

which appeared to be a  $\pi$  complex could be detected. A recent X-ray structure<sup>7</sup> of the solid from **3** and bromine has shown that it has the bromonium cation structure originally proposed. Our work shows that not only does the steric hindrance of **3** prevent rapid attack of external nucleophiles to cleave an "onium" ring formed by electrophilic attack, it also slows down rearrangement of aziridinium imide **5**, allowing its direct observation.

The ability to actually observe intermediate **5** will allow separation of the enthalpy and entropy of activation for the two steps of the cycloaddition, a rare opportunity for this type of reaction, which mechanistically mimics the much discussed addition of singlet oxygen.<sup>1</sup> Comparison of our results with what Greene and co-workers have reported suggests that the equilibrium constant for the addition to **5** has a much greater solvent sensitivity than the rearrangement of **5** to **4**, but quantitative studies of these effects remain to be done.<sup>8</sup>

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(8) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Wisconsin Alumni Research Foundation for partial financial support of this work, Prof. R. S. Sheridan and Douglas Kjell for a gift of **1** (R = Me), Prof. J. W. Taylor for the use of the FT-IR equipment, and Dr. Bruce R. Adams for assistance with the low-temperature NMR experiment.

## Alkyl Migration in an Iron(II) Alkylidene: A New Route to a Stabilized Bridgehead Olefin

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Small bicyclic, bridgehead olefins are distorted, strained, and highly reactive.<sup>1</sup> Three have been stabilized as  $\pi$ -complexes with platinum: (Z)-bicyclo[4.2.1]non-1-ene and -1(8)-ene with  $(\text{Ph}_3\text{P})_2\text{Pt}^0$ ,<sup>2</sup> (Z)-bicyclo[3.3.1]non-1-ene with  $(\text{Ph}_3\text{P})_2\text{Pt}^0$ , or  $(\text{Cl})_2(\text{C}_5\text{H}_5\text{N})\text{Pt}^{\text{II}}$ .<sup>3</sup> In each case the complex was prepared by "trapping" the preformed bridgehead olefin with the corresponding Pt(0)- or Pt(II)( $\eta^2$ -ethylene). We now report the first example of a stable bridgehead-olefin  $\pi$ -complex formed by intramolecular rearrangement of a transition-metal alkylidene.

An approximately 50:50 mixture of racemic **4** and **5**—prepared in 41% overall yield from racemic **1**<sup>4</sup> as outlined in Scheme I<sup>5-7</sup>—was mixed in  $\text{CH}_2\text{Cl}_2$  with a slight excess of  $\text{HBF}_4$  in  $\text{Et}_2\text{O}$

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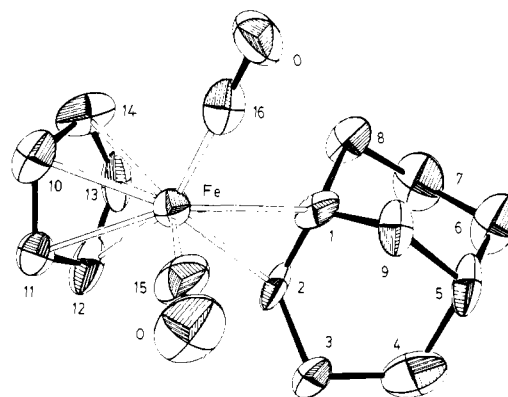
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(5) **2**: mp 91–92 °C, IR ( $\text{CH}_2\text{Cl}_2$ ) 2020, 1955, 1650  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  4.84 (s, 5 H, Cp), 2.26 (brs, 1 H, >CH), 2.0–1.30 (m, 12 H, >CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ )  $\delta$  262.1 (>C=O), 215.4, 215.2 (—C=O), 86.4 (Cp), 71.6 (>C<), 35.3 (>CH), and 42.6, 34.8, 32.1, 31.2, 28.5, 19.7 (>CH<sub>2</sub>); MS, *m/e* 314 [M]<sup>+</sup>, 286 [M - CO]<sup>+</sup>, 258 [M - 2CO]<sup>+</sup>, 230 [M - 3CO]<sup>+</sup>. Anal. Calcd for C<sub>16</sub>H<sub>18</sub>FeO<sub>3</sub>: C, 61.17; H, 5.78. Found: C, 60.48; H, 5.79.

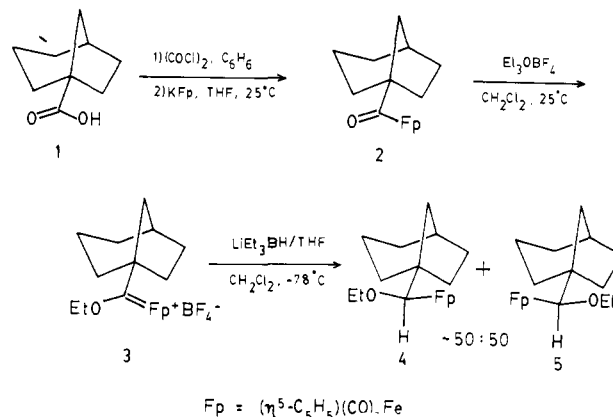
(6) **3**: IR ( $\text{CH}_2\text{Cl}_2$ ) 2070, 2020  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  5.4 (s, 5 H, Cp), 5.2 (q, 2 H, *J* 7.5 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 2.33 (brs, 1 H, >CH), 2.1–1.2 (m, 12 H, >CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CD}_2\text{Cl}_2$ , -5 °C)  $\delta$  343.7 (Fp=C(OEt)), 210.8, 210.6, 209.3, 209.1 (C=O), 88.0, 87.3 (Cp), 90.0, 83.5 (OCH<sub>2</sub>), 74.7, 73.5 (Fp=C(OEt)C<), 42.9, 42.4, 36.2, 35.4, 35.1, 34.6, 33.3, 32.7, 31.2, 31.1, 28.4, 28.2, 19.4, 14.3 (>CH, >CH<sub>2</sub>).

(7) **4** + **5**: IR ( $\text{CH}_2\text{Cl}_2$ ) 1995, 1935  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  4.90, 4.80 (s, s, 1 H, FpCH(OEt)'s), 4.75 (s, 5 H, Cp's), 3.6, 3.2 (m, 1 H, COCH<sub>2</sub>'s), 2.1 (brs, 1 H, >CH's), 1.9–0.9 (m, 12 H, >CH<sub>2</sub>'s); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , -10 °C)  $\delta$  216.7, 201.1 (C=O), 86.1, 85.9 (Cp's), 91.1, 89.6 (FpCH(OEt)'s), 65.9, 56.3, 56.1, 45.6, 45.0, 36.5, 36.3, 36.1, 35.4, 34.2, 32.7, 32.2, 29.8, 29.0, 20.3, 15.3, 15.2 (>C<'s, >CH's, and >CH<sub>2</sub>'s). Comparison of the relative areas of twinned resonances in these spectra indicate an ~50:50 mixture.

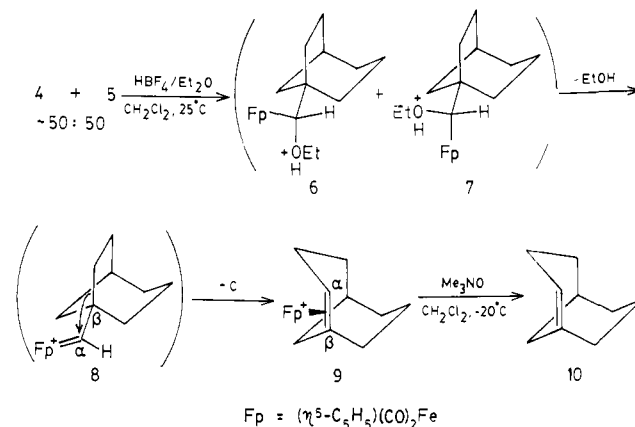


**Figure 1.** ORTEP plot of  $[\eta^2\text{-(Z)-bicyclo[3.3.1]non-1-ene}](\eta^5\text{-C}_5\text{H}_5\text{-(CO)}_2\text{Fe}$  cation showing thermal ellipsoids at the 50% probability level; unlabeled atoms are carbon. Selected bond distances (Å) and angles (deg): Fe–C(1) = 2.22 (1), Fe–C(2) = 2.23 (1), C(1)–C(2) = 1.37 (2), C(1)–C(8) = 1.50 (2), C(1)–C(9) = 1.51 (2), C(2)–C(3) = 1.52 (2); C(1)C(2)C(3) = 116 (1), C(2)C(3)C(4) = 104 (1), FeC(1)C(9) = 118.9 (9), FeC(2)C(3) = 120 (1), C(16)–Fe–the C(1)–C(2) midpoint = 92.7 (3), the C(1)–C(2) midpoint–Fe–Cp ring center = 125.7 (1).

### Scheme I



### Scheme II



and allowed to stand for 10 min at room temperature. Concentration under vacuum, dilution with  $\text{Et}_2\text{O}$ , and two recrystallizations of the resulting precipitate from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  produced a yellow, crystalline, air-stable complex **9**, mp 173–175 °C dec, in 92% yield. The terminal C=O stretches, single vinyl hydrogen resonance, and quaternary and vinyl carbon resonances<sup>8</sup> indicate

(8) **9**: IR ( $\text{CH}_2\text{Cl}_2$ ) 2080, 2040  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  5.5 (s, 5 H, Cp), 5.0 (t, 1 H, *J* = 7.2 Hz, >C=CHCH<sub>2</sub>), 3.1–0.8 (m, 13 H, 1 >CH + 12 >CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CD}_2\text{Cl}_2$ , -5 °C)  $\delta$  211.8, 207.3 (—C=O), 106.4 (>C=), 89.7 (Cp), 71.5 (=CH—), 37.8 (>CH), 43.3, 41.0, 32.3, 31.3, 31.0, 29.1 (>CH<sub>2</sub>). Anal. Calcd for C<sub>16</sub>H<sub>19</sub>BF<sub>4</sub>FeO<sub>2</sub>: C, 49.79; H, 4.96. Found: C, 49.56; H, 5.01.

it to be a single,  $\pi$ -complexed, bridgehead olefin. Attempts to decomplex **9** in the usual way with NaI/acetone<sup>9</sup> were unsuccessful; however, stirring the complex in CD<sub>2</sub>Cl<sub>2</sub> for 5 h at -20 °C with 1.5 equiv of anhydrous trimethylamine oxide<sup>10</sup> and filtering through Celite provided a single olefin whose <sup>13</sup>C{<sup>1</sup>H} NMR matches that reported for (*Z*)-bicyclo[3.3.1]non-1-ene (**10**),<sup>3,11</sup> Scheme II.

The structure of **9**, determined by single-crystal X-ray diffraction,<sup>12</sup> is shown in Figure 1. As the bond lengths and bond angles indicate, the cationic portion of the complex is octahedral with the olefin occupying one coordination site, the Cp three. The iron is located midway between the olefinic carbons. The double bond is lengthened slightly; its axis is essentially parallel to one Fe-CO bond and perpendicular to the other.<sup>13</sup> This structure confirms that **9** is indeed a  $\pi$ -complexed bicyclo[3.3.1]non-1-ene and establishes the geometry of the double bond as *Z*.

Our results establish rather clearly a new mode of reaction for transition metal alkylidenes:  $\beta$ - to  $\alpha$ -alkyl migration.<sup>14</sup> That **5** is converted to **9** rather than to a different bridgehead olefin complex indicates that ring enlargement is *not* concerted with the loss of ethanol from **7**. The considerable precedent for the formation of Fe(II) alkylidenes by protonation of Fe(II)  $\alpha$ -alkoxyalkyls<sup>15</sup> suggests **8** as an intermediate in this case. We formulate the reaction as shown in Scheme II.

The ring enlargement is regiospecific:<sup>16</sup> of the six bridgehead-olefin  $\pi$ -complexes that are possible only **9** is observed. Even through the rearrangement produces what is probably the most stable of these complexes, we presume that the observed specificity is kinetic rather than thermodynamic for there is no indication of the reaction being reversible. The ring enlargement relieves considerable strain<sup>1</sup> and hence is likely to be exothermic and to occur via an early transition state<sup>18</sup> in which the filled iron orbitals are not yet properly positioned for good overlap with the developing empty orbital at C( $\beta$ ).<sup>19</sup> Consequently, the bridgehead cation is probably a better model energetically for the transition state than is the  $\pi$ -complexed olefin. If the barrier to C( $\alpha$ )-C( $\beta$ ) rotation in **8** is small relative to the activation enthalpy of rearrangement,<sup>20</sup> ethano-bridge migration is expected to be about 4 kcal/mol more favorable than methano or propano migration.<sup>21</sup> When it occurs in the most stable conformer<sup>23</sup> (Scheme II), ethano-bridge migration generates the observed product, **9**.<sup>24</sup>

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We continue to examine both the mechanism and utility of this new reaction of transition-metal alkylidenes, this new route to a stabilized bridgehead olefin.

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**Supplementary Material Available:** Listings of atomic positional and thermal parameters (4 pages). Ordering information is given on any current masthead page.

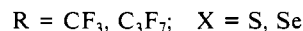
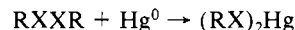
## Mercuration of the Se-Se Bond of a Chelating Se<sub>2</sub> Group with Hg<sup>0</sup>: Preparation and Crystal Structure of [(dmpe)<sub>2</sub>Ir( $\mu$ -Se)<sub>2</sub>Hg]<sub>4</sub>Cl<sub>4</sub>

A. P. Ginsberg\* and C. R. Sprinkle

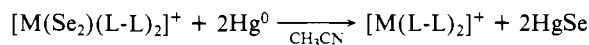
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It has been known for some time that Hg<sup>0</sup> can mercurate the S-S and Se-Se bonds of perfluoroalkyl disulfides and diselenides:<sup>1</sup>



We now report the first example of mercuration of the chalcogen-chalcogen bond of a dichalcogen group chelated to a transition metal in a complex. The mercuration occurs when the compound [Ir(Se<sub>2</sub>)(dmpe)<sub>2</sub>]Cl<sup>2</sup> in acetonitrile is treated with metallic mercury and leads to the tetrameric product [(dmpe)<sub>2</sub>Ir( $\mu$ -Se)<sub>2</sub>Hg]<sub>4</sub>Cl<sub>4</sub> in which Hg has inserted into an Se<sub>2</sub> group and also bridges to an adjacent Se<sub>2</sub> group. The reaction corresponds to oxidative addition of Hg across the Se-Se bond and is similar to insertion of low-valent metal complexes into the S-S and Se-Se bonds of S<sub>2</sub> and Se<sub>2</sub> groups chelating<sup>3</sup> or bridging<sup>4</sup> metal atoms. That Hg<sup>0</sup> mercurates Se<sub>2</sub> in [Ir(Se<sub>2</sub>)(dmpe)<sub>2</sub>]Cl, rather than stripping the selenium off as HgSe, is a striking example of the sensitive dependence of the reactivity of the Se<sub>2</sub> group in [M-(Se<sub>2</sub>)(L-L)<sub>2</sub>]Cl complexes on the nature of the metal M and the basicity of the ditertiary phosphine L-L: for both M = Rh, L-L = dmpe and M = Ir, L-L = dppe the only reaction observed with metallic mercury is



When [Ir(Se<sub>2</sub>)(dmpe)<sub>2</sub>]Cl (200 mg, 0.292 mmol) in acetonitrile (20 mL) was stirred with mercury (2.0 g, 10.0 mmol), the purple color of the Se<sub>2</sub> complex slowly faded and the solution became yellow.<sup>5</sup> After 4 days the yellow solution was concentrated to 10 mL and excess diethyl ether (70 mL) was added to precipitate the yellow product (208 mg, 80%) with stoichiometry [Ir-(Se<sub>2</sub>Hg)(dmpe)<sub>2</sub>]Cl.<sup>6</sup> The same mercury adduct is obtained when [Ir(Se<sub>4</sub>)(dmpe)<sub>2</sub>]Cl<sup>2</sup> in acetonitrile is stirred with excess mercury. In this case HgSe precipitates and the red Se<sub>4</sub> complex is converted to the purple Se<sub>2</sub> complex which is then mercurated.

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(6) Anal. Calcd for C<sub>12</sub>H<sub>12</sub>P<sub>4</sub>IrSe<sub>2</sub>HgCl: C, 16.26; H, 3.64; P, 13.98; Se, 17.81; Hg, 22.63; Cl, 4.00. Found (by analytische Laboratorien, Engelskirchen, West Germany, after drying at 55 °C (10<sup>-3</sup> mm)): C, 16.20; H, 3.67; P, 14.14; Se, 17.66; Hg, 22.58; Cl, 3.83.