 2 H), 5.95 (m, 2 H) (MeCp). ^{13}C NMR (benzene-d_6): δ 15.3 ($CpCH_3$), 18.3 (CH_3), 44.9 (CH_2), 107.9 111.3, 111.7, 116.4 (CpC), 126.4 (CpC_{ipso}).

Bis(η^5-methylcyclopentadienyl)chloro(1-hexyl)zirconium (8). To a suspension of 290 mg (1.01 mmol) of **4** in 10 mL of toluene was added 0.13 mL (1.01 mmol) of 1-hexene at room temperature. A clear yellow solution is formed within 5 min. After 10 min of additional stirring the solvent was removed in vacuo. The yellow oil was dissolved in 30 mL of pentane. The solvent was again removed in vacuo. Residual traces of solvent were removed at reduced pressure ($<10^{-3}$ bar, 2 h); yield 359 mg (97%). Anal. Calcd for $C_{18}H_{27}ClZr$ (370.1): C, 58.42; H, 7.35. Found: C, 57.01; H, 7.21. ^{1}H NMR (benzene-d_6): δ 0.97 (t, 3 H, CH_3), 1.04–1.09 (m, 2 H, CH_2), 1.30–1.45 (m, 6 H, CH_2), 1.49–1.67 (m, 2 H, CH_2), 2.07 (s, 6 H, $CPCH_3$), 5.34 (m, 2 H), 5.50 (m, 2 H), 5.67 (m, 2 H), 5.98 (m, 2 H) (MeCp). ^{13}C NMR (benzene-d_6): δ 14.5 (CH_3), 15.4 ($CpCH_3$), 23.3, 32.0, 34.2, 36.4 (CH_2), 53.9 ($ZrCH_2$), 107.9, 111.3, 111.7, 116.4 (MeCpC), 126.3 ($MeCpC_{ipso}$).

Alternative Preparation of 8 Starting from 2 and 3. (a) In THF/Toluene. Complexes **3** (160 mg, 0.63 mmol) and **2** (203 mg, 0.63 mmol) were dissolved in 20 mL of THF. The solvent was then removed in vacuo to give a white powder. A suspension of this material (200 mg, being equivalent to 0.70 mmol of **4**) in 20 mL of toluene was mixed with 0.1 mL (0.8 mmol) of 1-hexene at room temperature. A clear yellow solution was obtained after 5 min. The ^{1}H NMR spectrum of a sample showed that >90% of the hydrozirconation product **8** had been formed.

(b) In Toluene. A mixture of 540 mg (2.15 mmol) of **3** and 688 mg (2.15 mmol) of **2** in 20 mL of toluene was stirred for 30 min at room temperature. 1-Hexene (0.54 mL, 4.30 mmol) was added with stirring. After 2 min a slightly cloudy orange solution had formed. Its ^{1}H NMR spectrum was identical with that for **8**.

Reaction of 4 with 1-Phenyl-1-(trimethylsiloxy)ethene. A suspension of 240 mg (0.84 mmol) of **4** in 1.0 mL of benzene-d_6 was stirred at room temperature with 0.17 mL (0.84 mmol) of 1-phenyl-1-(trimethylsiloxy)ethene. A clear orange solution was obtained after 20 min. The ^{1}H NMR spectrum revealed the formation of bis(η^5-methylcyclopentadienyl)chloro(trimethylsiloxy)zirconium (**11**) and bis(η^5-methylcyclopentadienyl)chloro(1-phenylethyl)zirconium (**12**). ^{1}H NMR (benzene-d_6): δ 0.20 (s, 9 H, $Si(CH_3)_3$ (**11**)), 2.11 (s, 6 H, $CpCH_3$ (**11**)), 5.47 (m, 2 H), 5.60 (m, 2 H), 5.81 (m, 2 H), 5.93 (m, 2 H), 6.02 (m, 2 H) (MeCp (**11** and **12**)), 2.14 (s, 6 H, $CpCH_3$ (**11**)), 1.35, 2.90 (m, 2 H each, $ZrCH_2CH_2$ (**12**)), 7.15–7.35 (m) and 7.68–7.74 (m) (Ph (**11**)).

[μ-(O-η^1:C,O-η^2)-Formaldehyde]bis[bis(η^5-methylcyclopentadienyl)chlorozirconium] (13). A suspension of 810 mg (2.83 mmol) of **4** in 25 mL of toluene was stirred at ambient temperature in a CO atmosphere. The reaction mixture turned yellow within a few seconds. During 16 min 30.0 mL (1.40 mmol) of CO was taken up. From the resulting clear yellow solution the product **13** crystallized at −30 °C. It was washed once with 30 mL of pentane and dried in vacuo: yield 583 mg (69%); mp 140 °C. Anal. Calcd for $C_{25}H_{30}Cl_2OZr_2$ (599.9): C, 50.06; H, 5.04. Found: C, 49.96; H, 4.94. ^{1}H NMR (benzene-d_6): δ 2.09 (s, 12 H, $CpCH_3$), 2.88 (m, 2 H, CH_2), 5.40 (m, 4 H), 5.80 (m, 4 H), 5.88 (m, 4 H), 6.04 (m, 4 H) (MeCp). ^{13}C NMR (benzene-d_6): δ 15.6, ($CpCH_3$), 76.7 (CH_2O), 109.6, 111.1, 112.3, 115.4 (MeCpC), 124.9 ($MeCpC_{ipso}$).

Bis(η^5-methylcyclopentadienyl)chloro(phenylmethanimido)zirconium (14). (a) In Toluene Solvent. Benzonitril (0.30 mL, 2.93 mmol) was added with stirring to a suspension of 840 mg (2.93 mmol) of **4** in 20 mL of toluene at ambient temperature. A clear orange solution was formed within seconds. Solvent was removed in vacuo. The resulting orange oil solidified upon stirring with 20 mL of pentane. Filtration gave 900 mg (79%) of **14**: mp 83 °C dec. Anal. Calcd for $C_{19}H_{20}ClNZr$ (389.1): C, 58.66; H, 5.18; N, 3.60. Found: C, 57.73; H, 5.10; N, 3.36. IR (CH_2Cl_2): ν(CN) = 1671 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.99 (s, 6 H, $CpCH_3$), 5.53 (m, 2 H), 5.60 (m, 2 H), 5.77 (m, 2 H), 5.84 (m, 2 H) (MeCp), 7.04–7.22 (m), 7.55–7.61 (m) (5 H, PhH), 9.06 (s, 1 H, N=CH). ^{13}C NMR (benzene-d_6): δ 15.2 (CpCH$_3$), 107.5, 108.8, 111.4, 113.8 (CpC), 125.2 (CpC$_{ipso}$), 128.3, 129.0, 131.0 (PhC), 138.8 (PhC$_{ipso}$), 165.8 (N=C).

(b) In Tetrahydrofuran Solvent. Benzonitril (0.09 mL, 0.87 mmol) was added to a suspension of 250 mg (0.87 mmol) of **4** in 5 mL of THF at room temperature with stirring. After 15 s a clear yellow solution had formed. The ^{1}H NMR spectrum of a sample revealed the quantitative formation of **14**.

Bis(η^5-methylcyclopentadienyl)chloro[(*E*)-2-(trimethylsilyl)ethenyl]zirconium (15). To a suspension of 600 mg (2.10 mmol) of **4** in 20 mL of toluene at room temperature was added with stirring 0.30 mL (2.10 mmol) of (trimethylsilyl)acetylene. A clear solution was obtained within ca. 1 min. The solution was concentrated in vacuo to about 10-mL volume. Pentane (10 mL) was added. The product **15** precipitated from this mixture upon cooling to −50 °C: yield 720 mg (89%); mp 147–150 °C dec. Anal. Calcd for $\mathrm{C_{17}H_{25}ClSiZr}$ (384.2): C, 53.15; H, 6.56. Found: C, 53.16; H, 6.33. ^{1}H NMR (benzene-d_6): δ 0.15 (s, 9 H, Si(CH$_3$)$_3$), 2.05 (s, 6 H, CpCH_3), 5.42–5.52 (m, 4 H), 5.70 (m, 2 H), 5.77 (m, 2 H) (MeCp), 6.59 (d, J = 22.7 Hz; 1 H, =CH), 7.90 (d, J = 22.7 Hz, 1 H, =CH). ^{13}C NMR (benzene-d_6): δ −0.77 (q, J = 121 Hz, Si(CH$_3$)$_3$), 15.3 (q, J = 121 Hz, CpCH$_3$), 107.2 (d, J = 161 Hz), 109.4 (d, J = 161 Hz), 114.8 (d, J = 161 Hz), 115.9 (d, J = 161 Hz) (MeCpC), 125.8 (s, MeCpC$_{ipso}$), 143.9 (d, J = 141 Hz, =CH), 205.4 (d, J = 141 Hz, =CH).

Competition Experiments. A sample containing 390 mg (1.36 mmol) of **4** and 350 mg (1.36 mmol) of **1** was suspended in 2.0 mL of benzene-d_6. Acetophenone (0.05 mL, 0.43 mmol) was added at 25 °C and the mixture stirred for exactly 10 min. The clear supernatant solution was decanted. ^{1}H NMR analysis using the CpCH_3 singlets of **7** (δ 2.03, 2.10) and the Cp singlets of **7a** (δ 5.90, 5.93) revealed the formation of the hydrozirconation products **7** and **7a** in a 88:12 molar ratio. Analogously, a mixture of 300 mg (1.05 mmol) of **4** and 270 mg (1.05 mmol) of **1** is reacted with 1-hexene (0.04 mL, 0.34 mmol) to give **8** [δ 2.07 (CpCH_3)] and **8a** [δ 5.77 (Cp)] in a 86:14 ratio.

A suspension of 170 mg (0.59 mmol) of **4** in 5 mL of toluene was reacted for 10 min at 25 °C with a mixture of acetophenone (0.24 mL, 2.03 mmol) and 1-hexene (0.25 mL, 2.03 mmol). The solvent was then changed to benzene-d_6. Analysis by ^{1}H NMR revealed only the formation of the acetophenone hydrozirconation product **7**. The same result was obtained when mixtures of 120 mg (0.42 mmol) of **4**, 0.05 mL (0.42 mmol) of acetophenone, and 0.53 mL (4.20 mmol) of 1-hexene in 3.56 mL of toluene or 70 mg (0.25 mmol) of **4**, 0.03 mL (0.25 mmol) of acetophenone, and 1.50 mL (12.0 mmol) of 1-hexene in 2.10 mL of toluene were reacted analogously at 25 °C.

Bis(η^5-methylcyclopentadienyl)dihydridohafnium (17). To a solution of 10.0 g (24.5 mmol) of **16** in 50 mL of tetrahydrofuran at room temperature was added 6.30 mL (6.11 mmol) of a 0.97 M solution of LiAlH$_4$ in THF dropwise. The resulting suspension was stirred for an additional hour and then filtered. The white precipitate was washed twice with 20 mL of pentane and dried in vacuo: yield 3.0 g (72%); mp 188 °C. Anal. Calcd for $\mathrm{C_{12}H_{16}Hf}$ (338.8): C, 42.55; H, 4.76. Found: C, 42.53; H, 4.66. ^{1}H NMR (THF-d_8): δ 1.35 (t, J = 7.2 Hz, 2 H, Hf(μ-H)), 2.24 (s, 12 H, CpCH_3), 5.33 (m, 4 H), 5.38 (m, 4 H), 5.60 (m, 4 H), 5.83 (m, 4 H) (MeCp), 9.67 (t, J = 7.2 Hz, 2 H, HfH).

H/Cl Ligand Exchange between 17 and 16. Hydrohafnation of Alkenes. (a) Reaction with 1-Hexene. A suspension of 130 mg (0.38 mmol) of **17** and 155 mg (0.38 mmol) of **16** in 20 mL of tetrahydrofuran was stirred for 30 min at ambient temperature. Then 0.10 mL (0.76 mmol) of 1-hexene was added. After 12 min a clear yellow solution had formed. The solvent was removed in vacuo. The viscous residue contained about 75% of the hydrohafnation product **20** (characterized by NMR). ^{1}H NMR (benzene-d_6): δ 0.81–0.89 (m, 2 H, CH$_2$), 0.99 (t, 3 H, CH$_3$), 1.34–1.49 (m, 6 H, CH$_2$), 1.55–1.74 (m, 2 H CH$_2$), 2.09 (s, 6 H, CpCH_3), 5.29 (m, 2 H), 5.45 (m, 2 H), 5.61 (m, 2 H), 5.88 (m, 2 H) (MeCp). The product contains approximately 10% of **16** plus 15% of an as yet unidentified additional hafnium complex.

(b) Reaction with Ethylene. A suspension of 130 mg (0.38 mmol) of **17** and 155 mg (0.38 mmol) of **16** in 20 mL of tetrahydrofuran was stirred at room temperature in an ethylene atmosphere. During ca. 1 min 20 mL of ethylene (0.90 mmol) were taken up, yielding a clear yellow solution. NMR analysis revealed the presence of a mixture of (MeCp)$_2$HfCl$_2$ (**16**), (MeCp)$_2$Hf(Et)Cl (**21**), and (MeCp)$_2$HfEt$_2$ (**18**) in a 3:4:2 ratio. **21**: ^{1}H NMR (benzene-d_6) δ 0.86 (q, 2 H, CH$_2$), 1.62 (t, 3 H, CH$_3$), 2.08 (s, 6 H, CpCH_3), 5.24–5.30 (m), 5.40–5.46 (m), 5.65–5.74 (m, MeCp).

Bis(η^5-methylcyclopentadienyl)diethylhafnium (18). A suspension of 140 mg (0.41 mmol) of **17** in 20 mL of tetrahydrofuran was stirred in an ethylene atmosphere. Within 10 min 20 mL (0.91 mmol) of ethylene were consumed, resulting in the formation of a slightly yellow solution. The solvent was removed in vacuo to give the product **18** as an oil, yield 154 mg (95%). Anal. Calcd for $\mathrm{C_{16}H_{24}Hf}$ (366.8): C, 48.67; H, 6.13. Found: C, 47.76; H, 6.13. ^{1}H NMR (benzene-d_6): δ 0.15 (q, 4 H, CH$_2$), 1.46 (t, 6 H, CH$_3$), 1.92 (s, 6 H, CpCH_3), 5.50–5.56 (m, 8 H, MeCp). ^{13}C NMR (benzene-d_6): δ 14.7 (CH$_3$), 15.9 (CH$_3$), 49.1 (CH$_2$), 108.4, 111.2 (MeCpC), 121.6 (MeCpC$_{ipso}$).

Carbonylation Reactions. Bis(η^5-methylcyclopentadienyl)chloropropionylzirconium (23). A suspension of 2.10 g (7.34 mmol) of **4** in 30 mL of toluene was reacted with 184 mL (8.20 mmol) of ethylene. The resulting solution was stirred for 15 min at room temperature. Ethylene was removed from the solution in vacuo. Then an atmosphere of CO was introduced. After about 1 h 180 mL (8.03 mmol) of CO had been taken up by the solution. Solvent was removed in vacuo. The remaining solid was washed twice with 20 mL of pentane: yield 2.33 g (93%); mp 119 °C. Anal. Calcd for $\mathrm{C_{15}H_{19}ClOZr}$ (341.9): C, 52.68; H, 5.59. Found: C, 52.42; H, 5.48. IR (CDCl$_3$): ν(CO) 1546 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.04 (t, 3 H, CH$_3$), 1.81 (s, 6 H, CpCH_3), 2.61 (q, 2 H, CH$_2$), 5.24 (m, 2 H), 5.31 (m, 2 H), 5.44 (m, 2 H), 5.83 (m, 2 H) (MeCp). ^{13}C NMR (benzene-d_6): δ 8.4 (CH$_3$), 14.5 (CpCH$_3$), 40.3 (CH$_2$), 104.1 105.4, 109.8, 115.8 (MeCpC), 121.6 (MeCpC$_{ipso}$), 316.3 (C=O).

Bis(η^5-methylcyclopentadienyl)chloro[(*E*)-3-(trimethylsilyl)-1-oxo-2-propenyl]zirconium (24). A solution of 200 mg (0.52 mmol) of **15** in 15 mL of toluene was stirred in a CO atmosphere at 8 °C. During 2 h 11 mL (0.5 mmol) of CO was consumed to give a clear, orange solution. Solvent was removed in vacuo. The resulting brown viscous residue was stirred with 20 mL of pentane. The solvent was removed in vacuo to give a brown powder of **24**: 193 mg (90%); mp 118 °C. Anal. Calcd for $\mathrm{C_{18}H_{25}ClOSiZr}$ (412.2): C, 52.46; H, 6.11. Found: C, 52.22; H, 6.10. IR (CH$_2$Cl$_2$): ν(C=O) 1511 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 0.06 (s, 9 H, Si(CH$_3$)$_3$), 1.88 (s, 6 H, CpCH_3), 5.36 (m, 2 H), 5.50 (m, 4 H), 5.90 (m, 2 H) (MeCp), 7.05 (d, J = 18.4 Hz, 1 H, =CH), 7.62 (d, J = 18.4 Hz, 1 H, =CH). ^{13}C NMR (benzene-d_6): δ −2.1 (Si(CH$_3$)$_3$), 14.6 (CpCH$_3$), 104.0, 105.5, 110.0, 115.7 (MeCpC), 122.3 (MeCpC$_{ipso}$), 141.9, 163.4 (C=C), 305.0 (C=O).

Crystal Structure Analysis of 24: $\mathrm{C_{18}H_{25}ClOSiZr}$; M = 412.2; monoclinic, $P2_1/c$; a = 12.321 (2) Å, b = 12.553 (3) Å, c = 13.367 (1) Å, β = 105.77 (1)°; V = 1989.6 Å^3; Z = 4; δ_{calcd} = 1.38 g cm^{-3}; μ = 7.37 cm^{-1}; Enraf-Nonius diffractometer; 11598 measured reflections, 3946 observed ($\lambda \geq 2\sigma(I)$); direct method (SHELX 86); R = 0.033, R_w = 0.045 for 199 parameters. Further details are given in the supplementary material.

Bis(η^5-methylcyclopentadienyl)ethylpropionylhafnium (22). A solution of 118 mg (0.30 mmol) of **18** in 20 mL of tetrahydrofuran was stirred for 3 h in a CO atmosphere at room temperature. A volume of 6.0 mL (0.28 mmol) of carbon monoxide gas was taken up. The solvent was removed in vacuo to give **22** as a yellow oil, yield 119 mg (94%). IR (KBr): ν(C=O) 1523 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 1.04 (t, 3 H, CH$_3$(propionyl)), 1.05 (q, 2 H, CH$_2$(ethyl)), 1.54 (s, 6 H, CpCH_3), 1.87 (t, 3 H, CH$_3$(ethyl)), 2.56 (q, 2 H, CH$_2$(propionyl)), 4.98 (m, 2 H), 5.18–5.26 (m, 4 H), 5.60 (m, 2 H) (MeCp). ^{13}C NMR (CDCl$_3$): δ 7.9 (CH$_3$), 13.6 (CH$_3$), 16.5 (CH$_3$), 25.9 (CH$_2$), 41.3 (CH$_2$), 101.1, 101.5, 105.5, 112.6 (MeCpC), 115.7 (MeCpC$_{ipso}$), 331.6 (CO).

Acknowledgment. Financial support of this work from the Stiftung Volkswagenwerk, the Fonds der Chemischen Industrie, and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

Registry No. **1**, 37342-97-5; **2**, 12109-71-6; **3**, 77965-67-4; **4**, 122116-29-4; **5**, 12114-73-7; **6**, 122116-30-7; **7**, 122116-31-8; **7a**, 122116-42-1; **8**, 122116-32-9; **8a**, 54471-27-1; **9**, 122116-45-4; **11**, 122116-33-0; **12**, 122116-34-1; **13**, 122116-35-2; **14**, 122116-36-3;

15, 122116-37-4; **16**, 32985-20-9; **17**, 68183-88-0; **18**, 122116-38-5; **20**, 122116-43-2; **21**, 122116-44-3; **22**, 122116-39-6; **23**, 122116-40-9; **24**, 122116-41-0; acetophenone, 98-86-2; ethylene, 74-85-1; 1-hexene, 592-41-6; 1-phenyl-1-(trimethylsiloxy)ethene, 13735-81-4; benzonitrile, 100-47-0; (trimethylsilyl)acetylene, 1066-54-2.

Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, and selected interatomic distances and angles for **24** (6 pages); a listing of observed and calculated structure factors for **24** (18 pages). Ordering information is given on any current masthead page.

Preparation, Properties, and Reactions of Metal-Containing Heterocycles. 65.[1] The Behavior of Tetracarbonyl(η^2-ethene)ruthenium toward Activated Alkenes and Alkynes

Ekkehard Lindner,* Rolf-Michael Jansen, Hermann August Mayer, Wolfgang Hiller, and Riad Fawzi

Institut für Anorganische Chemie der Universität, Auf der Morgenstelle 18, D-7400 Tübingen 1, West Germany

Received March 1, 1989

(η^2-C_2H_4)Ru(CO)$_4$ (**1**) reacts with the activated olefins $R^1R^2C{=}CR^2R^1$ (**2a,b**) (**a**, R^1 = H, R^2 = CN; **b**, $R^1 = R^2$ = CN) to give the substitution products (η^2-$R^1R^2C{=}CR^2R^1$)Ru(CO)$_4$ (**3a,b**). Toward electron-poor alkynes, however, **1** is a suitable educt for different cyclization reactions. Under elimination of carbon monoxide and ethylene, **1** reacts with two alkyne molecules $ZC{\equiv}CZ$ (**4c,d**) (**c**, Z = CO_2CH_3; **d**, Z = $CO_2C_2H_5$) to form the tricyclic compounds **8c,d** containing two tricarbonylruthenacyclopentadiene rings. This reaction proceeds via nondetectable intermediates (η^2-$ZC{\equiv}CZ$)$_2$Ru(CO)$_3$ (**5c,d**) and $(OC)_3\overline{RuCZ{=}CZCZ{=}C}Z$ (**7c,d**). The empty coordination sites at the ruthenium atoms are occupied by two ester carbonyl donor bonds in each case. The dimeric structure of **8d**, showing an eight-membered ring in a chair conformation, was elucidated by an X-ray structural analysis. **8d** crystallizes in the monoclinic space group $P2_1/c$ with Z = 2. The cell dimensions are a = 13.101 (3) Å, b = 17.768 (4) Å, c = 9.536 (3) Å, and β = 96.43 (3)°. **8c,d** are catalysts for the cyclotrimerization of the alkynes **4c,d**. The turnover numbers for the formation of the benzenehexacarboxylic acid hexaalkyl esters **13c,d** are on the order of 200 h^{-1}. Both Ru–O bonds in **8c,d** are cleaved by carbon monoxide resulting in the formation of the ruthenacyclopentadienes $(OC)_4\overline{RuCZ{=}CZCZ{=}C}Z$ (**10c,d**). In contrast to the reaction of **1** with the alkynes **4c,d**, the action of hexafluoro-2-butyne (**4e**) on **1** affords the heterocycle **9e** which, on the basis of spectroscopical data, can be described as a ruthenabicyclo[3.2.0]heptene.

Introduction

Carbonyl olefin complexes of the iron triad transition metals constitute an important area of investigation from both the synthetic[2a] and theoretical[2b] point of view. For the simplest species (η^2-ethene)M(CO)$_4$ (M = Fe, Ru, Os) only two general methods of preparation are described. The groups of Wrighton,[3a] Takats,[3b] and Grevels[3c] investigated successfully the photochemical synthesis and the photochemistry of these compounds. Alternatively, the nucleophilic elimination cycloaddition method on ethane-1,2-diylbis(trifluoromethanesulfonate) with the $[M(CO)_4]^{2-}$ anions offers a very simple route to tetracarbonyl(η^2-ethene)metal complexes of iron,[4a] ruthenium,[4b] and osmium.[1] These compounds should be excellent starting materials for ligand exchange reactions[5] with other olefins and for C–C coupling reactions with alkenes or alkynes.[6] Form our own work we know that the η^2-ethene–ruthenium bond in (η^2-C_2H_4)Ru(CO)$_4$ (**1**) is very labile.[4b] The photochemistry of **1** shows that one or two CO ligands are substituted by the corresponding number of ethene molecules.[3a] Both results suggest that tetracarbonyl(η^2-ethene)ruthenium (**1**) should be a source of interesting reactions. Here we report the behavior of **1** toward activated alkenes and different substituted alkynes, depending on the reaction conditions.

Experimental Section

General Procedures. All preparations were carried out under an atmosphere of purified argon. *n*-Hexane, *n*-pentane, chloroform, acetonitrile, and acetone were rendered water- and oxygen-free by distillation from $LiAlH_4$ and K_2CO_3. Instrumentation: mass spectra, Varian MAT 711 A; IR, Bruker FT-IR spectrometers, Models IFS 113c and IFS 48; ^1H, $^{13}C\{^1H\}$ NMR, Bruker AC 80 and Bruker Cryospec WM 400 at 80.13, 20.15 and 400, 100.62 MHz, respectively; ^{19}F NMR, Bruker WP 80 at 75.26 MHz, internal standard C_6F_6 relative to $FCCl_3$. Elemental analyses were carried out with Carlo Erba Model 1106 and Perkin-Elmer Model 4000 atomic absorption spectrometers. A molecular weight determination was carried out with Knauer Dampfdruckosmometer. Research grade C_2H_4 was obtained from Messer-Griesheim. Tetracyanoethylene, fumaric acid dinitrile, and acetylenedicarboxylic acid dimethyl and diethyl esters were obtained from Merck Schuchardt. Hexafluoro-2-butyne was obtained from

---

[1] Part 64: Lindner, E.; Jansen, R.-M.; Hiller, W.; Fawzi, R. *Chem. Ber.* **1989**, *122*, in press.

[2] (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4. (b) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978**, *50*, 1.

[3] (a) Wuu, Y.-M.; Bentsen, J. G.; Brinkley, C. G.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 530. (b) Kiel, G.-Y.; Takats, J.; Grevels, F.-W. *J. Am. Chem. Soc.* **1987**, *109*, 2227. (c) Grevels, F.-W.; Reuvers, J. G. A.; Takats, J. *J. Am. Chem. Soc.* **1981**, *103*, 4069.

[4] (a) Lindner, E.; Schauss, E.; Hiller, W.; Fawzi, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 711. (b) Lindner, E.; Jansen, R.-M.; Mayer, H. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1008.

[5] Fleckner, H.; Grevels, F.-W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

[6] Hoberg, H.; Jenni, K.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 153.

0276-7333/89/2308-2355$01.50/0