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# Photoinduced Ring Expansion of Cycloalkyl Iron $\sigma$ -Complexes to Cyclic Iron Complexes

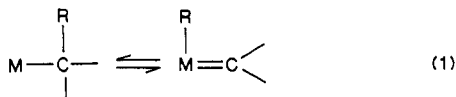
Yngve Stenström, A. E. Koziol,<sup>†</sup> Gus J. Palenik, and W. M. Jones\*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

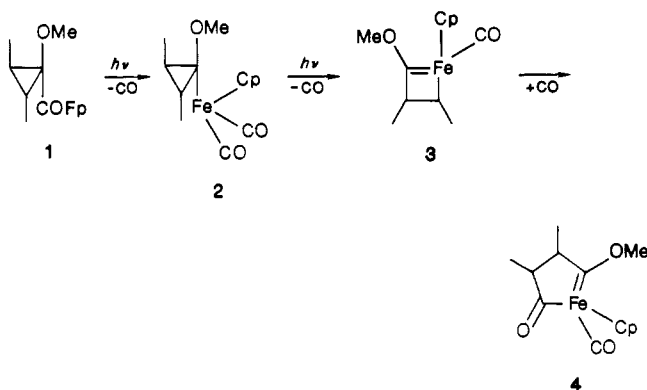
Received January 8, 1987

The kinetics of the reaction of triphenylphosphine with 1-carbonyl-1-( $\eta^5$ -cyclopentadienyl)-2-methoxy-1-ferracyclopentene (**8**) has been studied. The reaction is second order with  $k = (14.1 \pm 0.5) \times 10^{-3}$  L/(mol/s) at 50 °C. Activation parameters are  $\Delta H^\ddagger = 24.4 \pm 1.5$  kcal/mol and  $\Delta S^\ddagger = +8 \pm 2$  eu. Photolysis of dicarbonyl( $\eta^5$ -cyclopentadienyl)(1-methoxycycloalkyl)iron complexes with ring strain less than cyclobutyl (i.e. cyclopentyl and 2-norbornyl, **15** and **20**, respectively) leads to elimination of methanol rather than rearrangement. Photolysis of dicarbonyl( $\eta^5$ -cyclopentadienyl)[*trans*-2-(dialkylamino)cyclobut-1-yl]iron, **23a** and **23b**, gives the corresponding ring-expanded carbene complexes, **24a** and **24b**, respectively. Attempts to make  $\beta$ -amino  $\sigma$ -complexes of larger rings were unsuccessful.

Hückel calculations make the interesting prediction that rearrangement of transition-metal complexes of the type depicted in eq 1 should be facile.<sup>1</sup> And, indeed, examples



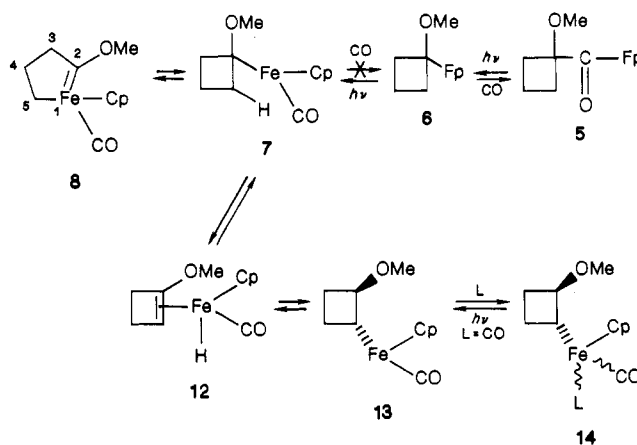
of migratory insertions (the reverse of eq 1) of H,<sup>2</sup> alkyl,<sup>3</sup> and aryl<sup>4</sup> have now been reported.<sup>5</sup> Rearrangement of hydrogen from saturated carbon to metal to give carbene complexes has also been frequently postulated, and occasionally the resulting metal hydrides have actually been observed.<sup>6</sup> However, to the best of our knowledge, with one exception in a nickel complex for which this kind of rearrangement was postulated,<sup>7</sup> rearrangement of an alkyl or aryl group from saturated carbon to metal to give a carbene complex had not been observed prior to our chancing upon the photoinitiated rearrangement of **1** to **4**.<sup>8-10</sup> At that time it was suggested that this reaction is



driven by a combination of relief of ring strain (possibly during the ring expansion to the metallacyclobutene **3** and most certainly when the metallacyclobutene expanded to the metallacyclopentenone **4**) and methoxy stabilization of the resulting carbene. This suggestion, which is consistent with Cooper and Green's postulate that the reason for the paucity of such rearrangements is thermodynamic in origin,<sup>11</sup> led us to the further expectation that the same kind of rearrangement should be at least as facile for  $\alpha$ -methoxycyclobutyl and cyclobutenyl complexes of iron since relief of strain in the primary rearrangement step should be even greater than in the cyclopropyl system.

<sup>†</sup> Permanent address: Maria Curie-Skłodowska University, 20-031 Lublin, Poland.

Scheme I



And, indeed, photolysis of both **5** (Scheme I)<sup>9</sup> and **9**<sup>10</sup> was found to give the hoped for carbene complexes **8**, **10**, and **11** in good yield. Furthermore, it was reported that re-

(1) Berke, H.; Hoffman, R. *J. Am. Chem. Soc.* **1979**, *100*, 7224. Goddard, R. J.; Hoffman, R. *Ibid.* **1982**, *102*, 7667.

(2) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. Kemball, C. *Catal. Rev.* **1971**, *5*, 33. Schultz, A. J.; Williams, J. M.; Schrock, R. R. *Catal. Rev.* **1971**, *5*, 33. Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, J. A.; Fellman, J. *J. Am. Chem. Soc.* **1979**, *101*, 1593. Foley, P.; Whitesides, G. *Ibid.* **1979**, *101*, 2732. Ahmed, K. J.; Chirsholm, M. H.; Rothwell, I. P.; Huffmann, J. C. *Ibid.* **1982**, *104*, 6453. Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *Ibid.* **1984**, *106*, 1847. Empsall, H. D.; Hyde, E. M.; Markham, M.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589. Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. Canastrani, M.; Green, M. L. H. *Ibid.* **1982**, 1789. Light, J. R. C.; Zeiss, H. H. *J. Organomet. Chem.* **1970**, *21*, 391. Sneedon, R. P. A.; Zeiss, H. H. *Ibid.* **1971**, *26*, 101. Farady, L.; Marko, L. *Ibid.* **1972**, *43*, 51. Green, J. C.; Green, M. L. H.; Morley, C. P. *Organometallics* **1985**, *4*, 1302.

(3) Taggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 5523. van Leeuwen, P. W. N. M.; Rooback, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 243. Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. Thorn, D. L. *Ibid.* **1985**, *4*, 192 and references cited therein.

(4) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. Jernakoff, P.; Cooper, N. J. *Ibid.* **1984**, *106*, 3026.

(5) Thorn, D. L. *Organometallics* **1985**, *4*, 192 and references cited therein.

(6) For examples, see: Fellman, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608. Turner, H. W.; Schrock, R. R.; Fellman, J. D. *Ibid.* **1983**, *105*, 4942.

(7) Miyashita, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

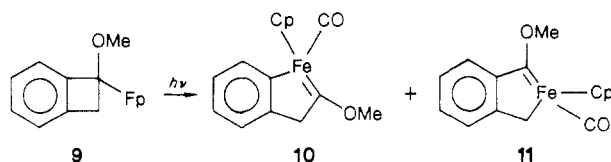
(8) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944.

(9) Stenstrom, Y.; Jones, W. M. *Organometallics* **1986**, *5*, 178.

(10) Stenstrom, Y.; Klauk, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155.

(11) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121.

arrangement of 7 to 8 is apparently reversible since treatment of 8 with CO gave 14 (L = CO), presumably via 7 as depicted in Scheme I.



As part of a program to assess the strain relief and stabilization required to induce rearrangement from saturated carbon to iron, we have now studied the dynamics of some of the reactions depicted in Scheme I and the photochemistry of a number of additional  $\sigma$  and acyl complexes of dicarbonyl( $\eta^5$ -cyclopentadienyl)iron. Included are two amino-substituted cyclobutanes (which rearrange) and two methoxy-substituted rings with less strain than cyclobutane (which do not give rearrangement products). The results of these investigations and an X-ray crystal structure of the amine-stabilized carbene 24b are reported here.

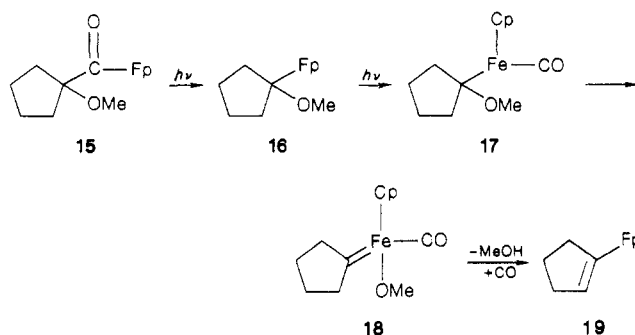
### Results

**Rearrangement of 8 to 14.** With an eye to at least placing boundaries on the energetics of the contraction of 8 to 7, the temperature-dependent  $^{13}\text{C}$  NMR spectrum of 8 was studied. No broadening of the C-3 and C-5 carbon resonances (which can become equivalent upon contraction to 7)<sup>12</sup> occurred. From this we conclude that the minimum energy barrier for the contraction of 8 to 7 is 15.1 kcal/mol (63.3 kJ/mol). An upper limit on the energy barrier for conversion of 8 to 7 was set by studying the reaction of 8 with  $\text{Ph}_3\text{P}$ . Initially, it was shown that 8 reacts with  $\text{Ph}_3\text{P}$  to give the two diastereomers of 14 (L =  $\text{Ph}_3\text{P}$ ). The diastereomers were separated by careful flash chromatography. However, over a period of a few hours they equilibrated back to the original mixture. They were therefore characterized as a mixture.

The absolute rate of the reaction of 8 with 1 equiv of  $\text{Ph}_3\text{P}$  in  $\text{C}_6\text{D}_6$  was determined at 50 °C by monitoring the increase in the Cp resonances at  $\delta$  4.36 and 4.13. A clean second-order plot was obtained to give a second-order rate constant of  $(14.1 \pm 0.5) \times 10^{-3} \text{ L}/(\text{mol}\cdot\text{s})$ , corresponding to  $\Delta G^\ddagger = 21.6 \pm 0.5 \text{ kcal/mol}$  (90.7 kJ/mol). For activation parameters, rates were also determined at 30, 54, and 60 °C. Typical Arrhenius treatment of the data led to  $\Delta H^\ddagger = 24.4 \pm 1.5 \text{ kcal/mol}$  and  $\Delta S^\ddagger = +8 \pm 2 \text{ eu}$ .

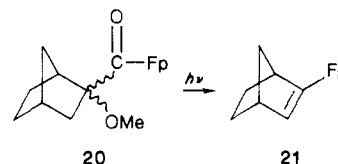
**$\alpha$ -Methoxy Fp-Acyl Complexes of Rings with Less Strain Than Cyclobutane.** In an attempt to determine if methoxy stabilization without substantial strain relief is sufficient to induce rearrangement to the carbene, the Fp-acyl complex 15 was prepared. Photolysis gave no sign of a carbene complex; instead, the only isolated products were the  $\sigma$ -complex 19 (61% isolated yield) and methanol

### Scheme II



(identified by vacuum transfer and comparison with authentic material). We considered this to be an interesting result because, although thermally induced (60 °C) elimination of methanol from an Fp-methoxyalkyl complex has previously been observed, a reaction which Casey noted was not accelerated by added acid,<sup>15</sup> we know of no reported case of photoinduced elimination of methanol from an  $\alpha$ -methoxy Fp-alkyl  $\sigma$ -complex. A reasonable mechanism for this elimination is suggested in Scheme II.<sup>16,19</sup>

In an attempt to determine if rearrangement could be induced by a combination of methoxy stabilization and strain relief that is less than cyclobutane expanding to a metallocyclopentene but might be more than cyclopentane expanding to metallocyclohexene, the norbornyl acyl complex 20 (as a 6:4 mixture of two diastereomers) was prepared and photolyzed.<sup>20</sup> However, once again the primary reaction was elimination of methanol; Fp-norbornene was the major product (>90%), and we could find no evidence for a carbene complex.



**Amine-Substituted Cycloalkanes.** Dialkylamine is a stronger electron donor than methoxy and should therefore induce the rearrangement in eq 1 in systems where less strain is relieved than in the cyclobutane to metallocyclopentene conversion. Unfortunately, synthesis of  $\alpha$ -amino acyl or alkyl complexes comparable to 5 and 15 posed synthetic problems. On the other hand, synthesis of  $\beta$ -amino  $\sigma$ -complexes that could rearrange in a manner analogous to 14 appeared straightforward. To test this idea the cyclobutyl system was initially studied. And, indeed, it was found that addition of either dimethylamine or diisopropylamine to the  $\pi$ -complex 22 led quite smoothly

(15) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* 1982, 104, 3761.

(16) Precedent for the suggested migration of alkoxy from saturated carbon to metal to give a carbene complex can be found for iron<sup>17</sup> and cobalt.<sup>18</sup> However, in neither case was the evidence more substantial than that presented here, i.e., a convenient way to rationalize the final products.

(17) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. J. *Am. Chem. Soc.* 1984, 106, 5363.

(18) Wulff, W. D.; Gilbertson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* 1986, 108, 520.

(19) Methanol elimination from 18 could occur by either migratory insertion of the  $\beta$ -hydrogen followed by reductive elimination or by a cyclic concerted reaction. We have no evidence at this time that would allow us to distinguish between these two possibilities.

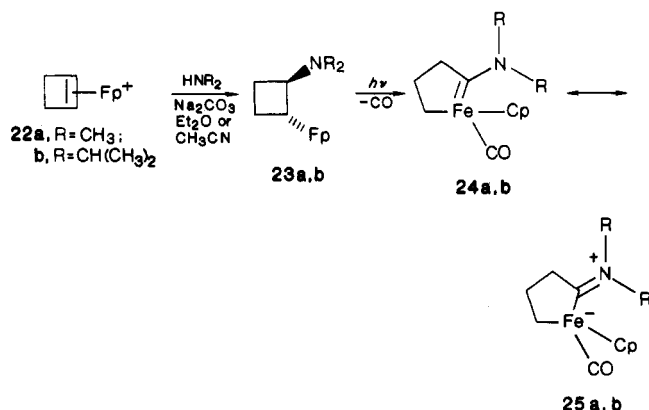
(20) The strain energies of the pertinent metallocyclooctenes are not known. However, from models it appears that the preferred 90° bond angle in the pseudooctahedral Fp-carbene complexes would lead to a modest decrease in strain relative to carbon analogues.

(12) 7 is not a symmetrical molecule. As a result, its mere formation does not automatically guarantee equivalence of C-3 and C-5 upon reexpansion. Once 8 has contracted to 7, C-3 and C-5 can become equivalent by two different routes. In one, the initially formed and presumably asymmetric iron in 7 could racemize. Although this racemization process has been studied both theoretically<sup>13</sup> and experimentally<sup>14</sup> for representative iron systems and although both suggest finite inversion barriers, to our knowledge the height of this barrier is unknown. C-3 and C-5 can also become equivalent, if the expansion of 7 to 8 simply takes place from a different conformation from that which was initially formed. Although these two conformations would be of different energies, it is presumed that their equilibration would be fast, relative to the expansion process.

(13) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 536.

(14) Cf. Flood, T. C.; Campbell, K. D. *J. Am. Chem. Soc.* 1984, 106, 2853.

to **23a** and **23b**, respectively. Furthermore, photolysis of either **23a** or **23b** gave the corresponding carbene complexes **24a** and **24b** in good yields. Structure assignments



to the two new carbene complexes are based on spectroscopic data and elemental analyses and, in one case, X-ray analysis. The <sup>13</sup>C NMR spectra provided the most convincing initial evidence for carbene structures; both **24a** and **24b** showed low-field carbene carbon resonances (**24a** at  $\delta$  286.79 and **24b** at  $\delta$  285.02) and high-field methylene resonances (**24a** at  $\delta$  11.33 and **24b** at  $\delta$  10.17) that are characteristic of saturated carbon bound to iron. In addition, each complex showed only one carbonyl carbon (in the <sup>13</sup>C and IR) which, from the IR frequencies, could be assigned to terminal carbonyls.

The carbene complex with the diisopropylamino group showed some unusual features in its <sup>1</sup>H NMR which we felt warranted closer examination. In the first place, the methyl resonances of the two isopropyl groups appeared as four resolved doublets which showed no change up to 78 °C. From this we conclude that rotation about the carbene-carbon nitrogen bond is slow on the NMR time scale ( $E_a > 16.1$  kcal/mol; 67.7 kJ/mol). This is presumably due to substantial contribution from resonance form **25**. Perhaps it should also be pointed out that if rotation is restricted around the carbene carbon-nitrogen bond, none of the four methyls are equivalent since the two methyl groups of each isopropyl group are diastereotopic.

Another very interesting feature of the <sup>1</sup>H NMR spectrum of **24b** is the chemical shift of one of the isopropyl methine hydrogens which appears at  $\delta$  5.17, nearly 2.5 ppm downfield from its progenitor and 1.81 ppm downfield from the methine of the other isopropyl. The most likely reason for this rather dramatic chemical shift is apparent from molecular models which show one of the methine hydrogens forced into the deshielding region of the cyclopentadiene ring. This conclusion was confirmed by nOe experiments (Table I) where it was found that irradiation of the Cp hydrogens led to a 15% increase in intensity of the low-field methine.<sup>21</sup> The nOe experiment also shed interesting light on the preferred conformation of the other isopropyl group. From decoupling experiments it was found that the highest and lowest field methyl doublets are coupled to the low-field methine while the two methyls in the middle belong to the high-field methine. In the nOe experiments, it was found that irradiation of the high-field methyl led to substantial enhancement of both methines (15% and 12% to the low- and high-field resonances, re-

Table I.<sup>a</sup> Nuclear Overhauser Effect Study of **24b**<sup>b</sup>

nOe	irradiation of						
	Cp	C8	C81 + C82	C7	C71	C72	C3
Cp		c	1.2	15.1	1.7	1.1	c
C81 + C82	1.8	15.7		c	c	c	14.5
C71	3.5	11.6	c	14.5		c	c
C72	c	c	c	12.4	9.2		c

<sup>a</sup> All numbers are percent increases. <sup>b</sup> See ORTEP plot for numbering. <sup>c</sup> No effect or percent increase too small to be significant.

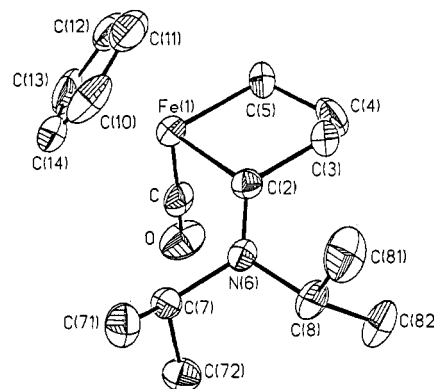


Figure 1. The 1-carbonyl-1-( $\eta^5$ -cyclopentadienyl)-2-(diisopropylamino)-1-ferracyclopentene (**24b**) molecules illustrating the atomic numbering and 35% probability thermal ellipsoids.

spectively) while irradiation of the two methyls coupled to the high-field methine led to an enhancement (16%) of its intensity while not affecting the low-field methine. From this we conclude that not only is rotation about the carbene-carbon nitrogen bond restricted but also that the isopropyl groups reside primarily in the conformation that is found in the solid state by X-ray crystallography (Figure 1).

The distances and angles of **24b** clearly support the carbene formulation. The Fe-C(2) distance of 1.927 (4) Å is significantly longer than the distances found in two other iron carbene complexes. In the dioxozirconacyclopenta-3,4-diylidene diiron group, a distance of 1.82 (2) Å was reported<sup>22</sup> while a distance of 1.827(6) Å was found in the ferracyclic ring of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C(OCH<sub>3</sub>)<sub>10</sub>. However, similar distances of 1.916 (2) Å were found in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)(C<sub>6</sub>H<sub>5</sub>)CNH(C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)<sub>23</sub> and 1.932 (3) Å in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)[(C=NC<sub>6</sub>H<sub>11</sub>)(CNHC<sub>6</sub>H<sub>11</sub>)CH{CNHC(CH<sub>3</sub>)<sub>3</sub>}].<sup>24</sup> The latter complex is particularly relevant, since the carbene carbon was bonded to a NHC(CH<sub>3</sub>)<sub>3</sub> group via a short (1.336 (4) Å) C-N bond. In both our structure and the latter complex there is appreciable double-bond character in the C-N bond, supporting the canonical form **25**. A pure C=N distance is about 1.28 Å,<sup>25</sup> which is significantly shorter than the value in **24b**, 1.317 (6) Å, or in the closely related structure, 1.336 (4) Å.<sup>24</sup> Consequently, longer Fe=C bonds appear when single bond forms such as **25** can be postulated for the metallocycle. The Fe-C(5) distance of 2.044 (5) Å is shorter than the "best" Fe-C(sp<sup>3</sup>) bond distance of 2.0977 (23) Å.<sup>26</sup>

(22) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* 1982, 104, 4712.

(23) Adams, R. D.; Chodos, D. F.; Golembeski, N. M.; Weissmann, E. C. *J. Organomet. Chem.* 1979, 172, 251.

(24) Aoki, K.; Yamamoto, Y. *Inorg. Chem.* 1976, 15, 48.

(25) (a) Naik, N. V.; Palenik, G. J. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* 1974, B30, 2396. (b) Palenik, G. J.; Rendle, D. F.; Carter, W. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1974, B30, 2390.

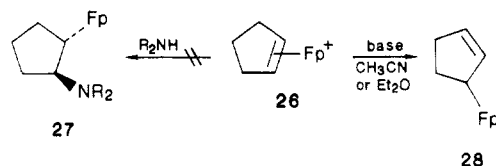
(26) Churchill, M. R.; Ni Chang, S. W.-Y. *J. Am. Chem. Soc.* 1973, 95, 5931.

(21) For some unexplained reason, the resolution of the <sup>1</sup>H NMR spectrum of this complex tended to decrease with broadening of the resonances as the field strength increased making the spectra obtained at 100 MHz generally superior to those obtained at either 60, 200, or 300 MHz. However, despite this, the resolution at 300 MHz was satisfactory for the nOe experiments.

However, the shorter Fe–C distances in metallacyclic rings have been noted previously.<sup>20</sup> Finally, torsion angles in the ferracyclopentene ring are typical of the half-chair conformation of a C<sub>5</sub> ring.

The distances H(7) to C(10) of 2.88 Å and to C(14) of 2.69 Å represent the short end of van der Waals contacts. However, the C(7)–H(7) distance of 0.95 Å is probably too short.<sup>27</sup> However, the main point is that H(7) is pointing toward the Cp ring, as predicted from the NMR results. The H(7)–Cp ring interaction is reflected in the possibly significantly longer Fe–C(10) and Fe–C(14) distances, 2.117 (7) and 2.119 (6) Å, relative to the other Fe–C ring distances of 2.103 (7), 2.085 (4), and 2.091 (5) Å. The C–C distances in the Cp ring, the ferracyclopentene ring, and the isopropyl groups are in agreement with the expected values.

Having found that  $\beta$ -amino Fp-cyclobutyl complexes rearrange, we next turned our attention to attempts (unsuccessful to date) to prepare the cyclopentyl  $\beta$ -amino complex 27 by treating the  $\pi$ -complex 26 with dimethylamine or diisopropylamine under slightly basic conditions. Unfortunately, instead of displacing the iron as was observed for the cyclobutene complex, in this case the only isolable iron containing product was the  $\beta$ -hydrogen abstraction product 28.<sup>28</sup> The result was the same whether



CH<sub>3</sub>CN or diethyl ether was used as the solvent and whether Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> was used as the base. In separate experiments it was confirmed that the proton abstraction was caused by the amines; treatment of the  $\pi$ -complex 26 with Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> in CH<sub>2</sub>CN required several days for proton abstraction while the reactions with the amines were complete in less than an hour. We are continuing our efforts along this line.

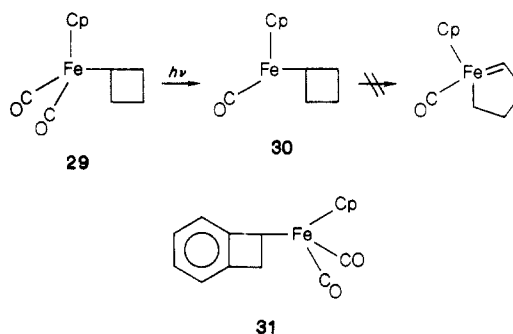
### Discussion

In a preliminary communication we reported our finding that a solution of 8 in C<sub>6</sub>D<sub>6</sub> under 6.5 atm of CO at room temperature lost its red color over a period of a few hours to give 14 (L = CO) in essentially quantitative yield.<sup>9</sup> The mechanism in Scheme I was proposed for this reaction with the further suggestion that, although none of the intermediates could be seen in the <sup>1</sup>H NMR, 8 is probably in equilibrium with 7, 12, and 13 at room temperature since the only obvious role of the added carbon monoxide to the overall scheme was trapping of 13. Since the hydrogens on C-3 and C-5 of 8 can become equivalent as a result of contraction to 7, followed by either (or both) inversion at the metal center of the 16-electron iron intermediate or expansion back to 8 from a different conformation,<sup>12</sup> the finding that treatment of 8 with CD<sub>3</sub>O<sup>−</sup> in CD<sub>3</sub>OD led to rapid and complete deuteration of both C-3 and C-5 lent strong support to the contention that 8 is in equilibrium with 7 at room temperature.

It has been suggested<sup>11</sup> that the reason alkyl groups normally do not migrate from saturated carbon to coordinatively unsaturated transition metals is thermodynamic in origin; i.e., the rearrangement would normally be en-

ergetically uphill. Our results are consistent with this suggestion for the carbonyl ( $\eta^5$ -cyclopentadienyl)iron system for the following reason. Although we have not yet been successful in measuring the absolute rate of the reaction, the facile deuterium scrambling between C-3 and C-5 of 8 at room temperature suggests a relatively low activation barrier for contraction of 8 to 7. This is supported by the activation parameters for the reaction of 8 with triphenylphosphine to give 14 (L = Ph<sub>3</sub>P) which limit the activation enthalpy for contraction to 7 to no more than 25–26 kcal/mol. This, in turn, places the same limit on the energy separating 8 from 7. Since this is in the range of the ring strain that could be relieved upon expansion of a cyclobutane ring<sup>29</sup> to a metallocyclopentene,<sup>30</sup> it is quite possible that rearrangement of an unstrained  $\alpha$ -methoxy  $\sigma$ -complex would be energetically uphill.

Furthermore, if the methoxy substituent stabilizes the carbene center of 8 more effectively than it does the  $\sigma$ -complex 7 (possibly by oxygen chelation to the metal), then rearrangement of an alkyl group from an unsubstituted 16-electron iron  $\sigma$ -complex to give its carbene isomer should be even less energetically favorable than the methoxy-substituted relative (strained or unstrained). That this is probably the case is supported by the fact that no rearrangement is observed when the unsubstituted 16-electron intermediate 30 is generated by photolysis of 29 and even 31, a system in which substantially more strain



relief would be realized<sup>10</sup> also shows no evidence of rearranging, unless an electron-donating substituent is present. It therefore appears highly likely that the rearrangement of an alkyl group from saturated carbon to the 16-electron iron system discussed here would be an energetically uphill process.

### Experimental Section

**General Data.** All reactions were performed in an atmosphere of nitrogen on a vacuum line using Schlenk-type flasks. Solvents and reagents were appropriately dried and purified. THF, hexane, and ether were distilled from K/Na alloy under nitrogen. Methylene chloride was distilled from Sicapent (MCB). Melting points: Thomas-Hoover melting point apparatus. All melting points are uncorrected. <sup>1</sup>H NMR spectra: Varian EM-360, JEOL FX-100, Varian XL-200, and Nicolet NT-300 spectrometers. <sup>13</sup>C NMR spectra: JEOL FX-100, Varian XL-200, and Nicolet NT-300 spectrometers. IR spectra: Perkin-Elmer 137 spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. Mass spectra: AEI MS-30 spectrometer. Photolyses were carried out by using a 450-W low-pressure Hg Hanovia lamp in a Pyrex well. Transfer needles from Aldrich were used (18 and 20 gauge, stainless steel, double tip). When

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(28) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Risan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. J. *Am. Chem. Soc.* 1976, 98, 3495.

(29) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

(30) The actual strain relieved would depend on the ring strain in 8. To our knowledge, no value is available for the strain energy of a ferracyclopentene, although models suggest that this may be less than the strain in cyclopentene.

referring to flash chromatography, 230–400-mesh silica gel was used.

**Photolysis of Acyl Complexes.** The acyl complex was dissolved in degassed  $C_6D_6$  in an NMR tube equipped with a boiling chip and a septum with a syringe needle joined to a  $N_2$  line. The photolyses were usually done at 15–25 °C, and the reactions were monitored by  $^1H$  NMR and by the evolution of CO. The products were isolated by flash chromatography. Both **15** and **20** gave methanol as identified by vacuum transferring it and comparing it with authentic material.

**Kinetic Measurements.** In a typical experiment 1 equiv of **8** was mixed with 0.85–1.2 equiv of  $Ph_3P$  in an accurately measured volume of  $C_6D_6$ . The reaction mixture was heated to a fixed temperature, and the progress of the reaction was monitored by the relative areas of the Cp's of two diastereomers of **14** ( $L = Ph_3P$ ) and the carbene **8**. Second-order plots were made to give the rate constants  $k_r$  for each reaction. The least-squares method was used for refinement of  $k_r$ .

**Synthesis of 1-Methoxycyclobutanecarboxylic Acid.** A solution of 5.0 g (50 mmol) of cyclobutanecarboxylic acid in 40 mL of THF was added to a solution of 125 mmol of lithium diisopropylamide (made from 12.6 g (125 mmol) of diisopropylamine and 83 mL of 1.5 M (125 mmol) MeLi in ether) in 200 mL of THF. The mixture was stirred overnight and the flask immersed in a cooling bath at room temperature. Dry oxygen was bubbled through the solution for ca. 2 h. The solution was washed thoroughly with 20%  $Na_2SO_3$ (aq). The aqueous phase was acidified with 6 N HCl, saturated with NaCl, and extracted several times with ether. The combined organic phases were washed with a small amount of water and brine, dried ( $MgSO_4$ ), and evaporated to give 5.85 g (100%) of the 1-hydroxycyclobutanecarboxylic acid as an oil. The crude product was dissolved in 220 mL of THF and added to 4.2 g (175 mmol) of NaH, and 25 g (176 mmol) of MeI was introduced. The mixture was kept at 25–30 °C for ca. 36 h when the reaction was quenched with 20 mL (20%) of  $Na_2SO_3$ (aq). After thorough stirring for ca. 1 h, the aqueous phase was acidified with 6 N HCl(aq), saturated with brine, and extracted several times with ether. The combined extracts were washed with a small amount of brine, dried ( $MgSO_4$ ), and evaporated to give 5.4 g (80%) of the  $\alpha$ -methoxy acid as an oil which gave white crystals upon standing. Although the crude product was pure enough for all practical purposes, the acid could be distilled by Kugelrohr (100–120 °C/0.025 mmHg) or recrystallized from pentane for analytical samples. The spectroscopic data have been published previously.<sup>9</sup>

**1-Methoxycyclobutanecarboxylic Acid Chloride.** To a solution of 1.64 g (12.6 mmol) of the carboxylic acid in 5 mL of ether was added 3.2 g (25.2 mmol) of oxalyl chloride. The mixture was stirred at room temperature for 3 h, carefully evaporated, and distilled on a Kugelrohr (50–60 °C/0.025 mmHg) to yield 1.61 g (86%): IR ( $CDCl_3$ ) 1775  $cm^{-1}$ ;  $^1H$  NMR (60 MHz,  $CDCl_3$ ):  $\delta$  1.4–2.5 (m, 6 H), 3.05 (s, 3 H,  $CH_3O$ );  $^{13}C$  NMR (25 MHz,  $CDCl_3$ ):  $\delta$  11.70 ( $CH_2$ ), 30.07 ( $CH_2 \times 2$ ), 52.10 ( $CH_3O$ ), 86.46 (C), 176.33 (C=O).

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)(1-methoxycyclobutyl-1-carbonyl)iron (5).** To a stirred suspension of 1.32 g (6.1 mmol) of KFp in 15 mL of THF cooled to 0 °C was added 0.82 g (5.6 mmol) of acid chloride in 5 mL of THF. The mixture was stirred overnight at room temperature when the solvent was evaporated. The residue was dissolved in  $CH_2Cl_2$ , filtered through Celite, evaporated, and flash chromatographed. A small amount of the  $\sigma$ -complex **6** and  $Fp_2$  could be eluted with methylene chloride–hexane, 6:4. Then the solvent was changed to ethyl acetate–hexane, 1:1, to give 1.14 g (71%) of **5**. The spectroscopic data have been published elsewhere.<sup>9</sup>

**Carbonyl(triphenylphosphine)( $\eta^5$ -cyclopentadienyl)-*trans*-2-methoxycyclobut-1-yl)iron (14) ( $L = Ph_3P$ ).** A mixture of 67 mg (0.29 mmol) of **8** and 85 mg (0.32 mmol) of  $Ph_3P$  in 0.5 mL of  $C_6D_6$  was heated to 70 °C for ca. 10 min.  $^1H$  NMR showed two new Cp's in a ratio of 58:42. Flash chromatography (ethyl acetate–hexane, 1:9 v/v) gave 78 mg (55%) and 60 mg (42%) of two compounds that equilibrated back to the original 58:42 mixture in a few hours at room temperature. Major isomer: IR ( $C_6D_6$ ) 1905  $cm^{-1}$ ;  $^1H$  NMR (100 MHz,  $C_6D_6$ )  $\delta$  1.1–1.4 (m, 3 H), 1.7–2.1 (m, 1 H), 2.2–2.4 (m, 1 H), 3.09 (s, 3 H,  $OCH_3$ ), 3.6–3.8 (m, 1 H), 4.38 (d,  $^3J_{PH} = 1.1$  Hz, 5 H, Cp), 6.9–7.1 (m, 3 H), 7.5–7.7

(m, 2 H);  $^{13}C$  NMR (25 MHz,  $C_6D_6$ )  $\delta$  25.86 (CH), 26.83 ( $CH_2$ ), 32.87 ( $CH_3$ ), 54.32 ( $OCH_3$ ), 84.82 (Cp), 89.21 (CH), 128.29 (CH), 129.36 (CH), 133.61 (d,  $^2J_{PC} = 10$  Hz, CH), 138.23 (d,  $^1J_{PC} = 39$  Hz, C), 224.00 (CO). Minor isomer: IR ( $C_6D_6$ ) 1905  $cm^{-1}$ ;  $^1H$  NMR (100 MHz,  $C_6D_6$ )  $\delta$  1.2–1.4 (m, 2 H), 1.7–2.1 (m, 2 H), 2.3–2.9 (m, 1 H), 3.05 (s, 3 H,  $OCH_3$ ), 3.2–3.6 (m, 1 H), 4.12 (d,  $^3J_{PH} = 1.2$  Hz, 5 H, Cp), 6.9–7.1 (m, 3 H), 7.5–7.7 (m, 2 H);  $^{13}C$  NMR (25 MHz,  $C_6D_6$ )  $\delta$  27.71 (CH), 29.17 ( $CH_2$ ), 32.58 ( $CH_2$ ), 54.90 ( $OCH_3$ ), 85.31 (Cp), 88.04 (CH), 128.29 (CH), 129.27 (CH), 133.56 (d,  $^2J_{PC} = 10$  Hz, CH), 137.84 (d,  $^1J_{PC} = 39$  Hz, C), 223.42 (CO). Anal. Calcd for the mixture of the two diastereomers ( $C_{29}H_{29}FeO_2P$ ): C, 70.17; H, 5.89. Found: C, 70.09; H, 6.15.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[(1-methoxycyclopentyl)carbonyl]iron (15)** was synthesized in exactly the same fashion as **5**. The  $\alpha$ -hydroxy acid was made quantitatively, the  $\alpha$ -methoxy acid<sup>31</sup> in 85% yield, and the acid chloride in 80%. A mixture of 3.08 g (14.3 mmol) of KFp in 35 mL of THF and 1.68 g (10.3 mmol) of acid chloride in 5 mL of THF followed by usual workup and flash chromatography (methylene chloride–hexane, 1:1, followed by ethyl acetate–hexane, 2:8) gave 1.91 g (61%) of **15**: IR ( $CDCl_3$ ) 2010, 1958, 1630  $cm^{-1}$ ;  $^1H$  NMR (100 MHz,  $C_6D_6$ )  $\delta$  1.2–1.8 (m, 8 H), 2.98 (s, 3 H,  $OCH_3$ ), 4.31 (s, 5 H, Cp);  $^{13}C$  NMR (25 MHz,  $C_6D_6$ )  $\delta$  24.59 ( $CH_2 \times 2$ ), 33.07 ( $CH_2 \times 2$ ), 51.69 ( $CH_3O$ ), 86.68 (Cp), 101.49 (C), 216.20 (terminal CO), 259.58 (bridging CO); mass spectrum,  $m/e$  276 ( $M^+ - CO$ ), 205 ( $FeCp(CO)_3^+$ ), 121 ( $FeCp^+$ ), 99 ( $M^+ - FeCp(CO)_3$ , 100). Anal. Calcd for  $C_{14}H_{16}FeO_4$ : C, 55.29; H, 5.30. Found: C, 55.03; H, 5.36.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)(1-cyclopentenyl)iron (19):** IR ( $CDCl_3$ ) 2005, 1995  $cm^{-1}$ ;  $^1H$  NMR (100 MHz,  $C_6D_6$ )  $\delta$  1.5–2.0 (m, 4 H), 2.1–2.6 (m, 4 H), 4.10 (s, 5 H, Cp), 5.69 (m, 1 H);  $^{13}C$  NMR (25 MHz,  $C_6D_6$ )  $\delta$  24.88 ( $CH_2$ ), 35.02 ( $CH_2$ ), 49.35 ( $CH_2$ ), 85.02 (Cp), 137.84 ( $CH=$ ), 141.74 ( $C=$ ), 216.79 (CO). The compound was not stable enough for either MS or elemental analyses. Anal. Calcd for  $C_{12}H_{12}FeO_2$ : C, 59.05; H, 4.96. Found: C, 56.95; H, 5.15. The structure seems likely from the NMR data and also by analogy with the reaction of **20** to give **21**.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[(1-methoxynorbornyl)carbonyl]iron (20)** was synthesized in the same manner. The  $\alpha$ -hydroxy acid was made quantitatively from the carboxylic acid; methoxylation gave 83% of a 62:38 mixture of the two epimeric acids after Kugelrohr (40–60 °C/0.05 mmHg). The acid chloride was made in 80% yield. A mixture of 3.30 g (15.3 mmol) of KFp in 40 mL of THF and 2.80 g (14.8 mmol) of acid chloride in 5 mL of THF gave after flash chromatography (acetone–hexane, 15:85) 3.26 g (65%) of **20** as a 6:4 mixture: IR ( $CDCl_3$ ) 2010, 1960, 1640  $cm^{-1}$ ;  $^1H$  NMR (100 MHz,  $C_6D_6$ )  $\delta$  0.9–3.0 (m,  $2 \times 10$  H), 2.93 (s, 3 H,  $OCH_3$  major isomer), 3.00 (s, 3 H,  $OCH_3$  minor isomer), 4.22 (s, 5 H, Cp minor isomer), 4.26 (s, 5 H, Cp major isomer);  $^{13}C$  NMR (25 MHz,  $C_6D_6$ )  $\delta$  22.35, 22.54, 28.59, 29.76, 35.41, 36.77, 37.16, 37.55, 37.94, 39.99, 41.74, 44.47 (aliphatic C's), major isomer, 51.01 ( $OCH_3$ ), 87.16 (Cp), 101.49 (C), 216.21, 216.50 (terminal CO's), 260.07 (bridging CO), minor isomer, 53.34 ( $OCH_3$ ), 86.77 (Cp), 99.35 (C), 216.01 (terminal CO's), 258.21 (bridging CO); mass spectrum,  $m/e$  (as a 6:4 mixture) 302 ( $M^+ - CO$ ), 125 ( $M^+ - FeCp(CO)_3$ , 100), 96 ( $C_5H_5OCH_3^+$ ). Anal. Calcd for  $C_{16}H_{18}FeO_4$  (as a 6:4 mixture): C, 58.21; H, 5.50. Found: C, 58.21; H, 5.57.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)(2-norbornenyl)iron (21):** IR ( $C_6D_6$ ) 2005, 1960  $cm^{-1}$ ;  $^1H$  NMR (100 MHz,  $C_6D_6$ )  $\delta$  0.6–3.1 (m, 8 H), 4.19 (s, 5 H, Cp), 5.98 (b s, 1 H);  $^{13}C$  NMR (25 MHz,  $C_6D_6$ )  $\delta$  24.59 ( $CH_2$ ), 27.81 ( $CH_2$ ), 44.96 (CH), 48.57 ( $CH_2$ ), 57.63 (CH), 85.12 (Cp), 144.96 ( $CH=$ ), 146.91 ( $C=$ ), 216.50 (CO), 216.79 (CO); mass spectrum,  $m/e$  270 ( $M^+$ ), 242 ( $M^+ - CO$ ), 214 ( $M^+ - 2 CO$ , 100), 186 ( $Cp_2Fe^+$ ), 121 ( $Fe - Cp^+$ ); high-resolution MS calcd for  $C_{13}H_{14}FeO$  ( $M^+ - CO$ ) 242.0394, found 242.0371; high-resolution MS calcd for  $C_{12}H_{14}Fe$  ( $M^+ - 2 CO$ ) 214.0444, found 214.0446. Anal. Calcd for  $C_{14}H_{14}FeO_2$ : C, 62.25; H, 5.22. Found: C, 62.11; H, 5.46.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[*trans*-2-(dimethylamino)cyclobut-1-yl]iron (23a).** Approximately 5 mL of dry, degassed  $CH_3CN$  was vacuum transferred to a flask containing 100 mg (0.32 mmol) of **22**, 41.7 mg (0.39 mmol) of  $Na_2CO_3$ , and a magnetic stirrer. Then ca. 0.5 mL (16 mmol) of  $Me_2NH$  was vacuum transferred into the same flask which was closed and

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heated up to  $-20$  to  $-10$  °C and stirred for 1.5 h. The mixture was stirred for another 1 h at 0 °C. The solvent was evaporated and the residue washed with ether and filtered through Celite. Evaporation, chromatography (basic alumina, activity III, ethyl acetate-hexane, 1:3) yielded 57.2 mg (65%) of **23a**: IR ( $\text{C}_6\text{D}_6$ ) 2000, 1940  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (60 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.5–2.3 (m, 4 H), 2.13 (s, 6 H), 2.8–3.2 (m, 2 H), 4.33 (s, 5 H);  $^{13}\text{C}$  NMR (25 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  24.49 ( $\text{CH}_2$ ), 25.66 (CH), 30.24 ( $\text{CH}_2$ ), 40.96 ( $\text{CH}_3 \times 2$ ) 75.37 (CH), 84.63 (Cp), 217.63 (CO), 218.16 (CO).

**1-Carbonyl-1-( $\eta^5$ -cyclopentadienyl)-2-(dimethylamino)-1-ferracyclopentene (24a).** A solution of 28.1 mg (0.10 mmol) of **23a** in 0.5 mL of  $\text{C}_6\text{D}_6$  in an NMR tube equipped with a boiling chip, a septum, and a  $\text{N}_2$  inlet was photolyzed for ca. 1 h. The reaction was monitored by  $^1\text{H}$  NMR. Evaporation followed by flash chromatography (ethyl acetate-hexane, 2:8) gave 20.9 mg (85%) of **24a**: IR ( $\text{C}_6\text{D}_6$ ) 1895  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.65–1.80 (m, 1 H), 1.85–2.10 (m, 4 H), 2.15–2.30 (m, 1 H), 2.17 (s, 3 H,  $\text{CH}_3$ ), 3.06 (s, 3 H,  $\text{CH}_3$ ), 4.26 (s, 5 H, Cp);  $^{13}\text{C}$  NMR (50 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  11.33 ( $\text{CH}_2$ ), 33.78 ( $\text{CH}_2$ ), 40.83 ( $\text{CH}_3$ ), 50.83 ( $\text{CH}_3$ ), 51.95 ( $\text{CH}_2$ ), 83.64 (Cp), 224.14 (CO), 286.79 (carbene C); mass spectrum,  $m/e$  calcd for  $\text{C}_{15}\text{H}_{17}\text{FeNO}$  247.0676, found 247.0659.

**Dicarbonyl( $\eta^5$ -cyclopentadienyl)[*trans*-2-(diisopropylamino)cyclobut-1-yl]iron (23b).** To a suspension of 100 mg (0.32 mmol) of **22** in 5 mL of ether was added 41.7 mg (0.39 mmol) of  $\text{Na}_2\text{CO}_3$  and 35.0 mg (0.35 mmol) of diisopropylamine. After 1 h of vigorous stirring at room temperature, the mixture was filtered over Celite, evaporated, and chromatographed (basic alumina, activity III, ethyl acetate-hexane, 1:9) to yield 76.3 mg (72%) of **23b**: mp (hexane) 38–39 °C; IR ( $\text{C}_6\text{D}_6$ ) 1997, 1940  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.93 (d,  $J = 6.5$  Hz, 6 H,  $\text{CH}_3 \times 2$ ), 1.08 (d,  $J = 6.7$  Hz, 6 H,  $\text{CH}_3 \times 2$ ), 1.4–1.6 (m, 1 H), 1.7–2.4 (m, 3 H), 2.9–3.2 (m, 4 H), 4.36 (s, 5 H, Cp);  $^{13}\text{C}$  NMR (25 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  21.96 ( $\text{CH}_3 \times 2$ ), 23.52 ( $\text{CH}_3 \times 2$ ), 29.07 (CH), 31.02 ( $\text{CH}_2$ ), 35.12 ( $\text{CH}_2$ ), 44.96 (CH  $\times 2$ ), 65.43 (CH), 84.43 (Cp), 218.16 (CO  $\times 2$ ); mass spectrum,  $m/e$  331 ( $\text{M}^+$ ), 303 ( $\text{M}^+ - \text{CO}$ ), 186 ( $\text{Cp}_2\text{Fe}^+$ ), 154 ( $\text{M}^+ - \text{Fp}$ ), 153 ( $\text{M}^+ - \text{FpH}$ ), 121 ( $\text{Fe}-\text{Cp}^+$ ), 96, 70, 28; high-resolution MS calcd for  $\text{C}_{17}\text{H}_{25}\text{FeNO}_2$  ( $\text{M}^+$ ) 331.1234, found 331.1272. Anal. Calcd for  $\text{C}_{17}\text{H}_{25}\text{FeNO}_2$ : C, 61.64; H, 7.61. Found: C, 61.55; H, 7.66.

**1-Carbonyl-1-( $\eta^5$ -cyclopentadienyl)-2-(diisopropylamino)-1-ferracyclopentene (24b).** Photolysis of a solution of a 200 mg (0.60 mmol) of **23b** in 1 mL of  $\text{C}_6\text{D}_6$  in an NMR tube as for **23a** for 2.5 h gave after evaporation and flash chromatography (ethyl acetate-hexane, 2:8) 122 mg (67%) of **24b**: mp (methylene chloride-hexane, 5:95) 95–96 °C; IR ( $\text{C}_6\text{D}_6$ ) 1885  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  0.79 (d,  $J = 7.0$  Hz, 3 H,  $\text{CH}_3$ ), 0.89 (d,  $J = 7.1$  Hz, 3 H,  $\text{CH}_3$ ), 0.93 (d,  $J = 7.2$  Hz, 3 H,  $\text{CH}_3$ ), 1.06 (d,  $J = 6.8$  Hz, 3 H,  $\text{CH}_3$ ), 1.2–2.1 (m, 2 H), 2.2–2.8 (m, 3 H), 2.9–3.1 (m, 1 H), 3.2–3.4 (m, 1 H), 4.28 (s, 5 H), 5.6–5.8 (m, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  10.17 ( $\text{CH}_2$ ), 20.01 ( $\text{CH}_3$ ), 20.16 ( $\text{CH}_3$ ), 22.26 ( $\text{CH}_3$ ), 22.55 ( $\text{CH}_3$ ), 34.05 ( $\text{CH}_2$ ), 50.25 (CH), 53.48 ( $\text{CH}_2$ ), 65.03 (CH), 83.48 (Cp), 224.62 (CO), 285.02 (carbene C); mass spectrum,  $m/e$  303 ( $\text{M}^+$ ), 275 ( $\text{M}^+ - \text{CO}$ ), 232 ( $\text{M}^+ - (\text{CO} + \text{CH}(\text{CH}_3)_2)$ ), 186 ( $\text{Cp}_2\text{Fe}^+$ ), 121 ( $\text{Fe} - \text{Cp}^+$ ); high-resolution MS calcd for  $\text{C}_{16}\text{H}_{25}\text{FeNO}(\text{M}^+)$  303.1285, found 303.1293. Anal. Calcd for  $\text{C}_{16}\text{H}_{25}\text{FeNO}$ : C, 63.38; H, 8.31. Found: C, 63.17; H, 8.37.

Crystals suitable for X-ray analyses were grown from a methylene chloride-hexane (5:95) solution by slow evaporation of the solvent at  $-20$  °C.

**Reaction of Amines with  $\pi$ -Complex 26 in Ether.** To a suspension of 100 mg (0.30 mmol) of **26** in 5 mL of ether was added 35.0 mg (0.35 mmol) of diisopropylamine and 41.7 mg (0.39 mmol) of  $\text{Na}_2\text{CO}_3$ . After the solution was stirred for 1 h, TLC showed only one major product. Filtration over Celite, evaporation, and chromatography over basic alumina, activity III (ethyl acetate-hexane, 1:9), gave 45 mg (62%) of the allylic  $\sigma$ -complex **28** with spectroscopic properties identical with those published in the literature.<sup>28</sup>

**In  $\text{CH}_3\text{CN}$ .** On the same scale as above replacing ether with 5 mL of  $\text{CH}_3\text{CN}$  and with a similar workup procedure, **28** was isolated in 67% yield with dimethylamine and in 61% yield with diisopropylamine.

**X-ray Data Collection, Structure Determination, and Refinement for 24b.** Crystals for X-ray analysis were grown from hexane by slow evaporation at  $-20$  °C. All measurements were made by using a Nicolet R3m diffractometer. Relevant crystal

**Table II. Crystal Data for  $\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)[\text{C}_4\text{H}_6\text{N}(\text{C}_3\text{H}_7)_2]$  (24b)**

formula	$\text{C}_{16}\text{H}_{25}\text{NOFe}$
fw	303.227
space group	<i>Pbca</i>
<i>a</i> , Å	12.735 (7)
<i>b</i> , Å	16.933 (5)
<i>c</i> , Å	14.768 (8)
<i>V</i> , Å <sup>3</sup>	3185 (3)
<i>Z</i>	8
<i>D</i> <sub>calcd</sub> / <i>D</i> <sub>obsd</sub> , g cm <sup>-3</sup>	1.26/1.20 (KI solution)
temp, °C	26
$\lambda(\text{Mo K}\alpha)$ , Å	0.71073; graphite monochromator
$\mu$ , cm <sup>-1</sup>	9.7
cryst size, mm	0.19 $\times$ 0.12 $\times$ 0.27
type of scan	$\theta$ - $2\theta$
scan width, deg	$K\alpha_1 - K\alpha_2 \pm 1.1$
scan speed, deg mm <sup>-1</sup>	2.0–2.93
bkgd counting	$1/2$ of peak-scan time on each side of the peak
data collection	1.5–45
range, $2\theta$ , deg	
total unique data	2082
data with $F \geq 2\sigma(F)$	1550
no. of parameters	172
refined	
<i>R</i> ( <i>F</i> )	0.059
<i>R</i> <sub>w</sub> ( <i>F</i> )	0.030
GOF	1.79
max $\Delta/\sigma$ for final cycle	0.06
max peak in diff map, e Å <sup>-3</sup>	0.32

**Table III. Final Positional Parameters ( $\times 10^4$ ) and Equivalent Isotropic Thermal Parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Fe}(\text{CO})(\text{C}_5\text{H}_5)[\text{C}_4\text{H}_6\text{N}(\text{C}_3\text{H}_7)_2]$  (24b)**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sup>a</sup>
Fe(1)	796 (1)	2301 (1)	907 (1)	44 (1)
C	424 (4)	2641 (3)	-128 (4)	53 (2)
O	157 (3)	2853 (2)	-844 (2)	87 (2)
C(2)	901 (4)	3357 (3)	1384 (3)	41 (2)
C(3)	33 (4)	3533 (3)	2048 (3)	54 (2)
C(4)	-942 (4)	3207 (3)	1602 (4)	67 (2)
C(5)	-729 (4)	2376 (3)	1331 (3)	66 (2)
N(6)	1573 (3)	3921 (2)	1181 (2)	37 (1)
C(7)	2394 (4)	3785 (3)	483 (3)	41 (2)
C(71)	3489 (4)	3873 (3)	871 (4)	60 (2)
C(72)	2219 (4)	4294 (3)	-338 (3)	61 (2)
C(8)	1582 (4)	4749 (3)	1561 (3)	48 (2)
C(81)	1794 (5)	4768 (3)	2564 (4)	73 (2)
C(82)	650 (4)	5239 (3)	1273 (4)	71 (2)
C(10)	2186 (6)	1878 (4)	1525 (5)	80 (3)
C(11)	1292 (7)	1524 (4)	1931 (4)	90 (3)
C(12)	803 (5)	1108 (3)	1255 (5)	83 (3)
C(13)	1330 (4)	1197 (3)	471 (4)	83 (3)
C(14)	2203 (5)	1675 (3)	641 (5)	80 (3)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

data and data collection parameters are summarized in Table II. The lattice parameters were determined by a least-squares fit of 25 reflections in the range  $5^\circ \leq 2\theta \leq 20^\circ$ . An analysis of the systematic absences unambiguously determined the space group to be *Pbca*. Two standard reflections measured after every 98 reflections showed a variation of  $\pm 3\%$ , less than  $\pm 3\sigma$  ( $\pm$ ).

The structure was solved by a combination of Patterson and Fourier syntheses. The least-squares refinement proceeded via isotropic and then anisotropic thermal parameters for all non-hydrogen atoms to an *R* of 0.079. A difference Fourier synthesis was used to locate 19 of the 25 hydrogen atoms. The six methyl hydrogens were located by using idealized torsion angles of 60 and 180°. The hydrogen atoms were included in the least-squares calculations but were not refined. The final *R* values etc. are given in Table II. The final parameters for the non-hydrogen atoms



**Table IV. Bond Distances (Å) and Bond Angles (deg) in Fe(CO)(C<sub>5</sub>H<sub>5</sub>)C<sub>4</sub>H<sub>8</sub>N(C<sub>5</sub>H<sub>7</sub>)<sub>2</sub> (24b)**

Bond Distances			
Fe(1)-C	1.700 (5)	Fe(1)-C(2)	1.927 (4)
Fe(1)-C(5)	2.044 (5)	Fe(1)-C(10)	2.117 (7)
Fe(1)-C(11)	2.103 (7)	Fe(1)-C(12)	2.085 (5)
Fe(1)-C(13)	2.091 (5)	Fe(1)-C(14)	2.119 (6)
C-O	1.167 (6)	C(2)-C(3)	1.507 (7)
C(2)-N(6)	1.317 (6)	C(3)-C(4)	1.512 (8)
C(4)-C(5)	1.487 (8)	N(6)-C(7)	1.487 (6)
N(6)-C(8)	1.509 (6)	C(7)-C(71)	1.515 (7)
C(7)-C(72)	1.503 (7)	C(8)-C(81)	1.506 (7)
C(8)-C(82)	1.509 (7)	C(10)-C(11)	1.420 (10)
C(10)-C(14)	1.350 (10)	C(11)-C(12)	1.373 (9)
C(12)-C(13)	1.347 (9)	C(13)-C(14)	1.399 (8)
Bond Angles			
C-Fe(1)-C(2)	91.9 (2)	C-Fe(1)-C(5)	89.4 (2)
C(2)-Fe(1)-C(5)	84.1 (2)	Fe(1)-C-O	178.0 (4)
Fe(1)-C(2)-C(3)	111.8 (3)	Fe(1)-C(2)-N(6)	129.4 (4)
C(3)-C(2)-N(6)	118.8 (4)	C(2)-C(3)-C(4)	104.3 (4)
C(3)-C(4)-C(5)	108.2 (4)	Fe(1)-C(5)-C(4)	108.3 (4)
C(2)-N(6)-C(7)	120.2 (4)	C(2)-N(6)-C(8)	126.4 (4)
C(7)-N(6)-C(8)	113.3 (3)	N(6)-C(7)-C(71)	111.7 (4)
N(6)-C(7)-C(72)	111.5 (4)	C(71)-C(7)-C(72)	112.6 (4)
N(6)-C(8)-C(81)	112.8 (4)	N(6)-C(8)-C(82)	113.6 (4)
C(81)-C(8)-C(82)	114.0 (4)	C(11)-C(10)-C(14)	108.3 (6)
C(10)-C(11)-C(12)	105.9 (6)	C(11)-C(12)-C(13)	110.0 (6)
C(12)-C(13)-C(14)	107.9 (5)	C(10)-C(14)-C(13)	108.0 (6)

are given in Table III, with the distances and angles given in Table IV. The molecule is shown in Figure 1, with the atomic numbering used and the final thermal ellipsoids. All calculations were carried out on a Model 30 Desktop Eclipse, using the programs and data in the Nicolet-SHELXTL package.<sup>32</sup>

(32) Sheldrick, G. M. *DESKTOP SHELXTL*; Nicolet X-ray Instruments: Madison, WI, 1986.

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**Supplementary Material Available:** Tables of the hydrogen atom positions and the thermal parameters for the non-hydrogen atoms (2 pages); a listing of observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

## Synthesis and Characterization of Polysilane Derivatives of Rhenium and Ruthenium<sup>1</sup>

Keith H. Pannell,\* James M. Rozell, and Woel-Min Tsai

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968-0513

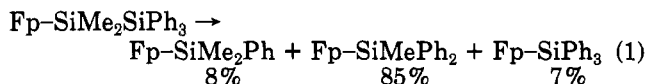
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The preparation of the silane-metal derivatives LM-Si<sub>n</sub>, LM = (CO)<sub>5</sub>Re or (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ru(CO)<sub>2</sub> (Rp) and Si<sub>n</sub> = Me<sub>3</sub>Si, Me<sub>5</sub>Si<sub>2</sub>, Me<sub>7</sub>Si<sub>3</sub>, CH<sub>2</sub>SiMe<sub>3</sub>, or CH<sub>2</sub>Si<sub>2</sub>Me<sub>5</sub>, is reported. Characterizations by <sup>29</sup>Si NMR and IR spectroscopy are included. In contrast to the related (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>- complexes, the new complexes of Re and Ru are not photolabile with respect to deoligomerization to monosilane metal derivatives. Base treatment of Rp-SiMe<sub>3</sub> results in migration of the silyl group from Ru to the cyclopentadienyl ring.

### Introduction

There is considerable current interest in the chemistry of organopolysilane compounds.<sup>2-4</sup> These materials are of interest due to their potential as commercially useful photoresist materials<sup>4</sup> and also as dopable semiconductors.<sup>3</sup> We have previously shown that (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>- (Fp)

substituents on short-chain polysilanes enhance their photochemical degradation relative to the completely permethylated analogues, eq 1.<sup>5</sup>



We are presently engaged in a program to enlarge the range of known polysilane metal derivatives, both in the field of high polymers and their lower homologues. In this paper we wish to report the synthesis and properties of new ruthenium and rhenium complexes.

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