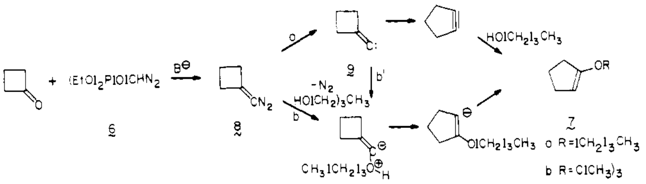


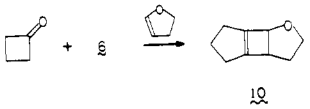
Figure 1. Possible mechanisms for formation of **7a**.

cloalkyne. The present communication addresses this question in the case of expansion of the four-membered to the five-membered ring.

Base-promoted reaction at 0 °C between cyclobutanone and diethyl (diazomethyl)phosphonate (**6**)[5] in 1-butanol afforded 1-(butyloxy)cyclopentene (**7a**) in 43% isolated yield (Figure 1).[6] The formation of **7a** finds close analogy in the production of enol ether **7b**, in 2–4% yield, from α-elimination of bromomethylenecyclobutane (**1**, n = 2, E = H, Hal = Br), with potassium *tert*-butoxide.[1a,4] For the present case, work by ourselves[7] and others[8] suggests scenarios like those outlined in Figure 1. The diazoethene **8**, a chemical relative of **2** (n = 3), is generated by reaction between cyclobutanone and **6** and is subsequently converted to **7a** by pathways that involve either (a) chemical equivalency of the vinylic carbon atoms in the form of cyclopentyne or (b) nonequivalency of these atoms at the time of interaction with 1-butanol.[9]

Repetition of the reaction between cyclobutanone and **6**, the latter now containing approximately 5% excess ^{13}C at the diazomethyl carbon atom,[10] produced **7a**, in which the label was equally distributed between atoms C-1 and C-2.[12] This is precisely as expected from a mechanism in which the vinylic carbon atoms of **7a** have become chemically equivalent before trapping by alcohol. The result can be accommodated by path b or b′ (Figure 1) with the proviso that nucleophilic attack occur with *equal* facility at both vinylic carbon atoms of **8** or **9**, but this impresses us as chemically untenable. The data are most economically rationalized by intervention of cyclopentyne as the exclusive precursor to **7a**.[14]

The question of whether cyclopentyne is formed under reaction conditions that yield cycloadducts has also been addressed. Execution of the base-promoted reaction between cyclobutanone and **6** in the presence of dihydrofuran gave the tricyclic adduct **10**[1c] in 28% yield (eq 2). Statistical analysis of the integrated ^{13}C NMR spectrum of **10** derived from ^{13}C-enriched **6** showed that the excess label again was equally distributed between the vinylic carbon atoms.[12] This result also clearly implicates cyclopentyne



(2)

as the reactive intermediate responsible for formation of the cycloadduct **10**. Consequently it is concluded that the products resulting from ring expansion of cyclobutylidenecarbene (**9**, Figure 1) in both protic and aprotic media arise from the cycloalkyne.

Acknowledgments. This research received support from the Robert A. Welch Foundation and the National Institute of General Medical Sciences. We thank Dr. Upali Weerasooriya for executing preliminary experiments and Dr. Ben Shoulders for assistance in the analysis of the ^{13}C spectral data.

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[5] Seyferth, D.; Marmar, R. M.; Hilbert, P. H. *J. Org. Chem.* **1971**, *36*, 1379.

[6] **7a**: ^1H NMR (CCl_4) δ 0.93 (3 H, t, J = 6 Hz), 1.23–2.10 (6 H, m), 2.27 (4 H, m), 3.63 (2 H, t, J = 6 Hz), 4.28 (1 H, m); ^{13}C NMR (neat) δ 18.34, 20.23, 28.03, 30.44, 30.83, 67.57, 91.44, 159.33; IR (CCl_4) 1650 cm^{-1} (C=C); molecular ion, m/e 140.1203 (calcd for $C_9H_{16}O$, 140.1201. Treatment of **7a** with 2,4-dinitrophenylhydrazine reagent afforded a 2,4-DNP derivative identical (mixture mp) with that from cyclopentanone.

[7] Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837 and references cited therein.

[8] Lahti, P.; Berson, J. *J. Am. Chem. Soc.* **1981**, *103*, 7011.

[9] Paths b and b′ are only two of several that predict nonequivalency of the key carbon atoms.

[10] Labeled (diazomethyl)phosphonate **6** was prepared[5] by using formaldehyde having ca. 5% isotopic enrichment. Mass spectral analysis of the CO_2 derived from combustion of enriched **6** indicated 4.3% excess ^{13}C in the sample.[11]

[11] We thank Professor P. L. Parker and Dr. Lee Entzeroth (UT Marine Sciences Institute) for this analysis.

[12] Error in the integrated ^{13}C spectrum is estimated at ±6%. The spectral data were obtained with a Bruker WH-90 spectrometer on a 40:60 (v:v) solution of benzene-d_6 and **7a** or **10** (microcell). The solutions were 0.1 M in $Cr(acac)_2$ to enhance relaxation.[13]

[13] Shoolery, J. N. *Prog. NMR Spectrosc.* **1977**, *11*, 79.

[14] A referee has suggested that **7a** may arise from attack on **9** following prior equilibration with cyclopentyne. Although consistent with our labeling data, calculations (MINDO/3 and MNDO) render such a mechanism questionable as the ring expansion is predicted to be *exothermic* by 4.7 (MINDO/3) and 1.6 (MNDO) kcal/mol (J. C. Gilbert, unpublished results). In any event, the equilibration still posits the cycloalkyne to achieve chemical equivalency of the vinylic carbon atoms.

Metal-Metal-Bonded Zirconium-Ruthenium and Zirconium-Iron Complexes

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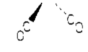
Current interest in heterobimetallic complexes incorporating both early and late transition metals stems from their potential importance in catalysis[1] and organic synthesis.[2] Among group 4 heterobimetallic complexes reported to date are complexes containing two different metal fragments linked by a bridging ligand,[3] complexes in which the group 4 metal bonds to a carbonyl oxygen of a second organometallic fragment[4–6] such as **1**-Ti[4a] and



1-Ti

1-Zr

2

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[2] For applications of pairs of early and late metal mononuclear complexes in organic synthesis see: (a) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333. (b) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *Ibid.* **1978**, *100*, 2254. (c) Negishi, E.; Van Horn, D. J. *Ibid.* **1977**, *99*, 3168.

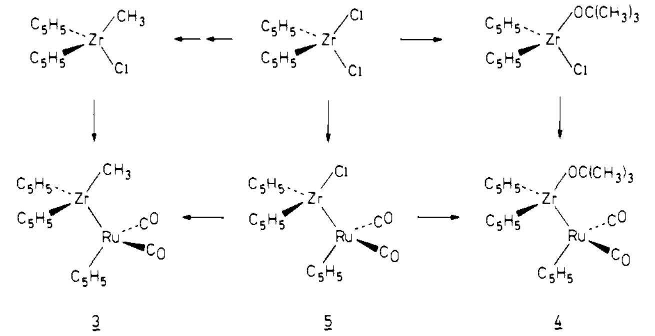
[3] (a) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Schore, N. E. *Ibid.* **1979**, *101*, 7410. (c) Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1981**, *103*, 2650. (d) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *Ibid.* **1979**, *101*, 218. (e) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Ibid.* **1981**, *103*, 5596. (f) Marsella, J. A.; Caulton, K. G. *Ibid.* **1980**, *102*, 1747.

[4] (a) $(C_5Me_5)_2Ti(CH_3)OCMo(CO)_2Cp$: Hamilton, D. M., Jr.; Willis, W. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 4255. (b) $Cp_2Zr(R)$-$OCMo(CO)_2Cp$: Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *Ibid.* **1982**, *104*, 6360. (c) $Cp_2Ti(Cl)OCCo_3(CO)_9$: Schmid, G.; Batzel, V.; Stutte, B. *J. Organomet. Chem.* **1976**, *113*, 67. (d) Cp_2Ti-$[OCCo_3(CO)_9]_2$: Stutte, B.; Batzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603. (e) For a related vanadium complex see: Haustein, H. J.; Schwarzhans, K. E. *Z. Naturforsch. B* **1978**, *33B*, 1108.

[5] $CpTi[OCCo_3(CO)_9]_2Co(CO)_4$: Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *111*, 1239.

[6] A complex in which Zr bonds to the oxygens of two carbonyl ligands that have coupled to form a C–C bond has been reported: Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712.

Scheme I



1-Zr,[4b] complexes containing metal–metal bonds bridged by CO[7] or other ligands,[8,9] and a single well-characterized case containing an unbridged metal–metal bond, **2**.[5,10] In an effort to develop a general synthesis for metal–metal-bonded heterobimetallic compounds and to elucidate the factors that determine whether linkage occurs via metal–metal or metal–carbonyl oxygen bonds, we have begun studies of the reactions of metal carbonyl anions with zirconium halides.[5,11] Here we report the synthesis of a series of metal–metal-bonded zirconium–ruthenium and zirconium–iron complexes.

The reaction of $Cp_2Zr(CH_3)Cl$[12] (Cp = η^5-C_5H_5) with 1 equiv of $K[CpRu(CO)_2]$[13] for 1 h at 25 °C in THF gave $Cp_2Zr(CH_3)Ru(CO)_2Cp$ (**3**, 83%), which was isolated as a bright yellow crystalline solid by evaporation of solvent and recrystallization from toluene.[14] The metal–metal-bonded structure of **3** was established by IR and ^{13}C NMR spectroscopy. The CO bands of **3** at 1950 (s) and 1880 (s) cm^{-1} are similar to those of $[NEt_4][Cp(CO)_2FeAlPh_3]$, which has been shown by X-ray crystallography to contain an Fe–Al bond.[15] The bands of **3** are shifted 45 and 120 cm^{-1} to higher energy from the corresponding bands of $K[CpRu(CO)_2]$ as expected for a Zr–Ru-bonded structure;[15] in contrast, bonding of Zr to a carbonyl oxygen would have resulted in a shift of one of the ν_{CO} bands to much lower energy.[4a,b,7b,16] Only one carbonyl signal, at δ 207, is seen in the −80 °C ^{13}C NMR spectrum of **3**. In contrast, two carbonyl peaks were observed in the −90 °C ^{13}C NMR spectrum of **1**-Zr in which Zr is bonded to a carbonyl oxygen of the $CpMo(CO)_3$ fragment.[4b,7b]

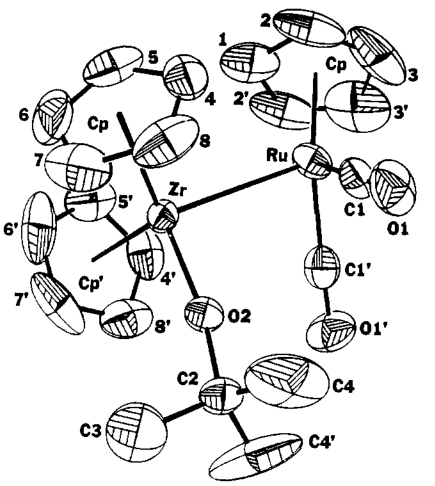


Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Zr[OC(CH_3)_3]Ru(CO)_2(\eta^5\text{-}C_5H_5)$ (**4**). Atoms labeled with and without a prime are related by the crystallographic mirror plane. Bond lengths (Å) and angles (deg) of interest are as follows: Ru-Zr, 2.910 (1); Ru–C(1), 1.839 (6); Ru–CNT, 1.943 (3); Zr–O(2), 1.910 (4); Zr–CNT, 2.274 (4); C(1)–O(1), 1.153 (7); CNT–Ru–Zr, 123.5 (2); CNT–Ru–C(1), 131.7 (4); C(1)–Ru–C(1)′, 88.7 (4); Zr–Ru–C(1), 81.4 (2); CNT–Zr–CNT′, 125.8 (4); CNT–Zr–O(2), 107.8 (3); Ru–Zr–O(2), 98.6 (2); Zr–O(2)–C(2), 169.6 (4); Ru–C(1)–O(1), 176.2 (5). CNT indicates the centroid of a Cp ring.

Compound **3** (Scheme I), while thermally stable, is rapidly hydrolyzed to $(Cp_2ZrCH_3)_2O$[3e] and $CpRu(CO)_2H$[17] upon exposure to air. The more hydrolytically stable $Cp_2Zr[OC(CH_3)_3]Ru(CO)_2Cp$ (**4**) was prepared by the reaction of $K[CpRu(CO)_2]$ with $Cp_2Zr[OC(CH_3)_3]Cl$[18] in THF and isolated as yellow crystals after recrystallization from toluene (75%).[19] Spectroscopic data for **4** also require a Zr–Ru-bonded structure.

Compounds **3** and **4** were also prepared by halide-substitution reactions involving the intact bimetallic framework of $Cp_2Zr(Cl)Ru(CO)_2Cp$ (**5**),[20] which was prepared by reaction of Cp_2ZrCl_2 with 1 equiv of $K[CpRu(CO)_2]$. Addition of 1 equiv of CH_3Li to a yellow THF slurry of **5** gave **3** (50%), and addition of 1 equiv of $K[OC(CH_3)_3]$ to **5** gave **4** (35%).[21]

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(9) For some related niobium compounds see: (a) Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979**, *18*, 1709. (b) Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Ibid.* **1979**, *18*, 136. (c) Pasynskii, A. A.; Skripkin, Yu. V.; Eremenko, I. L.; Kalinnikov, V. T.; Aleksandrov, G. G.; Andrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 49. (d) Hermann, W. A.; Biersack, H.; Zieglar, M.; Wülknitz, P. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 388.

(10) Several less well-characterized cases have also been reported: (a) Miyake, A.; Kondo, H.; Aoyama, M. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 520. (b) Cardin, D. J.; Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. A* **1970**, 2594. (c) Lappert, M. F.; Sanger, A. R.; *Ibid.* **1971**, 1314. (d) Abys, J.; Risen, W. M. *J. Organomet. Chem.* **1981**, *204*, C5. (e) See also: Martin, J.; Moise, C. *Ibid.* **1982**, *232*, C55.

(11) For recent examples of reactions of organometallic anions with halide complexes of later transition metals see: (a) Roberts, D. A.; Mercer, W. A.; Zahurak, S. M.; Geoffroy, G. L.; Debrosse, C. W.; Cass, M. E.; Pierpont, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 910. (b) Bars, V. O.; Braunstein, P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 308. (c) Mink, R. I.; Welter, J. J.; Young, P. R.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6928. (d) Fontana, S.; Orama, O.; Fischer, E. O.; Schubert, U.; Kriessl, F. R. *J. Organomet. Chem.* **1978**, *149*, C57. (e) Pandey, V. N. *Inorg. Chim. Acta* **1977**, *23*, L26. (f) Morse, D. L.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *125*, 71.

(12) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *33*, 181.

(13) Prepared by reduction of $[CpRu(CO)_2]_2$ with 2 equiv of K/benzophenone in THF; ^1H NMR (THF-d_8) δ 4.77 (s); IR (Nujol) 1905 s, 1760 s, 1685 sh, 1580 w cm^{-1}.

(14) **3**: ^1H NMR (benzene-d_6) δ 5.86 (s, 10 H, Cp_2Zr), 4.28 (s, 5 H, CpRu), −0.07 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 207.1 (CO), 111.8 (Cp_2Zr), 86.1 (CpRu), 39.7 (CH_3, J_{CH} = 118 Hz from gated decoupled spectrum); IR (Nujol) 1950 s, 1880 s cm^{-1}; exact mass 457.9388, calcd for $C_{18}H_{18}O_2RuZu$ 457.9382. Anal. Calcd: C, 47.14; H, 3.95. Found: C, 47.17; H, 4.12.

(15) Burlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hughes, R. E. *Inorg. Chem.* **1979**, *18*, 1097.

(16) (a) Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985. (b) Tilley, T. D.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 1772.

(17) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.

(18) Prepared by the reaction of Cp_2ZrCl_2 with 1 equiv $K[OC(CH_3)_3]$ in THF; ^1H NMR (benzene-d_6) δ 5.96 (s, 10 H), 1.06 (s, 9 H); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 113.3 (Cp), 79.4 (4 °C), 31.2 (CH_3); exact mass 328.0167, calcd for $C_{14}H_{19}ClOZr$ 328.0167.

(19) **4**: ^1H NMR (benzene-d_6) δ 5.92 (s, 10 H), 4.61 (s, 5 H), 1.16 (s, 9 H); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 207.9 (CO), 111.5 (CpZr), 86.8 (CpRu), 80.6 (4 °C), 32.1 (CH_3); IR (KBr) 1958 s, 1884 s cm^{-1}; exact mass 515.9805, calcd for $C_{21}H_{24}O_3RuZr$ 515.9805. Anal. Calcd: C, 48.81; H, 4.68. Found: C, 48.52; H, 4.62.

(20) **5**: ^1H NMR (benzene-d_6) δ 5.99 (s, 10 H), 4.37 (s, 5 H); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 206.1 (CO), 113.9 (Cp_2Zr), 87.0 (CpRu); IR (Nujol) 1953 s, 1892 sh, 1886 s, 1862 w cm^{-1}; exact mass 477.8839, calcd for $C_{17}H_{15}O_2ClRuZr$ 477.8839.

(21) For other recent examples of halide substitution reactions in bi- and polynuclear systems see: (a) Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046. (b) Masters, A. F.; Mertis, K.; Gibson, J. F.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 389. (c) Cotton, F. A.; Gage, L. D.; Mertis, K.; Shive, L. W.; Wilkinson, G. *J. Am. Chem. Soc.* **1976**, *98*, 6922.

We have also prepared the zirconium–iron compounds $Cp_2Zr(CH_3)Fe(CO)_2Cp$ (**6**)[22] and $Cp_2Zr[OC(CH_3)_3]Fe(CO)_2Cp$ (**7**)[23] in high yield by the reaction of $K[CpFe(CO)_2]$ with the appropriate zirconium halide. The spectroscopic data for these compounds are also most consistent with Zr–Fe-bonded structures.

An X-ray diffraction study was performed on the Zr–Ru *tert*-butoxy derivative **4**[24] to confirm the presence of metal–metal bonding in these heterobimetallic compounds. The molecular geometry is shown in Figure 1. The most interesting structural feature is the direct Zr–Ru bond (2.910 Å), which is the first example of an unbridged bond between zirconium and a later transition metal. The $OC(CH_3)_3$ and $Ru(CO)_2Cp$ groups reside in a crystallographically imposed symmetry plane, and there is no significant interaction between Zr and the CO ligands (Zr–O distance = 3.91 Å, Zr–C distance = 3.20 Å). As the spectroscopic data for **3** and **5**–**7** are nearly identical with those for **4**, these compounds undoubtedly have similar metal–metal-bonded structures.

In considering the factors that determine whether a Lewis acidic early-metal fragment will bond to the metal as in **3** or to a carbonyl oxygen of a metal carbonyl anion as in **1**-Ti and **1**-Zr, it should be recalled that thermodynamic protonation of mononuclear metal carbonyl anions invariably occurs at the metal center. Similarly Lewis acids such as $AlPh_3$ typically bond to the metal of metal carbonyl anions (e.g., $[NEt_4][Ph_3AlFe(CO)_2Cp]$[15] and $[PPN][Ph_3AlCo(CO)_4]$[15]) except in cases where such metal–metal-bonded structures would be extremely crowded (e.g., $[N(n\text{-}Bu)_4][Ph_3AlOCW(CO)_2Cp]$[15]). Even in some cases involving moderately crowded metal carbonyl anions and Lewis acids, metal–metal bond formation is observed (e.g., $[N(n\text{-}Bu)_4][Ph_3InW(CO)_3Cp]$[15] and $[N(n\text{-}Pr)_4][Ph_3InMn(CO)_5]$[15]). The striking structural difference between metal–metal-bonded **3** and metal–carbonyl oxygen bonded **1**-Ti and **1**-Zr may be rationalized in terms of this preference for metal carbonyl anions to form metal–metal bonds with Lewis acids in the absence of overriding steric factors. The low steric requirements of $CpRu(CO)_2^-$ allow bonding of the Lewis acid $Cp_2ZrCH_3^+$ at Ru, whereas with the more crowded $CpMo(CO)_3^-$ zirconium–oxygen or titanium–oxygen bonding is favored.

Electronic factors undoubtedly also play a role in determining the site of Lewis acid attachment to metal carbonyl anions. For example, the d^8 $CpM(CO)_2^-$ (M = Fe, Ru) anions have a high-energy filled d orbital ideally suited for metal–metal bond formation, whereas the $CpM(CO)_3^-$ (M = Mo, W) anions do not. Another factor, cited by others,[4b,15] is that the average CO stretching frequencies of the $CpM(CO)_3^-$ anions are lower than those of the $CpM(CO)_2^-$ anions, suggesting that the carbonyl oxygens in the former anions may be more basic than those in the latter. However, as changes in the electronic character of the metal carbonyl anion will simultaneously affect the basicity of both the metal and the carbonyl oxygen, the role of electronic factors is likely to be a complex one.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Science, and from the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Details of the X-ray structure solution and listings of fractional coordinates and thermal parameters, bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

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[22] **6**: ^1H NMR (benzene-d_6) δ 5.82 (s, 10 H), 3.75 (s, 5 H), −0.01 (s, 3 H) $^{13}C\{^1H\}$ NMR (THF-d_8) δ 218.2 (CO), 111.8 (Cp_2Zr), 82.4 (CpFe), 38.1 (CH_3) IR (Nujol) 1937 s, 1872 s cm^{-1}; exact mass 411.9697; calcd for $C_{18}H_{18}O_2FeZr$ 411.9694.

[23] **7**: ^1H NMR (benzene-d_6) δ 5.91 (s, 10 H), 4.10 (s, 5 H), 1.14 (s, 9 H); $^{13}C\{^1H\}$ NMR δ 219.7 (CO), 110.5 (Cp_2Zr), 82.4 (CpFe), 80.7 (4 °C), 31.6 (CH_3); IR (KBr) 1939 s, 1874 s cm^{-1}; exact mass 470.0115, calcd for $C_{21}H_{24}O_3FeZr$ 470.0111. Anal. Calcd: C, 53.49; H, 5.13. Found: C, 53.19; H, 5.09.

[24] Crystallographic data: a = 14.953 (3) Å, b = 10.744 (2) Å, c = 12.922 (3) Å, V = 2075.8 (8) $Å^3$, Z = 4 in space group *Pnam*; R_F = 0.0378, R_{wF} = 0.0366 for 1323 unique reflections ($I \geq 3\sigma(I)$) with anisotropic thermal parameters for all non-hydrogen atoms.

Synthesis and Thermal Isomerization of *trans*-Bicyclo[4.1.0]hept-3-ene

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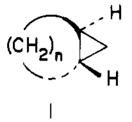
Several years ago, one of us suggested that the trans fusion of a sufficiently small ring to a cyclopropane should result in the formation of a novel "twist" bent σ bond that would impart unusual physical and chemical properties to the molecule in which it was contained.[1] Of the many studies that have been carried out on *trans*-bicyclo[*n*.1.0]alkanes (**1**),[2–4] none indicate the presence of significant strain in the *trans*-bicyclo[6.1.0]nonanes (*n* = 6),[2,3a–e] while limited evidence[3c,f,h] established the presence of slightly enhanced reactivity for the *trans*-bicyclo[5.1.0]octanes (*n* = 5).[3] In contrast, the one known example of a *trans*-bicyclo[4.1.0]heptane (*n* = 4)[4] has been reported to show only limited stability.[5] We now report the synthesis and thermal rearrangement of *trans*-bicyclo[4.1.0]hept-3-ene (**2**, Scheme I).[6]



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Esterification of commercially available *trans*-β-hydromuconic acid (**3a**) with refluxing methanol containing a catalytic amount of sulfuric acid gave the dimethyl ester, **3b**, in 85% yield. Simmons–Smith cyclopropanation[7] of **3b** gave 54% of **4**, which upon reduction with lithium aluminum hydride in ether gave a 97% yield of **5**. Treatment of **5** with *p*-toluenesulfonyl chloride in pyridine gave **6** in 97% yield. Refluxing of **6** in acetone containing lithium bromide yielded 97% of **7**. With utilization of high dilution techniques, **7** was refluxed with sodium sulfide in 95% ethanol to produce 39% of the bicyclic sulfide **8**. α-Chlorination of **8** was achieved in quantitative yield with *N*-chlorosuccinimide in refluxing carbon tetrachloride. In spite of its ease of formation, **9** proved to be quite labile, and as a result it was immediately oxidized with *m*-chloroperbenzoic acid in methylene chloride at 0–25 °C to give the α-chloro sulfone **10**, in 72% yield. Treatment of **10** with potassium *tert*-butoxide in ether at 0 °C in a classical Ramberg–Bäcklund reaction[8] gave 18% of distilled *trans*-bicy-

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[5] A second derivative of *trans*-bicyclo[4.1.0]heptane has been reported as a nonisolable intermediate. See: Casadevall, E.; Pouet, Y. *Tetrahedron* **1978**, *34*, 1921. For an example of an unsuccessful attempt to prepare a *trans*-bicyclo[4.1.0]hept-3-ene derivative by an acyloin condensation see: Delbaere, C. U. L.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 879. See also: Blancou, H.; Casadevall, E. *Tetrahedron* **1976**, *32*, 2907. For an additional unsuccessful approach see ref 3g.

[6] Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds except **9** (which was extremely labile).

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