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Reactions of Electrophiles with Neutral Cyclic Carbene Complexes of Iron

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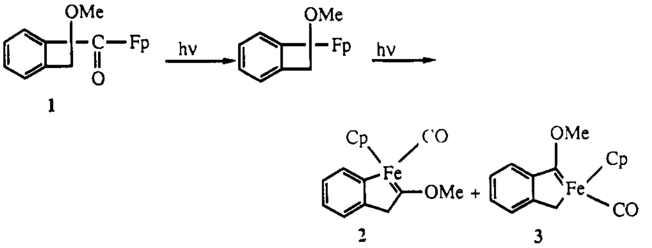
Reactions of the two benzannelated ferracyclopentadienes 2 and 3 with two electrophiles—anhydrous protic acid and trimethylsilyl triflate—have been studied. Reaction of 2 with either fluoroboric acid or trifluoromethanesulfonic acid under an atmosphere of CO leads to simple metal–carbon cleavage to give the new carbene complex 6. Similarly, in the presence of CO, 3 gives mostly the metal–alkyl cleavage product 10; but, in this case, a small amount (about 10%) of a new ring-opened product 13 is also formed. In the absence of CO, 13 becomes the predominant product. Structures of 6 and 10 were confirmed by independent syntheses. Structure assignment (including stereochemistry) of 13 is based on elemental analysis, NMR spectroscopy, and NOE difference experiments. The position of the deuterium of 13 from reaction of 3 with D$^+$ implicates an agostic intermediate (9) that reacts with CO to give 10 and reverts to 8 but does not equilibrate the methyl hydrogens. Treatment of 2 or 3 with trimethylsilyl triflate at -85 °C under an atmosphere of CO gives the known carbene complex 24. Two reasonable mechanisms for formation of 24—one involving a small-ring carbyne—are briefly discussed.

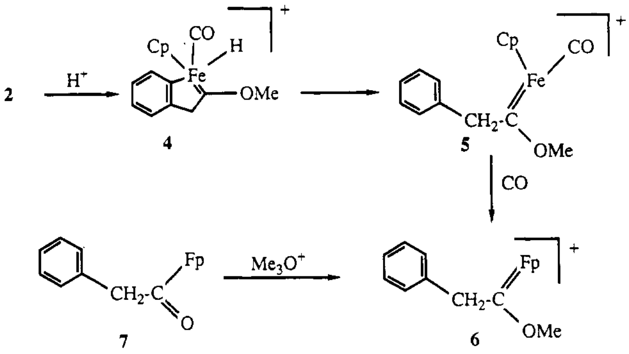
In the course of our investigations of rearrangements of carbon from saturated centers to transition metals to give carbene complexes (so-called α-eliminations of carbon)[1,2] and their reverse (carbene migratory insertions),[1b,c,2a,c] we have found that photolysis of α-methoxycyclobutyl and benzocyclobutenyl complexes of dicarbonyl (η^5-cyclopentadienyl)iron provides a source of reasonably stable complexes of iron substituted with both an alkyl or aryl group and a carbene ligand. Since this substitution pattern is unique, we thought it would be interesting to explore some of the chemistry of this unusual kind of carbene complex. At this time, we report the reaction of the two benzannelated complexes 2 and 3 (produced from photolysis of the benzocyclobutenylacyl complex of iron, 1) with two electrophiles: protic acids and trimethylsilyl triflate.



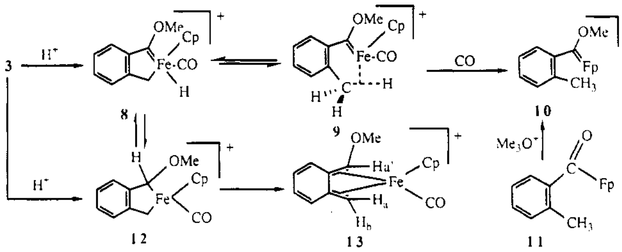
Results and Discussion

The benzocyclobutenylacyl complex of iron (1) was prepared[3] from reaction of KFp (Fp = dicarbonyl(η^5-cyclopentadienyl)iron) with α-methoxybenzocyclobutene carbonyl chloride, which was prepared as previously described.[2e] Photolyses were carried out in benzene-d_6 with a 450-W Hanovia medium-pressure mercury lamp. This gave a mixture of 2 and 3 in a ratio of 65:35 in an overall yield of 61%. Careful flash chromatography of the mixture over silica gel (230–400 mesh; 5% ethyl acetate/hexane) gave 3 as dark green prisms (from hexane at -20 °C) followed by 2 as blood red prisms (from CH_2Cl_2/hexane at -20 °C).

Scheme I



Scheme II



Reaction of 2 and 3 with Protic Acids. Reaction of the carbene complex 2 with HBF_4 (or CF_3SO_3H) in CH_2Cl_2 at -78 °C under an atmosphere of CO led to simple metal–alkyl cleavage with clean formation (65% recrystallized) of the expected carbene complex 6. The structure of this new complex was confirmed by independent synthesis from 7, as shown in Scheme I.

Reaction of the other isomer (3) with acid in methylene chloride proved more interesting. Under an atmosphere of CO, addition of HBF_4 at -78 °C gave a mixture of 10 and 13 in a ratio of about 9:1 (Scheme II) (62%:8% isolated). In the absence of CO, reaction of 3 with HBF_4 at

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[1] For rearrangements of cyclopropanes, see: (a) Lisko, J. R.; Jones, W. M. *Organometallics* 1985, *4*, 944. (b) Conti, N. J.; Jones, W. M. *Organometallics* 1988, *7*, 1666. (c) Conti, N. J.; Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* 1990, *9*, 175.

[2] For rearrangements of cyclobutanes and benzocyclobutenes, see: (a) Stenstrom, Y.; Jones, W. M. *Organometallics* 1986, *5*, 178. (b) Stenstrom, Y.; Klauck, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* 1986, *5*, 2155. (c) Stenstrom, Y.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* 1987, *6*, 2079. (d) Trace, R. L.; Jones, W. M. *J. Organomet. Chem.* 1989, *376*, 103. (e) Crowther, D. J.; Tivakornpannarai, S.; Jones, W. M. *Organometallics* 1990, *9*, 739.

[3] In earlier work,[2b] 2 and 3 were prepared by photolysis of the σ complex (prepared by the method of Giering[4]). However, since developing convenient syntheses of α-methoxybenzocyclobutenecarboxylic acid,[2d] we have found preparation of 2 and 3 from the acyl complex 1 to be superior.

[4] Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. soc.* 1973, *95*, 5430.

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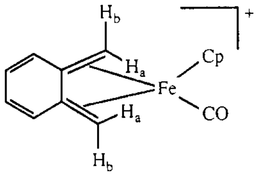
the same temperature gave mainly **13** (71% isolated).

The structure of **10** was confirmed by independent synthesis from **11**, as shown in Scheme II. The structure assignment for **13** (including stereochemistry) is based on analysis, ^{1}H and ^{13}C NMR spectroscopy, and NOE difference experiments. In the ^{1}H NMR spectrum of **13**, H_a appears at δ 0.05 ppm, J = 3.7 Hz. The high-field shift of H_a and the coupling constant are consistent with the data reported for **14**[5] (H_a; δ = 0.05, J_{ab} = 3.2 Hz). In the NOE experiments, it was found that irradiation of the signal at δ 0.05 (assigned to H_a in **13**) led to a 5% enhancement of the singlet at δ 3.20 (assigned to $H_{a'}$) and a 15% enhancement of the doublet at δ 3.72 (assigned to H_b). Irradiation of H_b showed no enhancement of $H_{a'}$. Attempts to release the diene from **13** by oxidation with Ce(IV) led only to intractables.



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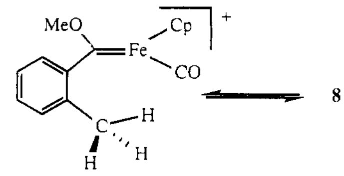
In the generally accepted mechanism of proton-induced alkyl cleavage from Fp-σ complexes, the iron is initially attacked by the proton followed by reductive elimination.[6] The same mechanism for formation of **6** and **10** is therefore eminently reasonable and is pictured as such for **10** [with an agostic modification (vide infra)] in Scheme II [protonation on Cp was excluded by deuterium labeling (vide infra)]. Two reasonable mechanisms for formation of **13** are included in Scheme II. In one, initially protonated iron undergoes carbene insertion to give **12**, which then ring-opens. Carbene insertions into metal–hydrogen bonds (**8**→**12**) have ample precedent.[7] In the other mechanism, **12** is formed by direct protonation of the carbene carbon.[8]

In the presence of 6.5 atm of CO, **10** is almost the exclusive product (ca. 90%). In the absence of added CO, **13** is formed in at least 71% yield. From these results, it is necessary that the precursors to **10** and product **13** be interconnected. In other words, either **13** adds CO to give **10** or, in the absence of CO, the intermediate that is trapped by CO isomerizes to **13**. The former was readily excluded by treating a solution of **13** with CO; no reaction of any kind occurred in 24 h. Thus, the intermediate that is trapped by CO must also be able to lead to **13**. The simplest picture that would explain these results is equilibrium between **15** and **8**, i.e. reversible reductive elimination of C–H. To test for this, **3** was treated with CF_3SO_3D. If reductive elimination were reversible, deuterium should be scrambled into the ortho methyl group, which, in turn, would lead to deuterium on the vinyl CH_2 of **13**. In fact, when **3** was treated with CF_3SO_3D at −80 °C in the absence of CO, within the limits of ^{1}H and ^{2}H NMR spectroscopy deuterium in the product was located exclusively α to the methoxy; none was on the vinyl methylene. In other words, if **15** is ever formed, it apparently does not reverse to an intermediate that can lead to **13**. To rationalize these apparently contradictory results requires an intermediate that can react with CO to give **10** but, in the absence of CO, reverses to **8** (which ultimately gives **13**) faster than deuterium can scramble. For this intermediate, the most attractive possibility is the agostic[11] species **9**, in which return to the metal hydride **8** is faster than scrambling of hydrogens on the methyl group (rotation around the methyl–phenyl bond).[12]



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Attempts to observe any of the intermediates in Scheme II failed because formation of both **10** and **13** is quite rapid (in both the presence and absence of added CO, reaction is complete at −80 °C before the NMR analysis can be run).

Finally, there are two paths by which **8** could revert to **12** and ultimately **13**. It could either undergo carbene insertion to give **12** directly or it could lose a proton to give **3**, which could then be reprotonated on the carbene carbon. We have no experimental evidence to distinguish between these possibilities, although Ocum's razor would favor the former.

Reaction of 2 and 3 with Trimethylsilyl Triflate. Due to their preferred linear geometry, alkynes confined to relatively small carbocyclic rings are highly strained.[15] However, despite this strain, there is compelling evidence for their transient existence in rings down to and including cyclohexyne **16**[16] and cyclopentyne **17**.[16] The strain in transition-metal carbynes incorporated into medium to relatively small rings should be significantly less than their

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(5) Roth, W. R.; Meier, J. D. *Tetrahedron Lett.* **1967**, 2053.

(6) Cf.: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 434–443 (see also references cited).

(7) For the later transition metals, see: (a) Casey, C. P.; Nagashima, H. *J. Am. Chem. Soc.* **1989**, *111*, 2353. (b) Brookhart, M.; Buck, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 559. (c) Fryzuk, M. D.; Joshi, K.; Chadha, R. K. *J. Am. Chem. Soc.* **1989**, *111*, 4498. (d) Fryzuk, M. D.; Bhangu, K. *J. Am. Chem. Soc.* **1988**, *111*, 4498. (e) For earlier references, see ref 6, pp 379–382, 580–583.

(8) In addition to the well-documented reactions of early-transition-metal "nucleophilic carbenes" (Schrock carbenes) with electrophiles at the carbene carbon,[9] there are isolated reports of direct reaction of electrophiles with carbene carbons of later transition metals.[10]

(9) Cf.: (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Reference 6, pp 129–134, 811–815.

(10) (a) Cf: Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (b) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079. (c) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713.

(11) Cf.: (a) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(12) Depending on the metal and its ligands, the bond from a transition metal to an agostic hydrogen may break (to give a C–H bond) slower[13] or it may appear to break faster[14] than does the bond from carbon to agostic hydrogen to give a M–H bond. The latter is only apparent because other slow processes may be involved in the fluxionality that requires a metal hydride. In the case at hand, the former must be invoked; i.e. methyl scrambling in **9** must be slower than metal hydride formation.

(13) (a) Brookhart, M.; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 691. (b) Brookhart, M.; Lincoln, D. M.; Volpe, A. F.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. (c) Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691. The authors are grateful to Professor Brookhart for providing this information prior to publication.

(14) (a) Brookhart, M.; Lamanna, W.; Humphrey, M. Beth *J. Am. Chem. Soc.* **1982**, *104*, 2117. (b) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417. (c) Brookhart, M.; Cox, K.; Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Bashkin, J.; Derome, A. E.; Grebenik, P. D. *J. Chem. Soc., Dalton Trans.* **1985**, 423. (d) Michael, G.; Kaub, J.; Kreiter, C. G. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 502.

(15) From molecular mechanics calculations performed elsewhere,[16] cyclooctyne and cycloheptyne have total strain energies of 20.8 and 31 kcal/mol, respectively. Similar calculations performed in these labs (MMX program kindly provided by Professor J. J. Gajewski, University of Indiana), assign total strain energies of 16.7, 27.7, 59, and 91 kcal/mol to cycloheptyne, cyclohexyne, cyclopentyne, and norbornyne, respectively.

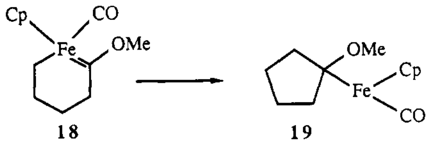
(16) Cf.: Johnson, R. P. in *Molecular Structures and Energetics*; Liebman, J. F.; Greenberg, A., Eds.; VCH: New York, 1986, Vol. 3, p 85.

16

17

carbocyclic analogues for two reasons. First, the C–M–C bond angle of an acyclic transition-metal carbyne complex need not invariably (if ever) prefer 180°,[17] as is the case for alkynes. Second, X-ray evidence suggests that the M–C–C bond of carbyne complexes may have a soft potential energy surface.[18] However, despite this optimistic outlook, to our knowledge, there are no reports of small-ring carbyne complexes.

One obvious reason for this void, at least for the later transition metals, is the expected instability of appropriate precursors. Of the three popular and general methods for preparing carbyne complexes,[21] the only one that might be potentially applicable to cyclic carbynes is the method so elegantly developed by Fischer: abstraction of a carbene stabilizing group such as methoxy from a carbene complex.[22] Unfortunately, for the later transition metals, appropriate precursors may not be isolable due to instability of the carbene complexes relative to their electron-deficient rearranged counterparts. For example, a methoxycarbene complex such as **18**, from which methoxy may be abstracted to give a cyclic carbyne, would be expected to be thermodynamically unstable relative to its highly reactive 16-electron relative **19**.[2c]

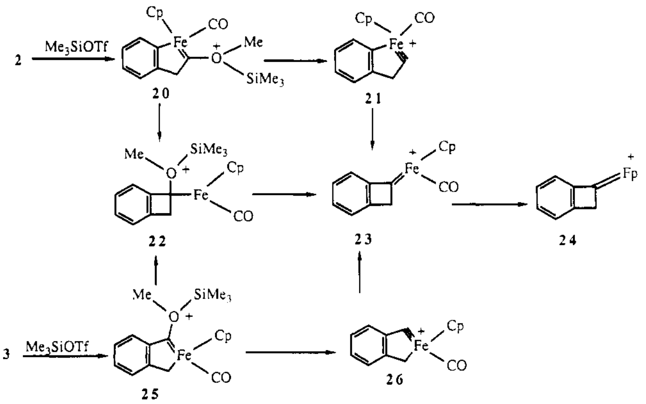


18 19

As mentioned above, benzannelated methoxy-substituted metallacyclopentadienes such as **2** and **3** are abnormally resistant to migratory insertion due to the strain in the resulting benzocyclobutene and, as a result, we thought that they may be suitable precursors to small-ring metallacarbynes. We, therefore, undertook studies of the reaction of **2** and **3** with the strong methoxy-abstractng reagents boron trihalide (Fischer's traditional reagent)[22] and trimethylsilyl triflate.

Reactions were typically carried out in carefully dried and degassed methylene chloride, most frequently at −80 °C. All reactions with boron halides in the presence or absence of added CO gave only very complex mixtures from which no single component could be isolated. However, if CO were present and extreme precautions were taken in preparing the trimethylsilyl triflate, fairly clean reaction with both **2** and **3** was observed[23] (Scheme III).

Scheme III



In a typical run, a methylene chloride solution of the carbene complex in a thick-walled NMR tube was frozen in liquid nitrogen followed by layering 1 equiv of Me_3SiOTf followed by sufficient CO to give about 3 atm at −85 °C. The reaction was complete by the time the mixture could be thawed and mixed and an NMR spectrum run at −80 °C. No transients could be detected in the ^1H NMR spectrum, and the primary and only identifiable product from both **2** and **3** was the known[4] carbene complex **24** (41% isolated and 28% by NMR analysis, respectively).

Two reasonable mechanisms for formation of **24** from either **2** or **3** are given in Scheme III. In one mechanism, an initially formed cyclic carbyne (**21** or **26**) undergoes carbyne migratory insertion to give **23**, which is then trapped by CO to give the known carbene **24**. This mechanism requires two rapid reactions: methoxy abstraction by trimethylsilyl triflate and carbyne migratory insertion. Although methoxy abstraction by trimethylsilyl triflate to give carbene complexes appears to be quite rapid,[24] to our knowledge, the ease of methoxy abstraction from a carbene complex with Me_3SiOTf to give a carbyne is unknown. Rapid migratory insertion of carbynes **21** and **26** is reasonable [despite the slow contraction of carbene **2** (E_a > 30–31 kcal/mol)[2b]] for two reasons. First, although not expected to be as strained as the corresponding cyclic alkyne, **21** and **26** would almost certainly be more strained than their carbene counterparts **2** and **3**. Second, **21** and **26** have no stabilizing electron donors to retard the insertion reaction as do the carbenes.

In the second mechanism, initially formed trimethylsilyl methyl ether complexes **20** and **25** undergo carbene migratory insertions in a reaction where the rearranging aryl or alkyl group either assists in the loss of trimethylsilyl methyl ether (to give **23** directly) or first gives the rearranged cation **22** which, upon loss of Me_3SiOMe and trapping by CO, gives **24**. In this case, ring contraction is induced solely by loss of methoxy stabilization of the carbene. In this mechanism, it is worth noting that a rapid unimolecular ring contraction of **20** or **25** at −80 °C would limit the activation barrier to no more than ca. 18 kcal/mol while the activation barrier for contraction of **2** must exceed 30–31 kcal/mol;[2b] i.e. this mechanism requires methoxy stabilization of the carbene complex **2** to exceed 12–13 kcal/mol.

Numerous attempts to directly detect either an intermediate carbene (such as **20** from **2**) or a carbyne complex failed; in all cases, rearrangement was complete before the NMR analysis could be run. Also, attempts to intercept carbyne **21** or **26** with nucleophiles compatible with the

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[17] Cf.: Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

[18] For instance, crystal structures of i and ii show M–C–C angles of 165°[19] and 169.5°[20], respectively. These deviations have been ascribed to crystal packing forces.

$OsCl(CO)(\equiv C\text{-}C_6H_4Me)L_2$ $OsCl_2(SCN)(\equiv C\text{-}C_6H_4NMe_2)L_2^+$

i ii

[19] Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. *J. Am. Chem. Soc.* **1980**, *102*, 6570.

[20] Clark, G. R.; Edmonds, N. R.; Pauptit, R. A.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Organomet. Chem.* **1983**, *244*, C57.

[21] (a) Reference 6, p 139. (b) Reference 17, p 181. (c) Schubert, U. In *Chemistry of the Metal–Carbon Bond*; Hartley, F. R.; Patai, S., Eds.; John Wiley and Sons: New York, 1982; Vol. 1, Chapter 5.

[22] (a) Cf.: Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59. (b) For the first example, see: Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Muller, J.; Hultner, G.; Lorenz, H. *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 564.

[23] Trimethylsilyl triflate was distilled from a proton sponge immediately before use. Even the slightest trace of protonic acid caused serious deviation from the desired reaction path.

[24] Cf.: (a) Thorn, D. L. *Organometallics* **1982**, *1*, 879. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (c) Brookhart, M.; Tucker, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 979.

reaction conditions (such as cyclopentene or phenylacetylene) failed. At this juncture, we therefore have no experimental evidence that permits us to make a choice between the two possibilities in Scheme III.

Experimental Section

General Procedure. All operations were carried out under a dry, oxygen-free nitrogen atmosphere by standard Schlenk-line or drybox techniques. ^1H NMR spectra were recorded either on a Varian XL-300 or on a QE-300 MHz spectrometer; the ^{13}C NMR spectra were recorded on a Varian XL-300 instrument at 75 MHz. Proton chemical shifts δ are reported (ppm) downfield from TMS; ^{13}C resonances were recorded with the resonance of the solvent, δ 53.8 for CD_2Cl_2 or δ 128.0 for C_6D_6, as the internal reference at all temperatures. Infrared (IR) spectra were recorded on a Perkin-Elmer 137 spectrometer. Melting points (uncorrected) were obtained by using a Thomas-Hoover apparatus. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. Photolyses were carried out by using a 450-W medium-pressure Hg Hanovia lamp in a Pyrex or quartz well. Transfer needles from Aldrich were used (18 and 20 gauge, stainless steel, double tip).

Solvents and Reagents. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from K/Na benzophenone ketyl. Reagent grade dichloromethane was washed with 5% sodium bicarbonate solution and water, dried with anhydrous calcium chloride overnight, and distilled from P_2O_5 under nitrogen. Reagent grade hexane and benzene were distilled from calcium hydride under nitrogen. Trimethylsilyl trifluoromethane sulfonate was distilled from Proton Sponge immediately prior to use. Column chromatography was carried out on 230–400-mesh silica gel.

Dicarbonyl(η^5-cyclopentadienyl)((1-methoxybenzocyclobuten-1-yl)carbonyl)iron. To a stirred suspension of 1.32 g (6.1 mmol) of KFp in 30 mL of THF cooled to −78 °C was added 0.82 g (4.3 mmol) of the acid chloride[2e] in 10 mL of THF. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure; the residue was digested in 50% benzene/hexane and filtered through Celite and sand. The Celite was washed several times with 50% benzene/hexane, and the filtrate was concentrated to ca. 10 mL at reduced pressure and eluted from a silica gel column with 10% ethyl acetate/hexane. Two fractions were collected: the first, a dark brown band, contained 0.94 g (65%) of pure acyl complex; the second, a red band, contained dicarbonyl(η^5-cyclopentadienyl)iron dimer (Fp_2). IR (Nujol): 2028, 1957 (CO), 1620 cm^{-1} (C=O). ^1H NMR (C_6D_6, δ): 2.9 (d, J = 3.5 Hz, 1 H, CH_2), 3.0 (s, 3 H, OMe), 3.4 (d, J = 3.5 Hz, 1 H, CH_2), 4.1 (s, 5 H, Cp), 6.7–7.1 (m, 4 H, aromatics). ^{13}C NMR (C_6D_6, δ): 38.3 (CH_2), 86.6 (Cp), 97.0 (–C–), 123.2, 123.5, 126.8, 129.2, 143.0, 145.5 (aromatic C), 252.1 (>C=O), 219.5, 219.6 (CO). Anal. Calcd for $C_{17}H_{14}O_4Fe$: C, 60.38; H, 4.17. Found C, 60.33; H, 4.18.

Photolysis of the Acyl Complex 1. A solution of 350 mg (1.036 mmol) of the acyl complex in 1 mL of C_6D_6 in an NMR tube equipped with a boiling chip, a septum, and a N_2 inlet was photolyzed for 2.5 h. The reaction was monitored by ^{13}C NMR spectroscopy, following the Cp resonance until no 1 remained (δ 86.6). Evaporation followed by flash chromatography (5% ethyl acetate/hexane) gave 0.12 g (41%) of carbene 2 and 58 mg (20%) of carbene 3. All spectroscopic data have been published elsewhere.[2b]

Reaction of the Carbene 2 with HBF_4 in the Presence of CO. A solution of 60 mg (0.21 mmol) of carbene 2 in 15 mL of dichloromethane was cooled in a 2-propanol/dry ice bath. CO was bubbled through the carbene solution for 5 min, and 0.04 mL (0.24 mmol) of 54% HBF_4/diethyl ether solution was added. The orange/red solution turned dark yellow immediately. CO was continuously bubbled for 5 min. After warming to room temperature, the solvent was removed under vacuum. The crude product was washed with 3 × 10 mL of diethyl ether. Recrystallizaton from dichloromethane/diethyl ether gave 55 mg (65%) of $6^+BF_4^-$. All spectroscopic data are the same as for an authentic sample obtained from an independent synthesis.

Dicarbonyl(η^5-cyclopentadienyl)(phenylacetyl)iron (7). To a stirred suspension of 1.102 g (5.1 mmol) of KFp in 30 mL of THF cooled to −78 °C was added 0.788 g (5.1 mmol) of phenylacetyl chloride in 5 mL of THF. The mixture was stirred for 6 h at room temperature. The solvent was removed under vacuum. The residue was extracted with 3 × 15 mL of hexane. The solvent was evaporated, and the product was flash-chromatographed over silica gel. The first yellow band was collected (30% ethyl acetate/hexane) to give 0.48 g (32%) of known 7.[25] IR ($CHCH_3$): 1998.3, 1938.7, 1640.3 cm^{-1}. ^1H NMR (C_6D_6, δ): 2.7 (s, 2 H, CH_2), 3.9 (s, 5 H, Cp), 6.8–7.2 (m, 5 H, aromatic). ^{13}C NMR (C_6D_6, δ): 5.4 (CH_2), 85.9 (Cp), 123.5, 127.7 (2), 127.75 (2), 127.8 (aromatic), 217.5 (CO), 254.1 (C=O). Anal. Calcd for $C_{15}H_{12}O_3Fe$: C, 60.85; H, 4.09. Found: C, 60.80; H, 4.10.

Conversion of Dicarbonyl(η^5-cyclopentadienyl)(phenylacetyl)iron to $6^+BF_4^-$. To a stirred solution of 0.228 g (0.773 mmol) of the title complex in freshly distilled dichloromethane (20 mL) was added 0.114 g (0.78 mmol) of $[Me_3O]BF_4$. Stirring at room temperature was continued overnight. The mixture was filtered through anhydrous $MgSO_4$ on a glass frit. The solvent was removed in vacuo. Recrystallization from dichloromethane/diethyl ether (50:50) gave 0.24 g (78%) of pure $6^+BF_4^-$. IR (Nujol): 2049.6, 2014.3 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 4.7 (br s, 2 H, CH_2), 4.8 (br s, 3 H, OCH_3), 5.2 (s, 5 H, Cp), 7.2–7.4 (m, 4 H, aromatic). ^{13}C NMR (CD_2Cl_2, δ): 61.0 (br, CH_2), 70.1 (br, OCH_3), 88.5 (Cp), 128.6 (2), 129.7 (2), 130.2, 133.0 (aromatic), 208.7 (CO), 338.5 (Fe=C). Anal. Calcd for $C_{16}H_{15}O_3FeBF_4$: C, 49.29; H, 3.80. Found: C, 49.15; H, 3.75.

Reaction of HBF_4 or CF_3SO_3H with the Carbene 3. To a stirred solution of 50 mg (0.18 mmol) of 3 in 10 mL of dichloromethane was added dropwise at −78 °C (by syringe) 0.2 mL of HBF_4/Et_2O. The mixture was stirred for 10 min at −78 °C and then slowly warmed to room temperature. The solvent was removed under vacuum, and the residue was washed with 3 × 10 mL of diethyl ether. ^1H NMR spectroscopy of the crude product showed a mixture of **10** (minor product) and **13**. Recrystallization from dichloromethane/ether gave 46 mg (71%) of golden yellow crystalline $\mathbf{13}^+BF_4^-$. IR (Nujol): 2026.1 cm^{-1} (CO). ^1H NMR (CD_2Cl_2, δ): 0.05 (d, J = 3.7 Hz, 1 H, CH), 3.2 (s, 1 H, CH), 3.7 (d, J = 4 Hz, 1 H, CH), 3.9 (s, 3 H, OMe), 4.5 (s, 5 H, Cp), 7.6–7.9 (m, 4 H, aromatic). ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 38.1 (CH_2), 62.9 (OMe), 88.0 (C), 89.5 (Cp), 95.3 (C), 108.1 (CH), 129.1, 132.9, 133.7, 134.1, (4 CH), 218.2 (CO).

When CF_3SO_3H was used, anion exchange was carried out by dissolving the crude product in acetonitrile, followed by addition of KPF_6. The mixture was stirred overnight and filtered through Celite and the solvent removed under vacuum. The crude residue was triturated with 3 × 15 mL of dichloromethane. Removal of the solvent followed by recrystallization from dichloromethane/diethyl ether gave a red crystalline $\mathbf{13}^+PF_6^-$. All spectroscopic data are the same as for $\mathbf{13}^+BF_4^-$.

Reaction of Carbene 3 with HBF_4 or CF_3SO_3H in the Presence of CO. A solution of 50 mg (0.18 mmol) of carbene 3 in 15 mL of dichloromethane was cooled in liquid nitrogen, and 0.06 mL (0.35 mmol) of HBF_4 or 0.03 mL (0.34 mmol) of CF_3SO_3H was added. The reaction mixture was then charged with enough CO to give 6.5 atm, at −78 °C. The mixture was warmed to −78 °C and stirred at this temperature for 15 min. After warming to 0 °C, the CO was released and the solvent was removed in vacuo. The crude product was washed several times with diethyl ether. By ^1H and ^{13}C NMR spectroscopy, the products of the reaction were found to be **13** and **10** formed in a 1:9 ratio. Recrystallization from dichloromethane/diethyl ether gave 44 mg (62%) of a yellow crystalline solid $\mathbf{10}^+BF_4^-$. IR (Nujol): 2054.4, 2011.5 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 2.1 (s, 3 H, CH_3), 4.1 (s, 3 H, OCH_3), 5.3 (s, 5 H, Cp), 6.8–7.4 (m, 4 H, aromatic). ^{13}C NMR (C_6D_6, δ): 19.0 (CH_3), 70.0 (OCH_3), 90.8 (Cp), 120.4, 120.5, 127.4, 131.4, 131.8 (aromatic C), 208.0, 208.4 (CO). Anal. Calcd for $C_{16}H_{15}O_3FeBF_4$: C, 48.29; H, 3.80. Found: C, 47.97; H, 3.68.

A second recrystallization of the mother liquor gave 5 mg (8%) of a golden yellow crystalline solid of $\mathbf{10}^+BF_4^-$.

Reaction of the Carbene 3 with CF_3SO_3D. To a stirred solution of 60 mg (0.21 mmol) of 3 in 10 mL of dichloromethane at −78 °C was added 0.025 mL (0.21 mmol) of CF_3SO_3D by syringe.

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[25] Abu, S.; Omar, M.; Bruce, M. *J. Chem. Soc., Dalton Trans.* **1974**, 2302.

The solution turned to reddish yellow immediately. The mixture was stirred at −78 °C for 15 min and slowly warmed to room temperature. The solvent was removed under vacuum, and the crude product was washed with 3 × 10 mL of diethyl ether. The residue was treated with 10 mL of acetonitrile, and excess KPF_6 (ca. 1 g) was added. Filtration through Celite gave a red/yellow filtrate. The solvent was removed and the residue was washed with ether until the washings became colorless. The residue was extracted with CH_2Cl_2 and filtered through $MgSO_4$. Removal of the solvent, followed by recrystallization from dichloromethane/diethyl ether, gave 61 mg (67%) of $\mathbf{13}^+PF_6^-$ as a red crystalline solid. IR (Nujol): 2025.8 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 0.14 (d, J = 4 Hz, 1 H, CH), 3.8 (d, J = 4 Hz, 1 H, CH), 4.0 (s, 3 H, OCH_3), 4.55 (s, 5 H, Cp), 7.67–7.8 (m, 4 H, aromatic). ^{2}H NMR (CH_2Cl_2, δ): 3.27 (=C—D). ^{13}C NMR (CD_2Cl_2, δ): 38.3 (=CH_2), 62.8 (OCH_3), 89.4 (Cp), 107.9 (=CD), 88.1 (=C-), 129.0 (=CH), 132.7 (=CH), 133.6 (=CH), 134.2 (=CH), 217.97 or 218.0 (CO). Anal. Calcd for $C_{15}H_{14}DO_2FePF_6$: C, 41.99; H + D as H, 3.53. Found: C, 42.74; H + D as H, 3.48.

Reaction of $\mathbf{10^+BF_4^-}$ with CO. A dichloromethane-d_2 solution of $\mathbf{10}^+BF_4^-$ (25 mg, 0.068 mmol) in an NMR tube was connected to the vacuum line and cooled in liquid nitrogen. The sample was degassed by the freeze–thaw method several times, and CO (1.5 atm) was introduced to the sample tube. The tube was flame-sealed. After 1 h in liquid nitrogen, the sample tube was transferred to a dry ice/2-propanol bath. After 12 h, there was no detectable change in its ^{1}H NMR spectrum.

Dicarbonyl(η^5-cyclopentadienyl)(*o*-tolylcarbonyl)iron (11). To a stirred suspension of 1.4 g (6.5 mmol) of KFp in 20 mL of THF cooled to −78 °C was added 1.0 g (6.5 mmol) of α-methylbenzoyl chloride in 5 mL of THF. The mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The residue was dissolved in 50% benzene/hexane, filtered through Celite, evaporated, and flash-chromatographed over silica gel. The first yellow band was collected (30% ethyl acetate/hexane) to give 1.43 g (75%) of **11** as a yellow oil. IR ($CHCl_3$): δ 2011.5, 1958.7, 1638.8 cm^{-1}. ^{1}NMR (C_6D_6, δ): 2.3 (s, 3 H, CH_3), 4.3 (s, 5 H, Cp), 6.9–7.1 (m, 4 H, aromatic). ^{13}C NMR (C_6D_6, δ): 19.7 (CH_3), 87.2 (Cp), 123.8, 126.1, 127.9, 131.2 (=CH, aromatic), 142.7, 153.5 (C, aromatic), 215.2 (CO), 255.0 (C=O). Anal. Calcd for $C_{15}H_{12}O_3Fe$: C, 60.85; H, 4.09. Found: C, 60.83; H, 4.10.

Conversion of Dicarbonyl(η^5-cyclopentadienyl)(*o*-tolylcarbonyl)iron to $\mathbf{10^+BF_4^-}$. To a stirred solution of the acyl complex (0.25 g, 0.84 mmol) dissolved in freshly distilled dichloromethane (20 mL) was added $[Me_3O]BF_4$ (0.125 g, 0.84 mmol). Stirring was continued overnight. The mixture was filtered through anhydrous $MgSO_4$ on a glass frit. The filtrate was layered with diethyl ether and stored at −20 °C for 1 week. This led to the isolation of $\mathbf{10}^+BF_4^-$ (0.21 g, 63%). IR (Nujol): 2054.4, 2011.5 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 2.1 (s, 3 H, CH_3), 4.1 (s, 3 H, OCH_3), 5.3 (s, 5 H, Cp), 6.8–7.4 (m, 4 H, aromatic). ^{13}C NMR (CD_2Cl_2, δ): 19.0 (CH_3), 70.0 (OCH_3), 90.8 (Cp), 120.4, 120.5 (2), 127.4, 131.4, 131.8 (aromatic), 208.0, 208.4 (CO), 332.9 (Fe=C). Anal. Calcd for $C_{16}H_{15}O_3FeBF_4$: C, 48.29; H, 3.80. Found: C, 47.97; H, 3.68.

Low-Temperature NMR Scale Reaction of Carbene 2 with Trimethylsilyl Trifluoromethanesulfonate (TMSOTf) in the Presence of CO. A 50-mg (0.18 mmol) sample of carbene **2** was placed in an NMR tube that was joined to a vacuum line by a 14/20 female joint. The NMR tube was cooled in liquid nitrogen and charged sequentially with CD_2Cl_2, Me_3SiOTf (37 mg, 0.17 mmol), and CO (3 atm at room temperature) followed by flame sealing. After about 20 min at liquid nitrogen temperature, the sample was thawed in the NMR probe, which had been preset at −85 °C. The NMR spectrum showed complete reaction, and the major product was carbene **24**. Recrystallization of the crude product from dichloromethane/diethyl ether gave 31 mg (41%) of pure carbene **24**. IR (Nujol): 2064.5, 2020.1 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 4.6 (s, 2 H, CH_2), 5.8 (s, 5 H, Cp), 7.5–7.9 (m, 4 H aromatic). ^{13}C NMR (CD_2Cl_2, δ): 62.2 (CH_2), 92.7 (Cp), 124.8, 125.6, 131.3, 145.2, 146.6, 164.2 (aromatic C), 206.5 (CO), 349.4 (Fe=C). All spectroscopic data are consistent with those reported in the literature.[4]

Low-Temperature NMR Scale Reaction of Carbene 3 with Trimethylsilyl Trifluoromethanesulfonate in the Presence of CO. A 50-mg (0.18 mmol) sample of carbene **3** was placed in an NMR tube that was joined to a vacuum line by a 14/20 female joint. The NMR tube was cooled in liquid nitrogen and charged sequentially with CD_2Cl_2, Me_3SiOTf (40 mg, 0.18 mmol), and CO (3 atm at room temperature) followed by flame sealing. After about 20 min at liquid nitrogen temperature, the sample was thawed in the NMR probe, which had been preset at −85 °C. The ^{13}C NMR spectrum of the reaction mixture showed a complex mixture that included 28% of **24**. There was no sign of transients.

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Registry No. 1, 132939-25-4; **2**, 104090-23-5; **3**, 104090-24-6; [**6**]BF_4, 132939-27-6; 7, 55622-66-7; [**10**]BF_4, 132939-29-8; **11**, 118962-42-8; [**13**]BF_4, 132939-31-2; [**13**]PF_6, 132939-32-3; [**24**]OTf, 132939-33-4; Fp_2, 12154-95-9; KFp, 60039-75-0; Me_3SiOTf, 27607-77-8; HBF_4, 16872-11-0; CF_3SO_3H, 1493-13-6; CF_3SO_3D, 66178-41-4; α-methoxybenzocyclobutene carbonyl chloride, 125476-35-9; phenylacetyl chloride, 532-27-4; α-methylbenzoyl chloride, 22414-26-2.