

be reduced by CO to a metal alkylidene complex and CO<sub>2</sub>, or even a metal acyl could be reduced to a metal carbyne and CO<sub>2</sub>.<sup>18</sup> The heterogeneous analogue of these reactions, the disproportionation of CO to CO<sub>2</sub> and C (which presumably goes through a dissociative mechanism), is well-known.<sup>19</sup>

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**Supplementary Material Available:** Tables of crystal and collection data, atomic coordinates and temperature factors, bond lengths and bond angles, and observed and calculated structure factors and a view of the unit cell of **3** (19 pages). Ordering information is given on any current masthead page.

(18) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 608-610.

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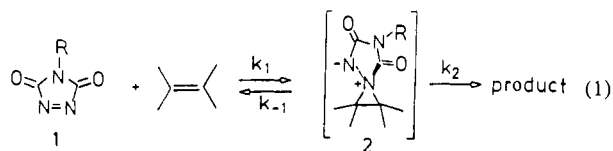
### Direct Observation of the Aziridinium Imide Intermediates in the Reaction of Biadamantylidene with Triazolinediones

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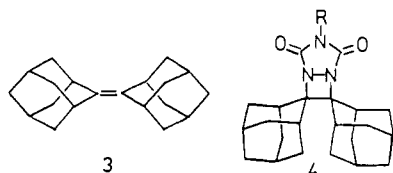
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Greene and co-workers<sup>1</sup> and Adam and co-workers<sup>2</sup> have extensively studied the reactions of 4-substituted 1,2,4-triazolinediones **1**, R = Me, Ph, with olefins. Ene products (*N*-allylurazoles) are formed when abstractable  $\alpha$ -hydrogens are present in the olefin, and diazetidines (formal 2 + 2 cycloaddition) when they are not, and in a few other cases (enol ethers, aryl-alkyl olefins). Rearrangements to five-membered ring urazoles are observed in some cases.<sup>2</sup> All of their experiments are consistent with the rate-controlling step being approach of **1** perpendicular to the plane of the olefin, forming an intermediate "with the structural characteristics of an aziridinium imide"<sup>1a</sup>, **2**, see eq 1. The



Stephenson isotope effect test provided important evidence for intermediate **2** in the ene reactions, while the reactivity pattern of various olefins which give diazetidine products was argued to be consistent with **2**. For example, norbornene is far less reactive than typical disubstituted olefins, but biadamantylidene **3** is as reactive. The activation parameters for **1**(R = Ph) + **3** were  $\Delta H^\ddagger$

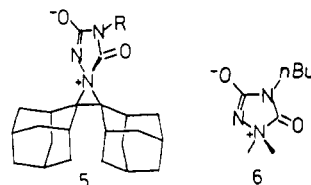


(1) (a) Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910. (b) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384.

(2) Adam, W.; Carballeira, N. *J. Am. Chem. Soc.* **1984**, *106*, 2874 and references therein.

= 10.6 kcal/mol  $\Delta S^\ddagger = -33$  eu<sup>1a</sup> in benzene, so  $\Delta G^\ddagger(25^\circ\text{C})$  is 20.4 kcal/mol, corresponding to a first half-life at 0.1 M concentration of reactants of 2.6 min. The structure of the product was verified by obtaining the X-ray crystallographic structure of **4** (R = Me). The reaction goes to completion, and **4** (R = Ph) only cleaves slowly to **3** at 70 °C. We report here that, surprisingly, an intermediate that we assign as aziridinium imide **5** builds up in chloroform solution in the reaction of **3** and **1**.

When the addition of **1** (R = Me) to **3** is followed by <sup>1</sup>H NMR in deuteriochloroform solution, an intermediate is formed which has an N-CH<sub>3</sub> 3 H singlet at  $\delta$  3.07, broad bridgehead 2 H signals at  $\delta$  2.75 and 3.09 (the latter overlapping with the N-CH<sub>3</sub> signal), and an upfield 2 H doublet at  $\delta$  1.4, as well as many other peaks which overlap with the adamantyl multiplets of **3** and **4** (R = Me). When 0.037 M **1** (R = Me) and 0.184 M **3** were mixed, the spectrum observed after 90 s showed no detectable **1** (R = Me) remaining, nor could the pink color of **1** (R = Me) be detected visually, and the ratio of intermediate to **4** was over two, as measured by integration of both the N-CH<sub>3</sub> and the bridgehead signals. A similar intermediate was observed in CDCl<sub>3</sub> from **1** (R = Ph) and **3**, which had bridgehead <sup>1</sup>H NMR absorptions at  $\delta$  2.85 and 3.17. The IR spectrum of the intermediate was obtained at room temperature under conditions where **1** (R = Me) had already disappeared, by subtracting the **4** (R = Me) signals from the observed FT-IR spectrum, giving a carbonyl region having absorptions at 1790 and 1686 cm<sup>-1</sup>. These absorptions should be compared with those of the model ammonium imide **6**, reported to be 1790 and 1670 cm<sup>-1</sup>.<sup>3</sup> Conversion of the intermediate to **4** (R = Me) is slow at -40 °C. A solution initially 0.20 M in **1** (R = Me) and 0.21 M in **3** which was reacted at room temperature for 30 s and rapidly cooled to -40 °C showed by <sup>1</sup>H NMR integration 15% **4** (R = Me), 2% **3**, and 83% intermediate after 2 h. The <sup>13</sup>C NMR of the intermediate shows peaks at  $\delta$  159.9 and 156.6 (C=O), 81.8 (C<sub>q</sub>), 36.8, 36.7, 35.5, 35.3, and 34.3 (CH<sub>2</sub>), 28.6, 26.0, 25.7, and 25.5 (CH), and 26.2 (CH<sub>3</sub>). Two of the three mirror symmetry planes which intersect at midpoint of olefin **3** have been lost in the intermediate. Our spectral data are consistent with the intermediate being **5** (R = Me).



The kinetics of the reaction of **1** (R = Me) with **3** in CDCl<sub>3</sub> at 23 °C have been measured by integration of the proton NMR signals, and also by visible spectroscopy, following disappearance of **1** (R = Me) using its 536-nm ( $\epsilon$  208) band.<sup>4</sup> All of our data are consistent with rate constants  $k_1 = 0.63 \pm 0.06$  M<sup>-1</sup> s<sup>-1</sup>,  $k_2 = 0.0048 \pm 0.0005$  s<sup>-1</sup> ( $\Delta G_1^\ddagger = 17.7$ ,  $\Delta G_2^\ddagger = 20.6$  kcal/mol). We do not yet have an accurate measure of  $k_{-1}$  but it is certainly no larger than 0.005 s<sup>-1</sup> and may be substantially smaller.

We find it very surprising that **5** (R = Me) is so stable that  $k_1/k_{-1}$  is large, but our results demonstrate that it is. The unusual steric properties of **3** have made it uniquely important in the study of electrophilic additions to olefins. Wynberg and co-workers<sup>5</sup> originally assigned the white solids with the solubility properties of salts which are isolated upon treatment of **3** with bromine and chlorine as halonium salts, although Olah and co-workers<sup>6</sup> concluded on the basis of NMR studies that, in solution, only a species

(3) Wadsworth, W. W.; Emmons, W. D. *J. Org. Chem.* **1967**, *32*, 1279.

(4) At initial concentrations (M) of **1** (R = Me) and **3** respectively of 0.037 and 0.012, 0.037 and 0.043, and 0.037 and 0.184 for the NMR studies and at 0.0217 and 0.0243 and 0.00325 and 0.00328 for the UV studies.

(5) (a) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907. (b) Wieringa, J. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1970**, 4579.

(6) Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581.

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>

(7) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

(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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(2) (a) Stamm, E.; Becker, K. B.; Engel, P.; Ermer, O.; Keese, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 685. (b) Stamm, E.; Becker, K. B.; Engel, P.; Keese, R. *Helv. Chim. Acta* **1979**, *62*, 2181.

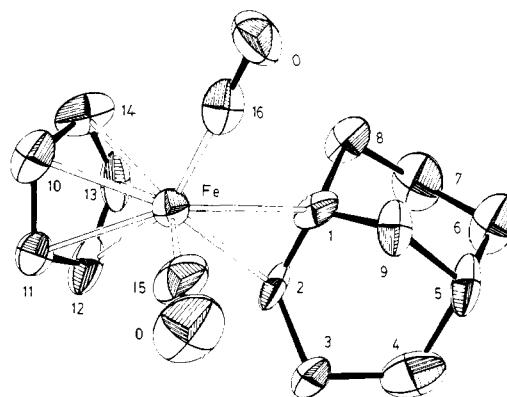
(3) Godleski, S. A.; Valpey, R. S.; Grundlach, K. B. *Organometallics* **1985**, *4*, 296.

(4) Chow, A. W.; Jakas, D. R.; Hoover, J. R. E. *Tetrahedron Lett.* **1966**, 5427.

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

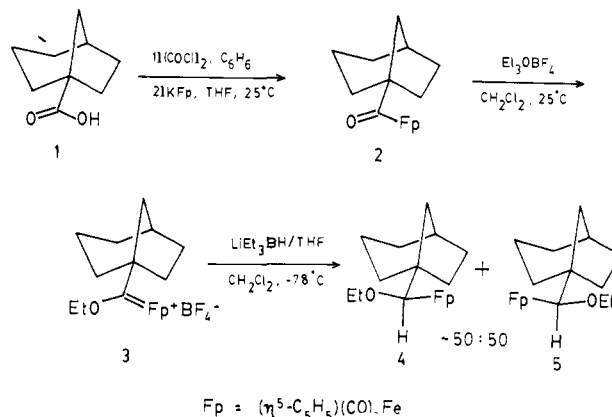
(6) **3**: IR ( $\text{CH}_2\text{Cl}_2$ ) 2070, 2020  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  5.4 (s, 5 H, Cp), 5.2 (q, 2 H,  $J = 7.5$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 2.33 (brs, 1 H,  $\text{>CH}$ ), 2.1–1.2 (m, 12 H,  $\text{>CH}_2$ ); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CD}_2\text{Cl}_2$ , -5 °C)  $\delta$  343.7 ( $\text{Fp}^+=\text{C}(\text{OEt})$ ), 210.8, 210.6, 209.3, 209.1 ( $\text{C=O}$ ), 88.0, 87.3 (Cp), 90.0, 83.5 ( $\text{OCH}_2$ ), 74.7, 73.5 ( $\text{Fp}^+=\text{C}(\text{OEt})\text{C<}$ ), 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 ( $\text{>CH}$ ,  $\text{>CH}_2$ ).

(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,  $\text{FpCH}(\text{OEt})$ 's), 4.75 (s, 5 H, Cp's), 3.6, 3.2 (m, 1 H,  $\text{COCH}_2\text{CH}_3$ 's), 2.1 (brs, 1 H,  $\text{>CH}$ 's), 1.9–0.9 (m, 12 H,  $\text{>CH}_2$ 's); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ , -10 °C)  $\delta$  216.7, 201.1 ( $\text{C=O}$ ), 86.1, 85.9 (Cp's), 91.1, 89.6 ( $\text{FpCH}(\text{OEt})$ '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 ( $\text{>C<}$ 's,  $\text{>CH}$ 's, and  $\text{>CH}_2$ 's). Comparison of the relative areas of twinned resonances in these spectra indicate an ~50:50 mixture.

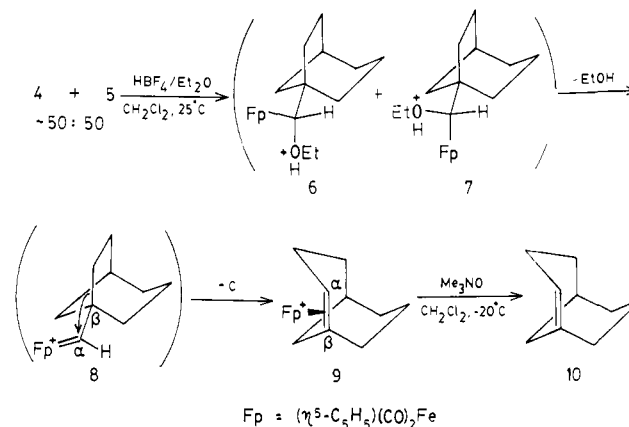


**Figure 1.** ORTEP plot of  $[\eta^2\text{-(Z)-bicyclo[3.3.1]non-1-ene}](\eta^5\text{-C}_5\text{H}_5\text{-(CO)}_2\text{Fe}$  cation showing thermal ellipsoids at the 50% probability level; unlabeled atoms are carbon. Selected bond distances (Å) and angles (deg): Fe–C(1) = 2.22 (1), Fe–C(2) = 2.23 (1), 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  $\text{C=O}$  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,  $\text{>C=CHCH}_2$ ), 3.1–0.8 (m, 13 H, 1  $\text{>CH}$  + 12  $\text{>CH}_2$ ); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CD}_2\text{Cl}_2$ , -5 °C)  $\delta$  211.8, 207.3 ( $\text{—C=O}$ ), 106.4 ( $\text{>C=}$ ), 89.7 (Cp), 71.5 ( $\text{=CH—}$ ), 37.8 ( $\text{>CH}$ ), 43.3, 41.0, 32.3, 31.3, 31.0, 29.1 ( $\text{>CH}_2$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{19}\text{BF}_4\text{FeO}_2$ : C, 49.79; H, 4.96. Found: C, 49.56; H, 5.01.