Table I. Thermal Decomposition of Pt Ketene Complexes 1, 3, and 4[a]

complexes	temp, °C	products,[b] %						
		CH_4	C_2H_4	C_3H_6	C_4H_8	CO	CH_2CO	*f*[c]
3	110		14	5	7	11	15	5
3	210		15	6	8	68	16	5
4	180	17	8	16	3	56	4	23
1	80		15	14	4	8	2	48
1	200	3	18	12	5	72	1	95

[a] Pyrolysis of the solid was performed under vacuum, and the products were collected on a cold finger cooled with liquid nitrogen. The temperature was raised from 20 °C to the specific point at a rate of 5 °C/min. [b] All products were identified by GC–MS (EI, 20 eV) and GC–IR using a short column of Durapak (octane on Porasil C) treated with trimethylsilyl ether. [c] $f = \sum^4_{m=1} m\text{-}(CH_2)_m/CH_2C{=}O$.

ligands was determined by means of IR and NMR spectroscopy.[1] The data are fully consistent with an η^2-(C,C) ketene structure for 1–4; the magnitude of $^1J_{PtC}$ or $^2J_{PtH}$ in NMR spectra of 1 and 3 reflects the s character of the carbon hybrid orbital involved in the Pt–C bonding, corroborating the platinacyclopropane structure.[10]

The ketene complexes thermally decompose to yield various hydrocarbons. Upon being heated at 55 °C in acetone, 2 decomposed to give C_2D_4 (17%), C_3D_6 (16%), and C_4D_8 (7%). From the decomposition residue, $Pt(CO)(PPh_3)_3$ was isolated in 36% yield.[11] This result may be ascribed to a C–C bond cleavage reaction of the ketene ligand of 2, followed by the formation of the kinetically viable metal–carbene–CO intermediate 5, the carbene fragment of which presumably oligomerizes to form olefins (Scheme I).[12] This observation is in accord with recent studies on the bridging ketene complex of Os which is in partially reversible equilibrium with the methylene complex.[4d,13] This rearrangement, which probably proceeds through metal–carbene species 5, is consistent with the formation of cyclopropane derivative 7 (36%) in carbene trapping experiments of 2 with Michael acceptors such as methyl acrylate.[14]

The ketene complexes 1, 3, and 4 readily decompose to yield hydrocarbons and CO as summarized in Table I. $Pt(CH_2{=}C{=}O)(PPh_3)_2$ (1) almost exclusively affords hydrocarbons, resulting in a large *f* value, whereas $PtCl_2(CH_2{=}C{=}O)$ (3) yields more ketenes. It was found that those 4 which have electron-donating phosphine ligands[15] gave larger *f* values affording less ketene compared with 3. The decomposition mode of the ketene complexes involving a C–C bond scission of the bound ketenes seems to be largely affected by the nature of the ligands coordinated to the metal center.[15] However, thermolysis of 1 in the presence of H_2 has led to the formation of C_2-oxygenated products, irrespective of its dominant decomposition route.

The ketene ligands of complexes 1–4 were found to be reduced by H_2 under mild condition. Hydrogenation of 1 by 3 atm of H_2 (26 °C) gave CH_3CHO (36%) and C_2H_5OH (20%), together with hydrocarbons [CH_4 (20%), C_2H_6 (2%), and C_3H_8 (5%)], while 3 afforded C_2H_5OH (55%), CH_3CHO (21%), and CH_3OH (2%) in addition to CH_4 (3%) and C_3H_8 (9%).

$$L_2Pt(CH_2{=}C{=}O) \xrightarrow[\text{acetone}]{H_2} C_2H_5OH + CH_3CHO + C_nH_{2n+2}$$

$$L_2Pt(CH_2{=}C{=}O) \xrightarrow[\text{THF}]{LiAlH_4} C_2H_5OH$$

Reduction of 1, 3, or 4 with $LiAlH_4$ in THF produced C_2H_5OH in 93, 87, or 92% yield, respectively. These observation may indicate that the ketene complexes can be substantially converted to C_2-alcohol and aldehyde along with hydrocarbons under mild conditions. Such hydrogenations appear to be important because of the potential relevance of ketene intermediates on catalyst surfaces during CO reduction chemistry.

Acknowledgment. We gratefully acknowledge the financial support of the Ministry of Education (Grant 580555) and the experimental assistance of Mr. S. Ikezu.

Registry No. 1, 96728-28-8; 2, 96705-37-2; 3, 96705-38-3; 4, 96705-39-4; 7, 90115-89-2; $Pt(PPh_3)_4$, 14221-01-3; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $[PtCl_2(C_2H_4)]_2$, 12073-36-8; $Pt(CO)(PPh_3)_3$, 15376-99-5; CH_2Br_2, 74-95-3; CH_2CO, 463-51-4; norcarane, 51592-70-2; methyl acrylate, 96-33-3; ketene-d_2, 4789-21-3; cyclohexene, 110-83-8.

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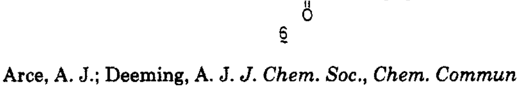
(9) 4: IR (KBr) 2990 (m, ν_{CH}), 2870 (m, ν_{CO}), 1722 (s, ν_{CO}), 325 (w, ν_{PtCl}); ^1H NMR (toluene-d_8) δ 1.62–1.70 (m, 14 H, CH_2, PMe) 7.2–7.4 (m, 10 H, Ph). Anal. Calcd for $C_{18}H_{24}OCl_2P_2Pt$: C, 36.99; H, 4.14; Cl, 12.13. Found: C, 37.28; H, 4.50; Cl, 11.82. Only one Pt–Cl stretching vibration, which is consistent with the trans-halogen structure, is observed. See: Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pilbrow, M. E. *J. Chem. Soc. A* **1969**, 227.

(10) Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, **1981**; p 38.

(11) Malatesta, L.; Cariello, C. *J. Chem. Soc.* **1958**, 2323. Chini, P.; Logoni, G. *J. Chem. Soc. A* **1970**, 1542.

(12) An alternative decomposition process involving platinacyclobutanone complex 6 is conceivable, although no cyclopropanone was detected on pyrolysis of 2. However, the experimental result that thermolysis of 2 in the presence of ca. 2 equiv of $CH_2{=}C{=}O$ yielded C_2D_4 and C_3D_6 as the major products along with cyclopropanone-d_2 (4%) and $C_2H_2D_2$ (2%) may exclude this possibility.



(13) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 364.

(14) The carbene fragment of 2 could be also trapped with cyclohexene to yield norcarane (17%). Norcarane and 7 were isolated by preparative GLC and identified by ^1H NMR and mass spectroscopy.

(15) Kosolapoff, G. M.; Maier, L. "Organic Phosphorus Compounds"; Wiley-Interscience: New York **1972**; Vol. 1, p 77.

(16) (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147. (b) Miyashita, A.; Takaya, H., to be submitted for publication.

Stable Titanacyclopentanes: Isolation, Characterization, and Reactions of 5,5-Bis(pentamethylcyclopentadienyl)-5-titanaspiro[2.4]heptanes Derived from $(\eta^5\text{-}C_5Me_5)_2Ti(CH_2{=}CH_2)$ and Methylenecyclopropanes

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Summary: 5,5-Bis(pentamethylcyclopentadienyl)-5-titanaspiro[2.4]heptanes prepared by the oxidative coupling of $(\eta^5\text{-}C_5Me_5)_2Ti(CH_2{=}CH_2)$ with methylenecyclopropanes have been isolated and characterized by spectroscopic and X-ray analyses. Divergent thermal reactions involving novel skeletal rearrangements and reductive eliminations giving cycloalkanes have been observed, which are highly dependent on the molecular structures of the metallacycles.

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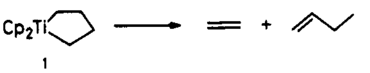
The preparation and study of metallacyclic compounds are of considerable current interest because many synthetically important transition-metal-assisted reactions proceed via metallacyclic intermediates. Although numerous metallacyclic compounds are known, only a limited number of such compounds of the elements of the first transition series have been isolated and characterized.[1,2]

Bis(cyclopentadienyl)titanacyclopentane (1) (Cp = cyclopentadienyl) is unstable in solution even at −30 °C. Its instability may be ascribed to a facile β-elimination reaction and β-carbon–carbon bond fission giving 1-butene and ethylene, respectively (eq 1).[2] Synthesis of structurally variant, isolable titanacyclopentanes might afford us an opportunity to carry out detailed structure-reactivity studies of this class of compounds. We report herein the isolation, structure, and thermal reactions of some new stable titanacyclopentanes.



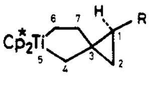
1

(1)

Treatment of a light green solution of Cp*$_2$Ti(CH$_2$=CH$_2$)[2c] (Cp* = pentamethylcyclopentadienyl) in hexane with a twofold excess of methylenecyclopropane (**2a**) at −10 °C for 48 h under argon led to formation of a deep red solution. Evaporation of the solvent and recrystallization of the residue from hexane at −80 °C gave the new titanacyclopentane **3a** as orange needles in 65% yield. The structure of **3a** was determined on the basis of its spectral data.[3] Solid **3a** is moderately stable (mp 156–158 °C dec), but in solution it slowly decomposes at 95 °C ($t_{1/2}$ = 91 min in toluene). No appreciable change in ^{1}H NMR signals of **3a** in toluene-d_8 were observed down to −90 °C, indicating that the flipping of the five-membered ring in **3a** is rapid even at −90 °C.

2a: R = H

2b: R = C_6H_5



3a: R = H

3b: R = C_6H_5

Similarly, complex **3b** was prepared by the reaction of Cp*$_2$Ti(CH$_2$=CH$_2$) with **2b** at 20 °C for 48 h. Recrystallization from toluene at −80 °C furnished deep red prisms of **3b** in 83% yield, mp 122–124 °C dec. Complex **3b** in toluene is less stable than **3a** ($t_{1/2}$ = ca. 3 min at 95 °C). The structure of **3b** was supported by spectral data.[4] Furthermore, a single-crystal X-ray study was carried out for **3b**.[5] The molecular structure is shown in Figure 1 together with some selected bond distance and angle data. Complex **3b** is monomeric and has the coordination geometry of a distorted tetrahedron that is defined by two pentamethylcyclopentadienyl ligands and two carbon atoms of the metallacyclopentane ring. The C(4)–Ti–C(6) angle is 80.6 (1)°, which is in contrast with the calculated value of 110° for d^0 titanocene, Cp$_2$TiH$_2$.[6] The five-membered ring of **3b** is fixed in a puckered form so that the C(1)–C(3) bond occupies a pseudoequatorial position.

Compound **3** can be considered to arise from a mixed-ligand complex bearing ethylene and the strained olefin **2** through an oxidative coupling of the two coordinated olefins. The selective formation of such a mixed ligand complex may be the consequence of a subtle balance of the coordination abilities of ethylene and methylenecyclopropane.[7] This is in remarkable contrast with the reported fact that the reactions of Cp*$_2$Ti(CH$_2$=CH$_2$) with terminal olefins do not give any metallacycles but result in the isomerization of the starting olefins to internal olefins.[2c] The observed stability of the metallacycles **3a** and **3b** might be ascribed to a strain effect and/or a steric effect exerted by a cyclopropane ring which makes the decomposition reactions shown in eq 1 more difficult.

Interestingly, when a solution of **3b** in ether was stirred with 0.1 N hydrochloric acid, no reaction took place. A smooth hydrolysis of **3b**, however, occurred upon treatment of a benzene solution of **3b** with column packing materials such as silica gel or alumina to give *trans*-1-ethyl-1-methyl-2-phenylcyclopropane in 88% yield.[8] Similar

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(1) For example: (a) Doyle, M. J.; McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376. (b) Takahashi, S.; Suzuki, Y.; Sonogashira, K.; Hagihara, N. *Ibid.* **1976**, 839. (c) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123. (d) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *Ibid.* **1981**, *103*, 5584. (e) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *Ibid.* **1982**, *104*, 7491. (f) Diversi, P.; Ingrosso, G.; Lucherini, A. *Inorg. Synth.* **1983**, *22*, 171. (g) Lindner, E.; Schauss, E.; Hiller, W.; Fawzi, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 711. (h) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952 and references cited therein.

(2) (a) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (b) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *Ibid.* **1978**, *100*, 2418. (c) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

(3) **3a**: ^{1}H NMR (400 MHz, C_6D_6) δ 0.37 (s, 2 H_1 and 2 H_2), 0.62 (s, 2 H_4), 0.63 (t, 2 H_6, $J_{6,7}$ = 6.8 Hz), 1.79 (t, 2 H_7), 1.87 (s, Cp*); ^{13}C NMR (100 MHz, C_6D_6) δ 12.32 (C_5Me_5, J_{C-H} = 126 Hz), 20.48 (C_1 and C_2, 157 Hz), 25.01 (C_3), 41.59 (C_7, 123 Hz), 63.48 (125 Hz) and 65.60 (125 Hz) for C_4 and C_6, 120.82 (C_5Me$_5$); IR (KBr) ν 3045 (w), 2960 (s), 2880 (s), 2800 (s), 1492 (w), 1434 (m), 1375 (s), 1314 (w), 1260 (w), 1188 (m), 1017 (m), 992 (m), 827 (w), 801 (w), 626 (w), 587 (w), 532 (w), 479 (w), 440 (w), 400 (m), 370 (w) cm^{-1}; mass spectrum, m/z 400 (M$^+$), 398 (M$^+$ − 2), 318 (M$^+$ − C_6H_{10}, base peak), 181 (M$^+$ − 219); calcd for $C_{26}H_{40}{}^{48}$Ti 400.2609, found 400.2584. Anal. Calcd for $C_{26}H_{40}$Ti: C, 77.98; H, 10.07. Found: C, 77.56; H, 9.58.

(4) **3b**: ^{1}H NMR (400 MHz, C_6D_6) δ −0.13 (ddd, H_{6a}, $J_{6a,6b}$ = 11.0 Hz, $J_{6a,7a}$ = 5.5 Hz, $J_{6a,7b}$ = 5.5 Hz), 0.09 and 0.39 (AB$_q$, 2 H_4, $J_{4a,4b}$ = 11.9 Hz), 0.88 (dd, H_{2cis}, $J_{1,2cis}$ = 6.1 Hz, $J_{2cis,2trans}$ = 4.1 Hz), 0.97 (dd, H_{2trans}, $J_{1,2trans}$ = 8.6 Hz), 1.33 (ddd, H_{6b}, $J_{6b,7a}$ = 11.0 Hz, $J_{6b,7b}$ = 5.8 Hz), 1.53 (ddd, H_{7a}, $J_{7a,7b}$ = 12.3 Hz), 1.63 (dd, H_1), 1.69 (s, Cp*), 1.87 (s, Cp*), 2.31 (ddd, H_{7b}), 7.10–7.30 (m, C_6H_5), the stereochemical assignments of ring methylene protons have not been done; ^{13}C NMR (C_6D_6) δ 12.08 (C_5Me_5, J_{C-H} = 127 Hz), 12.33 (C_5Me_5, 127 Hz), 28.74 (C_2, 157 Hz), 34.17 (C_1, 154 Hz), 34.85 (C_3), 44.15 (C_7, 122 Hz), 55.36 (C_4, 125 Hz), 64.98 (C_6, 123 Hz), 120.89 (C_5Me$_5$), 121.02 (C_5Me$_5$), aromatic carbons at 124.49, 127.49, 128.38, 142.52; IR (KBr) ν 3045 (w), 2970 (s), 2900 (s), 2800 (s), 1640 (m), 1601 (m), 1497 (m), 1445 (m), 1378 (s), 1304 (w), 1077 (w), 1063 (w), 1019 (m), 821 (m), 774 (m), 737 (m), 697 (s), 636 (m), 401 (w) cm^{-1}; mass spectrum, m/z 476 (M$^+$), 318 (M$^+$ − $C_{12}H_{14}$), 158 (M$^+$ − Cp*$_2$Ti), 129 (M$^+$ − 347, base peak); calcd for $C_{32}H_{44}{}^{48}$Ti 476.2921, found 476.2900. Anal. Calcd for $C_{32}H_{44}$Ti: C, 80.65; H, 9.31. Found: C, 80.17; H, 9.95.

(5) Crystals of **3b** grown from toluene solution at −20 °C are monoclinic of space group $P2_1/a$ with a = 21.832 (3) Å, b = 8.580 (1) Å, c = 14.759 (2) Å, β = 96.81 (1)°, U = 2744.9 (6) Å^3, Z = 4, D_{calcd} = 1.154 g cm^{-3}. Intensity data ($2\theta_{max}$ = 60°) were collected on a crystal of dimensions 0.40 × 0.32 × 0.22 mm on a Rigaku AFC5 four-circle diffractometer using graphite-monochromated Mo Kα radiation and an θ–2θ scan technique. The data were corrected for absorption (μ = 3.42 cm^{-1}) and averaged to give 4261 unique observed reflections with $|F_o| > 3\sigma(F_o)$. The structure was solved via application of the direct-methods program MULTAN 78 and refined by block-diagonal least squares. The atoms were refined anisotropically except for the hydrogen atoms, which were refined isotropically. The current R value is 0.053 (R_w = 0.056). Atomic coordinates, thermal parameters, and bond lengths and angles are listed in supplementary tables.

(6) The ideal value of the angle H–Ti–H in Cp$_2$TiH$_2$ has been calculated to be 110°. However, it was also shown that the total energy of the molecule is rather insensitive for this angle, and the energy differences are within 3 kcal/mol over the range 75–130°. This suggests that the present compound **3b** is not destabilized so much by the deformation of the angle C(4)–Ti–C(6): Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(7) Noyori, R.; Ishigami, T.; Hayashi, N.; Takaya, H. *J. Am. Chem. Soc.* **1973**, *95*, 1674.

(8) All hydrocarbon products reported here were identified by comparison of their ^{1}H NMR, ^{13}C NMR, mass spectra, and gas chromatographic retention times with those of authentic samples.

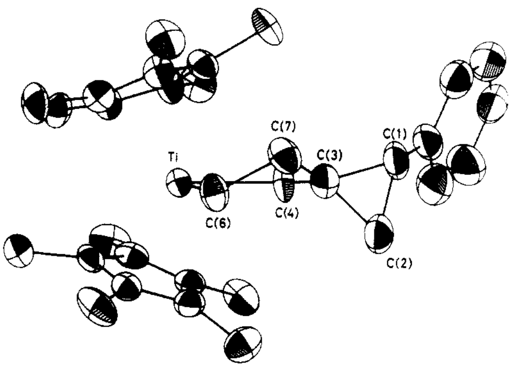
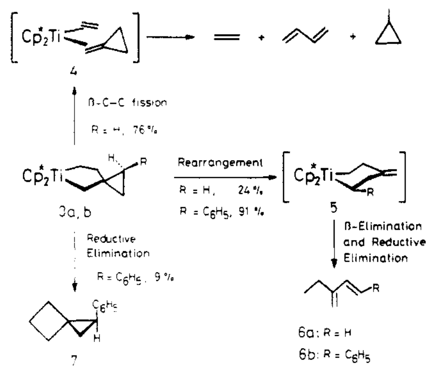


Figure 1. The molecular structure of **3b**. The hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles (deg) are as follows: C(3)–C(4) = 1.513 (5), C(3)–C(7) = 1.529 (5), Ti–C(4) = 2.214 (3), Ti–C(6) = 2.189 (3), C(6)–C(7) = 1.527 (4), Ti–Cp* (1) (centroid) = 2.146, Ti–Cp* (2) (centroid) = 2.150; C(3)–C(4)–Ti = 109.8 (2), C(3)–C(7)–C(6) = 109.0 (3), C(4)–C(3)–C(7) = 114.0 (3), C(4)–Ti–C(6) = 80.6 (1), Ti–C(6)–C(7) = 107.2 (2), Cp* (1) (centroid)–Ti–Cp* (2) (centroid) = 137.6.

treatment of **3a** with silica gel afforded 1-ethyl-1-methylcyclopropane in 96% yield. Complex **3a** also was hydrolyzed with water, though the reaction was very slow.

When a solid sample of **3a** was heated rapidly to 200 °C under reduced pressure, the complex underwent predominantly β-carbon–carbon bond cleavage to give ethylene (43%), 1,3-butadiene (31%), and methylcyclopropane (19%) (Scheme I).[9] The latter two products could be derived from regenerated methylenecyclopropane by either a metal-catalyzed rearrangement[10] or a reduction with a metal hydride species. The 1,3-diene **6a** also was formed in 16% yield, while no products arising from a direct β-hydrogen elimination reaction in **3a** were detected. In contrast, thermal decomposition of **3b** gave mainly **6b** (70%) accompanied by the reductive elimination product **7** (6%).[11] To our knowledge, this is the first example of the direct reductive elimination of cycloalkanes from metallacycles of group 4 transition metals.[12] The diene **6** can be considered to be derived from the intermediate six-membered metallacycle **5** by β-hydrogen elimination followed by reductive elimination. We think that the formation of **5** can be reasonably accounted for by a skeletal rearrangement from the cyclopropylcarbinyl to the allylcarbinyl structure.[13] Although the selective formation of the rearranged products implies that the reaction proceeds within the coordination sphere around titanium, it is still not clear whether the rearrangement proceeds in a concerted manner or through a dissociative mechanism involving homolysis or heterolysis of the alkyl–Ti bond.[17-19] The mechanism that involves a direct γ-elimination of one of the two C(2) methylene hydrogens leading to **6**, however, cannot be ruled out, though such an elimination process is unlikely in view of the long distances between Ti and these hydrogens (4.39 and 4.74 Å). The observed remarkable differences in reaction modes between **3a** and **3b** could be attributed partly to the presence of a reactive benzylic carbon–carbon bond in the latter complex. Subtle differences in the structure of the five-membered ring of **3b** from that of **3a** may be another factor which makes the β-carbon–carbon bond fission unfavorable,[20] and hence the hitherto unprecedented reductive elimination takes place.

Scheme I



Further investigations of the mechanism of formation of **6** are underway with use of deuterium-labeled substrates. Reactions of **3** with carbon monoxide and other unsaturated compounds are also the subject of our current studies.

Acknowledgment. We thank the Ministry of Education, Science and Culture, Japan, for financial support of this work (No. 59740256).

Registry No. **2a**, 6142-73-0; **2b**, 29817-09-2; **3a**, 96760-77-9; **3b**, 96791-11-6; **6a**, 3404-63-5; **6b**, 96760-78-0; **7**, 93714-50-2; $Cp_2{}^*Ti(CH_2{=}CH_2)$, 83314-27-6; *trans*-1-ethyl-1-methyl-2-phenylcyclopropane, 23194-72-1; 1-ethyl-1-methylcyclopropane, 53778-43-1; benzylidenecyclobutene, 5244-75-7.

Supplementary Material Available: Tables of atomic positions, thermal parameters, selected bond lengths and angles, and structure factors for **3b** and spectral data for **7**, ^1H NMR spectrum of **3a**, and ^{13}C NMR spectra of **3a** and **3b** (36 pages). Ordering information is given on any current masthead page.

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(9) Yields were determined either by gas chromatography or by ^1H NMR. Differences in detector responses between the products and standards in gas chromatography were corrected. In Scheme I, only product ratios were shown.

(10) (a) Takaya, H.; Hayashi, N.; Ishigami, T.; Noyori, R. *Chem. Lett.* **1973**, 813. (b) Binger, P.; Brinkmann, A.; Wedemann, P. *Chem. Ber.* **1983**, *116*, 2920.

(11) Compound 7 was prepared by the Simmons–Smith methylenation of benzylidenecyclobutane and was purified by preparative gas chromatography; ^1H NMR ($CDCl_3$) δ 0.85 (dd, H_{2trans}, $J_{1,2trans}$ = 8.85 Hz, $J_{2cis,2trans}$ = 5.49 Hz), 1.06 (dd, H_{2cis}, $J_{1,2cis}$ = 5.80 Hz), 1.83 (dd, H_1), 1.89–2.27 (m, cyclobutane ring protons), 6.95–7.27 (m, C_6H_5). ^{13}C NMR and IR spectra also were consistent with the assigned structure. Mass spectrum, *m/z* 158 (M^+), 143 ($M^+ - CH_3$), 130 ($M^+ - C_2H_4$, base peak), 115 ($M^+ - C_3H_7$), 104 ($M^+ - C_4H_6$); calcd for $C_{12}H_{14}$ 158.1095, found 158.1099.

(12) For compound 1, insertion of carbon monoxide followed by reductive elimination reaction to give cyclopentanone has been reported.[2a]

(13) Transition-metal catalyzed reactions of methylenecyclopropanes in the presence of olefinic substrates give a variety of homo- and cross-coupling products,[7,14,15] for which mechanisms involving similar type of rearrangements have been proposed.[10b,16]

(14) (a) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780. (b) Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *Ibid.* **1972**, *94*, 4018. (c) Noyori, R.; Yamakawa, M.; Takaya, H. *Tetrahedron Lett.* **1978**, 4823.

(15) (a) Binger, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 309. (b) Binger, P. *Synthesis* **1973**, 427.

(16) (a) Binger, P.; Doyle, M. J.; Benn, R. *Chem. Ber.* **1983**, *116*, 1. (b) Binger, P.; Martin, T. R.; Benn, R.; Rufinska, A.; Schroth, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39b*, 993.

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