

We have also prepared the zirconium-iron compounds  $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Fe}(\text{CO})_2\text{Cp}$  (**6**)<sup>22</sup> and  $\text{Cp}_2\text{Zr}[\text{OC}(\text{CH}_3)_3]\text{Fe}(\text{CO})_2\text{Cp}$  (**7**)<sup>23</sup> in high yield by the reaction of  $\text{K}[\text{CpFe}(\text{CO})_2]$  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**<sup>24</sup> 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  $\text{OC}(\text{CH}_3)_3$  and  $\text{Ru}(\text{CO})_2\text{Cp}$  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  $\text{AlPh}_3$  typically bond to the metal of metal carbonyl anions (e.g.,  $[\text{Net}_4][\text{Ph}_3\text{AlFe}(\text{CO})_2\text{Cp}]^{15}$  and  $[\text{PPN}][\text{Ph}_3\text{AlCo}(\text{CO})_4]^{15}$ ) except in cases where such metal-metal-bonded structures would be extremely crowded (e.g.,  $[\text{N}(n\text{-Bu})_4][\text{Ph}_3\text{AlOCW}(\text{CO})_2\text{Cp}]^{15}$ ). Even in some cases involving moderately crowded metal carbonyl anions and Lewis acids, metal-metal bond formation is observed (e.g.,  $[\text{N}(n\text{-Bu})_4][\text{Ph}_3\text{InW}(\text{CO})_3\text{Cp}]^{15}$  and  $[\text{N}(n\text{-Pr})_4][\text{Ph}_3\text{InMn}(\text{CO})_5]^{15}$ ). 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  $\text{CpRu}(\text{CO})_2^-$  allow bonding of the Lewis acid  $\text{Cp}_2\text{ZrCH}_3^+$  at Ru, whereas with the more crowded  $\text{CpMo}(\text{CO})_3^-$  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  $d^8$   $\text{CpM}(\text{CO})_2^-$  ( $M = \text{Fe}, \text{Ru}$ ) anions have a high-energy filled  $d$  orbital ideally suited for metal-metal bond formation, whereas the  $\text{CpM}(\text{CO})_3^-$  ( $M = \text{Mo}, \text{W}$ ) anions do not. Another factor, cited by others,<sup>4b,15</sup> is that the average CO stretching frequencies of the  $\text{CpM}(\text{CO})_3^-$  anions are lower than those of the  $\text{CpM}(\text{CO})_2^-$  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.

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**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.

(22) **6**:  $^1\text{H}$  NMR (benzene- $d_6$ )  $\delta$  5.82 (s, 10 H), 3.75 (s, 5 H), -0.01 (s, 3 H)  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ )  $\delta$  218.2 (CO), 111.8 ( $\text{Cp}_2\text{Zr}$ ), 82.4 ( $\text{CpFe}$ ), 38.1 ( $\text{CH}_3$ ) IR (Nujol) 1937 s, 1872 s  $\text{cm}^{-1}$ ; exact mass 411.9697; calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{FeZr}$  411.9694.

(23) **7**:  $^1\text{H}$  NMR (benzene- $d_6$ )  $\delta$  5.91 (s, 10 H), 4.10 (s, 5 H), 1.14 (s, 9 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  219.7 (CO), 110.5 ( $\text{Cp}_2\text{Zr}$ ), 82.4 ( $\text{CpFe}$ ), 80.7 (4 °C), 31.6 ( $\text{CH}_3$ ); IR (KBr) 1939 s, 1874 s  $\text{cm}^{-1}$ ; exact mass 470.0115, calcd for  $\text{C}_{21}\text{H}_{24}\text{O}_3\text{FeZr}$  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<sup>3</sup>,  $Z = 4$  in space group  $Pnam$ ;  $R_F = 0.0378$ ,  $R_w = 0.0366$  for 1323 unique reflections ( $I \geq 3\sigma(I)$ ) with anisotropic thermal parameters for all non-hydrogen atoms.

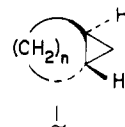
## Synthesis and Thermal Isomerization of *trans*-Bicyclo[4.1.0]hept-3-ene

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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  $\sigma$  bond that would impart unusual physical and chemical properties to the molecule in which it was contained.<sup>1</sup> Of the many studies that have been carried out on *trans*-bicyclo[ $n.1.0$ ]alkanes (**1**),<sup>2-4</sup> none indicate the presence of



significant strain in the *trans*-bicyclo[6.1.0]nonanes ( $n = 6$ ),<sup>2,3a-e</sup> while limited evidence<sup>3c,f,h</sup> established the presence of slightly enhanced reactivity for the *trans*-bicyclo[5.1.0]octanes ( $n = 5$ ).<sup>3</sup> In contrast, the one known example of a *trans*-bicyclo[4.1.0]heptane ( $n = 4$ )<sup>4</sup> has been reported to show only limited stability.<sup>5</sup> We now report the synthesis and thermal rearrangement of *trans*-bicyclo[4.1.0]hept-3-ene (**2**, Scheme 1).<sup>6</sup>

Esterification of commercially available *trans*- $\beta$ -hydromuconic acid (**3a**) with refluxing methanol containing a catalytic amount of sulfuric acid gave the dimethyl ester, **3b**, in 85% yield. Simmons-Smith cyclopropanation<sup>7</sup> 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**.  $\alpha$ -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  $\alpha$ -chloro sulfone **10**, in 72% yield. Treatment of **10** with potassium *tert*-butoxide in ether at 0 °C in a classical Ramberg-Bäcklund reaction<sup>8</sup> gave 18% of distilled *trans*-bicy-

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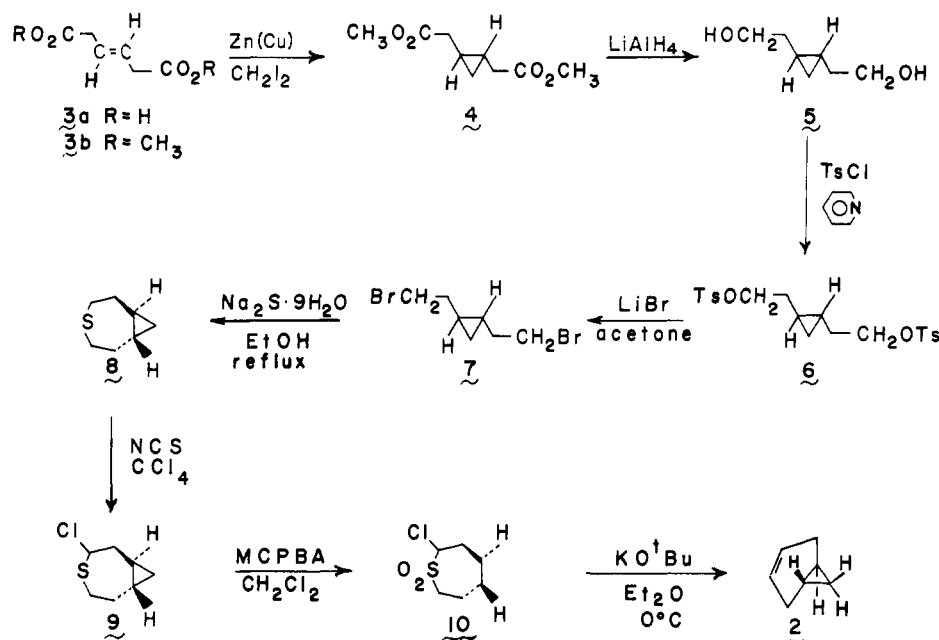
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(6) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds except **9** (which was extremely labile).

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Scheme I

**Table I.** Rates of Isomerization of *trans*-Bicyclo[4.1.0]hept-3-ene to *cis*-Bicyclo[4.1.0]hept-3-ene

| solvent             | temp, $\pm 2$ °C | rate, $s^{-1}$                   | $\Delta H^\ddagger$ kcal/mol | $\Delta S^\ddagger$ , eu |
|---------------------|------------------|----------------------------------|------------------------------|--------------------------|
| toluene- $d_8$      | 150              | $(1.28 \pm 0.01) \times 10^{-4}$ | $25.8 \pm 1.6$               | $-15.8 \pm 4.0$          |
|                     | 140              | $(6.98 \pm 0.15) \times 10^{-5}$ |                              |                          |
|                     | 130              | $(2.67 \pm 0.15) \times 10^{-5}$ |                              |                          |
|                     | 25 <sup>a</sup>  | $2.46 \times 10^{-10}$           |                              |                          |
| acetonitrile- $d_3$ | 130              | $(6.45 \pm 0.10) \times 10^{-6}$ |                              |                          |

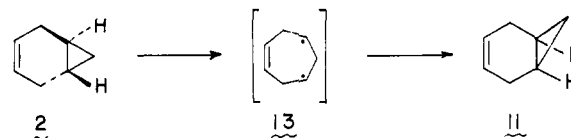
<sup>a</sup> Extrapolated from higher temperatures.clo[4.1.0]hept-3-ene (**2**), bp 45–50 °C (142 mmHg).

The structure of **2** was established on the basis of extensive spectral evidence and on its facile thermal conversion to the known<sup>9</sup> *cis*-bicyclo[4.1.0]hept-3-ene (**11**). The <sup>1</sup>H NMR spectrum of **2** was quite unusual. Absorptions occurred at  $\delta$  5.92 (2 H, olefinic protons), 2.85–1.85 (4 H, allylic protons), 1.27 (2 H, cyclopropyl methylene protons), and –0.50 (2 H, cyclopropyl methine protons). This can be compared with the spectrum of **11**, which had the corresponding protons absorbing at  $\delta$  5.42, 2.28, 0.59–0.24, and 0.98, respectively. Of particular interest is the reversal of positions of the cyclopropyl methylene and cyclopropyl methine hydrogens between **2** and **11**. In **11** the cyclopropyl methylene hydrogens are upfield from the cyclopropyl methine hydrogens as is common for anisotropically shifted hydrogens on 1,2-disubstituted cyclopropanes. The reversal of the chemical shift positions of the cyclopropyl hydrogens for **2**<sup>10</sup> is probably a result of the “twisted” nature of the cyclopropyl ring of **2** combined with an anisotropy effect of the twisted double bond. The <sup>13</sup>C NMR showed absorptions at  $\delta$  132.53 (d,  $J_{C-H}$  = 156.80 Hz), 32.95 (t,  $J_{C-H}$  = 129.35 Hz), 16.35 (d,  $J_{C-H}$  = 147.20 Hz), and 18.42 (t,  $J_{C-H}$  = 160.15 Hz). *trans*-Bicyclo[4.1.0]hept-3-ene showed an exact mass molecular weight of 94.0779 (calcd for C<sub>7</sub>H<sub>10</sub>, 94.0783) with a mass spectral cracking pattern identical with that of **11**. The Raman spectrum of **2** showed that C=C stretch at 1590 cm<sup>–1</sup> while the corresponding absorption for **11** occurred at 1665 cm<sup>–1</sup>.

Oxidation of **2** under single-sweep voltammetry conditions<sup>11</sup> showed an  $E_{1/2}$  vs. a saturated calomel electrode of 1.52 V. This can be compared to 1.98 V for **11**, 2.07 V for cyclohexene, and

2.17 V for *cis*-bicyclo[4.1.0]heptane (**12**). Because of the similarity of the  $E_{1/2}$  values for cyclohexene and **12**, it cannot be immediately determined whether the oxidation of **2** involves removal of an electron from the  $\pi$  bond of **2** or from the highly strained  $\sigma$  bond (C1–C6 bond) associated with the ring fusion. The ease of oxidation of **2** indicates that the energy level of its HOMO is very similar to that of the central bond of bicyclo[1.1.0]butanes.<sup>11</sup>

Attempted distillation of **2** at atmospheric pressure resulted in its partial isomerization to **11**. A detailed study of the thermal stability of **2** showed that it was quantitatively converted to **11** slowly at 120 °C and rapidly at 150 °C. Table I gives the rates of isomerization of **2** in toluene- $d_8$  and acetonitrile- $d_3$  as measured by <sup>1</sup>H NMR spectroscopy. The similarity of the rates of isomerization of **2** in toluene- $d_8$  and acetonitrile- $d_3$  suggested the absence of any type of highly polarized transition state and is consistent with the formation of the diradical **13** as an interme-



diolate. The  $E_a$  for the thermal isomerization of **2** was 26.4 kcal/mol. This can be compared to the values of 61.2 kcal/mol for the isomerization of *cis*-2,3-dimethylcyclopropane to *trans*-2,3-dimethylcyclopropane,<sup>12</sup> of 38.9 kcal/mol for the ring-flap inversion of 2-methylbicyclo[2.1.0]pentane,<sup>13</sup> and of 22 kcal/mol for the cleavage of [2.2.2]propellane to 1,4-dimethylenecyclohexane.<sup>14</sup> This extremely low  $E_a$  observed for the isomerization of **2** provides an adequate reflection of the unusually strained nature of this hydrocarbon.<sup>15</sup>

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We are continuing to investigate the chemistry of **2** and related trans-fused bicyclo[*n*.1.0]alkanes.

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**Registry No.** **2**, 84194-54-7; **3a**, 29311-53-3; **3b**, 25126-93-6; **4**, 53389-31-4; **5**, 84194-49-0; **6**, 2345-85-9; **7**, 84194-50-3; **8**, 84194-51-4; **9**, 84194-52-5; **10**, 84194-53-6.

(15) In studying this facile isomerization, we were very concerned about the possibility of either acid-catalyzed or transition-metal-promoted rearrangement of **2**. This was of special concern in view of the large observed negative entropy of activation ( $-15.8$  eu),<sup>16</sup> which would more commonly be associated with a bimolecular process than with a unimolecular process. Because of our long-term experience with both acid-catalyzed and transition-metal-promoted rearrangements of highly strained ring systems, precautions were taken to avoid such complications from the start. Since all rates were measured by  $^1\text{H}$  NMR, all tubes were carefully base treated prior to use. In addition, the NMR tubes used were new, and the rates were reproducible in different tubes. Any type of acid-catalyzed process could be rigorously excluded since treatment of **2** with *p*-toluenesulfonic acid in acetonitrile showed that **2** was only partially isomerized (40%) after 3 days at  $75^\circ\text{C}$ . Under these acidic conditions, **2** did not yield **11** but instead gave an olefin that was identified as 1,3-cycloheptadiene. Pirkle and Lunsford had observed  $\Delta S^\ddagger = -3.7$  eu for a related system<sup>3b</sup> while Berson and co-workers have observed  $\Delta S^\ddagger \approx -16$  eu for the unimolecular cleavage of the 1,4-carbon-carbon  $\sigma$  bond of 5-alkylidenebicyclo[2.1.0]pentanes followed by dimerization of the intermediate diradical.<sup>17</sup> It was suggested in the latter work that the relatively large observed  $\Delta S^\ddagger$  may signify a spin-forbidden transition state.

(16) The entropy of activation reported in Table I lists an error based on the reproducibility of the rates in several kinetic runs. If the uncertainty in  $\Delta S^\ddagger$  is calculated by using the temperature variation of the NMR spectrometer which was used in the kinetic measurements, an uncertainty in  $\Delta S^\ddagger$  of 15.6 eu is obtained. Thus, the reported  $\Delta S^\ddagger$  should not be overinterpreted. Berson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions"; *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, No. 21, p 8. We wish to thank Prof. J. Berson for bringing this reference to our attention.

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## Stereochemistry of Transmetalation in the Palladium-Catalyzed Coupling of Acid Chlorides and Organotins

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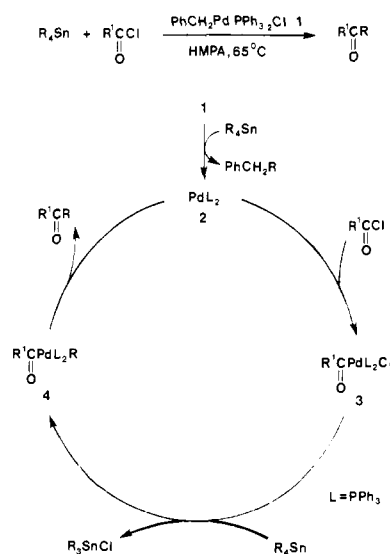
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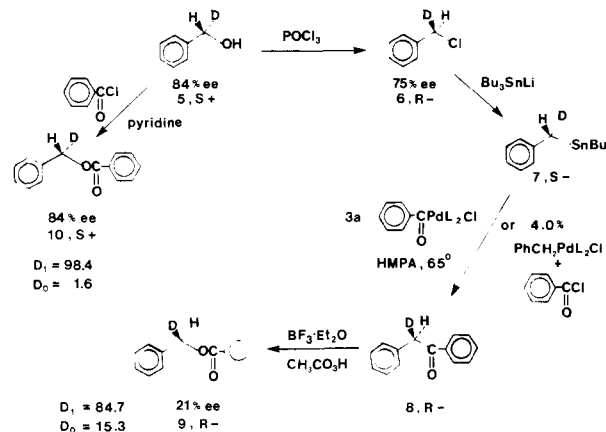
Although transmetalation reactions between organotin compounds and palladium halide complexes is an important step in the palladium-catalyzed cross-coupling of organic halides and organotin compounds,<sup>1,2</sup> there is essentially no mechanistic information available for this reaction. We report that this transmetalation occurs predominately with inversion of configuration at the saturated carbon being transferred.

The palladium-catalyzed coupling of acid chlorides and organotin gives ketones in high yield.<sup>2</sup> The proposed catalytic cycle<sup>2</sup> (Scheme I) involves a transmetalation reaction between an organotin and an acylbis(triphenylphosphine)palladium(II) chloride complex, **3**, to afford an acylalkylbis(triphenylphosphine)palladium(II) chloride complex, **4**, which releases the desired ketone by reductive elimination. The presence of **3** is directly observable by  $^{31}\text{P}$  NMR in the coupling of phenyltributyltin and benzoyl chloride catalyzed by 25% of **1**. After 1.5 h at  $65^\circ\text{C}$  in  $\text{CDCl}_3$  the peak corresponding to **1** at  $\delta$  28.7 disappeared, and a new peak

Scheme I



Scheme II



appearing at  $\delta$  19.8 was shown by comparison to an independently prepared sample<sup>3</sup> to be benzoylbis(triphenylphosphine)palladium(II)chloride, **3a**.

Since the reductive elimination of a saturated carbon is known to occur predominately with retention of configuration,<sup>4</sup> the only step of unknown stereochemical consequence in the catalytic cycle is the transmetalation reaction. Thus, by conducting a catalytic reaction with benzoyl chloride and (*S*)-(-)-( $\alpha$ -deuteriobenzyl)-tributyltin, **7**, in the presence of **1** and observing the absolute configuration of the  $\alpha$ -deuteriobenzyl phenyl ketone product, **8**, the stereochemistry of the transmetalation process could be unambiguously defined (Scheme II).

(*S*)-(+)-Benzyl- $\alpha$ -*d* alcohol (**5**,<sup>5</sup>  $[\alpha]_D^{20} +1.33^\circ$  (neat,  $l = 1$  dm), 84.2% ee) was treated with  $\text{POCl}_3$  in pyridine/ $\text{CH}_2\text{Cl}_2$  to give (*R*)-(-)-benzyl- $\alpha$ -*d* chloride (**6**,  $[\alpha]_D^{20} -1.15^\circ$  (neat,  $l = 0.1$  dm), 75.0% ee).<sup>6</sup> Tributyltin hydride was converted to lithium tributylstannate<sup>7</sup> and added to a THF solution of **6** at  $0^\circ\text{C}$  to yield (*S*)-(-)-( $\alpha$ -deuteriobenzyl)tributyltin (**7**,  $[\alpha]_D^{20} -0.328^\circ$ ,  $[\alpha]_{436}^{20} -0.790^\circ$  (neat,  $l = 1$  dm)). The absolute configuration of **7** was not directly determined; however, it is known that displacement reactions with lithium triorganostannates under similar conditions proceed with predominate inversion of configuration at carbon.<sup>8</sup>

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