3360 *Organometallics* **2002,** *21,* 3360−3366

Reactions of Zirconocene−Alkyne Complexes with Polar Functionalized Olefins[†]

Hongsui Sun,*[,‡] Vladimir V. Burlakov, Anke Spannenberg, Wolfgang Baumann,*
Perdita Arndt, and Uwe Rosenthal

Institut für Organische Katalyseforschung an der Universität Rostock e.V.,
Buchbinderstrasse 5-6, 18055 Rostock, Germany

Received February 20, 2002

The zirconocene−alkyne complex $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ reacts with methyl vinyl ketone to yield the zirconadihydrofuran $Cp_2\overline{ZrOCMe{=}CHC}H_2$ (**1**). In contrast, *rac*-(ebthi)-$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl) reacts with methyl vinyl ketone giving, for the first time, the 1,4-conjugated insertion product *rac*-(ebthi)-$\overline{ZrOCMe{=}CHCH_2C(SiMe_3){=}C}(SiMe_3)$ (**2**) in good yield. An X-ray crystallographic structure determination of **2** shows that the seven-membered ring is twisted in such a way to fit the steric demands of the "ebthi" and $SiMe_3$ groups. Treating *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with *tert*-butyl acrylate gives the zirconadihydrofuran *rac*-(ebthi)$\overline{ZrOC(O^tBu){=}CHC}H_2$ (**3**). The monomeric structure of **3** has been established by X-ray crystallography. A different type of zirconadihydrofuran, *rac*-(ebthi)$\overline{ZrOCMe(CH{=}CH_2)\text{-}C(SiMe_3){=}C}(SiMe_3)$ (**4**), results from the reaction with mesityl oxide. Complexes analogous to **4** and **2** were observed consecutively by NMR in the reaction of $Thi_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (Thi = η^5-tetrahydroindenyl) with methyl vinyl ketone. This lets one conclude that the carbonyl insertion products (e.g. **4**) are formed first as intermediates. Finally, *rac*-(ebthi)$\overline{ZrCH_2CHMe{=}CHC}H_2$ (**5**), a zirconacyclopentene, is obtained from *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and isoprene.

Introduction

Zirconocene complexes have attracted considerable attention due to their ability to function as highly active Ziegler−Natta type catalysts for the polymerization of olefins.[1] From a synthetic point of view, zirconocene−alkene and −alkyne complexes are of particular interest, as they are considered to be important reagents for selective carbon−carbon bond formation as well as a variety of synthetic transformations.[2] The fact that the zirconocene−alkyne complex $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$[3] is an excellent zirconocene "Cp_2Zr" precursor[4] has also been confirmed recently by Tilley and coworkers.[5] For comparison, the Negishi system,[6] which also generates the "Cp_2Zr" species, proved to be effective for coupling alkynes,[6a,7] but there are several practical difficulties in coupling functionalized diynes.[5d] Moreover, the latter system risks the formation of several byproducts.[8]

---

* To whom correspondence should be addressed. E-mail: H.S., hsun@chem.ubc.ca; W.B., wolfgang.baumann@ifok.uni-rostock.de.

[†] Dedicated to Professor Cornelius Gerhard Kreiter on the occasion of his 65th birthday.

[‡] Present address: Chemistry Department, The University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1.

(1) For recent reviews see: (a) Erker, G. *Acc. Chem. Res.* **2001**, *34*, 309. (b) Chum, P. S.; Kruper, W. J.; Guest, M. J. *Adv. Mater.* **2000**, *12*, 1759. (c) Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243. (d) Dahlmann, M.; Erker, G.; Bergander, K. *J. Am. Chem. Soc.* **2000**, *122*, 7986. (e) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (f) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem.* **1995**, *107*, 1225; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (g) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (h) Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (i) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57.

(2) (a) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. (b) Hoveyda, A. H.; Morken, J. P. *Angew. Chem.* **1996**, *108*, 1378; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262. (c) Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2835. (d) Suzuki, N.; Rousset, C. J.; Aoyagi, K.; Kotora, M.; Takahashi, T. *J. Organomet. Chem.* **1994**, *473*, 117. (e) Maler, M.; Oost, T. *J. Organomet. Chem.* **1995**, *505*, 95. (f) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (g) Takahashi, T.; Li, Y.; Ito, T.; Xu, F.; Nakajima, K.; Liu, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1144.

(3) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77.

(4) For reviews see: (a) Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burlakov, V. V.; Rosenthal, U. *Synlett* **1996**, 111 and references therein. (b) Rosenthal, U.; Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (c) Rosenthal, U.; Burlakov, V. V. in *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, 2002.

(5) (a) Nitschke, J. R.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 10183. (b) Schafer, L. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 2683. (c) Nitschke, J. R.; Tilley, T. D. *Angew. Chem.* **2001**, *113*, 2200; *Angew. Chem., Int. Ed.* **2001**, *40*, 2142. (d) Nitschke, J. R.; Zürcher, S.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 10345. (e) Liu, F.-Q.; Harder, G.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 3271. (f) Mao, S. S. H.; Liu, F.-Q.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 1193. (g) Nitschke, J. R.; Tilley, T. D. *J. Org. Chem.* **1998**, *63*, 3673. (h) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 7031. (i) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5365. (j) Schafer, L. L.; Nitschke, J. R.; Mao, S. S. H.; Liu, F.-Q.; Harder, G.; Haufe, M.; Tilley, T. D. *Chem. Eur. J.* **2002**, *8*, 74.

(6) (a) Negishi, E. I.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Sato, K.; Nishihara, Y.; Huo, S.; Xi, Z.; Takahashi, T. *J. Organomet. Chem.* **2001**, *633*, 18.

(7) Negishi, E. I.; Holms, S. J.; Tour, J.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

(8) (a) Soleil, F.; Choukroun, R. *J. Am. Chem. Soc.* **1997**, *119*, 2938. (b) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1997**, *16*, 1452.

10.1021/om0201415 CCC: $22.00
Publication on Web 07/10/2002

In recent years, we have been interested in zirconocene–alkyne complexes for their rich and varied chemistry toward unsaturated $C{=}X$[4a] (X = C, N, O) substrates, diynes/polyynes,[4b] and functionalized alkynes.[9] An extension of this approach into the field of polar functionalized olefins is presented in this paper. Our interest in such olefins is two-fold: first, the exploration of highly active catalysts for the controlled polymerization of polar functionalized monomers and copolymerization of these monomers with simple olefins has drawn much attention recently,[10] and second, the question what kind of functional groups in olefins are tolerated by metallocene units is still lacking a decisive answer, although recent work[2g] describes the zirconocene-mediated synthesis of nitrogen and oxygen heterocycles.

Carbonylation of group 4 metallocene complexes was found to result in carbonyl insertion into the metal–alkyl bond,[11] following the pioneering work of Floriani[12] on the reaction of carbon monoxide with zirconocenes. Zirconocene–alkyne complexes are also known to react with ketones or aldehydes, forming either oxazirconacycles (zirconadihydrofurans) through insertion of carbonyls into Zr–C bonds[2e,13,14] or η^2-ketone complexes[14e] by kicking out alkynes. Basic investigations in reactions of $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = tetrahydrofuran,[15] pyridine[3]) with acetone,[14c] formaldehyde, benzaldehyde, and benzophenone[14e] and in the reaction of $Cp_2Zr(thf)(\eta^2\text{-}Me_3SiC_2{}^tBu)$ with acetone[14b] have shown that the reaction products are determined decisively by the substituents of the carbonyl compounds. Moreover, the influence of the solvents has been investigated in the reactions of $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = tetrahydrofuran, pyridine) with methacrolein.[14f] In this contribution, we report new investigation results on the reactions of zirconocene–alkyne compounds with other polar functionalized olefins.

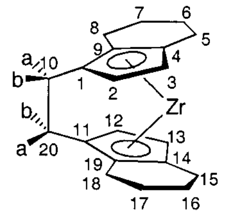


Figure 1. Numbering scheme used for the NMR spectra assignment of *rac*-1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl).

Experimental Section

General Considerations. All manipulations were conducted by standard Schlenk techniques under a dry argon atmosphere. Solvents were dried and freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. Methyl vinyl ketone, mesityl oxide, *tert*-butyl acrylate, and isoprene were purchased from Aldrich, dried over molecular sieves, and distilled under argon before use. The metallocene–alkyne compounds $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$,[3] *rac*-(ebthi)Zr($\eta^2$-$Me_3SiC_2SiMe_3$),[14d] and $Thi_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$[16] were prepared as described in the literature. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker ARX 400 spectrometer at ambient temperature, unless stated otherwise. Chemical shifts are given in ppm relative to TMS with the solvent signal as a secondary standard (C_6D_6, ^1H δ 7.16 ppm, ^{13}C 128.0 ppm; THF-d_8, ^1H δ 1.73 ppm, ^{13}C 25.2 ppm), and coupling constants are given in hertz. Signal assignments were confirmed by 2D shift correlation and NOE methods. The numbering scheme of *rac*-1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl) used for this purpose is illustrated in Figure 1. The zirconacyclic systems are numbered as a, b, c, ..., starting from the Zr-bound carbon atom (the one neighboring the methyl group for complex **5**). Mass spectra were obtained on a AMD 402 spectrometer operating in the electron ionization mode at 70 eV. Elemental analyses were carried out with a Leco CHNS-932 elemental analyzer. Melting points were measured in sealed capillaries on a Büchi 535 apparatus.

Preparation of the 2-Oxa-1-zirconacyclopent-3-ene 1. Methyl vinyl ketone (44 μL, 0.53 mmol) was added dropwise by syringe to a stirred *n*-hexane solution (15 mL) of $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (250 mg, 0.53 mmol) at ambient temperature. The color of the solution immediately changed from dark violet to yellow. The solution was stirred for 10 min, part of the solvent was removed in vacuo, and the remaining solution was cooled to −40 °C, yielding 109 mg of a red crystalline solid of **1** (70%). Mp: 59 °C dec. Anal. Calcd for $C_{14}H_{16}OZr$: C, 57.68; H, 5.53. Found: C, 57.19; H, 5.83. ^1H NMR (C_6D_6): δ 1.73 (3H, dt, $^4J \approx 0.5$, $^5J \approx 1.0$, Me), 1.76 (2H, dq, $^3J = 8.3$, $^5J = 1.0$, CH_2), 4.54 (1H, tq, $^4J = 0.5$, $^3J = 8.3$, $=CH$), 5.51 (10H, s, Cp). ^{13}C NMR (C_6D_6): δ 22.4 (Me, $^1J_{C,H} = 126.2$), 44.3 (CH_2, $^1J_{C,H} = 141.5$), 103.5 ($=CH$, $^1J_{C,H} = 155.4$), 106.5 (Cp, $^1J_{C,H} = 171.4$), 147.5 ($=C$(Me)O). MS (*m*/*z*): 290 $[M]^+$, 220 $[M - C_4H_6O]^+$, 155 $[M - C_4H_6O - Cp]^+$.

Preparation of the 7-Oxa-1-zirconacyclohepta-2,5-diene 2. Methyl vinyl ketone (20 μL, 0.24 mmol) was added dropwise to a stirred solution of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (128 mg, 0.24 mmol) in *n*-hexane (5 mL), resulting in an immediate color change from green to yellow. All volatiles were removed in vacuo, and the residue was crystallized in toluene/hexane (2:5); yellow crystals were obtained. Yield: 122 mg (84%). Mp: 141 °C. Anal. Calcd for $C_{32}H_{48}OSi_2Zr$: C, 64.48; H, 8.12. Found: C, 64.65; H, 8.41. ^1H NMR (C_6D_6):[17] δ 0.38 (9H, s, b-$SiMe_3$), 0.50 (9H, s, a-$SiMe_3$), 1.89 (3H, s, Me), 2.81

---

(9) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem.* **1994**, *106*, 1946; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1850.

(10) (a) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479. (b) Nguyen, H.; Jarvis, A. P.; Lesley, M. J. G.; Kelly, W. M.; Reddy, S. S.; Taylor, N. J.; Collins, S. *Macromolecules* **2000**, *33*, 1508. (c) Bolig, A. D.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7943. (d) Hölscher, M.; Keul, H.; Höcker, H. *Chem. Eur. J.* **2001**, *7*, 5419.

(11) (a) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (b) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668. (c) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. (d) Blaschke, U.; Erker, G.; Nissinen, M.; Wegelius, E.; Fröhlich, R. *Organometallics* **1999**, *18*, 1224.

(12) (a) Fachinetti, G.; Floriani, C. *J. Organomet. Chem.* **1974**, *71*, C5. (b) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946.

(13) (a) Buchwald, S.; Watson, B. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (b) Buchwald, S.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Erker, G.; Zwettler, R. *J. Organomet. Chem.* **1991**, *409*, 179.

(14) (a) Lefeber, C.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1995**, *501*, 179. (b) Lefeber, C.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *J. Organomet. Chem.* **1995**, *501*, 189. (c) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *J. Organomet. Chem.* **1994**, *484*, 203. (d) Lefeber, C.; Baumann, W.; Tillack, A.; Kempe, R.; Görls, H.; Rosenthal, U. *Organometallics* **1996**, *15*, 3486. (e) Peulecke, N.; Ohff, A.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1996**, *15*, 1340 and references therein. (f) Peulecke, N.; Ohff, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *J. Organomet. Chem.* **1996**, *520*, 235. (g) Baumann, W.; Ohff, A.; Ebener, M. *Helv. Chim. Acta* **1996**, *79*, 454.

(15) Rosenthal, U.; Ohff, A.; Michalik, M.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **1993**, *105*, 1228; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1193.

(16) Peulecke, N.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Eur. J. Inorg. Chem.* **1998**, 419.

(1H, c-H_{exo}), 3.11 (1H, c-H_{endo}), 4.60 (1H, d-H), 5.41 (1H, ^3J = 2.8, 12-H), 5.46 (1H, d, ^3J = 3.1, 2-H), 5.64 (1H, d, ^3J = 3.1, 3-H), 6.77 (1H, ^3J = 2.8, 13-H). ^{13}C NMR (C_6D_6):[17] δ 3.6 (b-$SiMe_3$), 6.6 (a-$SiMe_3$), 24.0 (e-Me), 37.6 (c-C), 97.4 (d-C), 103.1 (C-2), 104.5 (C-12), 112.7 (C-13), 113.5 (C-3), 161.2 (b-C), 161.3 (e-C), 215.7 (a-C). ^{29}Si NMR (C_6D_6): δ −16.6 (a-$SiMe_3$), −10.5 (b-$SiMe_3$). MS (*m*/*z*): 594 $[M]^+$, 424 $[M - Me_3SiC_2SiMe_3]^+$, 354 $[M - C_4H_6O - Me_3SiC_2SiMe_3]^+$.

Preparation of the 2-Oxa-1-zirconacyclopent-3-ene 3. **3** was prepared by following a procedure similar to that described for complex **2** from 105 mg (0.2 mmol) of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) and 30 μL (0.2 mmol) of *tert*-butyl acrylate in *n*-hexane (5 mL). THF/hexane (1:10) was used for crystallization; yield 84 mg (87%). Mp: 159 °C. Anal. Calcd for $C_{27}H_{36}O_2Zr$: C, 67.03; H, 7.50. Found: C, 67.22; H, 7.65. ^{1}H NMR (C_6D_6):[17] δ 1.21 (1H, dd, ^3J = 7.1, ^2J = 11.3, a-H_{down}), 1.46 (9H, s, CMe_3), 1.90 (1H, dd, ^3J = 10.6, ^2J = 11.3, a-H_{up}), 4.30 (1H, dd, ^3J = 10.6 and 7.1, b-H), 5.21 (1H, d, ^3J = 3.0, 12-H), 5.28 (1H, d, ^3J = 3.4, 3-H), 5.33 (1H, d, ^3J = 3.4, 2-H), 5.69 (1H, d, ^3J = 3.0, 13-H). ^{13}C NMR (C_6D_6):[17] δ 29.8 (CMe_3), 44.4 ($^1J_{C,H}$ = 141.0, a-C), 77.0 (CMe_3), 80.9 ($^1J_{C,H}$ = 157.7, b-C), 98.5 (C-2), 101.8 (C-12), 107.6 (C-3), 109.2 (C-13), 151.9 (c-C). MS (*m*/*z*): 425 $[M - {}^tBu]^+$.

Preparation of the 5-Oxa-1-zirconacyclopent-2-ene 4. A procedure similar to that described for complex **2** was used in the reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (240 mg, 0.46 mmol) with mesityl oxide (52 μL, 0.46 mmol) in 10 mL of *n*-hexane. All volatiles were removed in vacuo, and a yellow soft substance was obtained. Crystallization from *n*-pentane at −100 °C yielded 34 mg (12%) of **4** (which was still not pure enough for getting a satisfactory analysis; see discussion). Mp: 53 °C. ^{1}H NMR (C_6D_6):[17] δ 0.36 (9H, s, a-$SiMe_3$), 0.41 (9H, s, b-$SiMe_3$), 1.64 (3H, s, c-Me), 1.78 (6H, 2 d, CMe_2), 5.07 (1H, d, ^3J = 2.8, 12-H), 5.38 (1H, d, ^3J = 3.1, 2-H), 6.00 (1H, "sept", c-CH), 6.54 (1H, d, ^3J = 3.1, 3-H), 6.89 (1H, d, ^3J = 2.8, 13-H). ^{13}C NMR (C_6D_6):[17] δ 4.8 (b-$SiMe_3$), 6.3 (a-$SiMe_3$), 19.4 (*Z*-C=C*Me*), 27.1 (*E*-C=C*Me*), 32.3 (c-Me), 88.5 (c-C), 107.2 (C-2), 108.3 (C-13), 108.7 (C-12), 113.6 (C-3), 132.4 (c-CH, $^1J_{C,H}$ = 150), 132.2 ($C{=}CMe_2$), 192.7 (b-C), 217.2 (a-C). MS (*m*/*z*): 525 $[M - C_6H_{10}O]^+$, 452 $[M - Me_3SiC_2SiMe_3]^+$, 354 $[M - C_6H_{10}O - Me_3SiC_2SiMe_3]^+$.

Preparation of the Zirconacyclopent-3-ene 5. Isoprene (74 μL, 0.53 mmol) was added to a stirred *n*-hexane solution (10 mL) of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (389 mg, 0.74 mmol). The resulting red solution was concentrated to about 1 mL, and a red crystalline solid formed after 2 days. Yield: 240 mg (77%). Mp: 113 °C. Anal. Calcd for $C_{25}H_{32}Zr$: C, 70.86; H, 7.61. Found: C, 67.95; H, 7.73. ^{1}H NMR (C_6D_6):[17] δ −1.16 (2H, br d, a-H_{inward}), −0.07 (1H, br t, d-H_{inward}), 1.99 (3H, s, Me), 2.84 (1H, br t, d-$H_{outward}$), 2.99 (1H, br d, a-$H_{outward)}$, 4.61 (1H, d, ^3J = 3.3, 3-H), 4.69 (1H, d, ^3J = 2.9, 13-H), 4.83 (1H, t, ^3J = 10.6, c-H), 5.11 (1H, d, ^3J = 3.3, 2-H), 5.64 (1H, d, ^3J = 2.9, 12-H). ^{13}C NMR (C_6D_6):[17] δ 29.5 (Me), 48.6 (d-C), 57.7 (a-C), 97.2 (C-12), 98.1 (C-2), 103.5 (C-3), 106.3 (C-13), 110.4 (c-C), 126.4 (b-C). MS (*m*/*z*): 422 $[M]^+$, 354 $[M - C_5H_8]^+$.

NMR Investigations in the Formation of Complexes 6 and 7. $Thi_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (60 mg, 105 μmol) was dissolved in THF-d_8 (0.6 mL) in an NMR tube. Methyl vinyl ketone (12 μL, 140 μmol) was added at −78 °C. The dark green solution changed to yellow-green immediately. The first NMR spectrum, taken at −19 °C, revealed already complete conversion of the alkyne complex to the 5-oxa-1-zirconacyclopent-2-ene **6**. No further changes occurred while the sample was brought to room temperature (for data see Table 3 and the Supporting Information). Complex **6** remained unchanged while the solution was kept at −20 °C for 4 weeks. After it was heated to 60 °C for 2 h, **6** had disappeared by an almost quantitative rearrangement to complex **7**. ^{1}H NMR:[17] δ 0.18 (9H, s, b-$SiMe_3$), 0.20 (9H, s, a-$SiMe_3$), 1.72 (3H, s, e-Me), 2.56 (2H, br d, c-H), 4.41 (1H, t, ^3J = 7.8, d-H). ^{13}C NMR:[17] δ 3.0 (b-$SiMe_3$), 6.0 (a-$SiMe_3$), 22.5 (e-Me), 39.4 (c-C), 105.0 (d-C), 156.5 (e-C), 170.5 (b-C), 219.3 (a-C).

X-ray Crystallographic Study of Compounds 2 and 3. Diffraction data were collected on a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86[18]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[19]). All non-hydrogen atoms except the carbon atoms of disordered groups were refined anisotropically. The hydrogen atoms were placed in theoretical positions and refined by using the riding model. XP (Bruker AXS) was used for molecular graph drawings.

Crystal data for **2**: $C_{32}H_{48}OSi_2Zr$, M_r = 596.10, yellow prism, size 0.2 × 0.3 × 0.4 mm, triclinic, space group $P\bar{1}$, *a* = 11.067(2) Å, *b* = 11.134(2) Å, *c* = 13.521(3) Å, α = 108.19(3)°, β = 95.02(3)°, γ = 97.93(3)°, *V* = 1552.5(5) Å^3, *T* = 293 K, *Z* = 2, ρ_{calcd} = 1.275 g cm^{-3}, μ(Mo Kα) = 4.54 cm^{-1}, *F*(000) = 632, 8423 reflections measured, 4682 reflections independent of symmetry, 3876 reflections observed ($I > 2\sigma(I)$), 330 parameters, R1 = 0.039, wR2 (all data) = 0.109.

Crystal data for **3**: $C_{27}H_{36}O_2Zr$, M_r = 483.78, yellow-orange prism, size 0.2 × 0.3 × 0.4 mm, monoclinic, space group $P2_1/c$, *a* = 8.206(2) Å, *b* = 16.480(3) Å, *c* = 17.352(3) Å, β = 97.26(3)°, *V* = 2327.8(8) Å^3, *T* = 293 K, *Z* = 4, ρ_{calcd} = 1.380 g cm^{-3}, μ(Mo Kα) = 4.93 cm^{-1}. *F*(000) = 1016, 4683 reflections measured, 2415 reflections independent of symmetry, 2044 reflections observed ($I > 2\sigma(I)$), 267 parameters, R1 = 0.035, wR2 (all data) = 0.106.

Results

Reactions of Zirconocene−Alkyne Complexes with Methyl Vinyl Ketone. The reaction of $Cp_2Zr(py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with methyl vinyl ketone in *n*-hexane at ambient temperature, gives, after elimination of the alkyne $Me_3SiC_2SiMe_3$, the 2-oxa-1-zirconacyclopent-3-ene $Cp_2\overline{ZrOCMe{=}CHCH_2}$ (**1**) as a red solid. ^{1}H and ^{13}C NMR spectra of **1** show the signals of the former methylene group (5.72, 5.31, and 137.5 ppm in methyl vinyl ketone) now shifted upfield to the aliphatic region (1.76 and 44.3 ppm). This indicates the linkage of the now-saturated carbon a-C to the zirconium atom. The signal of the former carbonyl C atom is also shifted upfield from 197.2 to 147.5 ppm, showing the formation of Zr−O single bond and b-C=c-C double bond (enolate system). The mass spectrum of **1** gives peaks at *m*/*z* 290 for $[M]^+$ and *m*/*z* 220 for $[M - C_4H_6O]^+$. All spectral analyses support a 2-oxa-1-zirconacyclopent-3-ene (zirconadihydrofuran) structure for complex **1** (as shown in Scheme 1).

An isomeric zirconadihydrofuran with 1,4-coordinated methacrolein, $[Cp_2\overline{ZrOCH{=}CMeCH_2}]_2$ (**B**),[14f] was shown to be a dimer in the solid state. Inspection of a molecular model shows that analogous dimerization via a $\overline{ZrOZrO}$ core is disfavored for compound **1** because the methyl groups would come too close to the other Cp_2Zr moiety.[20]

The reaction between *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) and methyl vinyl ketone gives, under the same conditions, the unusual and unexpected 1,4-insertion product

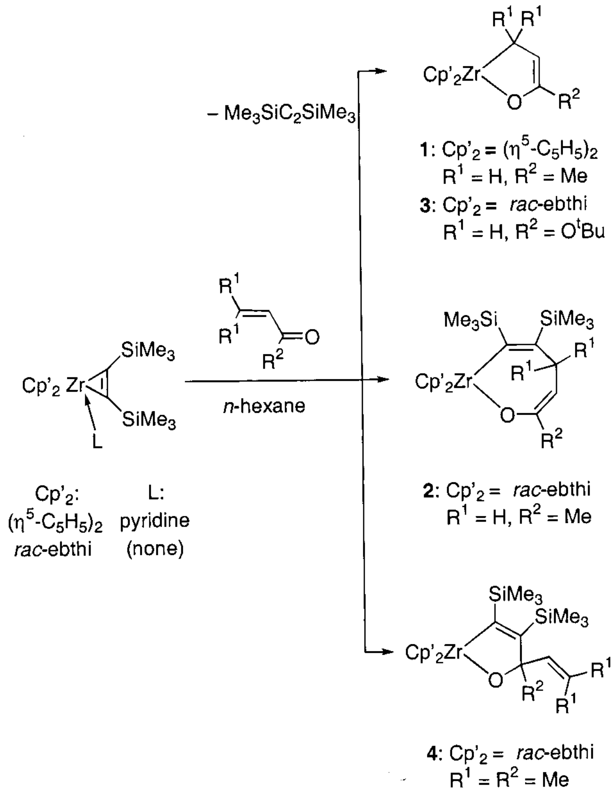
---

[17] Detailed ^{1}H, ^{13}C, and ^{29}Si NMR data, also on the ebthi and the tetrahydroindenyl ligand systems, are given in the Supporting Information.

[18] SHELXS-86: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[19] Sheldrick, G. M. SHELXL-93; University of Göttingen: Göttingen, Germany, 1993.

Scheme 1



rac-(ebthi)ZrOCMe=CHCH$_2$C(SiMe$_3$)=C(SiMe$_3$) (**2**) in 84% yield. ^{1}H and ^{13}C NMR spectra of **2** prove the presence of both the alkyne and the ketone linked together. Two SiMe$_3$ signals appear at δ 0.38 and 0.50 ppm, the upfield shifts for the methylene protons are less pronounced than described for complex **1** at 2.81 and 3.11 ppm, and for the methylene carbon 37.6 ppm is found, characteristic data for an allylic position; the carbonyl carbon shifts upfield to 161.3 ppm. Additionally, long-range couplings, between a-C and the methylene protons for instance, support the formulation of b-C−c-C single, d-C=e-C double, and Zr−O bonds. The mass spectrum of **2** (m/z 594 [M]$^+$, 424 [M − Me$_3$SiC$_2$SiMe$_3$]$^+$) is also in agreement with its structure (as shown in Scheme 1). Single crystals of **2** suitable for X-ray structure analysis were obtained by slowly cooling a saturated *n*-hexane/toluene (5:2) solution.

Crystallographic Analysis of Complex 2 (Figure 2 and Table 1). The crystal structure of **2** was determined by X-ray crystallography; the ORTEP diagram is shown in Figure 2, and selected bond lengths and angles are presented in Table 1. Methyl vinyl ketone 1,4-inserted into the zirconacyclopropene, giving the complex **2** with a nonconjugated seven-membered ring, in which the large deviation of atom C20 from the plane could help to avoid steric hindrance at the silyl groups. This deviation is obvious from the formation mechanism point of view (see Discussion) and maintained in solution (as recognized from ^{1}H NMR NOE correlations). The geometry of the Zr coordination sphere can be described as a distorted tetrahedron with the four angles 96.8, 102.0, 111.9, and 121.5° (see Table 1). The bond lengths of C18−C19 (1.318(6) Å) and C1a−C2 (1.365(5) Å) are in the range of carbon−carbon double bonds.

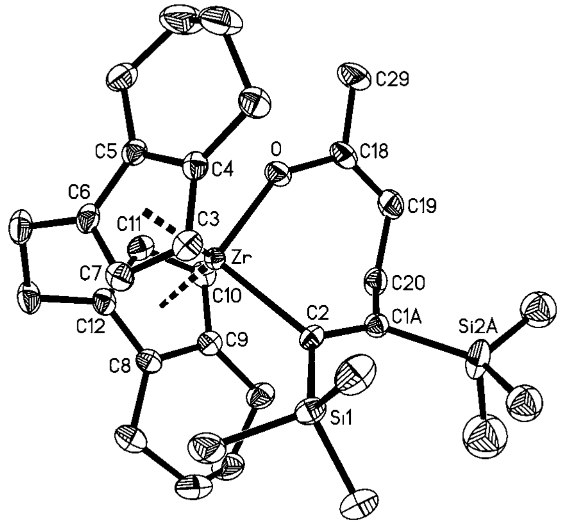


Figure 2. ORTEP plot of complex **2**. Hydrogen atoms and one position of the disordered group are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2[a]

Zr−C2	2.366(3)	Zr−O	2.001(2)
Zr−C3	2.536(4)	Zr−C4	2.619(4)
Zr−C5	2.604(3)	Zr−C6	2.557(4)
Zr−C7	2.487(4)	Zr−C8	2.650(3)
Zr−C9	2.657(4)	Zr−C10	2.536(4)
Zr−C11	2.458(3)	Zr−C12	2.567(3)
C1a−C2	1.365(5)	C2−Si1	1.884(4)
C1a−Si2a	1.912(5)	C1a−C20	1.547(5)
C19−C20	1.489(5)	C18−C19	1.318(6)
C18−C29	1.498(5)	C18−O	1.356(4)
O−Zr−C2	96.85(11)	O−Zr−X1a	102.0
C2−Zr−X1b	111.9	X1a−Zr−X1b	121.5
Zr−O−C18	144.4(2)	O−C18−C19	120.9(3)
C20−C1a−C2	121.4(3)	C18−C19−C20	122.1(3)
C1a−C2−Zr	113.4(3)	C19−C20−C1a	121.4(6)

[a] X1a and X1b are the centroids of the cyclopentadienyl rings C3−C7 and C8−C12, respectively.

Reaction of *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) with Mesityl Oxide. Unlike with methyl vinyl ketone, the carbonyl (1,2-) insertion complex *rac*-(ebthi)ZrOCMe(CH=CMe$_2$)C(SiMe$_3$)=C(SiMe$_3$) (**4**) is obtained as a golden yellow, amorphous solid of low density. Due to its extremely high solubility in any saturated hydrocarbon solvent, a purification has not been accomplished. However, the 5-oxa-1-zirconacyclopent-2-ene structure was established by NMR (see description of the analogous complex **6** below).

Reactions of *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) with *tert*-Butyl Acrylate and Isoprene. The 2-oxa-1-zirconacyclopent-3-ene *rac*-(ebthi)ZrOC(OᵗBu)=CHCH$_2$ (**3**) was obtained in 87% yield from the reaction of *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$) and *tert*-butyl acrylate. The orange-red crystals of **3** dissolve easily in THF, benzene,

---

(20) In C$_6$D$_6$ solution, a second species which undergoes slow chemical exchange with **1** is present (^{1}H NMR δ 1.84 (3H, Me), 4.92 (1H, =CH), 5.84 (10H, Cp); ^{13}C NMR δ 24.0 (Me), 110.7 (Cp), 112.1 (=CH), 150.8 (=*C*(Me)O)). This is presumably the dimeric form of **1**. Its cyclopentadienyl shifts are very close to that of the dimeric methacrolein complex **B**, and its quantity decreases with increasing temperature (ratio of ^{1}H Cp signal integrals of dimer to monomer: 0.15 at 295.1 K, 0.11 at 302.1 K, 0.08 at 309.0 K, 0.06 at 315.7 K, and 0.05 at 322.4 K).

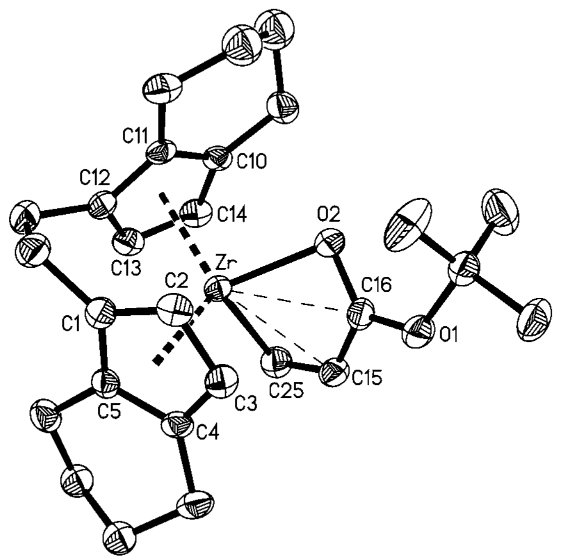


Figure 3. ORTEP plot of complex **3**. Hydrogen atoms and one position of the disordered groups are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

Scheme 2

5

and toluene and moderately in saturated hydrocarbon solvents. Slowly cooling an *n*-hexane solution (plus a little bit of THF) of **3** afforded prismatic red crystals suitable for X-ray crystallography. NMR spectra of **3** are completely consistent with the zirconadihydrofuran structure shown in Scheme 1, including the above-discussed upfield shift of the methylene group to the alkane region as well as indications for the formation of a new double bond (b-C=c-C).

The zirconacyclopentene compound *rac*-(ebthi)$ZrCH_2$-$CHMe{=}CHCH_2$ (**5**) was isolated from the reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) and isoprene (Scheme 2). Compound **5**, a red solid, has very good solubility in both polar and nonpolar solvents. Its structure was confirmed by spectroscopic analysis, MS, and elemental analysis and was found to be as expected for members of this well-established family (σ:η^2:σ-diene complexes).[22]

Solid-State Structure of Complex 3 (Figure 3 and Table 2). The double bond C15−C16 (1.362(7) Å) of the zirconacyclopentene folds toward the zirconium center, and interactions between the double bond and zirconium become possible. The distances Zr−C15 and Zr−C16 are 2.548(4) and 2.525(4) Å, respectively, and the angle between the planes defined by atoms O2, Zr, C25 and O2, C16, C15, C25 is 121.7° (the respective distances in typical s-cis-η^4-diene complexes are 2.55−2.71 Å[22c] and the folding angle 110−123°[22b,c]). The four angles at the "distorted tetrahedral" zirconium are 83.7, 102.1, 110.8, and 123.5° (see Table 2).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3[a]

Zr−C1	2.539(4)	Zr−C2	2.473(4)
Zr−C3	2.540(4)	Zr−C4	2.622(4)
Zr−C5	2.616(4)	Zr−C10	2.607(4)
Zr−C11	2.564(4)	Zr−C12	2.550(4)
Zr−C13	2.512(4)	Zr−C14	2.565(4)
Zr−C15	2.548(4)	Zr−C16	2.525(4)
Zr−C25	2.255(5)	Zr−O2	2.107(3)
O2−C16	1.331(5)	C15−C16	1.362(7)
C15−C25	1.471(7)		
O2−Zr−C25	83.7(2)	Zr−O2−C16	91.7(3)
O2−C16−C15	122.9(4)	C16−C15−C25	124.1(4)
C15−C25−Zr	83.4(3)	X1a−Zr−X1b	123.5
X1a−Zr−C25	110.8	X1b−Zr−O2	102.1

[a] X1a and X1b are the centroids of the cyclopentadienyl rings C1−C5 and C10−C14, respectively.

Table 3. Characteristic Chemical Shifts δ (^{13}C and ^{29}Si NMR Data) of Silyl-Substituted 5-Oxa-1-zirconacyclopent-2-enes[a]

	4	6	A[14f]	C[14g]
a-C	217.2	219.2	222.2	213.3
b-C	192.7	188.3	185.4	193.3
c-C	88.5	90.9	88.5	90.5
a-Si	−24.1	−22.7		−22.9
b-Si	−20.5	−20.2		−20.0
a-Si*Me*3	6.3	5.7	4.6	5.4
b-Si*Me*3	4.8	4.9	2.3	4.5

[a] Solvents used: benzene-d_6 for **4** and **C** and THF-d_8 for **6** and **A**.

Discussion

Seven-Membered-Ring Complexes: The Result of a 1,4-Conjugated Insertion Reaction and Mechanistic Investigation. The reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) with methyl vinyl ketone is the first example of a 1,4-conjugated insertion into a zirconacyclopropene, which leads to the 7-oxa-1-zirconacyclohepta-2,5-diene **2**. Earlier investigations showed that bis(trimethylsilyl)acetylene coordinated to a zirconocene or titanocene core is generally reluctant to participate in insertion reactions[4,23] with alkenes or alkynes and is easily replaced by other acetylenes,[24] diynes,[25] and polyynes.[26] Despite that, coupling with carbon dioxide or the carbonyl groups of ketones or aldehydes is achieved easily.[14,21] The reaction of methacrolein with $Cp_2Zr(\eta^2$-$Me_3SiC_2SiMe_3)$ gives, depending on reaction conditions, $Cp_2ZrOCH(CMe{=}CH_2)C(SiMe_3){=}C(SiMe_3)$

---

(21) Thomas, D.; Arndt, P.; Peulecke, N.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Eur. J. Inorg. Chem.* **1998**, 1351.

(22) Reviews: (a) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (b) Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (c) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

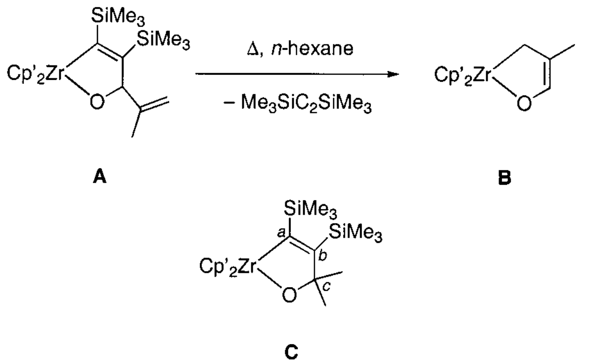
(23) (a) Sun, H.; Burlakov, V. V.; Spannenberg, A.; Baumann, W.; Arndt, P.; Rosenthal, U. *Organometallics* **2001**, *20*, 5472. (b) Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V.; Rosenthal, U. *Organometallics* **1995**, *14*, 3090. (c) Rosenthal, U.; Ohff, A.; Baumann, W.; Kempe, R.; Tillack, A.; Burlakov, V. V. *Angew. Chem.* **1994**, *106*, 1678; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1605.

(24) (a) Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T.; Shur, V. B.; Vol'pin, M. E.; Rosenthal, U.; Görls, H. *J. Organomet. Chem.* **1994**, *476*, 197. (b) Rosenthal, U.; Lefeber, C.; Arndt, P.; Tillack, A.; Baumann, W.; Kempe, R.; Burlakov, V. V. *J. Organomet. Chem.* **1995**, *503*, 221.

(25) Burlakov, V. V.; Ohff, A.; Lefeber, C.; Tillack, A.; Baumann, W.; Kempe, R.; Rosenthal, U. *Chem. Ber.* **1995**, *128*, 967.

(26) (a) Pellny, P.-M.; Peulecke, N.; Burlakov, V. V.; Tillack, A.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Angew. Chem.* **1997**, *109*, 2728; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2615. (b) Pellny, P.-M.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1999**, *18*, 2906.

Scheme 3[a]



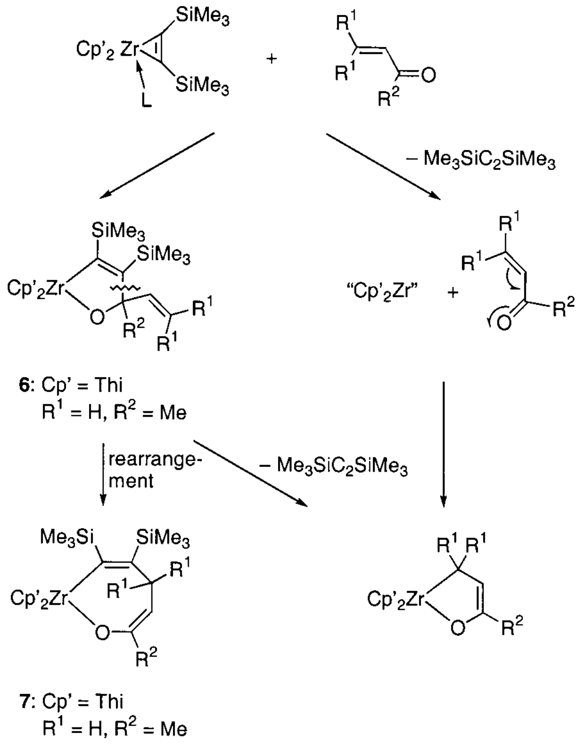
[a] Cp′ = η^5-C_5H_5 for all complexes. **B** forms a dimer in the solid state.

(**A**), a carbonyl (1,2-) insertion product, or $[Cp_2ZrOCH{=}CMeCH_2]_2$ (**B**), the dimer of a 1,4-coordination product (Scheme 3).[14f] Scott and Lippard[27] investigated reactions of the very reactive η^2-dibenzyl ketone complex [Hf(TC-3,5)(η^2-$OC(CH_2Ph)_2$)] (TC-3,5 is a tetraaza macrocyclic tropocoronand) with α,β-unsaturated ketones, in which coupling reactions took place for carbonyls but did not for olefinic bonds.

From the reactions described herein two types of insertion products were obtained, the 1,2-insertion product (5-oxa-1-zirconacyclopent-2-ene) **4** and the 1,4-insertion product (7-oxa-1-zirconacyclohepta-2,5-diene) **2**. To understand this, we tried to get some insight into their formation. The reaction of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) with methyl vinyl ketone, leading to **2**, appeared too fast to allow mechanistic studies. We happened to find that the reaction between $Thi_2Zr(thf)$(η^2-$Me_3SiC_2SiMe_3$)[16] (Thi = η^5-tetrahydroindenyl) and methyl vinyl ketone was ideal for monitoring by NMR spectroscopy. The first observable product which is already formed at low temperature results from carbonyl insertion into the zirconacyclopropene (Scheme 4, left branch). The resulting 5-oxa-1-zirconacyclopent-2-ene **6** is unambiguously identifiable from its very characteristic NMR data (Table 3). The vinyl group exhibits vicinal coupling constants ($^3J_{H,H}$ = 10.6 Hz, cis, and 17.5 Hz, trans), proving that it remained unchanged during complex formation. The presence of free bis(trimethylsilyl)acetylene and some unidentified complex species shows that **6** is formed preferentially, but not exclusively.

The thus obtained complex **6** disappears completely during heating the sample to 60 °C for 2 h. New signals, assigned to the 7-oxa-1-zirconacyclohepta-2,5-diene **7**, show up in the NMR spectra that exhibit features as they were discussed for the analogous complex **2** above. However, they are temperature-dependent. At −68 °C, there are six signals for the cyclopentadienyl protons. The nonplanar metal chelate (see the large out-of-plane deviation of C20 in Figure 2) makes the two π ligands inequivalent. Above room temperature, only three different cyclopentadienyl protons are observed. The enhanced flexibility of the bis(tetrahydroindenyl) ligand system (compared to the ebthi system) allows an inversion of the seven-membered ring, which makes it apparently planar.

Scheme 4. Possible Pathways for the Formation of Zirconacyclic Compounds



The single bond between b-C and c-C of silyl-substituted 5-oxa-1-zirconacyclopent-2-enes, in particular **C**,[14c,14g] is easily cleaved in numerous substitution reactions. Assuming the same reaction pattern for **6**, its conversion to **7** is straightforward (Scheme 4). Most notable is the vinyl group "hanging above" the zirconadihydrofuran ring. Following a cleavage of the central C−C bond, a rearrangement would immediately lead to complex **7**.[28] Steric restrictions at that point could explain why the reaction with mesityl oxide, which gives low yields anyway, cannot be driven beyond the five-membered ring **4**. Upon heating an NMR sample of **4** to 60−75 °C for several hours, no conversion to a complex analogous to **2** or **7** occurs. Liberation of bis(trimethylsilyl)acetylene and formation of many unidentified species is observed instead.

Small amounts of a second species are formed from **6**, in addition to **7**. A complete characterization was not achieved, but it is reasonable to assume that it is the 1,4-coordination product $Thi_2ZrOCMe{=}CHCH_2$, analogous to **1**, formed by alkyne elimination, because of its characteristic NMR signals,[29] in particular for the metalated CH_2 group (δ_H 1.33, δ_C 47.2). These observations, the formation of complex **4**, and the successful isolation of $Cp_2ZrOCH(CMe{=}CH_2)C(SiMe_3){=}C(SiMe_3)$ (**A**),[14f] complexes similar to intermediate **6**, evidence the mechanism depicted in Scheme 4 (left branch).

Five-Membered-Ring Complexes: The Result of 1,4-Coordination to Zr. The reactions of 1,3-buta-

---

[27] Scott, M. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 3411.

[28] The reviewers suggested that the seven-membered-ring compounds be formed by alkyne insertion into the 2-oxa-1-zirconacyclopent-3-enes, but we have no clear evidence for this assumption.

[29] Chemical shifts δ in THF-d_8: ^{1}H NMR at 297 K, =CH 4.66 (1H, t, ^3J = 8 Hz), Zr−CH_2 1.33 (2H, d, ^3J = 8 Hz); ^{13}C NMR at 205 K, =CH 101.3, Zr−CH_2 47.2, Me 23.1.

diene[22] and α-diketone[30] with zirconocenes have been well investigated, while the reactions of α,*β*-unsaturated ketones or esters, which can be considered as the combination of half a 1,3-butadiene molecule and half a α-diketone molecule, with zirconocenes are little known. The similarity of these reactions is the formation of zircona five-membered rings.

Two possible pathways in the first step of the reactions of $Cp'_2Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ with α,*β*-unsaturated ketones are shown in Scheme 4. If the reaction follows the right branch, i.e. the unstable zirconocene "Cp'_2Zr" species is generated first, the following addition of the α,*β*-unsaturated ketone gives the expected final product. This is a reaction mechanism similar to that found elsewhere.[4] According to findings described above, the left branch, an associative mechanism with an intermediate 5-oxa-1-zirconacyclopent-2-ene, must be considered as well. However, there is no hard evidence here for either mechanism.

Conclusions

The reactions of zirconocene alkyne complexes with α,*β*-unsaturated aldehydes/ketones/esters (polar functionalized olefins) give three different types of products through 1,2-insertion of the carbonyl into the zirconacyclopropene (such as **4**), 1,4-conjugated insertion of α,*β*-unsaturated ketones into the zirconacyclopropene (e.g., **2**), and alkyne elimination with 1,4-coordination of the α,*β*-unsaturated ketones or esters to zirconium (e.g., complexes **1** and **3**). A key compound is the product from carbonyl insertion (5-oxa-1-zirconacyclopent-2-ene), which is to be regarded the kinetically favored product and may serve as a precursor to all other observed species. This is in accord with earlier observations,[14f] but for the first time this intermediate could be converted to a seven-membered zirconacycle. Although answering the question how the ligands at zirconium, the substrates' substitution pattern, and even the solvent govern reaction path and issue requires much more work, the strong influence of these factors becomes manifest. Increasing the steric demand allows the observation of intermediates, and the combination of the hindered substrate mesityl oxide with the bulky ligand system ebthi stops the reaction at the stage of the first detectable intermediate (**4**).

Acknowledgment. The work was supported by the Max-Planck-Gesellschaft, the Deutsche Forschungsgemeinschaft (Project code AR 321/1-1), and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables giving detailed NMR data for the complexes **2**−**7** and tables of crystal data, data collection parameters, atomic coordinates, anisotropic displacement parameters, bond distances and bond angles for complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0201415

---

[30] Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem.* **1985**, *97*, 693; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712.