Table I. Orbitals and Parameters for the Extended Hückel Calculations

orbital	$-H_{ii}$/eV	ζ_1	ζ_2	C_1	C_2
Pd 5s	7.32	2.19			
Pd 5p	3.75	2.152			
Pd 4d	12.02	5.983	2.613	0.5264	0.6373
Ni 4s	9.17	2.10			
Ni 4p	5.15	2.10			
Ni 3d	13.49	5.75	2.30	0.5798	0.5782

study[21] for the concerted reductive elimination of ethane from $(PH_3)_2Pd(CH_3)_2$ gives a much lower value for the barrier (ca. 10 kcal mol^{-1}). This is due to the difficulties of dealing reliably with bond-breaking and bond-forming processes when the extended Hückel approach is used. For these reasons, a potential surface to optimize C–C bond formation relative to Pd–C bond breaking was not explored. A different choice of the transition state might lead to a different barrier. In spite of all these considerations, it should be pointed out that the qualitative conclusions remain valid, as a 30% decrease in activation energy for the migration must indeed correspond to an easier process. There are too many degrees of freedom involved in this reaction, and a better choice of the transition state would certainly lower the barrier.

Another point to consider is the choice of method. Even in an ab initio approach, there are many limitations when one deals with heavy atoms, such as palladium, and relatively large systems. The choice of which option to apply may result in very different values, as illustrated, for instance, in the work of Morokuma.[25]

Appendix

All the calculations were of the extended Hückel type[14] with modified H_{ii}'s.[26] The basis sets for the palladium, nickel, and platinum atoms consisted of *ns*, *np*, and (*n* − 1)d orbitals. The s and p orbitals were described by single Slater type wave functions, and d orbitals were taken as contracted linear combinations of two Slater type wave functions.

The geometry of the model $Pd(PH_3)_2RR'$ complexes was square planar with all the angles in the palladium coordination plane being 90°. The distances were taken as Pd—P = 2.30, P—H = 1.42, Pd—C(methyl) = 2.00, Pd—C(vinyl) = 2.05, C—H = 1.09, and C=C = 1.33 Å, respectively. The parameters used for the calculations were the standard ones for H, C, and P and were those reported in Table I for the metals.

Acknowledgment. N.A.C. thanks the Science and Engineering Research Council (U.K.) for postdoctoral support. M.J.C. thanks NATO for a fellowship, which permitted her to visit the laboratories of Professor R. Hoffmann at Cornell University, where most of the calculations were completed. Professor Hoffmann's interest and encouragement is greatly appreciated.

Reactions of (η^5-Ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium with Lithium Aluminum Hydride and with Organomagnesium Halides, Leading to 6-Metallocenylfulvenes

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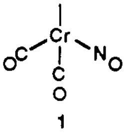
Reactions of (η^5-ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (**2**) with lithium aluminum hydride and with organomagnesium halides have been investigated. Treatment of **2** with $LiAlH_4$ in THF solution followed by hydrolysis did not produce the expected product, carbinol **4**, but instead 6-ferrocenylfulvene (**5**). A reaction between **4** and $LiAlH_4$ under the same conditions likewise formed **5**. Reactions of **2** with methylmagnesium iodide produced either the normal addition product, carbinol **7**, or 6-ferrocenyl-6-methylfulvene (**8**), depending on the reaction conditions, whereas only 6-ferrocenyl-6-phenylfulvene (**9**) could be isolated from reactions between **2** and phenylmagnesium bromide. Mechanistic considerations concerning degradation of the (η^5-cyclopentadienyl)dicarbonylnitrosylchromium substituent in **2** to form 6-ferrocenylfulvenes under these conditions are discussed. Fulvenes **5**, **8**, and **9** can also be prepared conveniently and in high yield from reactions under basic conditions between cyclopentadiene and formyl-, acetyl-, or benzoylferrocene, respectively. Carbonylbis[(η^5-cyclopentadienyl)dicarbonylnitrosylchromium] (**3**) has been prepared in 26% yield from a Friedel–Crafts reaction between (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (**1**) and (η^5-(chloroformyl)cyclopentadienyl)dicarbonylnitrosylchromium in the presence of aluminum chloride.

Introduction

Recent studies in our laboratory have focused on the formation, spectral properties, structural features, and chemical reactivities of ring-substituted derivatives of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (**1**).[1]



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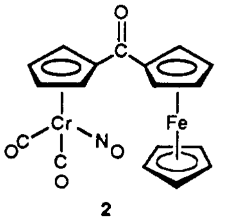

2

Acyl and carboxylic acid derivatives of **1** can be readily prepared by Friedel–Crafts acylation methods and undergo a wide variety of addition, reduction, and rearrangement

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(1) The trivial name cynichrodene has been proposed by analogy to the shortened names cymantrene and benchrotrene for (η^5-cyclopentadienyl)tricarbonylmanganese and (η^6-benzene)tricarbonylchromium, respectively.[2,3]

(2) Pittman, C. U., Jr.; Rounsefell, T. D.; Lewis, E. A.; Sheats, J. E.; Edwards, B. H.; Rausch, M. D.; Mintz, E. A. *Macromolecules* 1978, *11*, 560.

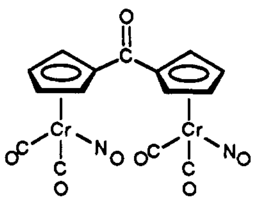
reactions that are typical of stable aromatic systems such as benzene or ferrocene.[3,4] Functionally substituted derivatives of 1 can also be obtained from reactions of [$C_5H_4C(O)R$]Na salts (R = H, Me, OMe) with $Cr(CO)_6$, followed by acidification of the resulting anions and subsequent nitrosylation.[5] (η^5-Vinylcyclopentadienyl)dicarbonylnitrosylchromium can be prepared from 1 in good overall yield, and this monomer undergoes homo- and copolymerization reactions in the presence of azo initiators.[2,6] A detailed study of the ^1H and ^{13}C NMR spectra of a series of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium-substituted carbonium ions has indicated that these cations are stabilized in a manner similar to isoelectronic ferrocenyl and cymantrenyl carbonium ions.[7] pK_{R^+} values of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium-stabilized carbonium ions have also been reported,[8] and a dimetallocenyl-stabilized carbonium ion, α-[(dicarbonylnitrosylchromio)-η^5-cyclopentadienyl]-α-ferrocenylmethylium tetrafluoroborate, has been synthesized and characterized.[9]

We report here on reactions of (η^5-ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (2) with lithium aluminum hydride and with organomagnesium halides, leading in some instances to degradation of the (η^5-cyclopentadienyl)dicarbonylnitrosylchromium moiety and formation of 6-ferrocenylfulvenes. Also described are the formation of carbonylbis[(η^5-cyclopentadienyl)dicarbonylnitrosylchromium] (3) and improved routes to a series of 6-metallocenylfulvenes.

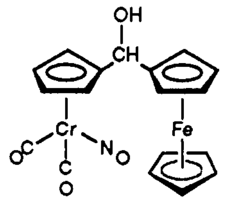
Results and Discussion

Formation of Carbonylbis[(η^5-cyclopentadienyl)dicarbonylnitrosylchromium] (3). Metallocenyl ketones have long played a key role in the development of metallocene and related chemistry, ever since the first metalloaromatic compound ferrocene was found to successfully undergo Friedel–Crafts acylation in 1952.[10] Several ketones that contain two metalloaromatic substituents are known, including diferrocenyl ketone,[11,12] ferrocenyl ruthenocenyl ketone,[11,13] dicymantrenyl ketone,[13,14] and cymantrenyl ferrocenyl ketone.[14] More recently, the synthesis of 2 has been reported,[15,16] and a ^{13}C NMR and X-ray structural investigation of this ketone has been undertaken.[17]

In an analogous manner, a reaction between (η^5-(chloroformyl)cyclopentadienyl)dicarbonylnitrosylchromium and aluminum chloride in methylene chloride solution followed be treatment with 1 has produced 3 as red crystals in 26% yield. The IR spectrum of 3 contained strong absorptions assignable to the organic carbonyl, terminal carbonyl, and nitrosyl substituents, whereas the mass spectrum contained a moderately intense peak corresponding to the molecular ion at m/e 432. The ^1H NMR spectrum of 3 exhibited two apparent triplets at δ 5.25 and 5.78 ppm, respectively. The ease of formation of ketones 2 and 3 makes them available for further investigations.

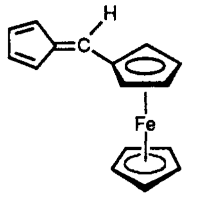


3

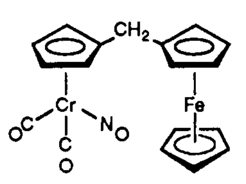


4

Reactions of 2 with Lithium Aluminum Hydride and with Organomagnesium Halides. As reported earlier, the reduction of 2 with sodium borohydride in aqueous ethanol proceeded in a straightforward manner to produce the normal reduction product [η^5-(hydroxyferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (4) in excellent yield (90%).[9] Previous reductions of acyl derivatives of 1[3] as well as (η^5-formylcyclopentadienyl)dicarbonylnitrosylchromium also produced good yields of the corresponding carbinols. In contrast, a reaction between ketone 2 and lithium aluminum hydride in THF at room temperature, followed by hydrolysis and column chromatography, afforded only a single product in addition to partial recovery of the starting ketone. The product was not the anticipated carbinol 4, but instead 6-ferrocenylfulvene (5), which was isolated in 45% yield.



5



6

Fulvene 5 obtained in this manner was identified by a comparison of its ^1H NMR, IR, and mass spectra with those of an authentic sample (vide infra).

It was of subsequent interest to ascertain the possible reactivity of carbinol 4 under these reaction conditions. Indeed, treatment of 4 with lithium aluminum hydride at room temperature followed by hydrolysis likewise afforded fulvene 5 in 61% yield.

Reduction of 2 by means of an equimolar mixture of lithium aluminum hydride and aluminum chloride in diethyl ether, however, did proceed in an expected manner. This reducing agent, which is known to reduce ketones to hydrocarbons in systems where stabilized intermediate carbonium ions can be formed,[18,19] produced [η^5-(ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (6) in 41% yield. No other reaction products such as fulvene 5 or carbinol 4 could be detected. Compound 6 was purified by vacuum sublimation and was identified by its ^1H NMR, IR, and mass spectra.

Previous studies involving reactions of Grignard reagents such as CH_3MgX and C_6H_5MgX with (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium and (η^5-

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(3) Rausch, M. D.; Mintz, E. A.; Macomber, D. W. *J. Org. Chem.* **1980**, *45*, 689.

(4) Rausch, M. D.; Wang, Y.-P. *J. Organomet. Chem.*, submitted for publication.

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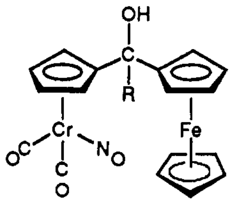
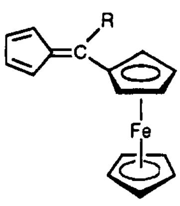
benzoylcyclopentadienyl)dicarbonylnitrosylchromium have shown that, following hydrolysis, tertiary carbinol addition products can be obtained in high yields.[3] Partial dehydration of the resulting carbinols often occurred during attempted distillation or column chromatography, and in these instances the alcohols were contaminated with the corresponding alkenes.[3]

Reactions of ketone 2 with several Grignard reagents were likewise investigated during the course of the present study. In these reactions, as in reductions of 2 with lithium aluminum hydride, unexpected products were obtained under certain reaction conditions.

When 2 was allowed to react with an excess of methylmagnesium iodide in diethyl ether at reflux for 30 min followed by hydrolysis, [η^5-(1-hydroxy-1-ferrocenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (7) was obtained in 83% yield. In contrast, when this same reaction was allowed to proceed for a 2-h reflux period rather than for 30 min, and the reaction mixture worked up in an analogous manner, carbinol 7 could not be detected. The only isolable product under these conditions was 6-ferrocenyl-6-methylfulvene (8), which was identified by ^{1}H NMR, IR, and mass spectral comparisons with an authentic sample (vide infra).



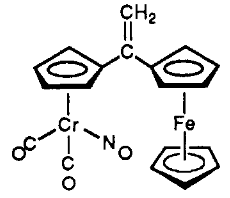
7 (R = CH_3)
10 (R = C_6H_5)



8 (R = CH_3)
9 (R = C_6H_5)

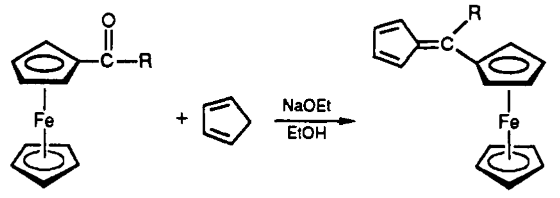
Reaction of ketone 2 and excess phenylmagnesium bromide in diethyl ether at room temperature for 1 h also produced an unexpected reaction product. Following hydrolysis and column chromatography, 6-ferrocenyl-6-phenylfulvene (9) was isolated in 59% yield, together with a 16% recovery of 2. Fulvene 9 was identified by ^{1}H NMR, IR, and mass spectral comparisons with an authentic sample (vide infra). Again, none of the expected addition product (10) could be detected. Further, when 2 and phenylmagnesium bromide were allowed to react in a 1:1 ratio at reflux for 30 min or at room temperature for 12 h, fulvene 9 was again obtained in yields of 33% and 21%, respectively, together with unreacted 2. No other reaction product could be detected under these conditions as well.

As anticipated from earlier studies,[3,6] carbinol 7 underwent acid-catalyzed dehydration in the presence of hydroquinone to afford [η^5-(1-ferrocenylvinyl)cyclopentadienyl]dicarbonylnitrosylchromium (11) in 54% yield, following column chromatography.



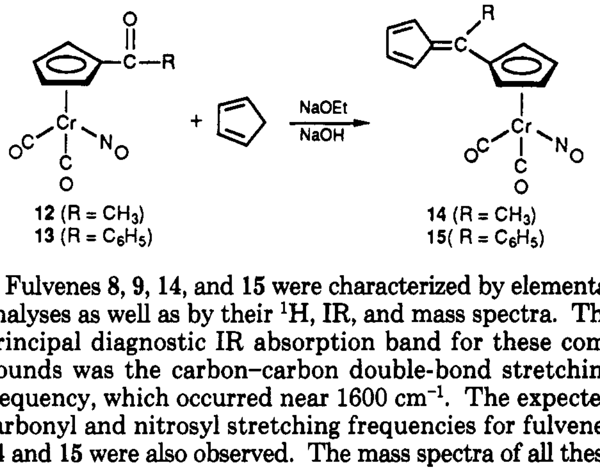
11

The unexpected isolation of various 6-ferrocenylfulvenes from reactions of 2 and lithium aluminum hydride or Grignard reagents as described above necessitated the synthesis of authentic samples of these substances. 6-Ferrocenylfulvene (5) could be obtained in 98% yield from a reaction between cyclopentadiene, ferrocenecarboxaldehyde, and sodium ethoxide, utilizing the procedure of Osgerby and Pauson.[20] In an extension of this method, we found that reactions of either acetylferrocene or benzoylferrocene with cyclopentadiene under basic conditions likewise afforded the respective fulvenes 8 and 9. Fulvene 8 was previously prepared in 44% yield in 1961 from acetylferrocene, cyclopentadiene, and ethanolic sodium hydroxide.[21] However, the present method is more satisfactory, since nearly quantitative yields of fulvenes 5, 8, and 9 can be obtained under these reaction conditions.



5 (R = H)
8 (R = CH_3)
9 (R = C_6H_5)

Since both (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (12) and (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (13) were available from previous studies,[6] it was of interest to determine if these metalloaromatic ketones could also be converted to corresponding fulvenes under similar conditions. Both reactions proved to be successful, and 6-methyl-6-[(dicarbonylnitrosylchromio)-η^5-cyclopentadienyl]fulvene (14) as well as 6-phenyl-6-[(dicarbonylnitrosylchromio)-η^5-cyclopentadienyl]fulvene (15) could be isolated in yields of 84% and 56%, respectively.



12 (R = CH_3)
13 (R = C_6H_5)

14 (R = CH_3)
15(R = C_6H_5)

Fulvenes 8, 9, 14, and 15 were characterized by elemental analyses as well as by their ^{1}H, IR, and mass spectra. The principal diagnostic IR absorption band for these compounds was the carbon–carbon double-bond stretching frequency, which occurred near 1600 cm^{-1}. The expected carbonyl and nitrosyl stretching frequencies for fulvenes 14 and 15 were also observed. The mass spectra of all these fulvenes exhibited molecular ions. These were generally intense for the ferrocenylfulvenes and relatively weak for the chromium-containing analogues. Fragmentation peaks consistent with the structural formulations of the fulvenes were also observed.

Mechanistic Considerations. Carbonium ions when generated adjacent to η^5-cyclopentadienyl transition-metal substituents have long been known to exhibit an unusual degree of stability. The positive charge associated with the cation is believed to be extensively delocalized over the organometallic system and especially onto the metal atom itself.[22] The enhanced stabilities of carbocations containing the (η^5-cyclopentadienyl)dicarbonylnitrosylchromium moiety have been demonstrated earlier.[7-9]

In bimetallic stabilized carbonium ions such as 16, the positive charge generated initially at the carbon center (16a) can be delocalized over *two* organometallic moieties:

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(20) Osgerby, J. M.; Pauson, P. L. *J. Chem. Soc.* **1961**, 4604.
(21) Furdik, M.; Toma, B.; Suchy, J. *Chem. Zvesti* **1961**, *15*, 547.
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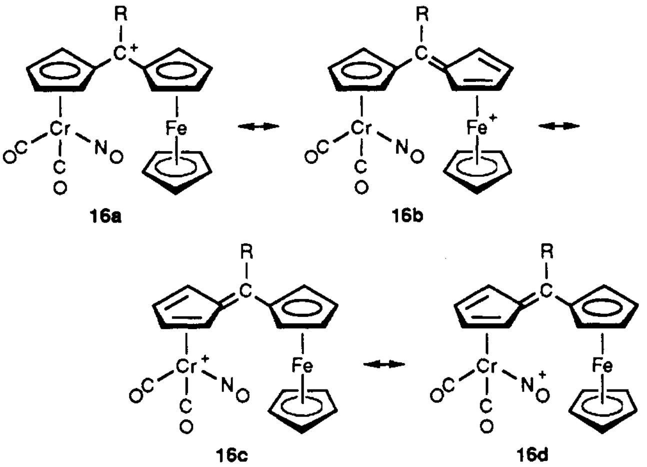
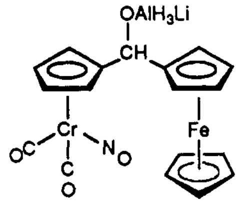


16a 16b 16c 16d

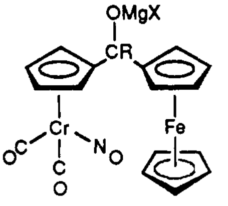
In structures **16b** and **16c**, the positive charge is localized on the iron atom and on the chromium atom, respectively. In the case of **16b**, the structure can formally be regarded as an iron complex of a 6-alkyl (or aryl)-6-[(dicarbonylnitrosylchromio)-η^5-cyclopentadienyl]fulvene, whereas structure **16c** is representative of a chromium derivative of a 6-alkyl (or aryl)-6-ferrocenylfulvene. Structure **16d**, in which the positive charge is delocalized onto the nitrosyl ligand, is also a reasonable contributer to the resonance hybrid cation **16**, since the nitrosyl ligand can formally accommodate such a charge.[23]

The methylium carbon in bimetallic stabilized carbonium ions such as **16** is therefore a relatively weak electrophilic center, since a significant amount of the positive charge originally generated at the α-carbon is delocalized onto the rest of the molecule. When cations **16** are allowed to react with reagents that are sufficiently nucleophilic, such as $LiAlH_4$ or RMgX, attack can occur at the $Cr(CO)_2NO$ moiety (**16c** and **16d**) as well as at the α-carbon. Such a process could subsequently lead to degradation of this unit and formation of the corresponding 6-ferrocenylfulvene.

Thus, in the reaction of either ketone **2** or carbinol **4** with $LiAlH_4$ in THF, ionization of the carbon–oxygen bond in the resulting intermediate (**17**) would generate the inter-



17



18 (R = CH_3, X = I)
19 (R = C_6H_5, X = Br)

mediate cation **16** (R = H) (THF is a more ionizing solvent than is diethyl ether). Subsequent nucleophilic attack at the $Cr(CO)_2NO$ moiety would lead to degradation and formation of fulvene **5**.

In a similar manner, reaction of **2** with CH_3MgI in diethyl ether should initially produce intermediate **18**, which on subsequent hydrolysis would lead to carbinol **7**. However, extended heating of **18** could promote ionization of the C–OMgI bond, and nucleophilic attack by excess CH_3MgI at the $Cr(CO)_2NO$ unit of the resulting cation (**16**, R = CH_3) would then lead to fulvene **8**. Ionizations of C–OMgX bonds in the formation of other types of anomalous products from reactions between ferrocenyl ketones and Grignard reagents have been postulated previously.[24-26]

Reactions of ketone **2** with either an equimolar amount or an excess of C_6H_5MgBr under various reaction conditions invariably led to the fulvene degradation product **9** and not the normal Grignard addition product **10**. Such a result could be due to more facile ionization of the C–OMgBr bond in the initial intermediate (**19**) compared to ionization in intermediate **18**. Two possible explanations for this result may be as follows: (1) enhanced stability of the cation (**16**, R = C_6H_5) due to the higher stabilizing ability of the phenyl group; (2) greater steric strain in the intermediate **19** compared to intermediate **18**.

Although a highly stabilized cation (**16**, R = CH_3) is also presumably an intermediate in the acid-catalyzed dehydration of carbinol **7**, no strong nucleophiles are present under these reaction conditions, and normal loss of a proton to form alkene **11** is the preferred reaction pathway.

Clearly, reactions of ketone **2** with various nucleophilic reagents leading to 6-ferrocenylfulvenes represent a novel and unexpected result. Several related reactions involving α-metallocenyl cations and nucleophiles, leading to 6,6-diphenylfulvene, have also been reported.[27,28] Additional studies to better elucidate the mechanisms of these unusual reaction pathways would be worthwhile.

Experimental Section

All operations were carried out under an argon atmosphere by using Schlenk techniques. The argon was dried with H_2SO_4 and P_2O_5, and trace oxygen was removed with activated BTS catalyst. Diethyl ether and tetrahydrofuran (THF) were predried over sodium wire and distilled under argon from sodium benzophenone ketyl radical. Hexane, dichloromethane, and benzene were distilled under argon from calcium hydride. All other solvents were used as obtained commercially. Column chromatography was carried out under argon by using Fisher silica gel. The silica gel was heated with a heat gun while mixing on a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen and then stored under argon until use. ^1H NMR spectra were recorded on either a Varian A-60 or Perkin-Elmer R-12A spectrometer. IR spectra were obtained on a Perkin-Elmer 237B or Beckman IR-10 spectrometer using KBr pellets or solutions and were calibrated versus polystyrene. Mass spectra were obtained by using a Perkin-Elmer-Hitachi RMU 6L mass spectrometer. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

Carbonylbis[(η^5-cyclopentadienyl)dicarbonylnitrosylchromium] (3). (η^5-Carboxycyclopentadienyl)dicarbonylnitrosylchromium (1.00 g, 4.05 mmol) was stirred with phosphorus pentachloride (0.930 g, 4.47 mmol) in 50 mL of benzene for 2 h at room temperature. The reaction mixture was filtered, and the filtrate was concentrated in vacuum at 50 °C to remove the benzene and phosphorus oxychloride, leaving a residue of (η^5-(chloroformyl)cyclopentadienyl)dicarbonylnitrosylchromium. Methylene chloride (100 mL) and aluminum chloride (0.540 g, 4.05 mmol) were added, and the mixture was stirred for 2 h and filtered. Subsequently, a solution of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (0.960 g, 4.73 mmol) in 25 mL of methylene chloride was added dropwise to the filtrate. After the addition was completed, the mixture was stirred at room temperature for 12 h. The reaction mixture was then cooled to 0 °C and slowly hydrolyzed with 50 mL of ice followed by 5 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated, and the aqueous layer was extracted twice with

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[24] Horspool, W. M.; Sutherland, R. G. *Tetrahedron Lett.* **1967**, 4165.

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[26] Horspool, W. M.; Sutherland, R. G.; Sutton, J. R. *Can. J. Chem.* **1969**, 3085.

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methylene chloride. The combined organic portion was washed once with water, once with sodium bicarbonate solution and once again with water and was dried with anhydrous magnesium sulfate. The solution was filtered, the filtrate was concentrated to 50 mL under vacuum, 20 g of silica gel was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane/benzene gave a red band, which upon removal of the solvent under vacuum gave ketone **3**, 0.45 g (26%). An analytical sample, mp 189–190 °C, was obtained by recrystallization from ethyl ether/benzene/hexane, followed by vacuum sublimation at ca. 100 °C: ^{1}H NMR ($CDCl_3$) δ 5.25 (4 H, t, $H_{3,4}$), 5.78 (4 H, t, $H_{2,5}$); IR ($CDCl_3$) 2960 (w), 2940 (w), 2875 (w), 2030 (vs), 1965 (vs), 1710 (vs), 1640 (m), 1465 (m), 1380 (m), 1300 (s), 1260 (s), 1110 (m), 1050 (s), 1030 (m), 890 (w), 800 (s), 700 (s), 635 cm^{-1} (s); MS *m/e* 432 (M^+). Anal. Calcd for $C_{15}H_8Cr_2N_2O_7$: C, 41.68; H, 1.87; N, 6.48. Found: C, 41.31; H, 2.11; N, 6.57.

[η^5-(1-Hydroxy-1-ferrocenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (7). A solution of methylmagnesium iodide was prepared from magnesium (0.959 g, 2.4 mmol) and excess methyl iodide in 5 mL of diethyl ether. To this solution was added rapidly (η^5-ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (0.55 g, 1.2 mmol) in 5 mL of diethyl ether, and the solution was refluxed for 30 min. The reaction mixture was hydrolyzed with 10 mL of ice water, followed by 5 drops of concentrated hydrochloric acid. Diethyl ether (50 mL) was added, the layers were separated, and the organic layer was dried with magnesium sulfate. The solution was filtered, and the solvent was removed under vacuum to give a residue. The latter was then dissolved in 50 mL of methylene chloride, 20 g of silica gel was added, and the solvent was removed under vacuum. This residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave a yellow band, which upon removal of the solvent under vacuum gave carbinol **7**, 0.43 g (83%). An analytical sample, mp 128 °C, was obtained as yellow crystals by recrystallization from methylene chloride/hexane: ^{1}H NMR ($CDCl_3$) δ 1.77 (3 H, s, CH_3), 2.41 (1 H, s, OH), 4.23 (9 H, s, ferrocenyl), 4.82 (2 H, t, $CrCpH_{3,4}$), 5.16 (2 H, t, $CrCpH_{2,5}$); IR ($CDCl_3$) 3560 (m), 3360 (m), 3100 (m), 2940 (w), 2020 (vs), 1955 (vs), 1710 (vs), 1440 (w), 1415 (m), 1372 (m), 1320 (m), 1265 (w), 1220 (w), 1205 (w), 1180 (m), 1080 (m), 1050 (w), 1030 (m), 1002 (s), 820 (s), 665 cm^{-1} (w); MS *m/e* 431 (M^+). Anal. Calcd for $C_{19}H_{17}CrFeNO_4$: C, 52.93; H, 3.97; N, 3.25. Found: C, 52.71; H, 4.06; N, 3.30.

When the reaction mixture was refluxed for 2 h instead of 30 min, elution of the column with hexane produced a 56% yield of 6-ferrocenyl-6-methylfulvene (**8**) (vide infra) and no carbinol **7**.

Reaction of (η^5-Ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (2) with Phenylmagnesium Bromide. A solution of phenylmagnesium bromide was prepared from magnesium (0.037 g, 3.0 mmol) and bromobenzene (0.47 g, 2.9 mmol) in 5 mL of diethyl ether. To this solution was rapidly added (η^5-ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (0.55 g, 1.2 mmol) in 5 mL of ether, and then the solution was allowed to stir at room temperature for 1 h. The reaction mixture was hydrolyzed with 20 mL of ice water, the aqueous and organic layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water and then dried with anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed under vacuum to give a residue. The latter was then dissolved in 50 mL of methylene chloride, 20 g of silica gel was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave a purple band, which upon removal of the solvent under vacuum gave 0.24 g (59%) of 6-ferrocenyl-6-phenylfulvene (**9**) (vide infra). Elution with benzene produced a 16% yield of ketone **2**.

Reaction of (η^5-Ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (2) with Lithium Aluminum Hydride. (η^5-Ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (0.55 g, 1.2 mmol) was dissolved in 10 mL in THF. Lithium aluminum hydride (0.070 g, 1.84 mmol) in 10 mL of THF was added slowly, and the mixture was stirred for 1 h at room temperature. The reaction mixture was hydrolyzed with 20 mL of ice water, the aqueous and organic layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water and then dried with anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed under vacuum to give a residue. The latter was then dissolved in 50 mL of methylene chloride, 20 g of silica gel was added, and the solvent was removed under vacuum. This residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave a dark red band, which upon removal of the solvent under vacuum gave 6-ferrocenylfulvene (**5**) (vide infra). Elution with benzene gave the starting compound **2** (10%).

Reaction of [η^5-(Hydroxyferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (4) with Lithium Aluminum Hydride. [η^5-(Hydroxyferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (0.13 g, 0.31 mmol) was dissolved in 10 mL of THF. Lithium aluminum hydride (0.020 g, 0.53 mmol) in 10 mL of THF was added, and the mixture was stirred for 1 h at room temperature. The reaction mixture was hydrolyzed with 20 mL of ice water, the aqueous and organic layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with water and dried with anhydrous magnesium sulfate. The solution was filtered, and the solvent was removed under vacuum to give a residue. The latter was then dissolved in 50 mL of methylene chloride, 20 g of silica gel was added, and the solvent was removed under vacuum. The resulting residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave 0.050 g (61%) of 6-ferrocenylfulvene (**5**) (vide infra).

[η^5-(1-Ferrocenylvinyl)cyclopentadienyl]dicarbonylnitrosylchromium (11). A solution of methylmagnesium iodide was prepared from magnesium (0.059 g, 2.4 mmol) and excess methyliodide in 5 mL of diethyl ether. To this solution was rapidly added (η^5-ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (0.55 g, 1.2 mmol) in 5 mL of ether, and the solution was refluxed for 30 min. The reaction mixture was hydrolyzed with 10 mL of ice water, followed by 5 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated, and 50 mL of ether was added. The organic layer was washed with water and then dried with anhydrous magnesium sulfate. The solution was filtered and the solvent was removed under vacuum to give a residue. The residue was dissolved in 25 mL of benzene, 2 mg of hydroquinone and 0.036 g (0.21 mmol) of *p*-toluenesulfonic acid were added, and the mixture was refluxed for 2 h. After cooling of the mixture to room temperature and removal of the solvent, 50 mL of methylene chloride and 20 g of silica gel were added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane/benzene (5:1) gave a red band, which upon removal of the solvent under vacuum gave 0.27 g (54%) of alkene **11**. An analytical sample was obtained as a red liquid by molecular distillation at 155 °C/0.1 Torr: ^{1}H NMR ($CDCl_3$) δ 4.17 (5 H, s, FeC_5H_5), 4.27 (2 H, t, $FeCpH_{3,4}$), 4.44 (2 H, t, $FeCpH_{2,5}$), 5.06 (2 H, t, $CrCpH_{3,4}$), 5.46 (2 H, t, $CrCpH_{2,5}$), 5.40 (1 H, s, $=CH_2$), 5.55 (1 H, s, $=CH_2$); IR ($CDCl_3$) 3100 (w), 2020 (s), 1950 (s), 1700 (s), 1550 (w), 1410 (w), 1000 (w), 815 (m), 620 (m), 500 cm^{-1} (m); MS *m/e* 413 (M^+). Anal. Calcd for $C_{19}H_{15}CrFeNO_3$: C, 55.23; H, 3.66; N, 3.39. Found: C, 55.18; H, 3.85; N, 3.19.

[η^5-(Ferrocenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (6). To a stirred suspension of lithium aluminum hydride (0.091 g, 2.3 mmol) in 3 mL of ethyl ether was added aluminum chloride (0.31 g, 2.3 mmol) slowly. After the vigorous reaction had subsided, (η^5-ferrocenoylcyclopentadienyl)dicarbonylnitrosylchromium (0.55 g, 1.2 mmol) in 4 mL of diethyl ether was added dropwise so as to maintain a gentle reflux. The reaction mixture was then refluxed for 30 min, followed by the addition of 10 mL of ice water and 2 drops of concentrated hydrochloric acid. The ether layer was separated, washed twice with water, and dried with magnesium sulfate. The solvent was removed under aspirator vacuum to give a residue, which was dissolved in 50 mL of methylene chloride, 20 g of silica was added, and the solvent was again removed under vacuum. The resulting residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave a yellow band, which upon removal of the solvent under vacuum gave **6**, 0.20 g (41%). An analytical sample, mp 115 °C, was obtained by vacuum sublimation at 100 °C/0.1 Torr: ^{1}H NMR ($CDCl_3$) δ 3.30 (2 H, s, CH_2), 4.12 (9 H, s, ferrocenyl), 4.93 (4 H, s, CrC_5H_4); IR ($CDCl_3$) 2035 (vs), 1965 (vs), 1717 (vs), 1600 (w), 1570 (w), 1440 (w), 1102 (w), 1000 (w), 840 cm^{-1} (w); MS *m/e* 401 (M^+). Anal. Calcd for $C_{18}H_{15}CrFeNO_3$: C, 53.89; H, 3.77; N, 3.49. Found: C, 53.75; H, 4.04; N, 3.53.

6-Ferrocenylfulvene (5). 6-Ferrocenylfulvene was prepared by a modification of a literature method.[20] Cyclopentadiene (1.01 g, 15.4 mmol) and ferrocenecarboxaldehyde (2.6 g, 7.5 mmol) in 50 mL of ethanol were added to a solution of sodium (2.0 g, 87 mmol) in 20 mL of ethanol. The mixture was heated to 80 °C for 30 min, then 200 mL of water was added, and the mixture was extracted with ether. The ether layer was separated, washed with water, and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum to give a residue, which was dissolved in 50 mL of methylene chloride. Silica gel (20 g) was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave a dark red band, which upon removal of the solvent under vacuum produced 1.9 g (98%) of 6-ferrocenylfulvene as a deep red oil: ^{1}H NMR ($CDCl_3$) δ 4.15 (5 H, s, C_5H_5), 4.45 (2 H, t, $H_{3,4}$), 4.62 (2 H, t, $H_{2,5}$), 6.1–7.1 (5 H, m, =CH); IR ($CDCl_3$) 3100 (s), 3064 (m), 3040 (w), 2960 (s), 2940 (s), 2860 (m), 1620 (vs), 1610 (vs), 1478 (m), 1439 (vs), 1410 (w), 1400 (w), 1380 (m), 1340 (s), 1280 (w), 1248 (m), 1210 (w), 1130 (w), 1100 (m), 1072 (m), 1042 (m), 1028 (m), 998 (m), 990 (s), 925 (w), 815 (vs), 752 (w), 672 (w), 610 cm^{-1} (s); MS *m/e* 262 (M^+).

6-Ferrocenyl-6-methylfulvene (8). Cyclopentadiene (0.54 g, 8.2 mmol) and acetylferrocene (1.0 g, 4.4 mmol) in ethanol (50 mL) were added to a solution of sodium (1.09 g, 47.4 mmol) in ethanol (20 mL). The mixture was refluxed for 6 h, then 200 mL of water was added, and the mixture was extracted with ether. The ether layer was separated, washed with water, and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum to give a residue, which was dissolved in 50 mL of methylene chloride. Silica gel (20 g) was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave a dark red band, which upon removal of the solvent under vacuum gave 6-ferrocenyl-6-methylfulvene (8), 1.13 g (93%), as a deep red oil. An analytical sample, mp 84–85 °C, was obtained by recrystallization from methanol/water: ^{1}H NMR ($CDCl_3$) δ 2.57 (3 H, s, CH_3), 4.20 (5 H, s, C_5H_5), 4.48 (2 H, t, $H_{3,4}$), 4.66 (2 H, t, $H_{2,5}$), 6.58 (4 H, m, =CH); IR ($CDCl_3$) 3100 (m), 2950 (m), 2920 (m), 1600 (m), 1435 (w), 1360 (m), 1120 (vs), 1040 (m), 1000 (s), 910 (s), 828 cm^{-1} (vs); MS *m/e* 276 (M^+). Anal. Calcd for $C_{17}H_{16}Fe$: C, 73.94; H, 5.84. Found: C, 73.67; H, 6.09.

6-Ferrocenyl-6-phenylfulvene (9). Cyclopentadiene (1.00 g, 15.1 mmol) and benzoylferrocene (2.2 g, 7.6 mmol) in ethanol (50 mL) were added to a solution of sodium (2.0 g, 87 mmol) in ethanol (20 mL). The mixture was refluxed for 6 h, then 200 mL of water was added, and the mixture was extracted with ether. The ether layer was separated, washed with water, and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum to give a residue, which was dissolved in 50 mL of methylene chloride. Silica gel (20 g) was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution with hexane gave a purple band, which upon removal of the solvent under vacuum gave 6-ferrocenyl-6-phenylfulvene (9), 2.31 g (90%), as a deep red oil. An analytical sample was obtained by vacuum distillation at 170 °C/0.1 Torr: ^{1}H NMR ($CDCl_3$) δ 4.12 (5 H, s, C_5H_5), 4.47 (4 H, s, C_5H_4), 5.86 (1 H, m, =CH), 6.38 (1 H, m, =CH), 6.62 (1 H, m, =CH), 7.08 (1 H, m, =CH), 7.37 (5 H, s, C_6H_5); IR ($CDCl_3$) 3105 (s), 3027 (m), 2925 (w), 1700 (w), 1580 (s), 1525 (s), 1455 (w), 1405 (w), 1365 (w), 1360 (s), 1328 (w), 1284 (w), 1100 (w), 1080 (w), 1050 (w), 1000 (s), 940 (w), 810 (s), 770 (m), 670 cm^{-1} (m); MS *m/e* 338 (M^+). Anal. Calcd for $C_{22}H_{18}Fe$: C, 78.12; H, 5.36. Found: C, 77.92; H, 5.53.

6-Methyl-6-[(dicarbonylnitrosylchromio)-η^5-cyclopentadienyl]fulvene (14). Cyclopentadiene (1.5 g, 24 mmol) and (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (1.35 g, 5.50 mmol) in ethanol (50 mL) were added to a solution of sodium (1.0 g, 43 mmol) in ethanol (20 mL). The mixture was refluxed for 6 h, then 200 mL of water was added, and the mixture was extracted with ether. The ether layer was washed with water and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum to give a residue, which was dissolved in 50 mL of methylene chloride. Silica gel (20 g) was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane/benzene gave a red band, which upon removal of the solvent under vacuum gave fulvene **14**, 1.35 g (84%). An analytical sample, mp 141–142 °C, was obtained as an orange solid by vacuum sublimation at 110 °C/0.1 Torr: ^{1}H NMR ($CDCl_3$) δ 2.32 (3 H, s, CH_3), 5.12 (2 H, t, $H_{3,4}$), 5.46 (2 H, t, $H_{2,5}$), 6.55 (4 H, s, =CH); IR ($CDCl_3$) 2030 (vs), 1960 (vs), 1710 (vs), 1610 (s), 1482 (m), 1464 (m), 1440 (w), 1410 (w), 1380 (m), 1370 (s), 1085 (w), 1065 (w), 990 (w), 890 (w), 880 (w), 828 (m), 769 (m), 720 (m), 630 cm^{-1} (vs); MS *m/e* 293 (M^+). Anal. Calcd for $C_{14}H_{11}CrNO_3$: C, 57.34; H, 3.78; N, 4.78. Found: C, 57.09; H, 4.11; N, 4.63.

6-Phenyl-6-[(dicarbonylnitrosylchromio)-η^5-cyclopentadienyl]fulvene (15). Cyclopentadiene (0.43 g, 6.5 mmol) and (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (1.00 g, 3.26 mmol) in ethanol (50 mL) were added to a solution of sodium (0.38 g, 16.3 mmol) in ethanol (20 mL). The mixture was refluxed for 6 h, then 200 mL of water was added, and the mixture was extracted with ether. The ether layer was separated, washed with water, and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum to give a residue, which was dissolved in 50 mL of methylene chloride. Silica gel (20 g) was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane gave a dark red band, which upon removal of the solvent under vacuum gave fulvene **15**, 0.65 g (56%). An analytical sample, mp 112–113 °C, was obtained as red crystals by vacuum sublimation at 100 °C/0.1 Torr: ^{1}H NMR ($CDCl_3$) δ 4.8–5.3 (4 H, m, C_5H_4), 5.5–6.8 (4 H, m, =CH), 7.1–7.4 (5 H, m, C_6H_5); IR ($CDCl_3$) 3070 (w), 2020 (vs), 1700 (vs), 1600 (w), 1490 (w), 1468 (w), 1442 (m), 1362 (w), 1340 (w), 1065 (w), 1030 (w), 820 (m), 775–700 (bm), 624 cm^{-1} (s); MS *m/e* 355 (M^+). Anal. Calcd for $C_{19}H_{13}CrNO_3$: C, 64.23; H, 3.69; N, 3.94. Found: C, 64.50; H, 3.86; N, 3.84.

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