plied. This resulted in transmission factors ranging from 0.96 to 1.00. The data were corrected for Lorentz and polarization effects. For a final refinement based on 1434 observed reflections ($I > 3.00r(I)$) and 280 variable parameters, the weighted and unweighted agreement factors were $R = 0.044$ and $R_w = 0.051$. The largest parameter shift in the final cycle was 0.01 times its esd. The standard deviation of an observation of unit weight was 0.93. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to down weight the intense reflections. Plots of $\sum w(|F_o - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin $\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum peak in the final difference Fourier map corresponded to 0.25 e$^-$/Å$^3$.

**($\eta^2$,$\eta^4$-2-*tert*-Butylcyclohexadienylidene-*exo*-ethane)Cr($CO)_3$ (22).** Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 14 carefully centered reflections in the range $39.73 < 2\theta < 39.98°$, corresponded to a monoclinic cell. On the basis of the systematic absences $h0l$ for $l \neq 2n + 1$ and $0k0$ for $k \neq 2n + 1$ and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (no. 14). Of the 2239 reflections that were collected, 2135 were unique ($R_{\rm int} = 0.040$). The intensities of three representative reflections that were measured after every 150 reflections and remained constant throughout the data collection, indicating that no decay correction was necessary. The linear absorption coefficient for Mo K$\alpha$ is 7.4 cm$^{-1}$. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. This resulted in transmission factors ranging from 0.88 to 1.00. The data were corrected for Lorentz and polarization effects. For a final refinement based on 1496 observed reflections ($I > 3.00r(I)$) and 172 variable parameters, the weighted and unweighted agreement factors were $R = 0.038$ and $R_w = 0.050$. The largest parameter shift in the final cycle was 0.00 times its esd. The standard deviation of an observation of unit weight was 1.49. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to down weight the intense reflections. Plots of $\sum w(|F_o - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin $\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.48, and −0.16 e$^-$/Å$^3$, respectively.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., and the University of Kansas General Research Fund for partial support of this project. J.A.H. acknowledges the efforts of Steven Gray in improving the yields of some products obtained in this study. M.E.T.-M. acknowledges the Graduate Professional Opportunities Program and Phillips Petroleum Corp. for fellowship supports.

**Supplementary Material Available:** Complete tables of X-ray crystallographic data for **5a** and **22**, including fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles (18 pages); tables of observed and calculated structure factors for **5a** and **22** (24 pages). Ordering information is given on any current masthead page.

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# $\alpha$-Elimination of Carbon Induced by Manganese

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Unlike the case for the $\alpha$-methoxycyclobutyl complex of dicarbonyl($\eta^5$-cyclopentadienyl)iron, photolysis of the $\alpha$-methoxycyclobutyl complex of $Mn(CO)_5$ does not lead to the ring-expanded metallacyclopentenes **27** (from $\alpha$-elimination of carbon); the dominant products are simply methoxycyclobutene and $\alpha$-methoxycyclobutanecarboxaldehyde (along with traces of methoxycyclobutane). The same results are found when reaction is induced by either heat or trimethylamine oxide. From the available evidence, these reactions are better explained by CO loss followed by $\beta$-hydrogen elimination than by homolysis of the carbon–metal bond followed by radical reactions. In contrast, $\alpha$-elimination of carbon occurs smoothly when strain relief is increased and methoxycyclobutene formation is retarded by benzannelation. This rearrangement gives the two isomeric cyclic carbene complexes **34** and **35**. The latter does not isomerize to **34** upon heating to 72 °C for 36 h.

Rearrangement of an alkyl or aryl group from a saturated carbon to an electron-deficient iron ($\alpha$-elimination of carbon)[1,2] appears to normally be thermodynamically unfavorable. However, we have recently found that if the carbene is stabilized by an electron-donating group and if sufficient ring strain is relieved during the rearrangement, the equilibrium between the 16-electron iron and its corresponding alkyl-substituted carbene can be induced to favor the carbene; for example, photolysis of **1**[5,7] or **4**[6] leads cleanly to **3** and **7**, respectively.

The purpose of the work reported herein was to determine if a metal other than iron would induce $\alpha$-elimination of carbon. For these studies, pentacarbonylmanganese(I) (and derivatives) was selected as the metal system because, when this work was begun, the only published[8] theoretical

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[1] Cf.: Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. For one example of a reaction where the published data are consistent with $\alpha$-elimination of carbon as one step in the mechanism, see: Miyashita, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

[2] The reverse of this reaction (carbene migratory insertion) is well documented[3] as are both $\alpha$-elimination of hydrogen (insertion of electron-deficient transition metal into $\alpha$-C–H) and its reverse.[4]

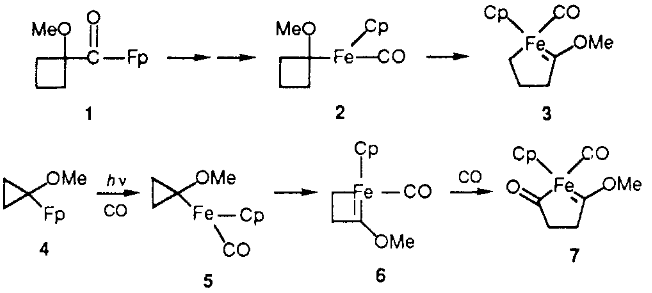
[3] (a) Ward, A. S.; Mintz, E. A.; Kramer, M. P. *Organometallics* **1988**, *7*, 8. (b) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282. (c) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 686. (d) Thorn, D. L. *Organometallics* **1985**, *4*, 192. (e) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026. (f) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. (g) Kleitzein, H.; Werner, H.; Serhadli, P.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46. (h) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (i) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (j) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648. (k) Threlkel, R. S.; Bercaw, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (l) Van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1977**, *142*, 243.

[4] Cf.: McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704.

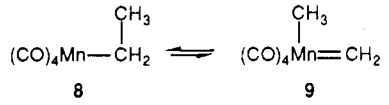
[5] Cf.: Stenstrom, Y.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079.

[6] (a) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 944. (b) Conti, N. J.; Jones, W. M. *Organometallics* **1988**, *7*, 1666.

[7] (a) Stenstrom, Y.; Jones, W. M. *Organometallics* **1986**, *5*, 178. (b) Stenstrom, Y.; Klauck, G.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155.



study of this kind of reaction predicted that the following equilibrium should be essentially thermally neutral with almost no activation energy:[9]



$$(CO)_4Mn(CH_3){-}CH_2 \rightleftharpoons (CO)_4Mn(CH_3){=}CH_2$$

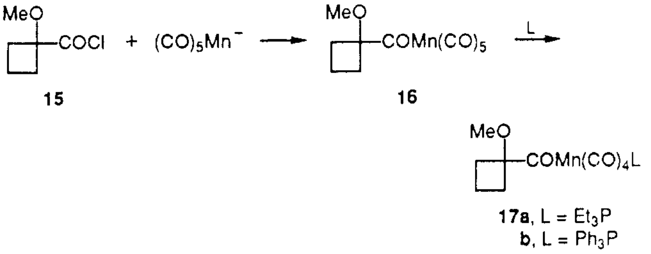
**8** **9**

To this end, manganese complexes **14**, **16**, and **17** were prepared for decarbonylation studies. The results of these investigations are reported at this time.

## Preparation of Organic Ligands and Acyl Complexes

The acid chloride **15** of α-methoxycyclobutanecarboxylic acid was prepared as previously reported.[5,7] α-Methoxybenzocyclobutenecarbonyl chloride was prepared from benzocyclobutenone as outlined in Scheme I.

Acyl complexes **14** and **16** were prepared by reaction of $(CO)_5Mn^-$ with the acyl chlorides. Phosphine-substituted acyl complexes **17** were prepared by simply warming **16** with the phosphine. One equivalent of triethylphosphine gave only one stereoisomer. This is believed to be the cis isomer because its phosphorus–acyl carbon coupling constant of 14.75 Hz is identical with that of the independently synthesized model complex **18** of known cis stereochemistry.[10] With 2 equiv of $Et_3P$ a second carbonyl was displaced to give 23% (isolated yield) of a bis(triethylphosphine) complex. One or more equivalents of $Ph_3P$ led to only monosubstitution but gave a mixture of cis and trans stereoisomers. On the basis of P–acyl carbon coupling constants, the major isomer ($J_{PC}$ = 14.1 Hz) is assigned the cis stereochemistry. Coupling in the minor isomer was to small to resolve. The cis and trans isomers could not be separated and were therefore characterized and used as a mixture.

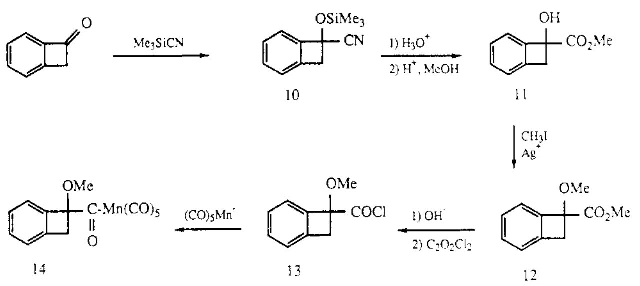


**17a**, L = $Et_3P$
**b**, L = $Ph_3P$

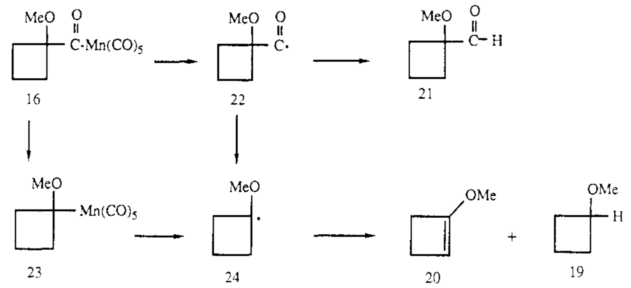
$$(CO)_4(Ph_3P)MnCOCH_3$$

**18**

### Scheme I



### Scheme II



### Scheme III

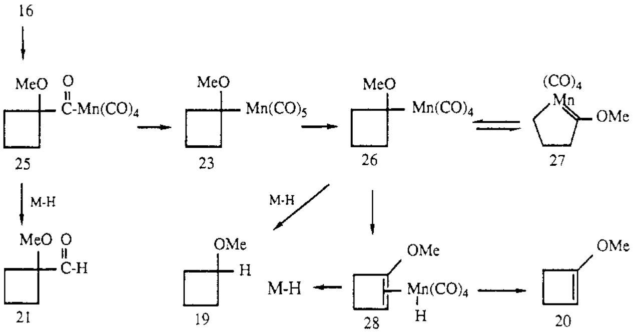


**Table I. Relative Amounts of Organic Products from Decomposition of 16**

| reacn conditions | 21[a] | 20[a] | 19[a] |
|---|---|---|---|
| 52 °C, benzene-$d_6$, 48 h | 1.02 ± 0.02 | 1.0 | 0.11 ± 0.01 |
| 25 °C, *hν*, benzene-$d_6$, 48 h | 1.06 ± 0.03 | 1.0 | 0.11 ± 0.02 |
| 2.2 equiv of $Me_3NO$, 25 °C, benzene-$d_6$ | 1.08 ± 0.03 | 1.0 | 0.15 ± 0.04 |
| 1 equiv of $CP(CO)_3WH$, 55 °C, benzene-$d_6$, 12 h | 2.03 ± 1.0 | 1.0 | 0.03 ± 0.02 |
| 52 °C, MePh-$d_8$, 48 h | 1.05 ± 0.01 | 1.0 | 0.06 ± 0.01 |
| 5 equiv of 1,4-cyclohexadiene, benzene-$d_6$, 52 °C | 1.04 ± 0.01 | 1.0 | 0.05 ± 0.01 |
| 20 equiv of 1,4-cyclohexadiene, benzene-$d_6$, 52 °C | 1.05 ± 0.01 | 1.0 | 0.04 ± 0.02 |

[a] Ratios determined by integration of the methoxy resonance in the $^1H$ NMR spectra.

## Thermolysis, Photolysis, and Chemical Decarbonylation of Manganese Derivatives of α-Methoxycyclobutane

Thermolyses were typically carried out in benzene-$d_6$ or toluene-$d_8$ at 52 °C. Photolyses were carried out in NMR tubes with use of a 450-W Hanovia medium-pressure lamp cooled in a Pyrex cold finger. Reactions were monitored by $^1H$ NMR spectroscopy. Specific conditions and results are recorded in Table I. Only **16** underwent significant reaction under these conditions; **17b** showed no reaction after 5 days of photolysis or heating at 70 °C for 1 week, and **17a** showed very slow thermal decomposition (about 10% after heating at 70 °C for 1 week) to the same

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[8] Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

[9] For a more recent theoretical study of this system that predicts α-elimination to be endoergic, see: Ziegler, T.; Versluis, L.; Tschinke, V. *J. Am. Chem. Soc.* **1986**, *108*, 612.

[10] Calderazzo, F.; Noack, K.; Schaerer, U. *J. Organomet. Chem.* **1966**, *6*, 265.

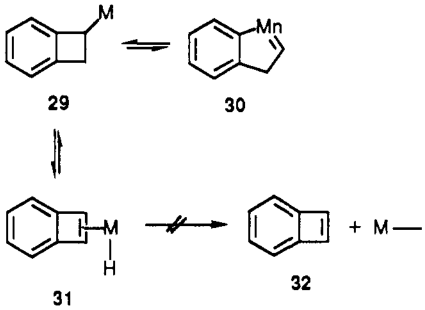
products as from **16**. Common to all decompositions of **16** was formation of $Mn_2(CO)_{10}$. Reactions were quite clean, and the only detectable organic-containing materials in any of the reactions were 1-methoxycyclobutene (**20**),[11] α-methoxycyclobutanecarboxaldehyde (**21**),[11] and traces of methoxycyclobutane (**9**).[11] Using quantitative $^{13}C$ NMR spectroscopy, it was possible to show that these products accounted for about 95% material balance. In no reaction was there any evidence for the carbene complex that would result from α-carbon elimination (no low-field methoxy resonance in the $^1H$ NMR spectra and no very low-field carbene resonance in the $^{13}C$ NMR spectra), nor was there evidence for organic dimers.

From the products of these reactions, we are forced to one of two mechanistic conclusions. Either the 16-electron manganese alkyl complex **23** preferred to follow a reaction path different from the rearrangement that is observed for the corresponding Fp (Fp = dicarbonyl($\eta^5$-cyclopentadienyl)iron) complex (which shows essentially exclusive rearrangement to the iron analogue of **27**) or the 16-electron metal alkyl complex is never formed and therefore has no chance to rearrange. Experiments were therefore undertaken to distinguish between these two possibilities.

The most likely alternatives for production of the three organic products **19**, **20**, and **21** are by a radical process or a decarbonylation–rearrangement sequence. These two mechanisms are outlined in Schemes II and III. In Scheme II, the radical mechanism, the key intermediates are the acyl radical **22** formed from homolytic cleavage of the acyl-manganese bond and the alkyl radical **24** formed from either decarbonylation of **22** or cleavage of the alkyl-manganese bond in **23**. Although homolytic cleavages of both acyl-[12] and alkyl-manganese[14,15] bonds are known, we doubt if Scheme II describes the mechanism of this reaction for the following reasons: (1) Both the photochemistry and thermal chemistry of pentacarbonylmanganese acyl and alkyl complexes appear to normally be dominated by CO loss[12,13] rather than homolytic cleavage. Consistent with the presumption of facile decarbonylation was the finding that warming **16** in the presence of triphenylphosphine or triethylphosphine gave the corresponding substituted acyl complexes **17a** and **17b**, respectively. (2) The substituted acyl complexes **17** were found to be stable to thermal conditions that readily decompose **16** (no reaction when heated at 72 °C for 48 h); phosphine ligands would be expected to accelerate homolysis.[16] (3) The relative yields of aldehyde and methoxycyclobutane did not increase when the reaction was run in the presence of radical traps such as toluene-$d_8$ or 1,4-cyclohexadiene. (4) No dimer of **24** could be detected.[17] (5) Not only could the decomposition of **16** be chemically induced with trimethylamine oxide[18] (in an essentially instantaneous reaction at room temperature) but also the results were identical with those from thermolysis or photolysis, suggesting a common mechanism. Furthermore, 2 equiv of amine oxide was required for complete reaction; with 1 equiv only half of the acyl complex reacted. This suggests that reactions of both the acyl and the σ complexes are induced by the amine oxide, an argument against homolytic cleavage of either **16** or **23**. (6) Finally, as elaborated in the next section, thermolysis of **14** does not give homolysis products despite the potential stabilizing effect of the benzene ring on a radical from homolysis of the alkyl–manganese bond.

From these observations, it would appear that the source of the three organic products from **16** is most likely as depicted in Scheme III. Each step has ample precedent,[12,13] including reduction of the two 16-electron intermediates **25** and **26** with metal hydrides.[16,19–21] Consistent with the suggested reduction of **25** by a metal hydride was the finding that thermolysis of **16** in the presence of added $Cp(CO)_3WH$ increased the relative yield of the aldehyde.

Scheme III includes a 16-electron complex (**26**) that is presumably a requisite for α-elimination of carbon. However, unlike its CpFe(CO) counterpart,[7] rather than **26** inducing this reaction to give a stable carbene complex (**27**), in this case, only β-hydrogen elimination followed by displacement of **20** is observed. In principle, this difference in behavior could be due to a poorer equilibrium between **26** and **27** (or slower formation of **27**), a more facile β-hydrogen elimination/displacement (or dissociation) to give **20**, or both.[22] With an eye to addressing these possibilities, we undertook to design an organic ligand that would both favor the α-carbon elimination and retard the β-hydrogen elimination/displacement reaction. For this, we ultimately settled on the methoxybenzocyclobutenyl ligand, where dissociation of the π complex should be retarded by the high energy of the resulting benzocyclobutadiene (**32**)[23] and the equilibrium giving **30** should be favored due to increased release of ring strain.[24] The requisite penta-



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(11) Structures of **19** and **20** were confirmed by comparison with known compounds. **19**: Rocek, J.; Aylward, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 5452. **20** [$^{13}C$ NMR (benzene-$d_6$, 75 MHz, ppm): 154.0 (C-1), 94.8 (C-2), 54.7 OMe), 31.9 (C-4), 20.0 (C-3)]: Gale, D. M. U.S. Patent 3,696,080, Oct 3, 1972. **21** could not be separated from **20**. It was therefore identified by $^1H$ and $^{13}C$ NMR difference spectra of the mixture. $^1H$ NMR (benzene-$d_6$, 300 MHz, ppm): 0.4–2.0 (mult, C-2, C-3), 2.4 (MeO), 9.5 (CHO). $^{13}C$ NMR (benzene-$d_6$, 75 MHz, ppm): 201.7 (CO), 83.0 (C-1), 51.8 (OMe), 27.8 (C-2), 12.0 (C-3).

(12) Gismondi, T. E.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *284*, 79.

(13) (a) Casey, C. P.; Cyr, C. R.; Grant, J. A. *Inorg. Chem.* **1974**, *13*, 910. (b) Casey, C. P. *Inorg. Chem.* **1976**, *15*, 1991.

(14) (a) Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6433. (b) Heinekey, D. M.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *232*, 335.

(15) Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326.

(16) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

(17) Gladysz[14a,15] has found high yields (65–90%) of ii from thermolysis of i.

(18) 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; p 264.

(19) Reference 18, pp 340–343.

(20) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33.

(21) Kovacs, I.; Hoff, C. D.; Ungvary, F.; Marko, L. *Organometallics* **1985**, *4*, 1347.

(22) Cf. Reference 18, Chapter 6. For a recent comparison of the rates of α- and β-hydrogen eliminations in a tungsten complex, see: McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704.

(23) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; p 144.

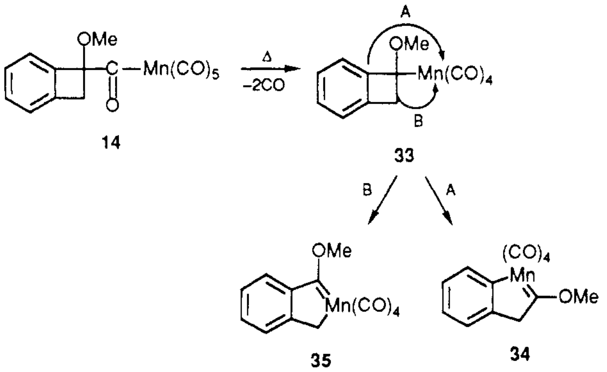
(24) The strain relieved when cyclobutane expands to metallalocyclopentene or when benzocyclobutene expands to metallaindene is not known. However, expansion of cyclobutane to cyclopentene relieves about 20 kcal/mol, while, on the basis of a reported heat of formation of about 48 kcal/mol for benzocyclobutene,[25] its expansion to indene should relieve at least 27 kcal/mol.[26]

(25) Roth, W. R.; Biermann, M.; Dekker, H.; Jochems, R.; Mosselman, C.; Hermann, H. *Chem. Ber.* **1978**, *111*, 3892.

carbonylmanganese acyl complex **14** was therefore prepared as described above and its thermal chemistry studied.

## Thermolysis of the Pentacarbonylmanganese Derivative of α-Methoxybenzocyclobutenecarboxylic Acid

The pentacarbonylmanganese acyl complex **14** is a white crystalline solid that is stable at room temperature but slowly decomposes upon exposure to air. Warming a benzene solution at ca. 70 °C leads to slow, steady gas evolution (presumably CO), which is complete after about 15 h. During this time, the yellow solution slowly turns to orange, from which the two carbene complexes **34** and **35**[27] were isolated by flash chromatography in 13% and 61% yield, respectively. Monitoring the reaction with use of $^{13}$C NMR spectroscopy showed only loss of starting material and carbene formation. We could find no evidence for the presumed intermediate σ complex **33**.



The two carbene complexes were identified by $^1$H and $^{13}$C NMR spectroscopy (each showed low-field resonances; $\delta$ = 328.8 and 398.5 ppm for **35** and **34**, respectively), C,H analysis of **35**, the major isomer, and high-resolution MS of both. Regioisomeric assignments are based on a comparison of NMR chemical shifts with those of analogous iron complexes. Particularly noteworthy are both $^1$H and $^{13}$C chemical shifts of the methylenes and the $^{13}$C chemical shifts of the carbene carbons. As would be expected, the methylene bonded to the metal is at significantly higher field than the one bonded to the carbene carbon (1.1 and 2.1 ppm higher for $^1$H and 50.7 and 38.5 ppm for $^{13}$C for Fe and Mn, respectively). The carbene carbon bonded to the phenyl is also higher than the one bonded to CH$_2$ (35.3 and 69.7 ppm for Fe and Mn, respectively). Formation of **35** as the major isomer is taken as evidence for preferential alkyl migration to manganese, which is in interesting contrast to preferential aryl migration in the carbonyl($\eta^5$-cyclopentadienyl)iron case. The manganese carbene complex **35** is similar to its iron analogue in that it does not undergo discernible carbene migratory insertion when warmed for an extended period of time; e.g., warming **35** to 72 °C for 36 h showed no detectable isomerization to **34**. From this it is possible to calculate an approximate minimum activation barrier for this reaction of about 29 kcal/mol (assuming a preexponential of $10^{13}$). Experimentally, the activation barrier for carbene migratory insertion in the carbonyl($\eta^5$-cyclopentadienyl)iron analogue must be at least 31 kcal/mol.[7] However, on the basis of the rate of contraction of **3** to **2**[28] and strain arguments, the actual barrier is probably not much greater than this minimum. If this is the case, then the stability of **35** to heating suggests that α-elimination induced by tetracarbonylmanganese in **26** is probably about as exothermic as it is for the carbonyl($\eta^5$-cyclopentadienyl)iron analogue **2**. This, in turn, suggests that the principal reason no carbene complex was observed upon thermolysis of **16** is facile β-hydrogen elimination–π-complex dissociation (or displacement) rather than poor thermodynamics for carbene formation.

## Experimental Section

Hexane, diethyl ether, and tetrahydrofuran were distilled from benzophenone ketyl. Methylene chloride was distilled from P$_2$O$_5$ and was degassed prior to use. Benzene was distilled from SilicaPent under nitrogen. The silica gel used was MCB 230–400 mesh. All chromatographic separations were accomplished by the low-pressure flash column method of Still.[29] The silica gel used was degassed overnight (0.25 Torr, 25 °C) prior to use. NMR spectra were taken on a Varian EM-360 (60 MHz), JEOL FX100 (100 MHz), Varian XL-200 (200 MHz), or Varian XL-300 (300 MHz) spectrometer. All spectra were recorded at room temperature unless specified otherwise. Infrared data were recorded on either a Perkin-Elmer 137 or a Nicolet 5DXB FTIR spectrometer. Atlantic Microlab, Inc., or the University of Florida Chemical Analysis Service performed C,H analyses. Melting points (uncorrected) were obtained by using a Thomas-Hoover apparatus. All solutions containing transition-metal complexes, as well as organometallic solids, were manipulated under inert-atmosphere (Schlenk line or glovebox) conditions.

**Synthesis of ((α-Methoxycyclobutyl)carbonyl)pentacarbonylmanganese (16).** Potassium pentacarbonylmanganate was prepared by the method of Gladysz.[30] To a slurry of 4.5 g (19.4 mmol) of freshly prepared KMn(CO)$_5$ in 30 mL of THF at 0 °C was slowly added 3.2 g (19.4 mmol) of α-methoxycyclobutanecarbonyl chloride[5] in 20 mL of THF, also at 0 °C, via double-ended cannula. The reaction mixture was stirred for 24 h while being warmed to room temperature. All volatiles were removed in vacuo, the resulting yellow-orange residue was extracted three times with 70 mL of hexane, and the extracts were filtered through Celite. The yellow-orange oil obtained after rotavapping was subject to flash chromatography on silica gel (visualized with 2 g of Du Pont No. 609 indicator/100 mL of silica gel, quartz column, short-wave UV). Elution with 85/15 hexane/ethyl acetate and removal of solvents gave 3.7 g (62%) of a yellow, air-sensitive oil. Anal. Calcd for C$_{11}$H$_9$O$_7$Mn: C, 42.87; H, 2.93. Found: C, 42.90; H, 2.91. Mass spectrum (CI, *m/e*): 309 (M + 1). $^1$H NMR (CDCl$_3$, 100 MHz, ppm): 3.4 (s, 3 H, -OCH$_3$), 2.3–1.1 (m's, 6 H, -CH$_2$-). $^{13}$C NMR (CD$_3$COCD$_3$, 25 MHz, ppm): 259.8 (acyl CO), 211.9 (M–CO), 94.1 (α-ring C), 51.9 (–OCH$_3$), 28.3 (β-ring C's), 12.3 (γ-ring C). IR (CCl$_4$, NaCl, cm$^{-1}$): 2112.3, 2046.8, 2017.5, 2007.0, 1645.8.

**Thermal Degradation of 16.** In a typical experiment, a 5-mm NMR tube was charged with 0.3 g of **16**, 0.7 mL of benzene-$d_6$, and a graphite boiling chip and capped with a rubber septum. The tube was immersed in an oil bath at a temperature of 62–65 °C and maintained under a N$_2$ atmosphere. Gas evolution was observed to be immediate, but slow, and thermolysis was allowed to continue for 48 h. The volatiles were transferred by bulb to bulb distillation and analyzed by $^1$H NMR spectroscopy with

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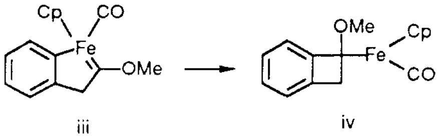
(26) This prediction gains support from our finding that the activation barrier for contraction of iii to iv must be at least 8–10 kcal/mol greater than that for **3** to **2**.



(27) To our knowledge, these are the first reported cyclic carbene complexes of manganese in which the metal is the sole heteroatom. These are also the first manganese carbene complexes with an alkyl or aryl group bonded directly to the metal.

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measurement of areas under methoxy absorptions. One reaction was also analyzed by using quantitative $^{13}C$ NMR spectroscopy with naphthalene as an internal standard. Not only did this show **19**, **20**, and **21** to be essentially the sole organic products but it also accounted for >95% of the starting material. Relative amounts of **19**, **20**, and **21** are listed in Table I. The nonvolatiles were examined by $^{1}H$ and $^{13}C$ NMR spectroscopy. In some cases, unreacted **16** remained but no other organic products could be detected; the major nonvolatile was $Mn_2(CO)_{10}$ (IR, TLC).

Thermal degradation of **16** was also carried out at 52 °C in the presence of up to 20 equiv of 1,4-cyclohexadiene and toluene-$d_8$ as reaction solvent. The volatiles were isolated and analyzed as before. Results are recorded in Table I.

**Photolysis of 16.** In a typical experiment, an NMR tube was charged with 0.3 g of **16** and 0.7 g of benzene-$d_6$ and subjected to photolysis with a 450-W Hg lamp. The reaction temperature was maintained at 25 °C with a circulating water bath. Decarbonylation was qualitatively slower than from thermolysis; even after 48 h, unreacted **16** remained. The volatiles from the reaction were analyzed as described before. Results are recorded in Table I.

**Reaction of 16 with Trimethylamine Oxide.** Trimethylamine oxide was obtained by sublimation of the dihydrate.[31] In the drybox, 0.3 g of **16** (1.28 mmol) was dissolved in 1.0 mL of benzene-$d_6$ in a flask with a magnetic stirbar. While the mixture was stirred at room temperature, 0.21 g of $Me_3NO$ (2.2 equiv) was slowly added. The ensuing reaction was quite vigorous, and a color change from yellow to orange occurred with the precipitation of an intractable orange solid. Analysis of the crude reaction by $^{1}H$ and $^{13}C$ NMR spectroscopy showed that only **19**, **20**, and **21** were formed. The volatiles were vacuum-transferred and analyzed as before. Results are recorded in Table I.

**Thermolysis of ((α-Methoxycyclobutyl)carbonyl)pentacarbonylmanganese in the Presence of $Cp(CO)_3WH$.** A solution of 0.3 g (1.28 mmol) of **16** and 0.43 g of $Cp(CO)_3WH$[32] (1.28 mmol) in 1.0 mL of benzene-$d_6$, was heated at 55 °C for 12 h, at which time no further decarbonylation was observed. Analysis of the volatiles, by usual methods, showed that the relative amount of 1-methoxycyclobutanecarboxaldehyde increased at the expense of the 1-methoxycyclobutene. These results are listed in Table I.

**((α-Methoxycyclobutyl)carbonyl)(triethylphosphine)tetracarbonylmanganese (17a).** A solution of 0.7 g of **16** (2.3 mmol), 0.19 g of $PEt_3$ (2.3 mmol), and 1.0 mL of benzene-$d_6$ was heated in an NMR tube at 45 °C. The reaction was closely monitored to detect completion. This was necessary since **16** and **17a** were found to cochromatograph. The contents of the NMR tube were chromatographed on silica gel (quartz column, indicator) with 10/90 ethyl acetate/hexane as eluent. In vacuo removal of solvents left a very viscous, pale yellow oil in 23% yield. Anal. Calcd for $C_{16}H_{24}O_6PMn$: C, 48.25; H, 6.07. Found: C, 48.38; H, 6.16. MS (CI, *m/e*): 399 (M + 1). $^{1}H$ NMR (benzene-$d_6$, 300 MHz, ppm): 3.20 (s, 3 H, $OCH_3$), 2.0–2.34 (m, 4 H, β-ring H's); 1.46–1.61 (m, 8 H, γ-ring H's and $PCH_2$); 0.61–0.77 (m, 9 H, $PCH_2CH_3$). $^{13}C$ NMR (benzene-$d_6$, 75 MHz, ppm): 271.84 ($J_{PC}$ = 12.3 Hz, acyl CO), 216.7 (M–CO), 93.0 (α-ring C), 50.60 ($OCH_3$), 27.4 (β-ring C's), 11.7 (γ-ring C). IR ($CCl_4$, $cm^{-1}$): 2054.7, 1978.9, 1960.9, 1944.0, 1583. A benzene-$d_6$ solution of this complex showed no reaction when either heated at 75 °C or photolyzed at 25 °C for 72 h.

**((α-Methoxycyclobutyl)carbonyl)(triphenylphosphine)tetracarbonylmanganese (17b).** A Schlenk tube was charged with 0.7 g of **16** (2.3 mmol), 0.93 g of triphenylphosphine (3.4 mmol), and 30 mL of benzene. The reaction mixture was heated at 40 °C under nitrogen for 2 days; it was then cooled to room temperature, 1.0 g of MeI (2 equiv based on phosphine) was added, and the solution was stirred for an additional 1 h. The crude product was filtered through Celite and chromatographed on neutral alumina. A bright yellow band was eluted with an 85/15 mixture of hexane/ethyl acetate. After removal of solvents, a yellow solid was obtained in 35% yield and was composed of cis (ca. 60%) and trans **17b**. An analytical sample was obtained by recrystallization from hexane. Anal. Calcd for $C_{28}H_{24}O_6PMn$: C, 62.00; H, 4.46. Found: C, 61.72; H, 4.41. Mp: 88–91 °C. $^{1}H$ NMR (benzene-$d_6$, 300 MHz, ppm): 7.72–6.96 (m, $P(C_6H_5)_3$), 3.29 (s, cis $OCH_3$), 3.20 (s, trans $OCH_3$), 1.4–2.6 (m, $CH_2$). $^{13}C$ NMR (benzene-$d_6$, 75 MHz, ppm): cis isomer, 272.15 (d, $J_{PC}$ = 14.5 Hz, acyl CO), 218–216 (M–CO), 92.6 (α-ring C), 50.3 ($OCH_3$), 27.6 (β-ring C's), 11.7 (γ-ring C); trans isomer, 264.3 (acyl CO), 227 (M–CO), 93.7 (α-ring C), 51.9 ($OCH_3$), 28.4 (β-ring C's), 11.4 (γ-ring C). IR ($CH_2Cl_2$, $cm^{-1}$): 2064.5, 1990.8, 1975.3, 1956.2, 1618.0. Thermolysis of a benzene-$d_6$ solution of **17b** at 73 °C for 48 h showed <10% reaction.

**Synthesis of ((α-Methoxycyclobutyl)carbonyl)bis(triethylphosphine)tricarbonylmanganese.** One gram of **16** (3.25 mmol) and 2.1 g of $PEt_3$ (6.5 mmol), dissolved in 25 mL of benzene, were heated at 45 °C for 48 h. Excess phosphine was precipitated with MeI as described above. Column chromatography on neutral alumina with 10/90 ethyl acetate/hexane gave the title compound. The yellow band was rotavapped to yield 0.7 g of a gummy solid containing some **17a**. Recrystallization from hexane at −40 °C gave 0.3 g (23%) of clear yellow crystals of the disubstituted acyl complex. Anal. Calcd for $C_{21}H_{39}O_5P_2Mn$: C, 51.64; H, 8.05. Found: C, 51.58; H, 7.98. Mp: 71–72 °C. MS (Cl, *m/e*): 489 (M + 1), 461 (M + 1 − CO). $^{1}H$ NMR (benzene-$d_6$, 300 MHz, ppm): 3.23 (s, $OCH_3$), 1.7 (m, $PCH_2CH_3$), 0.97 (m, $PCH_2CH_3$), 2.13–0.92 (m, ring H's). $^{13}C$ NMR (benzene-$d_6$, 75 MHz, ppm): 285.07, 284.82, 284.57 (acyl CO), 222.3, 222.1, 221.9 (M–CO), 91.92 (α-ring C), 48.99 ($OCH_3$), 27.31 (β-ring C's), 20.91, 20.61 ($PCH_2CH_3$), 12.49 (γ-ring C), 7.72 ($PCH_2CH_3$). IR ($CCl_4$, $cm^{-1}$): 2061.3, 2002.6, 1977.8, 1971.9, 1919.0, 1889.6, 1590. A benzene-$d_6$ solution of this complex showed no reaction when photolyzed for 72 h at 30 °C or when heated at 70 °C for 48 h.

**Synthesis of Cyanohydrin 10.** To a solution of 23.989 g (0.2033 mol) of benzocyclobutenone[34] in 150 mL of methylene chloride and a catalytic amount of zinc iodide was added 23.54 g (0.2372 mol) of trimethylsilyl cyanide dropwise under nitrogen. The reaction mixture was refluxed at 65 °C for 3 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure to yield the crude trimethylsilyl cyanohydrin as a dark brown liquid, which was used in the next step without purification.

To the crude trimethylsilyl cyanohydrin was added 100 mL of 3 N hydrochloric acid, and the mixture was refluxed for 1.5 h. After the mixture was cooled to room temperature, the product was extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure to yield 28.35 g (96%) of the cyanohydrin **10** as a light brown viscous liquid. IR ($CHCl_3$, $cm^{-1}$): 3300, 3015, 3060, 2498. $^{1}H$ NMR (300 MHz, $CDCl_3$, ppm): 3.37 (d, *J* = 14.4 Hz, 1 H, $CH_2$), 3.95 (d, *J* = 14.4 Hz, 1 H, $CH_2$), 4.40 (br s, 1 H, OH), 7.22–7.43 (m, 4 H, aromatics). $^{13}C$ NMR (75 MHz, $CDCl_3$, ppm): 142.8, 141, 131.5, 128.5, 124.2, 121.6 (aromatics), 119.8 (CN), 68.3 (C–OH), 47.7 ($CH_2$).

**Synthesis of Hydroxy Ester 11.** To a solution of 28.35 g (0.1985 mol) of cyanohydrin **10** in 50 mL of absolute methanol was added 250 mL of a solution of anhydrous HCl in diethyl ether with use of a double-ended cannula. The mixture was stirred at room temperature for 3 h. The resulting white precipitate was filtered, washed several times with anhydrous diethyl ether, and then dissolved in 50 mL of water. The resulting solution was extracted with 3 × 50 mL of diethyl ether and dried over anhydrous $MgSO_4$. Removal of the solvent gave 25.8 g (73%) of **11** as a colorless viscous liquid. Recrystallization from hexane gave colorless crystals. Mp: 56–57 °C. FTIR ($CHCl_3$, $cm^{-1}$): 3510, 1725. $^{1}H$ NMR (300 MHz, $CDCl_3$, ppm): 3.42 (d, *J* = 13.7 Hz, 1 H, $CH_2$), 3.86 (d, *J* = 13.7 Hz, 1 H, $CH_2$), 4.15 (br s, 1 H, OH), 7.18–7.40 (m, 4 H, aromatics). $^{13}C$ NMR (75 MHz, $CDCl_3$, ppm): 174.8 (C=O), 145.2, 142.8, 130.0, 127.6, 123.3, 121.1 (aromatics), 78.0 (C–OH), 53.0 ($OCH_3$), 45.6 ($CH_2$). HRMS (*m/e*): calcd for $C_{10}H_{10}O_3$, 178.06300; found, 178.06363. Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.10; H, 5.55.

**Synthesis of α-Methoxybenzocyclobutenecarboxylic Acid.** A mixture of 20.0 g (0.1124 mol) of hydroxy ester **11**, 40 mL (0.6425

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mol) of methyl iodide, and 27.137 g (0.1171 mol) of silver oxide in 150 mL of acetone was refluxed at 65 °C for 12 h. After the mixture was cooled, the inorganic salt was filtered off and the organic layer was washed with 50 mL of saturated sodium sulfite solution and finally with water. The ether layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure. The crude methoxy ester **12** was added to a mixture of 75 mL of 5% sodium hydroxide and 75 mL of tetrahydrofuran. The slightly cloudy and light yellow mixture was stirred at 40 °C for 12 h. The resulting yellow, clear solution was combined with 50 mL of water and washed once with ether. The basic aqueous layer was acidified with 50% sulfuric acid and extracted with 3 × 50 mL of ether. The organic layer was dried over anhydrous magnesium sulfate. Removal of the solvents gave a light yellow viscous liquid. Column chromatography over silica gel, with 35% ethyl ether/65% hexane as eluent, gave a colorless viscous liquid that crystallized to colorless crystals upon standing overnight; 13.68 g (68%) of the methoxy acid was isolated. Mp: 57–58 °C. IR ($CHCl_3$, $cm^{-1}$): 3600.01–2300.15, 1720, 1460, 1420, 1280, 1105, 1020, 940. $^1H$ NMR (300 MHz, $CDCl_3$, ppm): 3.36 (d, $J$ = 14.1 Hz, 1 H, $CH_2$), 3.43 (s, 3 H, $OCH_3$), 3.67 (d, $J$ = 14.1 Hz, 1 H, $CH_2$), 7.14–7.23 (m, 4 H, aromatics), 11.31 (br s, 1 H, OH). $^{13}C$ NMR (75 MHz, $CDCl_3$, ppm): 145.6 (C=O), 142.7, 142.3, 130.5, 127.6, 123.6, 122.5 (aromatics), 84.0 (*C*—$OCH_3$), 54.2 ($OCH_3$), 40.9 ($CH_2$). HRMS (*m/e*): calcd for $C_{10}H_{10}O_3$, 178.06299; found, 178.06223. Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.54; H, 5.58.

**Synthesis of α-Methoxybenzocyclobutenecarbonyl Chloride (13).** To a solution of 1.068 g (6.00 mmol) of the methoxy acid in 20 mL of methylene chloride was added 2.286 g (18.00 mmol) of oxalyl chloride. The mixture was stirred at room temperature for 3 h. Removal of the solvent gave the acid chloride **15** as a light yellow liquid, which was used in the next step without further purification.

**Synthesis of ((α-Methoxybenzocyclobutenyl)carbonyl)pentacarbonylmanganese (14).** To a slurry of 1.405 g (6.00 mmol) of freshly prepared $KMn(CO)_5$ in 30 mL of THF at −78 °C was slowly added 1.019 g (5.186 mmol) of α-methoxybenzocyclobutenecarbonyl chloride in 10 mL of THF. A double-ended cannula was used for the addition of the acid chloride. The reaction mixture was stirred for 2 h, while being warmed to room temperature; then the solvent was removed on line. The resulting orange-yellow residue was flash-chromatographed over silica gel, with 5% ethyl acetate/95% hexane as eluent. The second light yellow band was collected. Removal of solvents and recrystallization from hexane at −10 °C gave 1.20 g (62%) of **14** as white crystals. Mp: 79–80 °C. FT IR (Nujol, $cm^{-1}$): 2097, 2014, 2008, 1995, 1643. $^1H$ NMR (300 MHz, $C_6D_6$, ppm): 2.95 (d, $J$ = 3.6 Hz, 1 H, $CH_2$), 3.11 (s, 3 H, OMe), 3.64 (d, $J$ = 3.6 Hz, 1 H, $CH_2$), 6.87–7.05 (m, 5 H, aromatics). $^{13}C$ NMR (75 MHz, $C_6D_6$, ppm): 255.2 (acyl CO), 210.1 (M–CO), 97.8 (C), 51.6 ($OCH_3$), 37.7 ($CH_2$), 144.3, 143.1, 129.9, 127.4, 123.9, 123.4 (aromatic C's). MS (EI, *m/e*): 356 ($M^+$), 328 (M − CO), 300 (M − 2CO), 272 (M − 3CO), 244 (M − 4CO), 216 (M − 5CO), 55 ($Mn^+$). Anal. Calcd for $C_{15}H_9O_7Mn$: C, 50.56; H, 2.53. Found: C, 50.43; H, 2.56.

**Thermolysis of ((α-Methoxybenzocyclobutenyl)carbonyl)pentacarbonylmanganese (14).** A 5-mm NMR tube was charged with 0.10 g (0.2809 mmol) of **14**, 0.7 mL of benzene-$d_6$; and several graphite boiling chips. The tube was immersed in an oil bath held at 67–72 °C while under a nitrogen atmosphere. Gas evolution was immediate, and the color changed from light yellow to orange. The reaction was monitored periodically by using $^{13}C$ NMR spectroscopy. After 15 h, $^{13}C$ NMR spectra showed no trace of the starting acyl complex. The crude reaction mixture was flash-chromatographed over silica gel with hexane as eluent. Removal of the solvent from the second band gave 0.051 g (61%) of the carbene complex **35** as an orange oil. Recrystallization from hexane at −10 °C gave pure orange crystals. Mp: 83–84 °C. FTIR ($CHCl_3$, $cm^{-1}$): 1935, 1976, 1997, 2062. $^1H$ NMR (300 MHz, $C_6D_6$, ppm): 2.62 (s, 2 H, $CH_2$), 4.09 (s, 3 H, $OCH_3$), 6.74 (t, 1 H, $J$ = 7.38 Hz, aromatic), 7.04 (t, 1 H, $J$ = 7.38 Hz, aromatic), 7.17–7.24 (m, 2 H, aromatics). $^{13}C$ NMR (75 MHz, $C_6D_6$, ppm): 328.8 (M=C), 215.3 (M—CO), 169.5, 152.1, 134.4, 129.1, 124.0, 119.0 (aromatic C's), 67.6 ($OCH_3$), 21.2 ($CH_2$). HRMS (*m/e*): calcd for M − CO ($C_{12}H_9O_4Mn$), 271.98813; found, 271.98947. Anal. Calcd for $C_{13}H_9O_5Mn$: C, 52.03; H, 3.02. Found: C, 51.99; H, 3.03.

Removal of the solvent from the third colored band gave 0.01 g (13%) of **34** as a pale yellow solid. Mp: 120–121 °C. $^1H$ NMR (300 MHz, $C_6D_6$, ppm): 3.52 (s, 3 H, $OCH_3$), 4.68 (s, 2 H, $CH_2$), 6.77–6.79 (d, 1 H, $J$ = 7.37 Hz, aromatic), 6.98–7.03 (t, 1 H, $J$ = 7.38 Hz, aromatic), 7.16–7.23 (m, 2 H, aromatic). $^{13}C$ NMR (75 MHz, $C_6D_6$, ppm): 398.5 (M=C), 209.4 (M—CO), 69.9 ($OCH_3$), 59.5 ($CH_2$). HRMS (*m/e*): calcd for M − CO ($C_{12}H_9O_4Mn$), 271.98813; found, 271.98949.

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