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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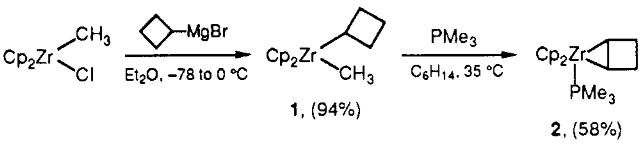
Summary: The first structurally characterized transition-metal complex of cyclobutene is described. The complex is formed by the elimination of methane from cyclobutylmethylzirconocene with subsequent trapping by trimethylphosphine. The reactivity of the complex with unsaturated organic molecules and 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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(1) Camille & Henry Dreyfus Teacher-Scholar Awardee, 1989–1994; American Cancer Society Junior Faculty Research Awardee, 1987–1989; Eli Lilly Grantee, 1988–1990; Alfred P. Sloan Research Fellow, 1988–1990; Union Carbide Innovation Recognition Program Awardee, 1989.

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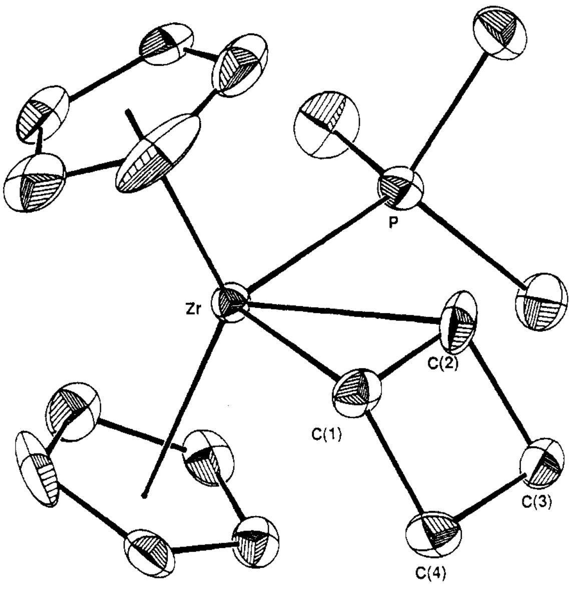
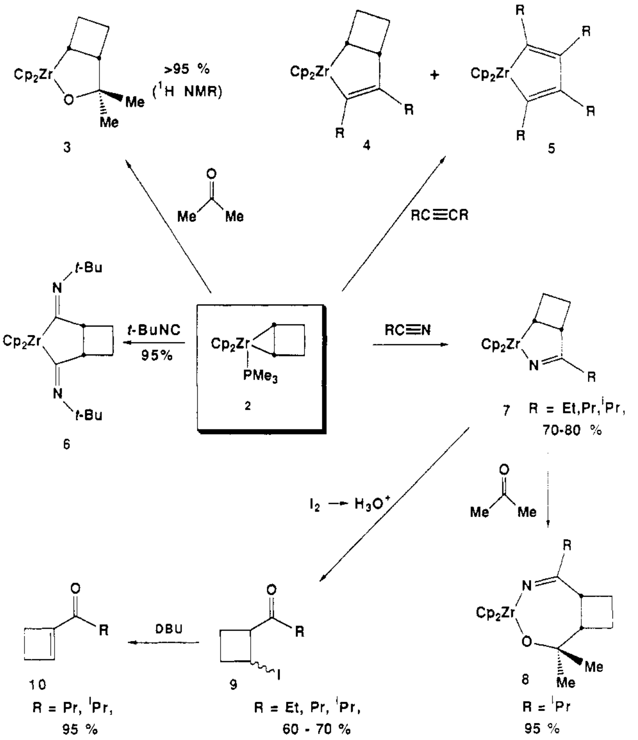


Figure 1. Molecular structure of **2**. Selected bond lengths (Å): Zr–C(1), 2.333 (9); Zr–C(2), 2.334 (8); C(1)–C(2), 1.49 (1); C(2)–C(3), 1.52 (1); C(3)–C(4), 1.55 (1); C(1)–C(4), 1.52 (1); Zr–P, 2.680 (3). Selected bond angles (deg): C(1)–Zr–C(2), 37.2 (3); P–Zr–C(1), 111.8 (2); C(1)–C(2)–C(3), 89.9 (9); C(2)–C(3)–C(4), 89.9 (7); C(3)–C(4)–C(1), 89.0 (7); C(4)–C(1)–C(2), 92.3 (7).

to 35 °C for 12 h results in the elimination of methane and the formation of the cyclobutene complex as its trimethylphosphine adduct **2** (~85% by ^{1}H NMR spectroscopy). Partial precipitation of the product occurs during the course of the reaction, which greatly facilitates the isolation of **2**. Recrystallization from hexanes/ether (10:1) affords pure **2** as a thermally sensitive crystalline orange solid.

Complex **2** was characterized by single-crystal X-ray diffraction, and the ORTEP diagram, along with selected bond distances and angles, is shown in Figure 1.[6] The gross structural features of the zirconocene fragment are in accord with those of previously characterized zirconocene complexes.[2i–k,4b,c] The atoms of the cyclobutene ring are essentially planar with no deviations greater than 0.05 Å; the internal bond angles are 90°. A notable lengthening of the C(1)–C(2) bond distance relative to that of free cyclobutene[7] is observed, indicating this bond possesses primarily single-bond character. The dihedral angle between the plane of the four-membered ring and the ligands in the plane of the wedge (defined by Zr, P, C(1), and C(2)) is 122.7°. These two structural features indicate that substantial back-bonding from the metal d orbitals to the π^* ligand orbitals is occurring, consistent with the representation of **2** as a zirconacyclopropane.

Scheme I



Complex **2** undergoes insertion reactions with a variety of unsaturated groups to afford good yields of the novel bicyclo[3.2.0]metallacycles as shown in Scheme I. Nitriles are conveniently coupled by direct treatment of solutions of **1**, prepared in situ, with a slight excess of nitrile followed by heating to 40 °C; no trimethylphosphine is required. The cyclobutene complex **2** reacts rapidly with 1 equiv of acetone to provide a species whose ^{1}H and ^{13}C NMR spectra are consistent with structure **3**. Compound **3** is unstable to removal of solvent, and attempts to isolate it from the reaction mixture have thus far been unsuccessful. Alkynes react reversibly with **2** to yield an inseparable mixture of the desired insertion product **4** and the metallacyclopentadiene **5**.[8] Treatment of mixtures of **4** and **5** with an excess of alkyne converts **4** into **5**. Complex **2** undergoes a rapid reaction at room temperature with 2 equivalents of *tert*-butyl isocyanide to provide the novel double-insertion product **6**. Treatment of **2** with less than 2 equiv of the isocyanide results in partial conversion to **6**; the single-insertion product has not been observed in the reaction mixture.

The azametallacycles **7** formed in the nitrile coupling reactions serve as useful intermediates for the further functionalization of the cyclobutane ring. Compound **7c** cleanly inserts 1 equiv of acetone to give the metallacycle **8**. The conversions of **2** to **6** and **2** to **8** (via **7**) represent rare examples of the formation of vicinal carbon–carbon bonds in the reaction of a cycloalkene. More generally, iodinolysis of the azametallacycles provides good isolated yields of the α-iodoacylcyclobutanes **9** as single diastereomers.[9] Although the relative stereochemistry of the β-iodo ketones has not been unambiguously determined, spectroscopic evidence suggests that the iodo and acyl groups are trans. These β-iodo ketones can be readily dehydrohalogenated by treatment with DBU in chloroform to form the cyclobutenyl ketones **10** in high yield.[10]

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(6) Single crystals of **2** were grown from a 10:1 hexane–ether solution at −40 °C. A suitable crystal (0.25 mm × 0.15 mm × 0.18 mm) was mounted on a glass fiber under a cold N_2 stream. Data were collected at −77 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7169 Å): monoclinic, space group $P2_1/n$, a = 8.182 (4) Å, b = 15.610 (3) Å, c = 12.384 (6) Å, β = 95.68 (2)°, V = 1574 (2) Å^3, Z = 4, d(calcd) = 1.484 g/cm^3. A total of 2192 data ($I > 3\sigma(I)$) were collected with use of an ω–2θ scan to a 2θ value of 55.2° (reflection to parameter ratio 12.7). The structure was solved by the Patterson method and refined without complications. Anisotropic refinement of all non-hydrogen atoms by full-matrix least squares (fixed hydrogen parameters, d_{C-H} = 0.95 Å) resulted in R = 0.060 and R_w = 0.070. A full report of the data collection and structure solution and refinement is given in the supplementary material.

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Further investigations of the diverse reactivity of 2 as well as investigations into the chemistry of other alkene complexes of group 4 metals are ongoing in our laboratory.

Acknowledgment. We gratefully acknowledge the National Institutes of Health (Grant No. GM 34917), Eli Lilly, and, in part, the Office of Naval Research for their support of this work. We also thank Dr. W. M. Davis of the MIT X-Ray Diffraction Facility for his crystallographic assistance and the U.S. Department of Energy (Grant No. DE-FG05-86ER-75292) for funding for the Rigaku AFC6R diffractometer.

Supplementary Material Available: An experimental section containing details of the preparation and spectroscopic characterization of compounds, a listing of crystallographic data and a description of data collection procedures, an ORTEP diagram of 2, and listings of final positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes (32 pages); a listing of structure factors (25 pages). Ordering information is given on any current masthead page.

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Alkyl Group Isomerization Studies with Unusually Stable Alkylmetal Complexes of Palladium and Platinum. Secondary-Primary Alkyl Isomerization Equilibria in the Absence of Steric Influences from Ancillary Ligands

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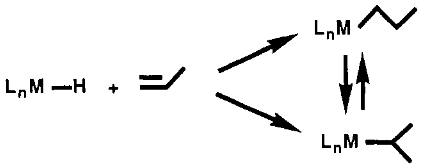
Summary: The unusually stable palladium(II) and platinum(II) derivatives $[R_2NCS_2]M(PR'_3)(alkyl)$ (R = Me, Et; R' = Et, Ph) undergo isomerization of the alkyl ligand when heated (Pt, 120 °C; Pd, 75 °C) in solution. For primary/secondary alkyl pairs (alkyl = *n*-propyl/isopropyl, *n*-butyl/*sec*-butyl) the positions of the isomerization equilibria are similar, 9/1.0 for platinum and 10/1.0 for palladium. This 1.6–1.7 kcal/mol free energy difference between the isomers represents the bond energy difference of primary versus secondary alkylmetal complexes in the absence of steric constraints imposed by other ligands in the coordination sphere.

Scheme I



The insertion of alkenes into metal–hydride bonds, a reaction that is important to many processes catalyzed by transition metals,[1] can lead to isomeric mixtures of alkylmetal complexes (Scheme I). The various isomers, which are generally in rapid equilibrium, can control the types of products produced in these reactions.[2] While a number of alkyl isomerization reactions of alkylmetal complexes have been reported,[3-7] fundamental information on the factors that determine the bonding preferences is still lacking. We report here investigations with unusually stable palladium(II) and platinum(II) derivatives of the formula $[R_2NCS_2]M(PR'_3)(alkyl)$ (R = Me, Et; R' = Et, Ph) in which the isomerization of the alkyl ligand (e.g., isopropyl, *n*-propyl) can be carefully studied by varying the ancillary ligands and the alkyl group. An important feature of the system is the ability to prepare complexes in which the ancillary ligands have minimal steric influences on the alkyl isomerization reaction. Steric effects have dominated earlier studies.

The new $[R_2NCS_2]M(PR'_3)(alkyl)$ complexes are prepared from the reaction of $[R_2NCS_2]M(PR'_3)Cl$ with alkyllithium or Grignard reagents.[8] With platinum, the synthesis is successful for alkyl = methyl for both R' = Et and R' = Ph, but stable alkylpalladium complexes containing β-hydrogen atoms, such as the *n*-propyl and isopropyl complexes, have only been prepared for R' = Et. The complexes $[Me_2NCS_2]Pd(PEt_3)(Pr)$ can be heated in toluene solution at 60 °C for extended periods without noticeable decomposition, and at 75 °C decomposition is ca. 1%/h. These complexes appear to be the most thermally stable simple alkyl derivatives containing β-hydrogen atoms that have been prepared for this metal. In general, palladium complexes with nonchelated alkyl ligands containing β-hydrogen atoms are not stable above room temperature.[9] The platinum complexes can be prepared for

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(9) The complexes *cis*- and *trans*-$[Pd(Et)_2(PMe_2Ph)_2]$ decompose in solution at room temperature and are "too unstable for microanalysis".[10] $Pd(DPPE)(Et)_2$ decomposes rapidly in solution at 60 °C.[10b] $CpPd(PPh_3)(Bu)$ decomposes in solution at 35 °C and $CpPd(PPh_3)(CH_2CH_2CH(COMe)_2)$ at 50 °C.[11] The low thermal stability of alkylpalladium complexes with β-hydrogen atoms has been extensively exploited in organic synthesis.[12]

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