

Substitutions with chelating ligands are also enhanced; 100% yields of  $\text{Ru}_3(\text{CO})_{10}(\text{L}_2)$ ,  $\text{L}_2 = \text{dppm}$ , bis(diphenylphosphino)methane, or  $\text{dppe}$ , bis(diphenylphosphino)ethane, are obtained within 3 min.<sup>12</sup>

Salts of the anions  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , or  $\text{NO}_2^-$  are milder catalysts promoting substitutions over a broad range of rates.<sup>13,14</sup> These may be expressed in terms of the half-life for disappearance of  $\text{Ru}_3(\text{CO})_{12}$  under standard reaction conditions<sup>7a</sup> using a ratio  $\text{PPH}_3:\text{Ru}_3(\text{CO})_{12} = 4:1$ . The following are found for the  $[\text{PPN}^+]$  salts,  $t_{1/2}$  (min):  $[\text{CN}^-]$  or  $[\text{CH}_3\text{CO}_2^-]$ , <1;  $[\text{F}^-]$ , <2;  $[\text{Cl}^-]$ , 7;  $[\text{Br}^-]$ , 10;  $[\text{I}^-]$ , 17;  $[\text{NO}_2^-]$ , 45. With  $[\text{PPN}][\text{Cl}]$  as catalyst, integrated rate data show zero-order dependence on  $\text{Ru}_3(\text{CO})_{12}$ .<sup>13b</sup> The mildest catalysts do not give pure monosubstituted product even when only a stoichiometric amount of ligand is present: their enhancement of the first (rate determining) step is not fast enough to exclude formation of subsequent substitution products.

Greater amounts of the  $[\text{PPN}^+]$  salts of the nucleophiles may be introduced through their acetone or  $\text{CH}_2\text{Cl}_2$  solutions.<sup>7c,11</sup> The action of the halide anions, however, is attenuated in  $\text{CH}_2\text{Cl}_2$ . Catalysis is prevented in the presence of strongly hydrogen-bonding solvent (i.e.,  $\text{CH}_3\text{OH}$ ) or if the nucleophile is irreversibly consumed by chemical reaction such as conversion shown in reaction 1 which occurs in competition with coordination by weakly nucleophilic ligands.

In attempts to extend the catalysis of substitution reactions to  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$ , we found instead a rapid deprotonation. Treatment of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  with a stoichiometric amount of  $[\text{PPN}][\text{Cl}]$  in THF gives  $[\text{PPN}][\text{Ru}_4(\mu\text{-H})_3(\text{CO})_{12}]$  in 100% yield in 15 min,<sup>15</sup> paralleling the deprotonation of  $[\text{HMo}(\text{CO})_2(\text{dppe})_2]^+$ ,<sup>16</sup> or  $\text{Os}_4\text{H}_3(\text{CO})_{12}\text{X}$ ,  $\text{X} = \text{Cl}$  or  $\text{I}$ .<sup>17</sup>

Our present observations reveal a novel aspect of the chemistry of ruthenium cluster complexes in the presence of highly dissociated salts. This greatly extends the range of reactions that can be investigated at ambient temperatures.

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**Supplementary Material Available:** Supplements to ref 8, 9, and 15, and two figures of the concentration of  $\text{Ru}_3(\text{CO})_{11}\text{PPH}_3$  as a function of time and rate data for disappearance of  $\text{Ru}_3(\text{CO})_{12}$  (4 pages). Ordering information is given on any current masthead page.

(11) Acceleration of the substitutions with  $\text{AsPh}_3$  and trialkyl or triaryl phosphites observed for  $[\text{PPN}][\text{CN}]$  may be achieved with  $[\text{PPN}][\text{acetate}]$  by using considerably larger amounts (0.075 mmol) added in  $\text{CH}_2\text{Cl}_2$  solution;<sup>7c</sup> under these conditions, disubstituted products are obtained.

(12) (a) Synthesis of  $\text{Ru}_3(\text{CO})_{10}(\text{dpmm})$ . Under experimental conditions in ref 7, a molar ratio of 1:1 of  $\text{Ru}_3(\text{CO})_{12}/\text{dpmm}$  is used. Yield after chromatographic purification and recrystallization, orange crystals, 90%; IR, carbonyl region in cyclohexane ( $\text{cm}^{-1}$ ) 2082 m, 2022 m, 2011 vs, 2001 s, 1983 w, 1958 m, 1942 w, cf. ref 6 and 12b,c. Bridge closing was found to be slow in  $\text{Ru}_3(\text{CO})_{11}(\text{dppe})_6$ ; the dissociated salts also accelerate the bridge closing reaction. (b) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 3369-3371. (c) Coleman, A. W.; Jones, D. F.; Dixneuf, P. H.; Brisson, C.; Bonnet, J.-J.; Lavigne, G. *Ibid.* **1984**, *23*, 952-956.

(13) (a) Results using solid  $[\text{PPN}][\text{Cl}]$ <sup>7a</sup> were found to be erratic. Under rigorous exclusion of moisture no catalysis of substitution is observed; the catalytic amounts of  $[\text{Cl}^-]$  are irreversibly consumed according to reaction 1. Catalysis of the substitution reaction by  $[\text{PPN}][\text{Cl}]$  requires a trace of moisture. (b) Integrated rate data for disappearance of  $\text{Ru}_3(\text{CO})_{12}$  using  $[\text{PPN}][\text{Cl}]$  as the catalyst is given as supplementary material, Figure 2.

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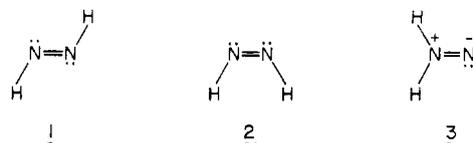
## Low-Temperature Matrix Isolation of $\text{H}_2\text{NN}$ . Electronic and Infrared Characterization

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Much of our understanding of the structures of the isomers of  $\text{H}_2\text{N}_2$  (1-3) comes from theory<sup>1</sup> due to the limited experimental characterization of these reactive species.<sup>2,3</sup> Firm spectroscopic evidence exists only for the trans 1,2-isomer 1.<sup>2</sup> In 1976, it was



reported that vacuum pyrolysis of cesium tosylhydrazide affords a colorless  $\text{H}_2\text{N}_2$  product ( $\lambda_{\text{max}}$  260 nm) on a cooled surface ( $-196^\circ\text{C}$ ) that differs in physical and chemical properties from the yellow trans 1,2-isomer, 1 ( $\lambda_{\text{max}}$  386 nm).<sup>2j</sup> This "isomeric diazene" was assigned to the 1,1-diazeno 3. However, subsequent theoretical work indicates that 3 is a colored species due to relatively low lying  $n,\pi^*$  electronically excited states ( $T_1$ , 0.6 eV;  $S_1$ , 2.2 eV).<sup>1n</sup> Recent experimental evidence from the study of persistent 1,1-diazenes, such as *N*-(2,2,6,6-tetramethylpiperidyl)nitrene and *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene, reveal that they are indeed violet species ( $\lambda_{\text{max}}$  543-497 nm,  $n,\pi^*$ ) and have considerable NN double bond character ( $1638\text{-}1595\text{ cm}^{-1}$ ,  $\text{N}=\text{N}$  stretch).<sup>4</sup>

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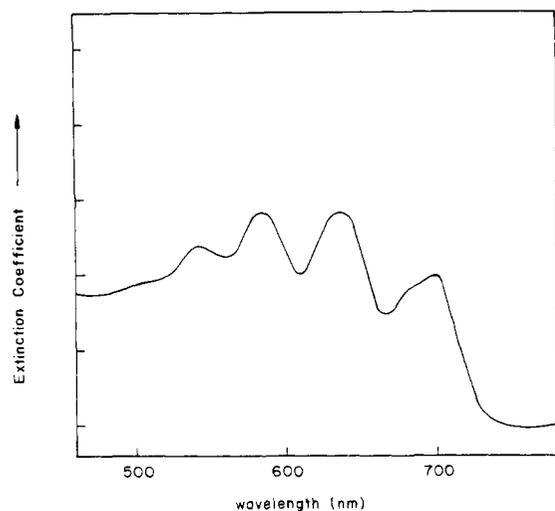
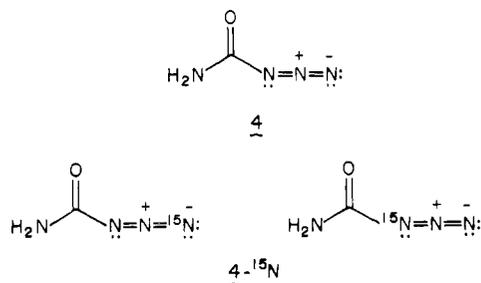


Figure 1. Electronic spectrum of H<sub>2</sub>NN (2 MTHF, 80 K).

We report the photochemical generation of H<sub>2</sub>NN (**3**) in a glass at 80 K and an argon matrix at 10 °K and the isotopically substituted species, D<sub>2</sub>NN (**3-d<sub>2</sub>**), H<sub>2</sub>N<sup>15</sup>N (**3-<sup>15</sup>N**) and D<sub>2</sub>N<sup>15</sup>N (**3-d<sub>2</sub>,<sup>15</sup>N**), facilitating the electronic and infrared spectral characterization of **3**. Irradiation of carbamoyl azide (**4**)<sup>5</sup> in a



rigid medium (2-methyltetrahydrofuran (2-MTHF) at 80 K<sup>6</sup>) with a 1000-W Xenon lamp through Corning filters CS-7-54 (UV transmitting, visible 440–660 cut-out filters)<sup>7</sup> affords a blue-violet glass. Electronic absorption spectroscopy (80 K) reveals a structured absorption spectrum in the visible ( $\lambda_{\max}$  636 nm) (Figure 1). This is assigned to the  $n, \pi^*$  transition for H<sub>2</sub>NN.<sup>8</sup> The vibrational progression shows an average spacing of 1300 cm<sup>-1</sup>, presumably the N–N stretching frequency of S<sub>1</sub> of H<sub>2</sub>NN.<sup>10</sup>

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(6) The low-temperature apparatus is of conventional design employing an Air Products Displex CSW-202 DMX-1E with rotating optical shroud. Suprasil outer windows were used for photolysis experiments and electronic spectroscopy. The inner cell and solution inlet system have been described previously.<sup>4a,c</sup> KBr outer windows and CsI inner windows were used for infrared spectroscopy. High vacuum ( $\leq 10^{-7}$  mbar) was achieved with an Edwards Mk.2 Diffstack. The apparatus was equipped with an APD-E temperature controller with iron-doped gold/chromel thermocouple, 2–300  $\pm$  0.1 K.

(7) IR filter and quartz optics.

(8) We presume the photoreaction of **4**  $\rightarrow$  **3** + N<sub>2</sub> + CO is proceeding by a photo-Curtius rearrangement,<sup>7</sup> **4**  $\rightarrow$  H<sub>2</sub>NNCO + N<sub>2</sub>, which then photodecarbonylates to H<sub>2</sub>NN and CO.

(9) Lwowski, W. f. DeMauriac, R. A.; Thompson, M. *J. Org. Chem.* **1975**, *40*, 2608.

(10) Average vibrational spacings observed for persistent 1,1-diazenes are 1000–1250 cm<sup>-1</sup>.<sup>4</sup>

(11) The characterization of the products from the thermal decomposition is under investigation and will be deferred to a full manuscript. However, one thermal product from **3**, assigned tentatively on the basis of spectral comparison ( $\lambda_{\max}$  386 nm), appears to be the trans 1,2-isomer, **1**. It is not yet known whether the thermal rearrangement **3**  $\rightarrow$  **1** is unimolecular or bimolecular.

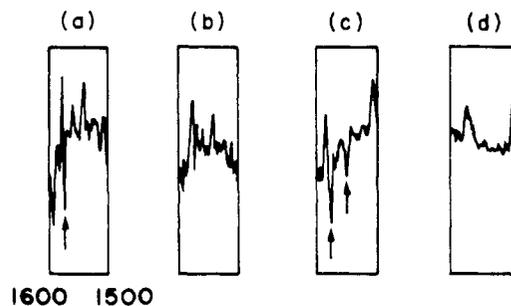


Figure 2. Infrared spectra (1600–1500 cm<sup>-1</sup>) of an argon matrix at 10 K after 2 h of photolysis of **4**. (a) Spectrum of H<sub>2</sub>NN with scale subtraction of starting material **4**. Arrow indicates the 1574-cm<sup>-1</sup> peak. (b) Same after 1 h of photolysis in the visible. (c) Spectrum of a mixture of H<sub>2</sub>NN and H<sub>2</sub>N<sup>15</sup>N from photolysis of **4-<sup>15</sup>N**. Arrows indicate 1574- and 1548-cm<sup>-1</sup> peaks. (d) Same after 1 h of photolysis in the visible.

Warming the glass to softening (90 °K) results in loss of the blue-violet species.<sup>11</sup> Irradiation of **4-d<sub>2</sub>**<sup>12</sup> affords a similar electronic absorption spectrum.

1,1-Diazenes have been shown to be photolabile on irradiation in the visible.<sup>4b</sup> Irradiation of the blue-violet glass at 80 °K with visible light (1000 W Xenon lamp, Corning filter CS-3-70, CS-1-75) results in decolorization. The products observed from photolysis of the blue-violet species at 80 °K in a glass are H<sub>2</sub> and N<sub>2</sub> in apparent quantitative yield.<sup>13</sup>

For infrared studies, the carbamoyl azide (**4**) was isolated in an argon matrix<sup>14</sup> at 10 °K<sup>7</sup> and the infrared spectrum was recorded.<sup>15</sup> Irradiation in the UV with visible cutout filters results in loss of all infrared bands due to **4** and appearance of new infrared bands at 2865, 2808, 2141, 1863, 1574, and 1003 cm<sup>-1</sup>. The 2141-cm<sup>-1</sup> band is assigned to carbon monoxide.<sup>16</sup> Of interest is the band at 1574 cm<sup>-1</sup> which is observed to grow in as a shoulder on the NH<sub>2</sub> bending mode band of the starting material **4**. Scaled subtraction of the infrared spectrum of **4** from the irradiated sample spectrum displays the 1574-cm<sup>-1</sup> band clearly (Figure 2a). Irradiation of this sample in the visible results in loss of the 1574-cm<sup>-1</sup> band (Figure 2b).

In order to support the assignment of the 1574-cm<sup>-1</sup> band to the NN stretch of H<sub>2</sub>NN, H<sub>2</sub><sup>14</sup>N<sup>15</sup>N was synthesized for comparison. It has been shown that isotopic labeling with <sup>15</sup>N of the terminal "nitrene" nitrogen in persistent 1,1-diazenes results in the expected Hooke's law shift to lower frequency.<sup>4</sup> Carbamoyl azide (**4**) was allowed to react with excess [1-<sup>15</sup>N]sodium azide<sup>17</sup> in dry acetonitrile affording **4-<sup>15</sup>N**, with the <sup>15</sup>N label distributed equally between the two terminal nitrogens of the azide moiety.<sup>18</sup> Photodecomposition of **4-<sup>15</sup>N** is expected to afford a mixture of H<sub>2</sub><sup>14</sup>N<sup>14</sup>N and H<sub>2</sub><sup>14</sup>N<sup>15</sup>N. Irradiation of **4-<sup>15</sup>N** in an argon matrix at 10 °K results in the same set of product infrared bands including the 1574-cm<sup>-1</sup> band and a single new band at 1548 cm<sup>-1</sup> (Figure 2c). Irradiation with visible light results in loss of the 1548-cm<sup>-1</sup> band and all infrared bands previously assigned to **3** (Figure 2d). On this basis the 1574- and the 1548-cm<sup>-1</sup> bands are assigned to the <sup>14</sup>N<sup>14</sup>N and <sup>14</sup>N<sup>15</sup>N stretch of **3**, respectively (Figure 2c).

In addition, D<sub>2</sub>NN and D<sub>2</sub><sup>14</sup>N<sup>15</sup>N were examined by infrared

(12) Deuterium exchange of **4** in excess D<sub>2</sub>O afforded **4-d<sub>2</sub>**.

(13) The photochemical sequence **4**  $\rightarrow$  **3** + CO + N<sub>2</sub>  $\rightarrow$  H<sub>2</sub> + N<sub>2</sub> + CO + N<sub>2</sub> would be expected to afford a ratio of N<sub>2</sub>:H<sub>2</sub>:CO of 2.0:1.0:1.0. We find the ratio of N<sub>2</sub>:H<sub>2</sub>:CO to be 1.96:1.01:1.00 by analytical VPC (1/8 in  $\times$  3 ft sieve 5A column). The absolute yield of CO was 90  $\pm$  10%.

(14) Linde UHP argon was used as received. Carbamoyl azide (**4**) was sublimed from a -20 °C bath and codeposited with argon at 3–5 mmol of gas mixture per h at 20 K. We estimate that the ratio of **4**:argon is in the range of 1:500 to 1:1000.

(15) Shimadzu IR-435 with built-in microprocessor routine for scaled subtraction and expansion at high resolution. Wavenumber accuracy is  $\pm$  2 cm<sup>-1</sup>.

(16) A control deposition of CO in argon (1:3500) at 10 K was carried out for comparison.

(17) Prochemical Limited, New Jersey; 97 atom % [1-<sup>15</sup>N]NaN<sub>3</sub>.

(18) <sup>15</sup>N incorporation was analyzed via infrared, <sup>15</sup>N NMR, and high-resolution mass spectroscopy.

spectroscopy. Photolysis of **4-d<sub>2</sub>** isolated in an argon matrix at 10 °K results in product bands at 2109, 1599, 1571, 1195, 913, 900, and 794 cm<sup>-1</sup> plus the CO band at 2141 cm<sup>-1</sup>. The bands at 1599 and 1571 cm<sup>-1</sup> are in the N=N stretch region. Irradiation of **4-<sup>15</sup>N**, **d<sub>2</sub>** prepared via <sup>15</sup>N azide exchange of **4-d<sub>2</sub>**, results in the same set of product infrared bands obtained from **4-d<sub>2</sub>** together with a single new band at 1552 cm<sup>-1</sup>, which is assigned to <sup>14</sup>N=<sup>15</sup>N stretch for D<sub>2</sub>N<sup>15</sup>N. Irradiation with visible light results in a decrease of all bands due to D<sub>2</sub>NN as well as the 1552-cm<sup>-1</sup> band. The 1571- and 1552-cm<sup>-1</sup> bands are assigned to the <sup>14</sup>N=<sup>14</sup>N and <sup>14</sup>N=<sup>15</sup>N stretch of D<sub>2</sub>NN.

In summary, H<sub>2</sub>NN is a blue-violet species (λ<sub>max</sub> 636 nm, n,π\*) with an N=N stretching frequency of 1574 cm<sup>-1</sup>. This can be compared to the trans 1,2-isomer, **1**, which is yellow (λ<sub>max</sub> 386 nm) with a Raman N=N stretch of 1529 cm<sup>-1</sup>. At 90 °K, one thermal product from H<sub>2</sub>NN appears to be the trans 1,2-isomer **1**.<sup>11</sup> The photodecomposition of H<sub>2</sub>NN in the visible at 80 K affords H<sub>2</sub> and N<sub>2</sub>.

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## Bond Dissociation Energies in Ferrocene

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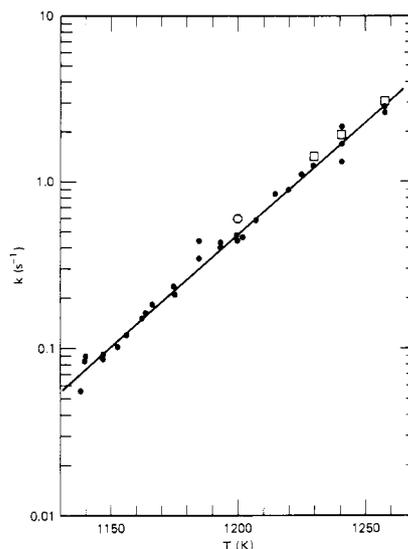
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Cyclopentadienyl (C<sub>5</sub>H<sub>5</sub>) is an important ligand in organometallic chemistry, in addition to its role in forming interesting sandwich compounds, such as ferrocene, Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. As a small, polydentate, strongly bound ligand, it is useful in producing partially unsaturated, extremely reactive species of value in modeling basic organometallic reaction chemistry, in synthesizing organometallic compounds containing particularly labile or reactive ligands, and for developing novel asymmetric ligands. Despite extensive literature on these compounds, reliable values for metal-cyclopentadienyl bond dissociation energies (BDE) are not available. The average values, which have been measured for metallocenes,<sup>1</sup> do not necessarily correspond to the individual bond strengths. We report here our measurements of the thermal decomposition rates of ferrocene by very low-pressure pyrolysis (VLPP) and derive the first and second bond energies.

The VLPP method has been widely used and is described in detail elsewhere.<sup>2</sup> The chosen gas, flowing at low pressure through a heated Knudsen cell, is heated rapidly by collisions with the walls and pyrolyzes if the temperature is high enough. The decomposition rate is measured relative to the known rate of escape into the analysis mass spectrometer. Two residence times, that is, exit aperture sizes, can be used, and gas-gas collisions are avoided at the low millitorr pressures used. Ferrocene was monitored at the parent peak (*m/e* 186 amu) relative to the signal level when the flow bypassed the heated reactor. Temperatures were measured by thermocouples.

The results are shown in Figure 1. Several observations indicate that decomposition is not wall catalyzed. Data taken both increasing and then decreasing the temperature, and data with carbon coated or bare quartz reactor walls, show no disparity.



**Figure 1.** Very low-pressure pyrolysis data for ferrocene decomposition. Dots are small aperture, squares are large aperture. The line is the calculated fit, including falloff for  $\log k_{\infty} = 16.34 - (91.4/2.3RT)$ . The open circle is the fit for a higher  $A$  factor as described in the text.

When the temperature is lowered below 1120 K after a run, no decomposition is observed. Thus, these rates represent the homogeneous gas-phase decomposition of ferrocene. We note, however, the prolonged exposure of the walls to ferrocene at high temperature does produce a catalytic wall coating. Attempts to perform a similar experiment for nickelocene produced rapid catalytic decomposition near 800 K. This was previously observed by Hedaya.<sup>3</sup>

A least-squares Arrhenius fit of the data gives  $\log A = 15.5$  and  $E_a = 86.8$  kcal/mol. However, the fact that the reaction is slightly in the falloff regime where energy-transfer collisions with the walls partially contribute to the rate must be taken into account. We have utilized a reduced Kassel formalism developed by Troe<sup>4</sup> which reproduces the results of full RRKM calculations. The rate constant is expressed as a correction to the Lindemann-Hinshelwood model:

$$\log k = \log (k_0 / (1 + (k_0/k_{\infty}))) + \log F / (1 + (\log k_0/k_{\infty})^2)$$

Here,  $k_0$  is the known strong collision rate with the walls,<sup>2</sup>  $k_{\infty}$  is calculated from assumed Arrhenius parameters which we are attempting to derive via the fit, and  $F$  is calculated<sup>4</sup> from  $E_a$  and the ferrocene vibrational frequencies.<sup>5</sup> The fit shown in Figure 1 is for  $\log A = 16.34 \pm 0.54$  and  $E_a = 91.4 \pm 3.0$  kcal/mol. The degree of falloff,  $k/k_{\infty}$ , ranges from  $\sim 0.88$  at 1150 K to  $\sim 0.75$  at 1250 K. In general, it is not possible to uniquely determine both  $A$  and  $E_a$  from VLPP data, hence the range of values. An increase in both  $A$  and  $E_a$  is partially compensated for by an increase in the falloff and its temperature dependence. Thus, this value of  $E_a$  represents a minimum for scission of the first cyclopentadienyl ligand from ferrocene. Much larger values of  $A$  and  $E_a$ , however, are unlikely, since the fit in Figure 1 will show curvature not evident in the data when this is attempted. For example, using  $\log A = 17.5$  and  $E_a = 97.5$  kcal/mol, we fit the data as before at 1150 and 1250 K, but the fit at 1200 K, shown in Figure 1 as the open circle, is clearly above the data.

In an attempt to resolve this ambiguity further, a laser pyrolysis experiment was undertaken at higher temperature. Experimental details are given in a recent paper on metal-carbonyl bond energies.<sup>6</sup> A mixture of 100 torr N<sub>2</sub> bath gas, SF<sub>6</sub> absorber, and

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