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In search of α-eliminations of carbon induced by sixteen electron iron: photolysis and thermolysis of derivatives of phenyl substituted cyclobutanes and cyclopropanes

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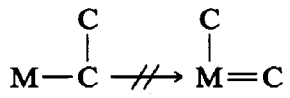
Abstract

Photolysis of dicarbonyl(η^5-cyclopentadienyl)(1-phenylcyclobutane-1-carbonyl)iron is proposed to give the hydride complex Ph(cyclobutenyl)Fe(Cp)-(CO)H which dissociates to 1-phenylcyclobutene and FpH (Fp = η^5-cyclopentadienyldicarbonyliron). The FpH complex can oxidatively add to the sixteen electron acyl or σ complexes (Ph(cyclobutyl)-C(O)FeCp(CO) and Ph(cyclobutyl)FeCp(CO) respectively) to produce phenylcyclobutane and 1-phenylcyclobutane carboxaldehyde. Photolysis of dicarbonyl(η^5-cyclopentadienyl)(1-phenylcyclopropyl-1-carbonyl)iron gives a σ complex with no further reaction. Substitution of CO with PPh_3 and thermolysis produced a centrally substituted π-allyl complex. In neither the cyclobutyl nor the cyclopropyl case did the reactions give isolable carbene complexes; apparently the phenyl substituent does not provide adequate stabilization of the carbene complex to allow its detection or isolation.

Normally, α-eliminations of carbon induced by electron deficient transition metals to give carbene complexes are energetically unfavorable [1]. However, we have recently found that this rearrangement can be biased in favor of the carbene by



combining ring strain relief with carbene stabilization. For instance, in Fp systems (Fp = η^5-cyclopentadienyldicarbonyliron) we have found that methoxy (or amine for 3) stabilization of the carbene combined with the strain relieved upon expansion of either cyclopropane to ferracyclobutene [2], cyclobutane to ferracyclopentene [3] or benzocyclobutene to ferraindene [4] provides sufficient bias to give the carbene complexes as the thermodynamically favored products. On the other hand, relief of

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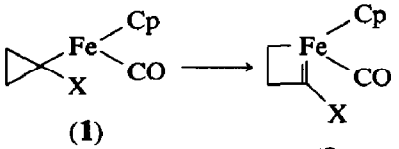
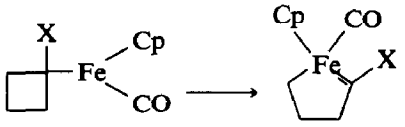
either cyclopropane, cyclobutane, or benzocyclobutene strain without any carbene stabilization (**1**, **3**, or **5**; X = H) is apparently not sufficient to induce this rearrangement.



(**1**) (**2**)



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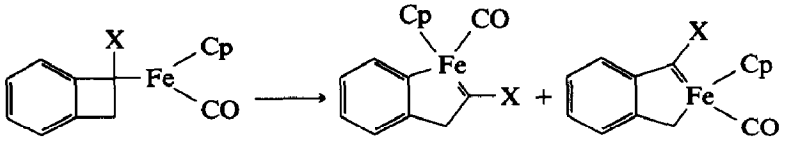


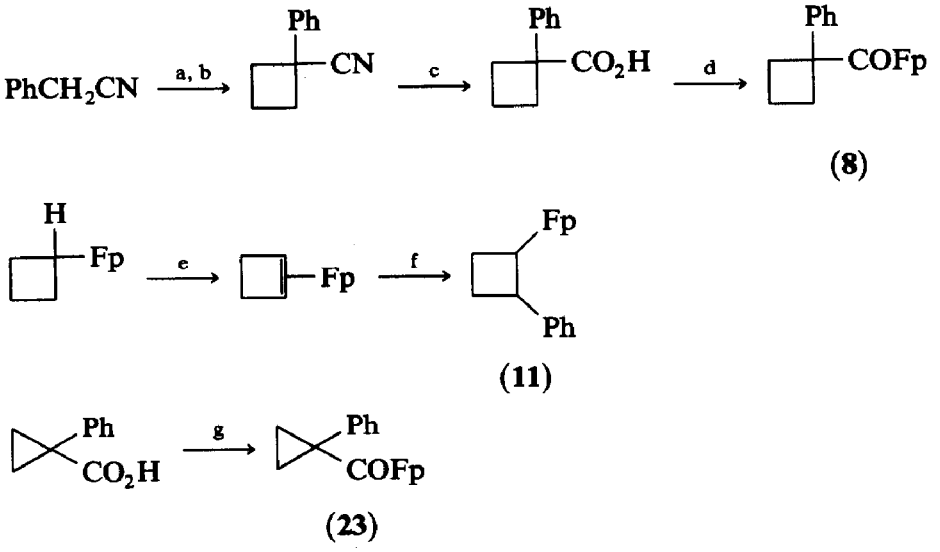
(**5**) (**6**) (**7**)

With an eye to ascertaining whether a combination of ring strain relief and stabilization by a phenyl ring would provide sufficient bias to induce ring expansion of either cyclobutane or cyclopropane, we have now prepared the two Fp–acyl complexes **8** and **23** (X = Ph) and studied their photochemistry (and, in one case, thermal chemistry). The results of these investigations are reported here.

Results and discussion

Expansion of cyclobutane to ferracyclopentene probably relieves more ring strain than does expansion of cyclopropane to metallocyclobutene [5]. We therefore elected to study the cyclobutyl system first. The acyl complexes **8** and **23** (X = Ph) were readily prepared by standard reactions as outlined in Scheme 1. The corresponding very unstable σ complex **13** was formed from either photolysis or chemically induced decarbonylation (with trimethylamine oxide) of **8**. The isomeric σ complex **11** was prepared as outlined in Scheme 1 but only in very poor yield. For independent photolysis studies, **11** that was isolated from photolysis reactions of **8** was therefore used.

Photolysis studies were carried out under a nitrogen atmosphere in degassed solvent (usually benzene-d_6) in NMR tubes sealed with septa vented to a nitrogen atmosphere with a hypodermic needle. Reactions were followed by monitoring their ^{13}C NMR spectra. Reactions of **8** were significantly more rapid (typically half reaction of about 2 h) than **11**. Under all conditions, both reactions gave mixtures consisting of predominately Fp_2, 1-phenylcyclobutene, and phenylcyclobutane (Scheme 2). Photolysis of **8** also gave some **16**. Structures of both **17** and **19** were confirmed by independent syntheses. Careful monitoring of the reaction of **8** as it progressed showed the buildup and decline of what was presumed to be the σ



Scheme 1. (a) NaH, DMSO, RT [6]; (b) 1,3-dibromopropane [6]; (c) HCl, HOAc, H_2O [6]; (d) oxalyl chloride followed by KFp in THF, 0 °C; (e) $Ph_3C^+ BF_2^-$; (f) PhMgBr or PhLi; (g) oxalyl chloride followed by KFp in THF, 0 °C.

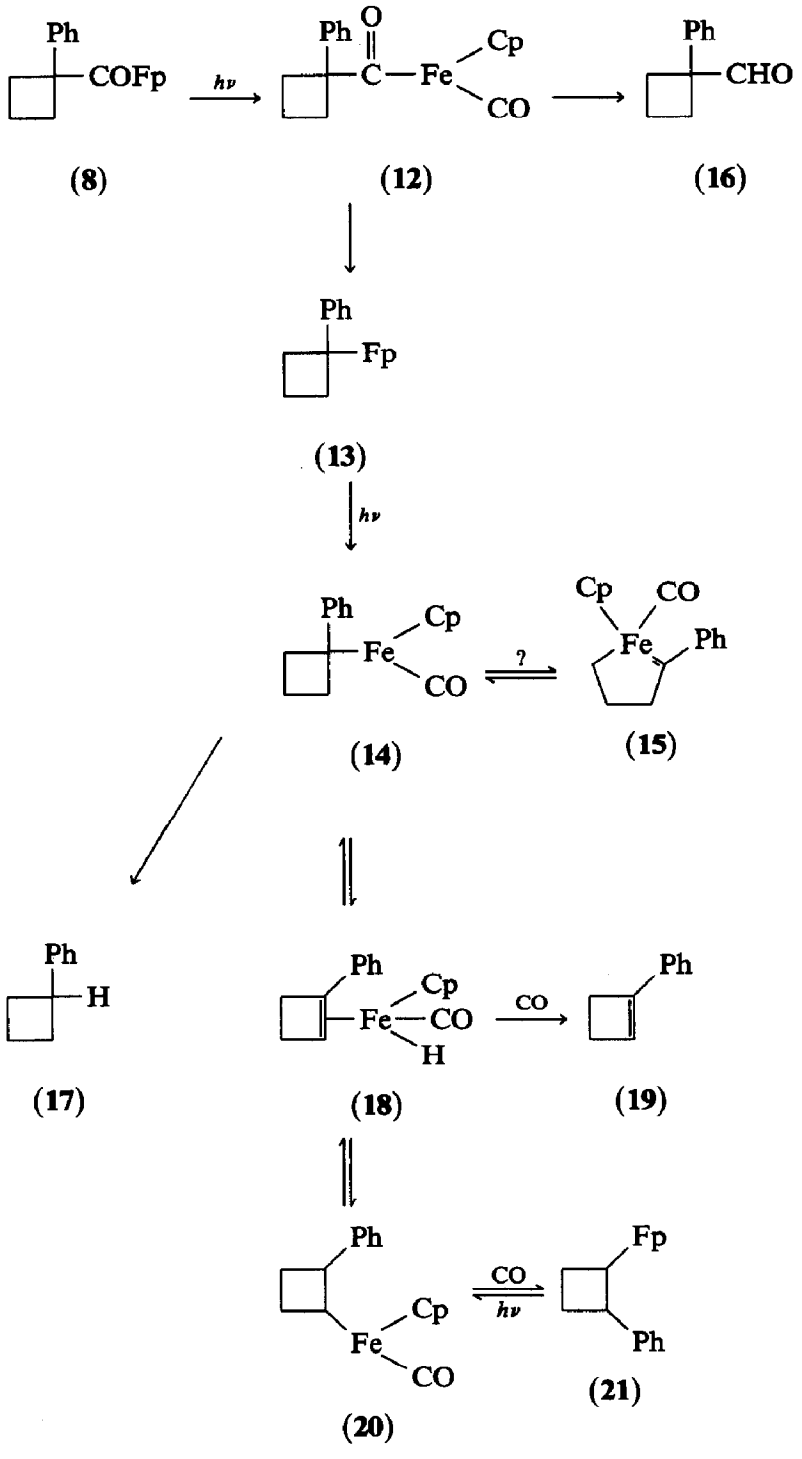
complex **13**. This presumption was confirmed by stopping the reaction before completion and isolating and characterizing this new material.

The origin of the organic products is important because they could be explained by either of two mechanisms, one of which includes the decarbonylation of **8** and **13** as pictured in Scheme 2 which would mean the rearrangement manifold had been entered but, instead of giving **15**, had gone astray. In the other, a radical process (Scheme 3) (much less likely from **11** than from **13**) the reaction manifold of interest is never entered and nothing is learned about the α-elimination question. We therefore undertook to distinguish between these possibilities.

The key steps in the decarbonylation mechanism in Scheme 2 are the rearrangements of the sixteen electron iron complexes **14** and **20** to the metal hydride π complex **18** [7]. Dissociation of this would give the observed phenylcyclobutene and FpH which could reduce **14** to phenylcyclobutane. All of these steps, including reductions of sixteen electron sigma and acyl complexes with metal hydrides [8] have ample precedent. Furthermore, even when the carbene corresponding to **15** is stabilized by a methoxy group there is strong evidence for a facile equilibrium with the π-complex that corresponds to **18** [1a].

In the alternative radical mechanism (Scheme 3) the acyl or σ complex undergoes homolytic cleavage to give the phenyl stabilized radical **22** which could give phenylcyclobutane and 1-phenylcyclobutene by either simple disproportionation or reactions with the Fp radical and FpH. An analogous (although less likely) mechanism for product formation by a radical mechanism from **11** can also be envisaged.

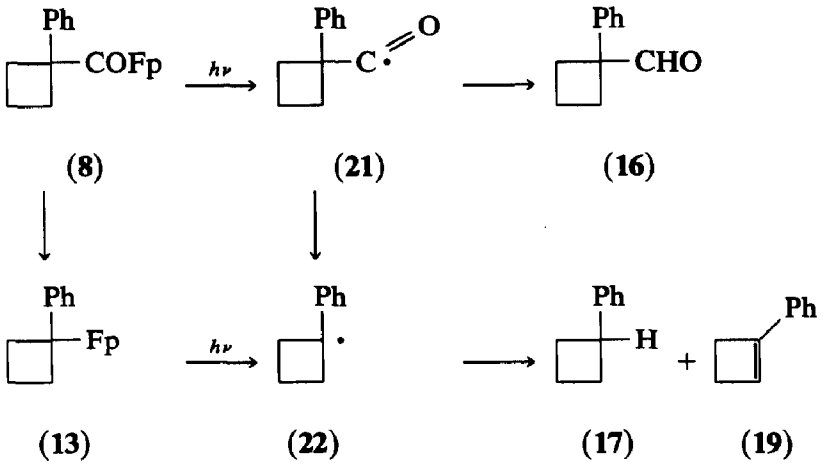
Two tacks were taken to assess the importance of the radical mechanism. In the first, photolysis of **8** was carried out in a large excess of 1,4-cyclohexadiene to see if **21** could be intercepted before it decarbonylated (very unlikely) or **22** before it disproportionated. This would appear as either formation of the aldehyde **16** or an



Scheme 2

increase in the phenylcyclobutane/1-phenylcyclobutene ratio, or both. In fact, no aldehyde appeared and no change in the ratio was observed.

Second, the 1-phenylcyclobutyl radical (**22**) was independently generated by



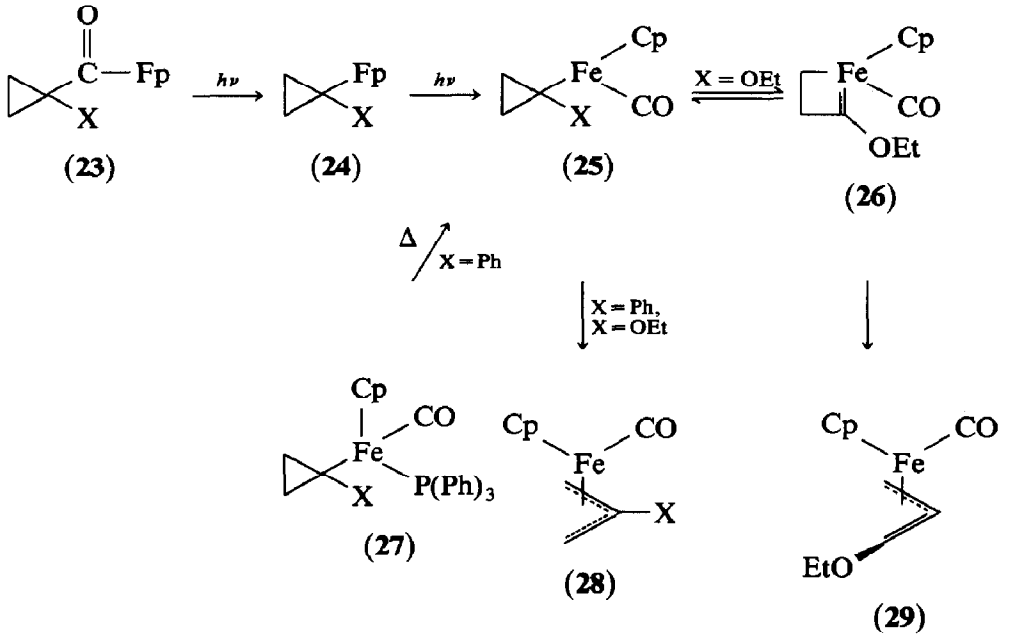
Scheme 3

warming the corresponding diacyl peroxide. This was a very messy reaction that gave only trace amounts of phenylcyclobutane and 1-phenylcyclobutene. However, most important, it gave ca. 10% of 1-phenylcyclobutyl dimer. In other words, **22** behaved like its acyclic counterpart, the cumyl radical [9]. Careful examination of the products from photolysis of either **8** or **11** revealed no trace of the phenylcyclobutyl dimer.

From these results we conclude that photolysis of **8** and **11** leads to the sixteen electron complexes **14** and **20** which behave like their methoxy substituted counterparts in that they undergo β-hydrogen elimination to give **18**. However, unlike the methoxy substituted complex, rather than giving the rearranged carbene **15**, the π-complex dissociates [10*]. Consistent with this conclusion was the observation of a transient resonance in the ^{1}H NMR spectrum at -11.8 ppm, the shift expected of FpH [11]. Finally, it must be recognized that these results do not distinguish between a kinetic and a thermodynamic reason for not observing the carbene complex. It is quite possible that the sixteen electron intermediate **14** is in equilibrium with **15** but that phenyl stabilization is insufficient to prevent decomposition via the π complex **18**. All attempts to detect **15** as a transient failed.

Although expansion of cyclobutane to ferracyclopentene probably relieves more strain than cyclopropane to ferracyclobutene, the latter has the advantage that even transient formation of a rearranged carbene might be detected by a unique product. Thus, we have found that the ferracyclobutene **26** (Scheme 4) rearranges to the terminal π-allyl complex **29** in competition with rearrangement of the cyclopropane **25** (X = OEt) to the centrally-substituted π-allyl complex **28** [2b]. We therefore prepared **23** (X = Ph) and studied its photochemistry. In contrast to the phenyl substituted cyclobutyl complex, photolysis of **23** (X = Ph) led cleanly to the σ complex **24** (X = Ph) and the reaction stopped. No further reaction was observed even when the photolysis was continued for several hours. With the exception of qualitative changes in the rate of decarbonylation of the acyl complex, changing the solvent to tetrahydrofuran showed no effect on the course of this reaction.

* Reference number with asterisk indicates a note in the list of references.



Scheme 4

Thermally-induced extrusion of a phosphine ligand to give a sixteen electron η^5-cyclopentadienylcarbonyliron complex is normally more facile than CO extrusion [26]. The phosphine substituted complex **27** (X = Ph) was therefore prepared by photolysis of **23** (X = Ph) in the presence of triphenylphosphine. Upon heating a solution of this complex in benzene-d_6 to 75 °C, the reaction proceeded quite cleanly to give a single new product that was identified by spectroscopy as the centrally substituted π-allyl complex **28** (X = Ph). From formation of this product, we conclude that the desired sixteen electron iron intermediate was formed. However, from its substitution pattern, it is equally clear that the π-allyl complex did not arise from the rearranged carbene complex corresponding to **26**.

Thus, it would appear that changing methoxy to phenyl on either a cyclobutane or a cyclopropane changes the chemistry of the iron complex substantially. With a methoxy substituent, in both cases α-elimination to the carbene complex dominates. With phenyl in place of methoxy, the reactions are totally diverted to non-carbene products suggesting that, if rearrangement does occur in either the phenylcyclobutyl or phenylcyclopropyl complexes, it is reversible and all products originate from the unrearranged complex.

Experimental

General. All reactions were performed under an inert atmosphere of N_2. THF and ether were distilled from Na/K alloy and benzophenone. Hexane was distilled from Na/K alloy. Methylene chloride was distilled from Sicapent (MCB). Melting points: Thomas–Hoover melting point apparatus. ^{1}H NMR spectra: JEOL FX-100, Varian XL-200, Varian XL-300. ^{13}C NMR spectra: JEOL FX-100, Varian XL-200,

Varian XL-300. IR spectra: Perkin–Elmer 137, Nicolet 5-DXB FTIR. Gas chromatograph: Hewlett–Packard 5790 A Series, Silicone FS 1265. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. Mass spectra: AEI MS-30. Photolyses were carried out at room temperature using a 450-W low pressure Hg-Hanovia lamp in a Pyrex well. When referring to flash chromatography, 230–400 mesh silica gel was used.

1-Phenylcyclobutanecarboxylic acid chloride. To 3.2 g (25.2 mmol) oxalyl chloride in 5 ml dry diethyl ether was added 1.0 g (7.42 mmol) 1-phenylcyclobutanecarboxylic acid. The acid was prepared as previously reported [12] via 1-phenylcyclobutanecarbonyl nitrile. The mixture was stirred overnight and the acid chloride purified by Kugelrohr distillation (90–105 °C/70 mmHg) giving 1.053 g (70%) of a pale yellow liquid. IR ($CDCl_3$); 2880–3100, 1750–1800, 1449, 1150 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$): δ 7.30–7.60 (5H, m, aryl),1.55–3.20 (6H, m, CH_2); ^{13}C NMR (25 MHz, C_6D_6): δ 15.91 (CH_2), 32.82 (CH_2), 62.30 (C), 127.26, 128.00, 129.11, 140.24 (aryl CH), 176.98 (C=O).

Dicarbonyl(η^5-cyclopentadienyl)(1-phenylcyclobutyl-1-carbonyl)iron (5). To a stirred suspension of 1.16 g (5.30 mmol) KFp in 20 ml dried THF at 0 °C was added 1.22 g (6.30 mmol) 1-phenylcyclobutanecarboxylic acid chloride from above. The reaction was warmed to room temperature and stirred for 5 h (or overnight). The solvent was removed in vacuo and the residue dissolved in methylene chloride, filtered over Celite, evaporated, and flash chromatographed. Using 10% ethyl acetate/hexane, the first yellow band collected was the σ complex **13**. The acyl complex was then eluted as a second yellow band. Removal of the solvent gave 0.81 g (45%) of a yellow solid. Sublimed (50 °C/0.05 mmHg), decomposition point 98 °C. IR (C_6D_6): 1950, 2010, 1670 cm^{-1}. ^1H NMR (100 MHz, C_6D_6): δ 7.07–7.29 (5H, m, aryl CH), 4.07 (5H, s, Cp), 1.64–2.72 (6H, m, CH_2); ^{13}C NMR (25 MHz, C_6D_6): δ 252.16 (CO), 216.70 (CO), 143.90, 127.32, 128.88, 129.46 (CH), 87.50 (Cp), 75.30 (C), 32.90, 16.01 (CH_2). Anal. Found: C, 64.20; H, 4.80. $C_{18}H_{16}FeO_3$ calcd.: C, 64.31; H, 4.80%.

Photolysis of 8 and 23. In a typical experiment 100 mg (0.30 mmol) of the acyl complex was dissolved in 1 ml of C_6D_6 in an NMR tube with a boiling chip. The materials were photolyzed under N_2 in an H_2O bath at room temperature. The reactions were monitored by ^1H and ^{13}C NMR and were terminated upon the disappearance of approximately 50% of the starting material. The mixtures of new products could be separated by flash chromatography.

From the photolysis of **8**, three new organometallic species were isolated. Initially, pure hexane was used to separate the organic components which came down as a colorless band (visible by ultra violet, using luminescence 609 Phosphor and a quartz column). By spectroscopy the organic products of the reaction were found to be phenylcyclobutane and 1-phenylcyclobutene formed in a 1/1 ratio. The second compound to be eluted with hexane was the σ complex **13** as a bright yellow band (7%). Changing the solvent system to 5% ethyl acetate/hexane, gave **11** as the second yellow band (10%) followed by a third yellow band which was **8**. The final fraction, Fp_2, can be retrieved with 20% ethyl acetate/hexane as a red band giving a red solid upon evaporation of the solvent (33%). (FpH could not be isolated by column chromatography.)

In the photolysis of **23**, the sigma complex, **25**, was isolated as given in the latter portion of this experimental section.

Photolysis of 8 in the presence of 1,4-cyclohexadiene. The acyl complex **8** was dissolved in C_6D_6 in an NMR tube with a boiling chip and freshly distilled, degassed 1,4-cyclohexadiene. The concentration of the 1,4-cyclohexadiene was varied from 2 to 20 molar equivalents (based on acyl complex). After photolysis was approximately 75% complete, the mixture was column chromatographed (silica gel, 100% hexane) and the first band (colorless), monitored by TLC, was collected. The solvent was evaporated, and the components as well as their concentrations were analyzed by gas chromatography. The gas chromatograms showed the presence of 1,4-cyclohexadiene, benzene-d_6, 1-phenylcyclobutene, and phenylcyclobutane. The ratio of phenylcyclobutane to 1-phenylcyclobutene was consistently $1.5/1.0 + 0.3$ in the presence and absence of cyclohexadiene. In no case, regardless of the amount of 1,4-cyclohexadiene, were the relative concentrations of the organic products effected.

Dicarbonyl(η^5-cyclopentadienyl)(1-phenylcyclobutyl)iron (13). Although solutions of **13** appeared to be relatively stable, concentration led to rapid decomposition and as a result, attempts to isolate and characterize it as a pure material were unsuccessful. In a typical experiment, a solution of 100 mg (0.30 mmol) of **13**, in 1.0 ml of C_6D_6 was photolyzed until **8** had disappeared (monitored using ^{13}C NMR following the Cp resonances). The resulting mixture was chromatographed (flash) over silica gel eluting with 5% ethyl acetate/hexane. Removal of the solvent from the first yellow band gave **13** as an unstable brown oil. Although the NMR spectra showed impurities, the following resonances were sufficiently dominant to be assigned with some confidence to **13**. ^1H NMR (75 MHz, C_6D_6): δ 3.74 (Cp); ^{13}C NMR (75 MHz, C_6D_6): δ 18.78, 43.03 (CH_2), 87.56 (Cp), 122.65 (C), 124.44, 127.89, 127.94 (aryl CH), 218.08 (C=O).

It was also possible to chemically decarbonylate **8** to give **13**. To 0.056 g (0.17 mmol) **8** in 1–5 ml C_6D_6 or acetone-d_6 was added 0.038 g (0.34 mmol) trimethylamineoxide [13]. Similarly, to 5 mg (0.0015 mmol) **8** in 1–5 ml acetonitrile-d_3 was added 0.13 g (0.018 mmol) of bis(triphenylphosphine)dichlororhodium [14].

Each of the above reactions were mixed vigorously in an NMR tube since the dimer and the amineoxide were only slightly soluble in the solvents used. They were allowed to react for three to seven days at room temperature with frequent mixing. The spectra of the products formed in these reactions confirmed clean decarbonylation, but, again, the σ complex could not be isolated due to its instability.

Dicarbonyl(η^5-cyclopentadienyl)(trans-2-phenylcyclobuy-1-yl)iron (11). The best samples of **11** were isolated from the photolysis of the acyl complex **8**. In a typical experiment **8** was dissolved in an NMR tube containing C_6D_6 and a boiling chip. The photolysis was monitored by ^{13}C NMR, following the Cp resonances until no **8** (δ 87.50) or **13** (δ 87.56) remained. These materials, being very photo-reactive, decreased rapidly while the concentrations of **11** (δ 84.48) steadily increased. **11** could be isolated in small yields as a yellow band using flash chromatography, eluting with 5% ethyl acetate/hexane. Typically, this gave a 20–30% yield of **11** as a yellow oil. Like **13** the compound was very unstable once the solvent was removed. The following spectral data were obtained. IR (C_6D_6): 1950, 2000^{-1} cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 1.30–3.30 (4H, m, CH_2), 3.36 (2H, m, CH), 3.97 (5H, s, Cp), 7.13–7.50 (5H, m, aryl); ^{13}C NMR (75 MHz, C_6D_6): δ 32.48 (CH), 34.11, 34.30 (CH_2), 57.98 (CH), 84.48 (Cp), 126.48, 127.48, 128.57, 145.65 (aryl), 217.61, 217.90 (C=O). Verified by APT.

1-Phenylcyclobutene (19). 1-Phenylcyclobutene was synthesized by dehydration of 1-phenylcyclobutanol (23%) [15]. 1-Phenylcyclobutanol was prepared by addition of phenyllithium to cyclobutanone (49%) [16], cyclobutanone was prepared by oxidation of cyclobutanol with CrO_3 [17], and cyclobutanol was synthesized via ring opening of cyclopropylcarbinol [17]. Spectra of 1-phenylcyclobutene were consistent with the literature. ^{13}C NMR (25 MHz, C_6D_6): δ 25.92, 28.41 (CH_2), 124.05, 126.50, 127.60, 128.00 (aryl), 134.93, 146.36 (alkenyl C).

Phenylcyclobutane (17). **17** was prepared via Na/NH_3 reduction of **19** (30%) [15]. Spectra are consistent with the literature. ^{13}C NMR (75 MHz, C_6D_6): δ 18.52, 30.01, 40.72 (CH_2), δ 126.56, 126.01, 128.48, 149.23 (aryl).

Independent generation of 1-phenylcyclobutyl radical [18]. To test for dimer formation from the 1-phenylcyclobutyl radical, 1-phenylcyclobutyryl peroxide was prepared by the method of Kane and Brown and thermolyzed. The reactions were run at temperatures from -78–$0\,^\circ C$ and the concentrations, with respect to the acid chloride, of the solutions varied from 0.10 to 1.00 *M*. The following represents a typical procedure. To 4 ml of methylene chloride was added 0.50 g (2.58 mmol) of 1-phenylcyclobutylcarboxylic acid chloride. The solution was brought to $0\,^\circ C$ and stirred under N_2. To this mixture was added 0.40 g (4.99 mmol) Na_2O_2 (slowly and with protection!) and the reaction was stirred for 1 h, warmed to room temperature, and stirred an additional 4 h. The excess acid chloride was hydrolyzed with H_2O and the H_2O layer drawn off and extracted 4 times with methylene chloride. The organic layers were combined, dried over $CaCl_2$, and the solvent evaporated (with care in case any diacyl peroxide remained) by a stream of N_2. The residue was then redissolved in benzene, refluxed for one hour to assure complete peroxide decomposition. The solvent was then removed by a stream of N_2. In the crude reaction mixture, 1-phenylcyclobutene phenylcyclobutane, and 1-phenylcyclobutyl dimer were identified by ^{13}C NMR. Comparison of these spectra was made with those obtained by their respective alternative syntheses as given in this experimental. The ratios of the phenylcyclobutane and 1-phenylcyclobutene varied with the concentration of the reaction mixtures. 1-Phenylcyclobutene generally being formed in greater amounts than phenylcyclobutane ranging from a $1.5/1.0 \pm 0.30$ ratio respectively to exclusive formation of the alkene and only trace amounts of the alkane. (These values were obtained using ^1H NMR spectroscopy as the compounds were very easily resolved and their protons integrated.) As the concentrations of the reaction mixtures increased, so did the amount of 1-phenylcyclobutene to phenylcyclobutane. Using column chromatography (silica gel, 100% hexane) the 1-phenylcyclobutyl dimer was removed from the mixture as the first colorless band. The solvent was evaporated giving a 8–10% yield. Spectral data are contained in the synthetic procedure for the 1-phenylcyclobutyl dimer.

1-Phenylcyclobutyl dimer. The 1-phenylcyclobutyl dimer was independently synthesized as reported [19] by coupling of 1-phenylcyclobutanol with titanium trichloride and $LiAlH_4$ (69%). ^{13}C NMR (75 MHz, C_6D_6): δ 15.62, 30.35, 53.50 (alkyl), 125.58, 127.12, 128.17, 146.51 (aryl).

1-Phenylcyclopropanecarboxylic acid chloride. 1-Phenylcyclopropanecarboxylic acid chloride (70%) was prepared in the same way as 1-phenylcyclobutanecarboxylic acid chloride described above [20].

Dicarbonyl(η^5-cyclopentadienyl)(1-phenylcyclopropyl-1-carbonyl)iron (23, X = Ph). To 0.96 g (4.43 mmol) KFp in 20 ml dry THF at $0\,^\circ C$ was added 0.80 g (4.43 mmol)

of 1-phenylcyclobutane carboxylic carboxylic acid chloride in 5 ml THF. The solution was stirred under N_2 at 0 °C for one hour, warmed to room temperature, evaporated, and purified by column chromatography. Using silica gel, 100% hexane eluted a yellow band which upon evaporation of the solvent was found to be the σ complex **24**. The solvent was changed to 2% ethyl acetate/hexane and another yellow band was collected. The solvent was removed under vacuo to give **23** (X = Ph) as a yellow solid (50%). (This band was immediately followed by Fp_2.) Recrystallization from hexane, m.p. 66–68 °C. IR ($CDCl_3$): 1626, 1963, 2021 cm^{-1}; ^1H NMR (75 MHz, C_6D_6): δ 1.51–1.55 (2H, m, alkyl), δ 4.00 (5H, s, Cp), δ 7.09–7.17 η δ 7.32, δ 7.35 (5H, m, aryl); ^{13}C NMR (75 MHz, C_6D_6): δ 15.26, 54.54 (alkyl), 85.79 (Cp), 127.03, 128.45, 131.49, 142.25 (aryl), 215.04, 249.25 (C=O). Anal. Found: C, 63.19; H, 4.42. $C_{17}H_{14}FeO_3$ calcd.: C, 63.38; H, 4.38%.

Dicarbonyl(η^5-cyclopentadienyl)(1-phenylcycloprop-1-yl)iron (25, X = Ph). 100 mg **23** (X = Ph) was photolyzed in C_6D_6 for 3 hours. The mixture was purified by flash column chromatography (silica gel). Using 100% hexane, the first yellow band was collected and the solvent evaporated giving **25** (X = Ph) as a yellow oil, 0.035 g (38%). IR (C_6D_6): 1952, 2008 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 0.82–0.95 (4H, m, alkyl), 3.90 (5H, s, Cp), 6.94–7.32 (5H, m, aryl); ^{13}C NMR (75 MHz, C_6D_6): δ 9.68, 17.42 (CH_2), 87.00 (Cp), 123.88, 128.12, 128.89, 159.86 (aryl), 217.51 (C=O). Analysis Found: C, 65.07; H, 4.88. $C_{16}O_{14}O_2Fe$ calcd.: C, 65.33; H, 4.80%.

Carbonyl(triphenylphosphine)(η^5-cyclopentadienyl)(1-phenylcycloprop-1-yl)iron (27). To **25** (X = Ph) from above was added 1 equivalent of triphenylphosphine and the mixture was photolyzed in C_6D_6. The reaction was monitored by ^1H NMR and was terminated when all of **25** had been converted to **27**. The mixture was purified by column chromatography elution first with 100% hexane gave unreacted starting material. The solvent was then changed to 5% ethyl acetate/hexane. **27** eluted as an orange band and the solvent was evaporated giving an orange solid, 0.028 g (45%). Recrystallization from hexane. Decomp. 122 °C. IR ($CDCl_3$): 1910 cm^{-1}; ^1H NMR (60 MHz, C_6D_6), 0.085–1.30 (4H, m, CH_2), 4.40 (5H, d, Cp), δ 6.50–7.50 (20H, m, aryl); ^{13}C NMR (25 MHz, C_6D_6): δ 1.06 (d, C, J 21.97 Hz), 19.86 (d, CH_2, J 56.15 Hz), 86.68 (CP), 122.74, 127.67, 128.29 (C, aryl), 128.63 (C), 129.6 (d, C, aryl), 133.95 (d, C, aryl), 137.02 (d, C, aryl), 162.31 (C, aryl). Mass spectrum *m/e*: 528 (M^+), 500 ($M^+ - CO$), 238 ($M^+ - CO - P(Ph)_3$).

Carbonyl(η^5-cyclopentadienyl)(2-phenylpropenyl)iron. For a general procedure, compound **27** from above was dissolved in C_6D_6, in an NMR, tube and heated to reflux. (Oil bath temperature was 95 °C.) The mixture was heated for 12–24 hours. The products were separated by column chromatography (flash/silica gel 230–400 mesh) using pure hexane to remove excess triphenylphosphine and 2% ethyl acetate/hexane to remove the allyl **28** as a yellow band, giving a yellow solid, 30–40%. IR: 1946 cm^{-1}. ^1H NMR (C_6D_6, 300 MHz): δ 0.65–0.66 (2H, d, CH), 3.33–3.34 (2H, d, CH), 3.81 (5H, s, Cp), 6.99–7.40 (5H, m, aryl). ^{13}C NMR (C_6D_6, 75 MHz): δ 31.10 (CH_2), 81.47 (Cp), 87.08 (CH), 125.09, 127.20, 128.60, 144.09 (aryl), 223.03 (CO).

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