We are currently examining the kinetics of the polymerization and are preparing various alkyl derivatives of this scandium system in order to elucidate the nature of the active catalyst.

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Supplementary Material Available: Experimental details describing the syntheses of $Li_2\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}$, $\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}ScCl$, $\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)\}ScCH(SiMe_3)_2$, and details of the structure determination, including listings of final atomic coordinates, thermal parameters, and bond distances and angles (15 pages); a listing of structure factors (10 pages). Ordering information is given on any current masthead page.

Carbon-Unsubstituted Germoles: Palladium-Catalyzed Reactions of Germylenes with Acetylene

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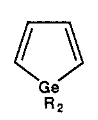
Summary: Dimesityl- and dibutylgermylenes react with acetylene in the presence of a catalytic amount of palladium complexes to yield the corresponding C-unsubstituted germoles **1b** and **1c**, which are characterized by their spectral data and by their reactions with maleic anhydride and diiron nonacarbonyl.

Although group 14 metalloles have proven to be quite interesting and important synthetic intermediates for various ring systems,[1,2] many of these studies have been carried out with metalloles possessing at least two substituents on the ring carbons. Regarding C-unsubstituted germoles, only 1,1-dimethylgermole (**1a**) has been isolated by the catalytic vacuum-flow dehydration of 1,1-dimethyl-1-germacyclopent-4-en-3-ol[3a] or by the thermolysis of the corresponding *N*-phenylcarbamate.[3b,c] We report here a novel synthesis of C-unsubstituted germoles **1b** and **1c** by the palladium-catalyzed reactions of germylenes with acetyloene.[4]



1a (R = Me)
1b (R = Mes)
1c (R = ⁿBu)

Mes = 2,4,6-trimethylphenyl

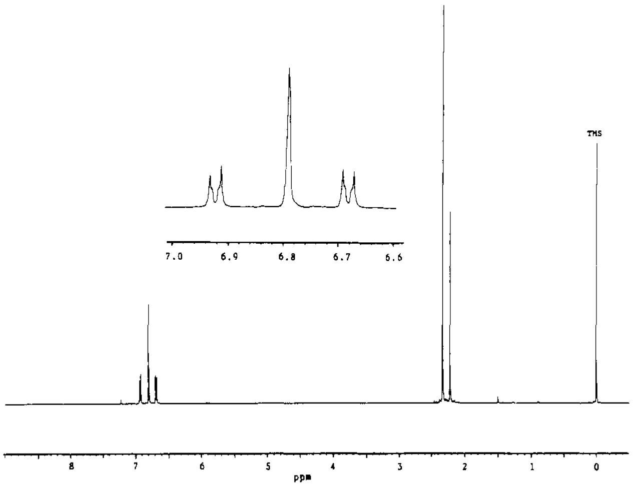
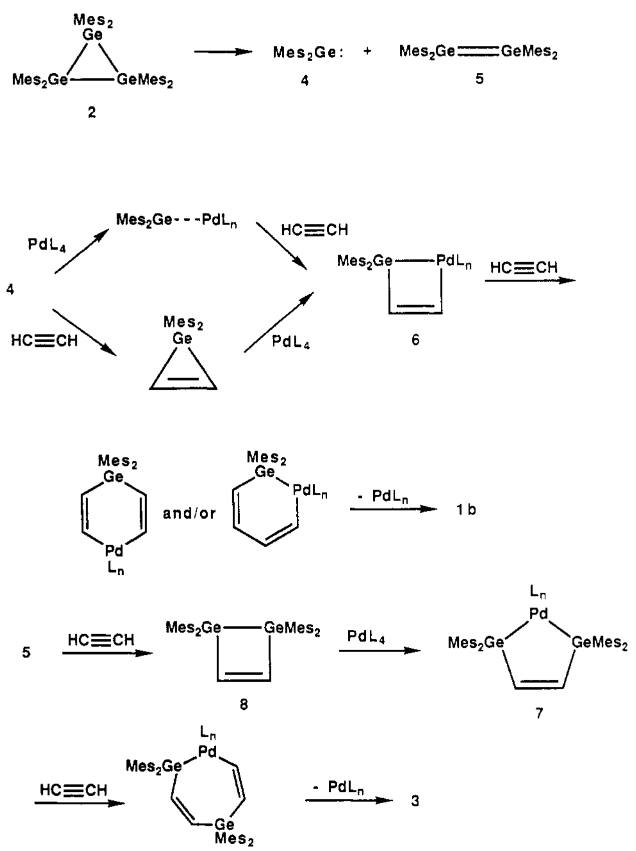


Figure 1. ^1H NMR spectrum of 1,1-dimesitylgermole (**1b**) in $CDCl_3$ (500 MHz).

Scheme I



When acetylene was bubbled into a toluene solution of hexamesitylcyclotrigermane (**2**)[5] in the presence of

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[1] Barton, T. J. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1983; Chapter 9.2, p 205.

[2] Pant, B. C. *J. Organomet. Chem.* **1974**, *66*, 321.

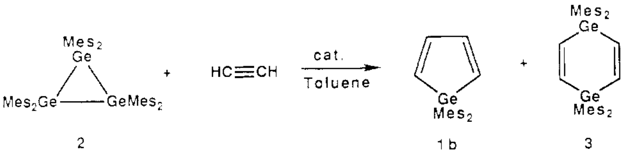
[3] (a) Laporterie, A.; Manuel, G.; Dubac, J.; Mazerolles, P.; Iloughmane, H. *J. Organomet. Chem.* **1981**, *210*, C33. (b) Laporterie, A.; Iloughmane, H.; Dubac, J. *J. Organomet. Chem.* **1983**, *244*, C12. (c) Guimon, C.; Pfister-Guillouzo, G.; Dubac, J.; Laporterie, A.; Manuel, G.; Iloughmane, H. *Organometallics* **1985**, *4*, 636.

[4] A similar synthetic method from a disilane or siliranes gives C-substituted siloles; see: (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Orgamomet. Chem.* **1975**, *86*, C27. (b) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43. (c) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. (d) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57 and references cited therein. (e) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417. (f) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

[5] Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514.

0276-7333/90/2309-0869$02.50/0

$Pd(PPh_3)_4$ (10 mol %) at 80 °C, a colorless crystalline product identified as 1,1-dimesitylgermole (**1b**)[6] was obtained in 85% yield. Also formed was 1,1,4,4-tetramesityl-1,4-digermacyclohexa-2,5-diene (**3**) in 68% yield (eq 1).[7,8] Also, it was found that $PdCl_2(PPh_3)_2$ catalyzed the

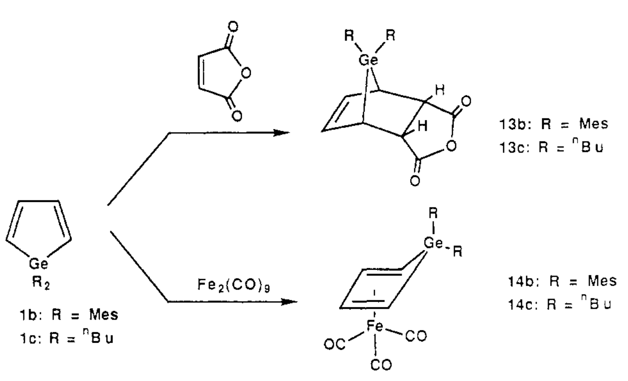


(1)

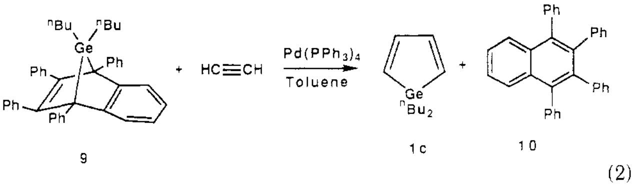
reaction, giving **1b** (72%) and **3** (28%). The presence of palladium catalysts is essential for the formation of **1b** and **3**. Compound **1b** thus obtained is thermally stable and does not dimerize even when heated to its melting point of 83–85 °C. This thermal stability toward dimerization probably is due to the steric protection by mesityl groups. The ^1H NMR spectrum of **1b** shows the characteristic AA′XX′ pattern centered at δ 6.68 and 6.92 ppm (Figure 1).

Reasonable mechanisms for the formation of the products obtained are shown in Scheme I. Because the cyclotrigermane **2** decomposes to dimesitylgermylene (**4**) and tetramesityldigermene (**5**) at 80 °C,[9] the products **1b** and **3** are best rationalized as arising from **4** and **5**, respectively. The formation of **1b** can be best explained in terms of the reaction of 1,2-palladagermetene **6** with acetylene. Product **3** seems to be formed by the reaction of the palladadigermacyclopentene intermediate **7**, produced from the insertion of a palladium complex into the Ge–Ge bond of digermetene **8**, with acetylene. Although evidence for the intermediates **6** and **7** has not yet been obtained, similar types of compounds have been isolated in silicon systems.[4e,f,10]

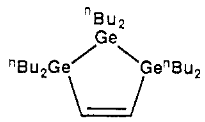
Scheme II



When a 7-germanorbornadiene[11] was used as the precursor of the germylene, C-unsubstituted germole could be isolated as well. A toluene solution of 7,7-di-*n*-butyl-7-germanorbornadiene **9**[11b] and a catalytic amount of $Pd(PPh_3)_4$ was heated to 70 °C, and acetylene was bubbled into the solution for 3 h. In this reaction the C-unsubstituted germole **1c**[12] and 1,2,3,4-tetraphenylnaphthalene (**10**) were obtained in 63% and 85% yields, respectively (eq 2). C-Unsubstituted germole **1c** could be readily separated from **10** by flash column chromatography (silica gel, hexane) or Kugelrohr distillation (80–90 °C/0.04 Torr). Heating of **9** and acetylene in the absence of Pd catalyst under the same conditions afforded **11**[13] in 24% yield and not **1c**. In contrast to the thermal stability of **1b**, pure **1c** easily dimerizes to form the Diels–Alder product **12**[14] even when stored at −20 °C. When **1c** was stored as a dilute CCl_4 solution, **1c** survived as a monomer for a long period.



(2)



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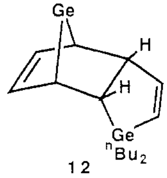

12

The structures of C-unsubstituted germoles **1b** and **1c** were also confirmed by the following reactions. **1b** and **1c** reacted with maleic anhydride smoothly at room temperature to produce the Diels–Alder addition products

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(6) Compound **1b**: colorless crystals; mp 83–85 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 6 H), 2.33 (s, 12 H), 6.68 (AA′XX′, 2 H), 6.79 (s, 4 H), 6.92 (AA′XX′, 2 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 20.9 (q), 24.5 (q), 128.6 (d), 133.5 (s), 134.7 (d), 138.2 (s), 140.4 (d), 143.2 (s); MS *m/e* (relative intensity) 364 (69, M^+), 245 (21, $M^+ - Mes$), 219 (23, $M^+ - Mes - C_2H_2$), 193 (49, MesGe), 178 (100). High-resolution MS: calcd for $C_{22}H_{26}Ge$, *m/e* 364.1246; found, *m/e* 364.1215.

(7) Compound **3**: colorless crystals; mp 238–239 °C; ^1H NMR (100 MHz, $CDCl_3$) δ 2.19 (s, 24 H), 2.22 (s, 12 H), 6.70 (s, 8 H), 7.33 (s, 4 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 20.9 (q), 24.3 (q), 128.8 (d), 135.4 (s), 137.9 (s), 143.1 (s), 147.7 (d); MS *m/e* (relative intensity) 674 (3, M^+), 555 (100, $M^+ - Mes$), 457 (39, $Mes_3GeC_2H_2$), 384 (29, $M^+ - 2Mes - C_4H_4$), 364 (68, $Mes_2GeC_4H_4$), 338 (98, $Mes_2GeC_2H_2$), 193 (29, MesGe). Anal. Calcd for $C_{40}H_{48}Ge_2$: C, 71.28; H, 7.18. Found: C, 71.17; H, 7.25.

(8) Experimental procedure: A typical experimental procedure is represented by the reaction of **2** with acetylene in the presence of $Pd(PPh_3)_4$ as a catalyst. Acetylene was bubbled into a solution of **2** (932 mg, 1 mmol) and $Pd(PPh_3)_4$ (102 mg, 0.1 mmol) in toluene (20 mL), and the mixture was heated at 80 °C. After it was heated for 3.5 h, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. Hexane was added to give colorless crystals of **3** in 68% yield. The filtrate was separated by column chromatography (silica gel, 1/4 benzene/hexane) to give **1b** in 85% yield.

(9) Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770.

(10) (a) Liu, C. S.; Cheng, C.-W. *J. Am. Chem. Soc.* **1975**, *97*, 6746. (b) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43.

(11) (a) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897. (b) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

(12) Compound **1c**: colorless oil; ^1H NMR (60 MHz, $CDCl_3$) δ 0.8–1.6 (m, 18 H), 6.26 (AA′XS′, 2 H), 6.95 (AA′XS′, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.98 (t), 13.77 (q), 26.00 (t), 28.16 (t), 131.99 (d), 143.03 (d); MS *m/e* (relative intensity) 240 (8, M^+), 211 (32, $M^+ - C_2H_5$), 183 (93, $M^+ - Bu$), 154 (41, $M^+ - Bu - C_2H_5$), 140 (19, $M^+ - Bu - C_3H_7$), 126 (100, $M^+ - 2Bu$). High-resolution MS: calcd for $C_{12}H_{22}Ge$, *m/e* 240.0930; found, *m/e* 240.0935.

(13) Compound **11**: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, $J = 7.2$ Hz, 12 H), 0.90 (t, $J = 7.2$ Hz, 6 H), 0.92–1.46 (m, 36 H), 7.27 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.31 (t), 13.75 (q), 13.77 (q), 15.24 (t), 26.48 (t), 26.50 (t), 28.82 (t), 30.83 (t), 152.32 (d); MS *m/e* (relative intensity) 586 (58, M^+), 529 (77, $M^+ - Bu$), 473 (100, $M^+ - Bu - C_4H_8$), 417 (93, $M^+ - Bu - 2C_4H_8$), 361 (78, $M^+ - Bu - 3C_4H_8$), 305 (39, $M^+ - Bu - 4C_4H_8$). Anal. Calcd for $C_{26}H_{56}Ge_3$: C, 53.25; H, 9.62. Found: C, 53.22; H, 9.74. Similar types of compounds were isolated in the reaction of dimethylgermylene with acetylenes; see: Billeb, G.; Neumann, W. P.; Steinhoff, G. *Tetrahedron Lett.* **1988**, *29*, 5245.

(14) Compound **12**: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.80–1.50 (m, 36 H), 1.96 (dd, $J = 1.9, 9.1$ Hz, 1 H), 2.23 (dd, $J = 1.9, 4.4$ Hz, 1 H); 2.35 (dd, $J = 2.3, 4.4$ Hz, 1 H), 3.67 (dddd, $J = 2.3, 2.3, 2.3, 9.1$ Hz, 1 H), 5.94 (dd, $J = 4.5, 6.5$ Hz, 1 H), 6.09 (dd, $J = 2.3, 9.4$ Hz, 1 H), 6.23 (dd, $J = 4.4, 6.5$ Hz, 1 H), 6.36 (dd, $J = 2.3, 9.4$ Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.87 (t), 13.76 (q), 13.81 (q), 13.83 (q), 13.86 (q), 14.95 (t), 15.15 (t), 17.07 (t), 26.04 (t), 26.21 (t), 26.48 (t), 27.21 (t), 27.71 (t), 27.75 (t), 27.87(t), 28.72 (d), 29.43 (t), 36.04 (d), 38.05 (d), 53.75 (d), 131.18 (d), 131.51 (d), 133.41 (d), 151.54 (d); MS *m/e* (relative intensity 478 (3, M^+), 292 (100, $M^+ - Bu_2Ge$,, 235 (78, $M^+ - Bu_2Ge - Bu$), 178 (50, $M^+ - Bu_2Ge - 2Bu$). High-resolution MS: calcd for $C_{24}H_{44}{}^{72}Ge^{74}Ge$, *m/e* 478.1867; found *m/e* 478.1822.

13b[15] and **13c**[16] in 67% and 71% yields, respectively (Scheme II). One of the two possible isomers was formed and was tentatively identified as the endo isomer. The reactions of **1b** and **1c** with diiron nonacarbonyl in benzene at 70–80 °C gave the corresponding C-unsubstituted π-complexes **14b**[17] and **14c**[18] in 97% and 42% yields, respectively. Both C-unsubstituted π-complexes **14b** and **14c** are yellow compounds and show characteristic AA′XX′ patterns in their ^{1}H NMR spectra. We are continuing to explore this and related systems.

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(15) Compound **13b**: colorless crystals; mp 212–213 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.22 (s, 3 H), 2.23 (s, 3 H), 2.42 (s, 6 H), 2.46 (s, 6 H), 3.30 (ddt, J = 1.4, 2.9, 3.7 Hz, 2 H), 3.71 (t, J = 1.4 Hz, 2 H), 6.47 (dd, J = 2.9, 3.7 Hz, 2 H), 6.83 (s, 2 H), 6.84 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.91 (q), 20.92 (q), 22.67 (q), 24.17 (q), 40.70 (d), 47.28 (d), 129.03 (d), 129.33 (d), 130.22 (s), 132.88 (d), 134.55 (s), 139.61 (s), 139.72 (s), 142.21 (s), 143.32 (s), 173.54 (s); MS *m/e* (relative intensity 312 (94, Mes_2Ge), 193 (100, MesGe), 122 (16, $C_7H_6O_2$), 106 (14, C_7H_6O); IR (KBr) 1850, 1760 cm^{-1} (CO–O–CO). Anal. Calcd for $C_{26}H_{28}O_3Ge$: C, 67.73; H, 6.12. Found: C, 67.63; H, 6.18.

(16) Compound **13c**: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (t, J = 7.2 Hz, 3 H), 0.85 (t, J = 7.2 Hz, 3 H), 0.97 (t, J = 7.2 Hz, 2 H), 0.99 (t, J = 7.2 Hz, 2 H), 1.20–1.40 (m, 8 H), 2.73 (ddt, J = 1.5, 3.6, 3.7 Hz, 2 H), 3.66 (t, J = 1.5 Hz, 2 H), 6.34 (dd, J = 3.6, 3.7 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.10 (t), 13.58 (q), 13.69 (q), 17.43 (t), 25.78 (t), 26.01 (t), 26.80 (t), 28.58 (t), 35.88 (d), 47.77 (d), 132.76 (d), 173.64 (s); MS *m/e* (relative intensity) 183 (53, $BuGeC_4H_4$), 126 (100, GeC_4H_4); IR (neat) 1830, 1760 cm^{-1} (CO–O–CO). Anal. Calcd for $C_{16}H_{24}O_3Ge$: C, 57.03; H, 7.18. Found: C, 56.70; H, 7.11.

(17) Compound **14b**: yellow crystals; mp 189–190 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 2.05 (s, 3 H), 2.12 (s, 3 H), 2.23 (AA′XX′, 2 H), 2.31 (s, 6 H), 2.48 (s, 6 H), 5.19 (AA′XX′, 2 H), 6.61 (s, 2 H), 6.79 (s, 2 H); ^{13}C NMR (125 MHz, C_6D_6) δ 20.91 (q), 21.10 (q), 23.59 (q), 24.24 (q), 54.62 (d), 89.77 (d), 129.30 (d), 129.31 (d), 134.83 (s), 138.30 (s), 139.05 (s), 140.75 (s), 141.50 (s), 143.30 (s), 211.94 (s); MS *m/e* (relative intensity) 476 (4, M^+ – CO), 448 (27, M^+ – 2CO), 420 (57, M^+ – 3CO), 301 (100, M^+ – Mes – 3CO); IR (KBr) 2050, 1960 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_3GeFe$: C, 59.71; H, 5.21. Found: C, 59.81; H, 5.30.

(18) Compound **14c**: yellow oil; ^{1}H NMR (500 MHz, C_6D_6) δ 0.42 (t, J = 7.3 Hz, 2 H), 0.87 (t, J = 7.3 Hz, 3 H), 0.93 (t, J = 7.3 Hz, 3 H), 1.12–1.53 (m, 10 H), 1.71 (AA′XX′, 2 H), 5.26 (AA′XX′, 2 H); ^{13}C NMR (125 MHz, C_6D_6) δ 13.93 (q), 14.01 (q), 15.81 (t), 23.46 (t), 26.21 (t), 26.42 (t), 27.33 (t), 28.43 (t), 48.15 (d), 89.80 (d), 212.75 (s); MS *m/e* (relative intensity) 380 (6, M^+), 352 (21, M^+ – CO), 296 (100, M^+ – 3CO), 240 (36, M^+ – $Fe(CO)_3$), 183 (39, M^+ – $Fe(CO)_3$ – Bu); IR (neat) 2050, 1800 cm^{-1} (CO). High-resolution MS: calcd for $C_{15}H_{22}O_3GeFe$ *m/e* 380.0128; found, *m/e* 380.0143.

Synthesis, Structure, and Reactivity of a Zirconocene Complex of Cyclobutene

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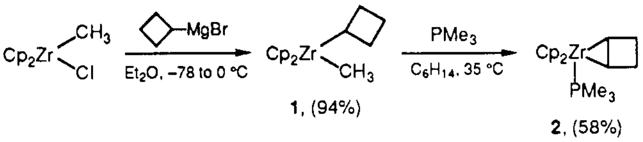
Summary: The first structurally characterized transition-metal complex of cyclobutene is described. The complex is formed by the elimination of methane from cyclobutylmethylzirconocene with subsequent trapping by trimethylphosphine. The reactivity of the complex with unsaturated organic molecules and its X-ray crystal structure are reported.

Early-transition-metal complexes of arynes and alkynes have been the subject of numerous recent publications.[2] Interest in these complexes stems from their novel structures and their use as intermediates in the selective synthesis of organic molecules. Olefin complexes of early transition metals have not been studied to the same extent, in part due to difficulties encountered in their synthesis and isolation. Until very recently, the only structurally characterized group 4 metal complex of an olefin was the $Cp^*{}_2Ti(\eta^2$-ethylene) complex reported by Bercaw and coworkers.[3] Renewed interest in the chemistry of alkene complexes of the group 4 metals has resulted in several recent reports of alkene complexes of titanium, zirconium, and hafnium.[4] In this communication, we report the synthesis, structure, and reactivity of zirconocene complex of cyclobutene. This represents the first structurally characterized group 4 metal complex of a cyclic olefin and the only structurally characterized transition-metal complex of cyclobutene.[5]

Treatment of ethereal solutions of zirconocene (methyl) chloride with cyclobutylmagnesium bromide at –78 °C, followed by warming to 0 °C, cleanly forms cyclobutylmethylzirconocene, which can be isolated as a thermally sensitive waxy yellow solid in ca. 90% yield. Adding excess trimethylphosphine to hexane solutions of 1 and warming



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