reduced pressure and identified by comparison of the NMR spectra with independently prepared authentic samples.[4]

Acknowledgment. Support of this work by the Office of Naval Research and by the National Science Foundation (Grant No. CHE77-06810) is gratefully acknowledged.

Registry No. 1, 23582-02-7; **2**, 12150-46-8; **4**, 17185-29-4; MMA, 80-62-6; methyl α-formylisobutyrate, 13865-20-8; methyl β-formylisobutyrate, 13865-21-9; styrene, 100-42-5; divinylbenzene, 1321-74-0.

Formation and Reactions of Ring-Substituted Derivatives of (η^5-Cyclopentadienyl)dicarbonylnitrosylchromium

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Friedel–Crafts acylation of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (1) produces the corresponding ketones and esters in good yield. Hydrolysis of [η^5-((methylthio)carbonyl)cyclopentadienyl]dicarbonylnitrosylchromium gives (η^5-carboxycyclopentadienyl)dicarbonylnitrosylchromium ($pK_a = 5.1$) in 50% yield. Reduction of ketone derivatives of 1 with sodium borohydride produces the corresponding secondary alcohols in high yield, whereas reduction with lithium aluminum chloride–aluminum chloride leads to products of hydrogenolysis in 55–65% yield. High yields of tertiary alcohols have been obtained by treating ketone derivatives of 1 with alkyl or aryl Grignard reagents. Dehydration of [η^5-(1-hydroxy-1-methylethyl)cyclopentadienyl]dicarbonylnitrosylchromium produces (η^5-isopropenylcyclopentadienyl)dicarbonylnitrosylchromium in 81% yield. (η^5-Ethynylcyclopentadienyl)dicarbonylnitrosylchromium has been prepared by reaction of (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium with phosphorus oxychloride in dimethylformamide, followed by decomposition of the resulting chloro aldehyde in refluxing basic dioxane solution.

Introduction

Since the discovery that ferrocene exhibits aromatic-type reactivity analogous to that of benzene and its derivatives, there has been a steady growth in interest in metalloaromatic systems, that is, organometallic compounds in which "aromaticity" is induced by virtue of coordination of an unsaturated organic ring system to a transition metal, utilizing delocalized covalent or synergic-type bonding. This aromatic reactivity is exemplified by the ability of ferrocene to undergo electrophilic aromatic substitution reactions such as Friedel–Crafts acylation[1-3] and alkylation,[4,5] formylation,[3,6,7] mercuration,[8,9] sulfonation,[10] aminomethylation,[11,12] and arylation with diazonium salts.[8] Ferrocene will also undergo metalation with organolithium reagents.[8,13]

Several other π-bonded cyclopentadienyl organometallic compounds have also been found to exhibit aromatic-type reactivity similar to that of ferrocene. These include the sandwich compounds ruthenocene and osmocene,[14,15] the mixed (η^5-cyclopentadienyl)carbonylmetal compounds cymantrene[16-18] and its technetium and rhenium[19-21] analogues, and (η^5-cyclopentadienyl)tetracarbonylvanadium.[22,23] (η^5-Cyclopentadienyl)dicarbonylnitrosylchromium (cynichrodene)[24] (1) is the only known example of a nitrosyl-containing (η^5-cyclopentadienyl)metal compound which exhibits aromatic-type reactivity.[25] The following order of decreasing reactivity toward Friedel–Crafts acetylation has been established by Fischer et al.:[26] ferrocene > anisole > ruthenocene > cymantrene > osmocene > cynichrodene $\gtrsim$ (η^5-cyclopentadienyl)tetracarbonylvanadium ≈ benzene > (η^5-cyclopentadienyl)tricarbonylrhenium.

Until the current work was undertaken, very little was known about the aromatic-type reactivity of 1 even though it was first reported in 1955.[27] In contrast, the chemistry

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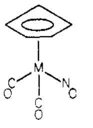
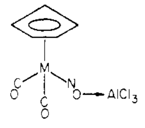
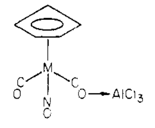
Table I. Carbonyl and Nitrosyl Stretching Frequencies for (η^5-Cyclopentadienyl)dicarbonylnitrosylmetal Complexes and Their Aluminum Chloride Adducts

	IR stretching frequencies (cm^{-1}) in CH_2Cl_2 solution					
						
	ν(NO)	ν(CO)	ν(NO)	ν(CO)	ν(NO)	ν(CO)
$(\eta^5\text{-}C_5H_5)Cr(CO)_2NO + AlCl_3$[a]	1695	2025, 1955	1500	2090, 2030		
$(\eta^5\text{-}C_5H_5)Mo(CO)_2NO + AlCl_3$[b]	1670	2025, 1950	1450	2087, 2025	1710	2065, 1735
$(\eta^5\text{-}C_5H_5)W(CO)_2NO + AlCl_3$[b]	1655	2010, 1930	1450	2075, 2010		

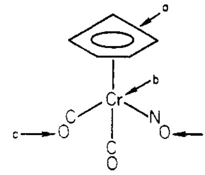
[a] This work. [b] Reference 35.

of carbonyl group substitution of 1 has been extensively investigated.[28-34]

Results and Discussion

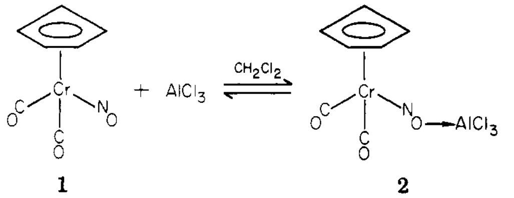
Ring-Substitution Reactions of 1. Although 1 has long been known to undergo Friedel-Crafts acetylation with acetyl chloride and aluminum chloride,[25] initial attempts to expand this reaction proved to be uniformly unsuccessful when extended to other acid chlorides such as benzoyl chloride, phenylacetyl chloride, etc., under the original conditions.[25,26]

In order to ascertain the reason for this apparent lack of reactivity of 1 under Friedel-Crafts conditions, a study was undertaken to examine the interaction of aluminum chloride with 1. There are four types of nucleophilic sites in 1 that could possibly interact with Lewis acids such as aluminum chloride: (a) the π cloud of the cyclopentadienyl ring; (b) a lone pair of electrons on chromium; (c) the carbonyl oxygen atoms; (d) the nitrosyl oxygen atom.

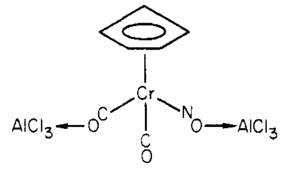


1

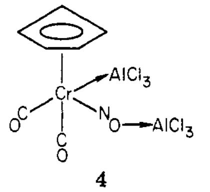
The IR spectrum of 1 in methylene chloride solution exhibits carbonyl stretching bands at 2025 and 1955 cm^{-1} and a nitrosyl stretching band at 1695 cm^{-1}. Upon the addition of aluminum chloride to this solution, the carbonyl band at 2025 cm^{-1} broadens and the intensities of both the carbonyl band at 1955 cm^{-1} and the nitrosyl band at 1695 cm^{-1} diminish, with the commensurate appearance and growth of strong new bands at 2090 and 1500 cm^{-1}. These spectral changes are consistent with the complexation of aluminum chloride and the nitrosyl oxygen of 1 to give complex 2 (eq 1). The simple changes in the IR spectrum continue to occur until approximately 1 equiv of $AlCl_3$/mol of 1 has been added. At this point, based on the IR spectrum, there is clearly a mixture of free 1 and complex 2. Upon the addition of excess aluminum chloride (up to 3 equiv), the IR spectrum becomes much more complicated, with a large number of new bands appearing in the carbonyl and nitrosyl region. These new bands are most likely due to complexes such as 3 and 4. Even with a threefold excess of aluminum chloride, there is still some free 1, as evidenced by the bands at 1955 and 1695 cm^{-1}.



1 2 (1)



3



4

Lokshin and co-workers[35] have recently published the results of a related study concerning the interaction of aluminum chloride with the molybdenum and tungsten analogues of 1. The results of that study, together with our results, are summarized in Table I.

The NMR spectrum of complexes 2-4 is much less diagnostic than the IR spectrum. When slightly more than 1 equiv of aluminum chloride is added to a solution of 1, the cyclopentadienyl resonance is shifted to lower field from δ 5.0 to 5.3. Upon the addition of water, the cyclopentadienyl resonance is shifted back to its original position at δ 5.0.

From the IR and NMR data it is clear that the complexation of 1 by aluminum chloride (eq 1) is reversible, being fast in comparison with the NMR time scale and slow with respect to the IR time scale. It should also be noted that aluminum chloride slowly caused the decomposition of 1 in solution.

On the basis of the above spectral results, we have subsequently found that preforming the Perrier-type complex 5 (eq 2) in the absence of 1 and then subsequently allowing this complex to react with 1 lead to the desired acylated derivatives of 1 in moderate to good yields. In this manner, ketone derivatives of 1 such as (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (6) and [η^5-(phenylacetyl)cyclopentadienyl]dicarbonylnitrosylchromium (7), as well as the ester derivative [η^5-((methylthio)carbonyl)cyclopentadienyl]dicarbonylnitrosylchromium (8), could be readily prepared (eq 3).

Reactions of Carbonyl and Alcohol Derivatives of 1. Hydrolysis of ester 8 with potassium hydroxide in 1:1 ethanol-water gave (η^5-carboxycyclopentadienyl)di-

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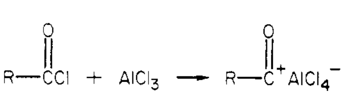
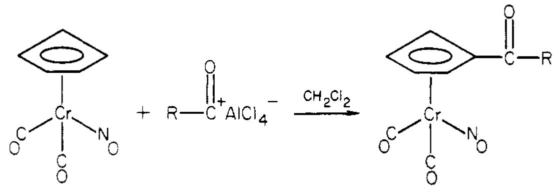


$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}Cl + AlCl_3 \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{}^{+}AlCl_4^{-}} \quad (2)$$

5

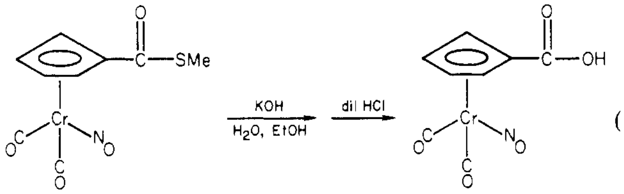


(3)

1

6, R = Ph
7, R = CH$_2$Ph
8, R = SMe

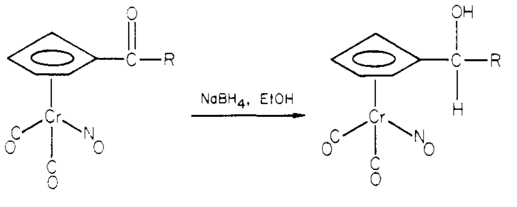
carbonylnitrosylchromium (**9**) in approximately 50% yield (eq 4). The pK_a of **9** in aqueous solution was determined to be 5.1. Thus, **9** is a weaker acid than ferrocenoic acid (pK_a = 4.4)[36] or benzoic acid (pK_a = 4.2)[37] and approximately as strong an acid as *m*-(methylamino)benzoic acid (pK_a = 5.1).[37] This would suggest that **9** is more electron donating than ferrocene and approximately as electron donating as a *m*-(methylamino)phenyl substituent.



(4)

8 9

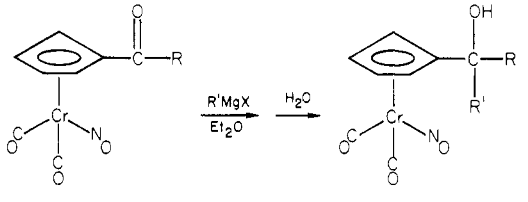
Reduction of ketone derivatives **10**,[38] **6**, and **7** with sodium borohydride in 95% ethanol produced the corresponding secondary alcohols **11**, **12**, and **13** in high yields (eq 5). Excellent yields of the tertiary alcohols **14**, **15**, and **16** could also be obtained by treating ketones **10** and **6** with alkyl- and arylmagnesium halides (eq 6).



(5)

10, R = Me
6, R = Ph
7, R = CH$_2$Ph

11, R = Me
12, R = Ph
13, R = CH$_2$Ph

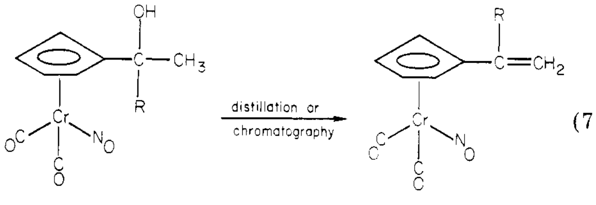


(6)

10, R = Me
6, R = Ph

14, R = R′ = Me
15, R = Me, R′ = Ph
16, R = R′ = Ph

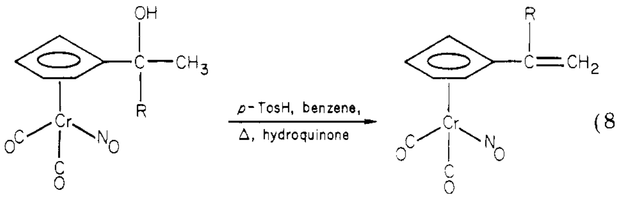
[η^5-(1-Hydroxy-1-phenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (**15**) and [η^5-(1-hydroxy-1-methylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (**14**) could not be obtained "analytically pure" by distillation or by column chromatography, since under these conditions partial dehydration occurred to give a mixture of the alcohol and the corresponding olefins, **17** and **18**, respectively (eq 7). Total dehydration of **15** or **14** to give **17** or **18**, respectively, could be carried out by simply chromatographing the alcohols on activated silica gel. A more reliable synthesis of (η^5-isopropenylcyclopentadienyl)dicarbonylnitrosylchromium (**18**) was developed which involved the acid-catalyzed dehydration of **14** in refluxing benzene using *p*-toluenesulfonic acid in the presence of hydroquinone as a radical inhibitor (eq 8).



(7)

15, R = Ph
14, R = Me

17, R = Ph
18, R = Me



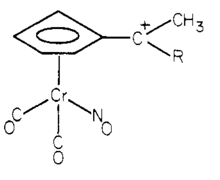
(8)

14, R = Me
19, R = H

18, R = Me
20, R = H

This method has been previously employed in the dehydration of [η^5-(1-hydroxyethyl)cyclopentadienyl]dicarbonylnitrosylchromium (**19**) to give the vinyl derivative **20** in high yield.[38]

These facile dehydrations of alcohols **14**, **15**, and **19** are indicative of the ready formation of stabilized carbonium ion intermediates **21**–**23**, respectively, which subsequently undergo loss of a proton to give the corresponding olefins. ^{1}H and ^{13}C NMR evidence for the facile formation of stabilized carbonium ions such as **21**–**23** has previously been presented.[39]



21, R = Me
22, R = Ph
23, R = H

Another reaction typical of stabilized carbonium ion intermediates is the hydrogenolysis of alcohols and ketones with lithium aluminum hydride and aluminum chloride.[40] Treatment of **6**, **12**, or **13** with 1:1 lithium aluminum hydride–aluminum chloride led to products of hydrogenolysis in 55–65% yield (eq 9 and 10).

(η^5-Ethynylcyclopentadienyl)dicarbonylnitrosylchromium (**27**) has likewise been prepared by using a method similar to that used for the synthesis of ethynylferrocene.[41] Acetyl derivative **10** was treated with an

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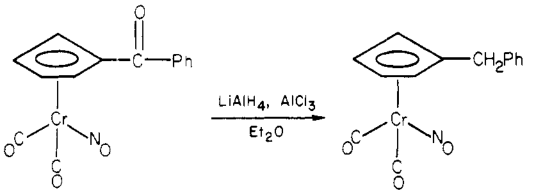
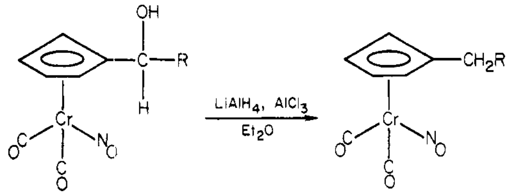


(9)

6 24

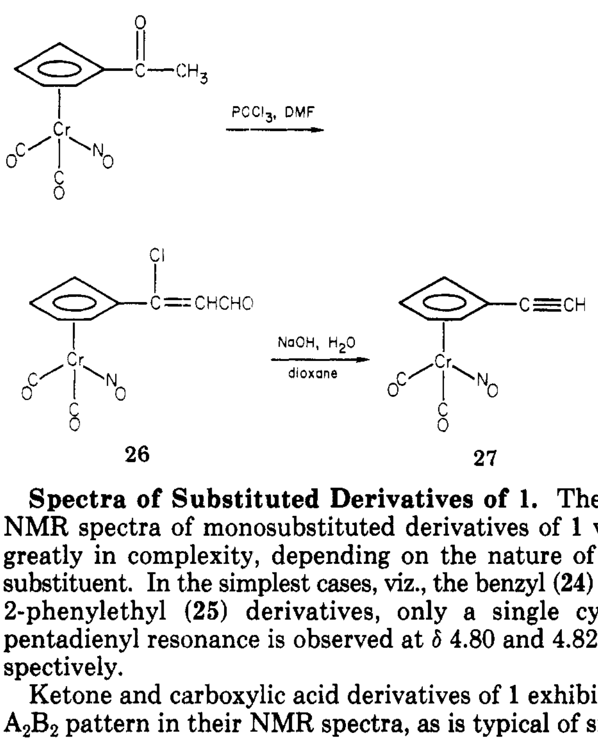


(10)

12, R = Ph
13, R = CH_2Ph

24, R = Ph
25, R = CH_2Ph

excess of phosphorus oxychloride in dimethylformamide to give the chloro aldehyde **26**, which decomposed in refluxing basic dioxane solution to produce the acetylene **27** in 77% yield (eq 11).



(11)

26 27

Spectra of Substituted Derivatives of 1. The ^1H NMR spectra of monosubstituted derivatives of **1** vary greatly in complexity, depending on the nature of the substituent. In the simplest cases, viz., the benzyl (**24**) and 2-phenylethyl (**25**) derivatives, only a single cyclopentadienyl resonance is observed at δ 4.80 and 4.82, respectively.

Ketone and carboxylic acid derivatives of **1** exhibit an A_2B_2 pattern in their NMR spectra, as is typical of similarly substituted cyclopentadienyl ring protons in many other metallo-aromatic systems.[42-46] The spectra consist of a pair of apparent triplets, in which the downfield triplet can be assigned to the $H_{2,5}$ protons. This assignment is made on the basis that the protons nearest the electron-withdrawing carbonyl group would be expected to be deshielded to a greater extent than the protons on the more distant 3- and 4-positions. Analogous assignments have been made unequivocally for monosubstituted ferrocenes from the NMR spectra of 2,5-dideuterioferrocene derivatives.[47]

The NMR spectra of alcohols **14** and **16** also exhibit an A_2B_2 pattern, typical of similarly substituted cyclopentadienyl ring protons in related metallo-aromatic systems.[48,49] The spectra consist of a pair of apparent triplets, in which the downfield triplet can be assigned to the $H_{2,5}$ protons by analogy to other metallo-aromatic systems.[48,49] Alcohols **11**, **12**, and **15**, in which R and R′ are dissimilar, exhibit an A_2BB' pattern in their NMR spectra, due to H_2 and H_5 being diastereotopic. This result is likewise typical of similarly substituted cyclopentadienyl ring protons in many other metallo-aromatic systems.[48,49] The spectra of these alcohols generally exhibit two closely spaced quartets of relative intensity 1 H downfield from δ 5.0 and a triplet of relative intensity 2 H upfield from δ 5.0. The two downfield quartets have been assigned to the $H_{2,5}$ protons on the basis that the protons nearest to the alcohol would be expected to show the greatest diastereotopic effect, whereas a proton at either the 3- or 4-position would show little or no diastereotopic effect.

It is of interest to compare the ^1H NMR spectra of monosubstituted derivatives of **1** with the analogously substituted ferrocene[45] and cymantrene[46] derivatives. As can be seen from the data in Table II, the chemical shifts of protons on derivatives of **1** occur at slightly lower field than those of the protons on analogously substituted cymantrenes, and at significantly lower field than those of the protons on the analogous ferrocene derivatives. The data in Table II also demonstrate that substitution on the cyclopentadienyl ring in these isoelectronic metallo-aromatic systems produces very similar changes in their NMR spectra.

The IR spectra of **1** and its ring-substituted derivatives all exhibit two carbonyl stretching bands, the symmetric mode occurring at 2010–2030 cm^{-1} and the asymmetric mode at 1945–1970 cm^{-1}. A nitrosyl stretching band is also observed between 1690–1705 cm^{-1}. In the ring-substituted derivatives of **1**, the normal absorbance of the organic carbonyl group of ketones and carboxylic acid derivatives is obscured by the NO stretching band; however, other functional groups show their characteristic absorbances.

The mass spectra of all derivatives of **1** studied in this program exhibit a parent peak and the expected chromium isotopic pattern. Fragment peaks at $(M - CO)^+$, $(M - 2\ CO)^+$, and $(M - 2\ CO - NO)^+$ are also always observed.

Experimental Section

All operations were conducted under either an argon or nitrogen atmosphere by means of Schlenk techniques. The argon or nitrogen was dried with H_2SO_4 and P_2O_5, and trace oxygen was removed by BASF catalyst. Hexane, pentane, benzene, methylene chloride, and dimethylformamide were dried over calcium hydride and freshly distilled under argon from calcium hydride. Ethyl ether was predried over sodium and distilled under argon from sodium benzophenone. Tetrahydrofuran was predried with potassium hydroxide and then with sodium and finally distilled under argon from sodium benzophenone. All other solvents were used as commercially obtained.

Column chromatography was carried out with Fisher silica gel or Ventron-Alfa neutral grade alumina. The silica gel and alumina were heated with a heat gun while mixing on a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen. The alumina was then deactivated with 5% (by weight) argon-

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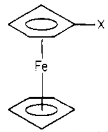
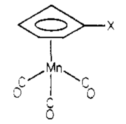
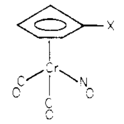
Table II. ^{1}H NMR Comparisons of Ferrocene,[a] Cymantrene,[b] and Cynichrodene (1)[c] Derivatives

						
X	δ(2,5)	δ(3,4)	δ(2,5)	δ(3,4)	δ(2,5)	δ(3,4)
H	4.04 (4.14)	4.04 (4.14)	4.73	4.73	5.00	5.00
$C(O)CH_3$	4.66 (4.77)	4.36 (4.49)	5.34	4.79	5.75	5.18
$C(O)C_6H_5$	4.80 (4.90)	4.43 (4.57)	5.42	4.82	5.72	5.16

[a] Recorded in CCl_4[45] (recorded in $CDCl_3$[42]). [b] Recorded in CCl_4.[46] [c] Recorded in $CDCl_3$, this work.

saturated water. The silica gel and alumina were stored under argon or nitrogen until use. Chromium hexacarbonyl was obtained from Pressure Chemical Co.

Proton NMR spectra were recorded on either a Varian A-60 or a Perkin-Elmer R-12A spectrometer. IR spectra were obtained on either a Perkin-Elmer 2378 or a Beckman IR-10 spectrometer and were calibrated vs. polystyrene. Mass spectra were obtained by Eugene Guzik, of this department, using a Perkin-Elmer Hitachi RMU 6L mass spectrometer. Melting points were determined on a Mel-Temp apparatus in sealed tubes under argon or nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst.

(η^5-Cyclopentadienyl)dicarbonylnitrosylchromium (1). This compound was prepared by a modification of the method originally described by Alt.[29] Sodium sand (3.14 g, 137 mmol) was added to a 500-mL three-neck round-bottom flask equipped with condenser and gas inlet and outlet valves. To this was added 250 mL of THF, and the contents were cooled to 0 °C. Cyclopentadiene (16 mL, 190 mmol) was added slowly in four portions, and the mixture was allowed to stir at 0 °C until all of the sodium had reacted and a clear red solution had formed. The THF was then removed under aspirator vacuum, followed by high vacuum (10^{-3} torr) to remove the excess cyclopentadiene. DMF (200 mL) was subsequently added to the flask containing the solid sodium cyclopentadienide, followed by chromium hexacarbonyl (24.0 g, 110 mmol). The mixture was refluxed for 6 h, the solution allowed to cool, and the DMF removed under vacuum (10^{-3} torr). THF (200 mL) was then added, followed by the dropwise addition of 98% acetic acid (13 mL, 220 mmol), and the mixture was stirred at room temperature for 2 h. To this was added slowly *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, 30 g, 140 mmol), and stirring was continued for 30 min at room temperature. The THF was removed under aspirator vacuum and the resulting black oil extracted with seven 100-mL portions of pentane. The pentane was then removed under aspirator vacuum to give a red oil, which was triturated with water to give a red-brown solid. This solid was then sublimed twice at 60 °C under high vacuum to give 17.5 g (78%) of 1 as orange-red crystals: mp 67 °C (lit.[25] mp 67–68 °C); IR (KBr) 3120 (w), 2020 (vs), 1945 (vs), 1680 (vs), 1415 (m), 1050 (w), 995 (m), 910 (w), 817 (s), 660 (m), 632 (s), 620 (s), 545 (w), 480 (m), 460 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.00 (5 H, s, C_5H_5).

Interaction of (η^5-Cyclopentadienyl)dicarbonylnitrosylchromium (1) and Aluminum Chloride. The IR spectrum of 1 in methylene chloride solution exhibits carbonyl stretching bands at 2025 (vs) and 1955 (vs) cm^{-1} and a nitrosyl stretching band at 1695 (vs) cm^{-1}. Upon addition of 1 equiv of aluminum chloride to the solution of 1, the carbonyl bands are shifted to higher energy (2090 and 2030 cm^{-1}, both vs), while the nitrosyl band is shifted to lower energy (1500 cm^{-1}, vs). Corresponding carbonyl and nitrosyl bands due to 1 at 1955 (m) and 1695 (m) cm^{-1} are still present, although greatly reduced in intensity. The carbonyl band at 2025 cm^{-1} for 1 overlaps the new carbonyl band at 2030 cm^{-1} for the complex (2) formed from 1 and aluminum chloride. If a large excess (up to 3 equiv) of aluminum chloride is added to the solution, a number of additional new bands appear in the carbonyl and nitrosyl region [2220 (w), 2130 (w), 1870 (w), 1780 (m), 1740 (w), 1640 (m), 1400 (m) cm^{-1}].

(η^5-Acetylcyclopentadienyl)dicarbonylnitrosylchromium (10). This compound was prepared by the general method described by Fischer and Plesske;[25] however, the product was purified much more conveniently by column chromatography on silica gel rather than by distillation as in the original procedure. In this manner, acetyl derivative **10** could be obtained as red crystals: mp 27 °C (lit. mp 27–28 °C), in yields of 70–80%; IR (neat) 3125 (w), 2030 (s), 1950 (s), 1705 (s), 1475 (m), 1380 (m), 1285 (s), 1120 (m), 1040 (w), 1020 (w), 885 (w), 830 (w), 630 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.28 (3 H, s, methyl), 5.18 (2 H, t, $H_{3,4}$), 5.75 (2 H, t, $H_{2,5}$).

(η^5-Benzoylcyclopentadienyl)dicarbonylnitrosylchromium (6). To a stirred solution of benzoyl chloride (3.45 mL, 4.18 g, 29.7 mmol) in 110 mL of methylene chloride was added aluminum chloride (7.9 g, 59 mmol), and the mixture was stirred at room temperature for 1 h to give a yellow solution of the corresponding acylium ion. The solution was filtered into a Schlenk tube to remove excess $AlCl_3$, and (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (1) (6.0 g, 29 mmol) in 25 mL of CH_2CH_2 was added slowly. This mixture was allowed to stir at room temperature for 12 h and then cooled to 0 °C. The reaction mixture was slowly hydrolyzed with ice water (150 mL) followed by 3 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated, and the aqueous layer was extracted twice with methylene chloride. The combined organic portion was washed once with water, once with sodium bicarbonate solution, and once again with water and dried over magnesium sulfate. The solution was filtered, 20 g of silica gel was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 8 cm) of silica gel. Elution of the column with 1:1 ether–hexane gave a red band which upon removal of the solvent under vacuum gave 3.9 g (43%) of **6**. Recrystallization from ether–hexane gave a red crystalline solid: mp 58 °C; IR (neat) 3120 (m), 2020 (s), 1955 (s), 1700 (s), 1650 (s), 1600 (m), 1455 (m), 1375 (m), 1340 (w), 1315 (m), 1290 (s), 1170 (m), 1040 (m), 855 (m), 725 (m), 695 (m), 670 (m), 625 (m), 475 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.16 (2 H, t, $H_{3,4}$), 5.72 (2 H, t, $H_{2,5}$), 7.25–7.85 (5 H, m, Ph); mass spectrum, *m/e* 307 (M^+).

Anal. Calcd for $C_{14}H_9CrNO_4$: C, 54.73; H, 2.95. Found: C, 55.03; H, 3.04.

(η^5-(Phenylacetyl)cyclopentadienyl)dicarbonylnitrosylchromium (7). To a stirred solution of phenylacetyl chloride (2.8 g, 18 mmol) in 50 mL of methylene chloride was added aluminum chloride (3.9 g, 29 mmol). The mixture was stirred at room temperature for 5 min to give a red solution of the corresponding acylium ion. The solution was filtered into a Schlenk tube, and (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (1) (3.0 g, 15 mmol) in 20 mL of methylene chloride was added slowly. After this mixture was allowed to stir at room temperature for 12 h, workup as described above produced 1.93 g (41%) of **7**. Recrystallization of the product from ethyl ether–hexane and subsequent sublimation under high vacuum gave **7** as a red crystalline solid: mp 57–58 °C; IR (KBr) 2020 (s), 1945 (s), 1690 (s), 1455 (w), 1400 (w), 1380 (w), 1235 (m), 1065 (m), 1035 (m), 880 (w), 830 (m), 775 (w), 720 (s), 695 (w), 625 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.84 (2 H, s, CH_2), 5.11 (2 H, t, $H_{3,4}$), 5.69 (2 H, t, $H_{2,5}$), 7.32 (5 H, s, Ph); mass spectrum, *m/e* 321 (M^+).

Anal. Calcd for $C_{15}H_{11}CrNO_4$: C, 56.08; H, 3.45; Cr, 16.19; N, 4.36. Found: C, 55.82; H, 3.32; Cr, 16.3; N, 4.33.

[(η^5-((Methylthio)carbonyl)cyclopentadienyl]dicarbonylnitrosylchromium (8). To a solution of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (1) (6.0 g, 30 mmol) in 60 mL of methylene chloride was slowly added a previously prepared and filtered solution of aluminum chloride (7.8 g, 58 mmol) and methyl chlorothioformate (4.9 g, 44 mmol) in 120 mL of methylene chloride. After the addition was completed, the reaction mixture was stirred at room temperature for 11 h. Workup as described above followed by vacuum distillation gave 5.8 g of **8** (71%) as a deep red liquid: bp 100 °C (0.1 torr); IR (neat) 3120 (w), 2935 (w), 2335 (w), 2025 (vs), 1955 (vs), 1815 (m), 1700 (vs), 1650 (s), 1450 (m), 1420 (w), 1375 (m), 1250 (m), 1050 (m), 1030 (m), 945 (w), 830 (s), 670 (m), 635 (s), 625 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.38 (3 H, s, CH$_3$), 5.09 (2 H, t, H$_{3,4}$), 5.78 (2 H, t, H$_{2,5}$); mass spectrum *m/e* 277 (M$^+$).

Anal. Calcd for $C_9H_7NO_4S$: mol wt, 276.9500. Found: mol wt, 276.9484.

(η^5-Carboxycyclopentadienyl)dicarbonylnitrosylchromium (9). [η^5-((Methylthio)carbonyl)cyclopentadienyl]dicarbonylnitrosylchromium (2.0 g, 7.2 mmol) was dissolved in 25 mL of ethanol and the resulting solution diluted with 25 mL of water. Potassium hydroxide (1.14 g, 20.4 mmol) was added and the resulting mixture refluxed for 2 h. The solution was cooled to room temperature and poured into 150 mL of ice water. The aqueous layer was acidified with dilute hydrochloric acid to precipitate the product, which was separated by filtration and dried under high vacuum at room temperature to give 0.89 g (50%) of **9** as a red-brown solid. An analytical sample was obtained by sublimation at 110 °C under high vacuum: mp 193 °C dec; IR (KBr) 2030, 1955, 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.30 (2 H, t, H$_{3,4}$), 5.81 (2 H, t, H$_{2,5}$); mass spectrum *m/e* 247 (M$^+$).

Anal. Calcd for $C_8H_5CrNO_5$: C, 38.88; H, 2.04; N, 5.67. Found: C, 38.79; H, 2.02; N, 5.62.

[η^5-(Hydroxybenzyl)cyclopentadienyl]dicarbonylnitrosylchromium (12). (η^5-Benzoylcyclopentadienyl)dicarbonylnitrosylchromium (1.0 g, 3.2 mmol) was dissolved in 30 mL of 95% ethanol, sodium borohydride (0.1 g, 2.6 mmol) was added, and the mixture was stirred at room temperature for 1 h. To this solution was added 1 mL of 6 N sodium hydroxide, and the reaction mixture was heated on a steam bath for 15 min. The solution was concentrated by removing approximately half of the solvent under aspirator vacuum; 100 mL of water was then added and the product precipitated. The latter was removed by filtration and dried under high vacuum at room temperature to give 0.8 g (79%) of **12** as a red-orange crystalline solid. An analytical sample was obtained by sublimation under high vacuum: mp 57–58 °C; IR (KBr) 3320 (m), 2005 (s), 1935 (s), 1680 (s), 1260 (m), 1070 (w), 1035 (m), 1005 (m), 795 (m), 735 (m), 700 (m), 625 (s), 465 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.28 (1 H, d, OH), 4.96 (2 H, t, H$_{3,4}$), 5.06 (1 H, q, H$_2$ or H$_5$), 5.29 (1 H, q, H$_2$ or H$_5$), 5.49 (1 H, d, HCOH), 7.46 (5 H, s, Ph); mass spectrum, *m/e* 309 (M$^+$).

Anal. Calcd for $C_{14}H_{11}CrNO_4$: C, 54.37; H, 3.58; N, 4.53. Found: C, 54.50; H, 3.58; N, 4.61.

[η^5-(1-Hydroxyphenethyl)cyclopentadienyl]dicarbonylnitrosylchromium (13). In a manner similar to that described above, [η^5-(phenylacetyl)cyclopentadienyl]dicarbonylnitrosylchromium (0.85 g, 2.6 mmol) was reduced with excess sodium borohydride in 30 mL of 95% ethanol to produce, following workup, 0.50 g (59%) of **13**, mp 52–54 °C. The sample was purified by vacuum sublimation: IR (KBr) 3350 (m), 2020 (vs), 1945 (vs), 1685 (vs), 1400 (m), 1240 (m), 1150 (m), 1050 (m), 845 (m), 820 (m), 760 (m), 730 (s), 690 (s), 665 (m), 625 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.96 (1 H, d, OH), 2.93 (2 H, d, CH$_2$), 4.52 (1 H, dt, HCOH), 4.91 (3 H, d, H$_{2,3,4}$), 5.19 (1 H, q, H$_5$), 7.28 (5 H, s, Ph); mass spectrum, *m/e* 323 (M$^+$).

Anal. Calcd for $C_{15}H_{13}CrNO_4$: C, 55.73; H, 4.05; N, 4.33. Found: C, 55.91; H, 3.81; N, 4.29.

(η^5-Benzylcyclopentadienyl)dicarbonylnitrosylchromium (24). Method A. Aluminum chloride (0.2105 g, 1.58 mmol) was added slowly to a stirred suspension of lithium aluminum hydride (0.0613 g, 1.62 mmol) in 3 mL of ethyl ether. After the vigorous reaction had subsided, (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (0.5051 g, 1.64 mmol) in 4 mL of ethyl ether was added dropwise so as to maintain gentle reflux. The reaction mixture was then stirred at room temperature for 10 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, followed by vacuum distillation to give 0.30 g (59%) of **24**: bp 80 °C (0.01 torr); IR (neat) 2020 (vs), 1945 (vs), 1690 (vs), 1480 (w), 1430 (w), 1025 (w), 925 (w), 820 (w), 760 (w), 705 (m), 635 (s), 625 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.47 (2 H, s, CH$_2$), 4.80 (4 H, s, H$_{2-5}$), 7.14 (5 H, s, Ph); mass spectrum, *m/e* 293 (M$^+$).

Anal. Calcd for $C_{14}H_{11}CrNO_3$: C, 57.34; H, 3.78; N, 4.78. Found: C, 57.25; H, 3.93; N, 4.77.

Method B. Aluminum chloride (0.2108 g, 1.58 mmol) was added slowly to a stirred suspension of lithium aluminum hydride (0.0656 g, 1.73 mmol) in 3 mL of ethyl ether. After the vigorous reaction had subsided, [η^5-(hydroxybenzyl)cyclopentadienyl]dicarbonylnitrosylchromium (0.5091 g, 1.65 mmol) in 10 mL of ethyl ether was added dropwise so as to maintain a gentle reflux. The reaction mixture was stirred at room temperature for 10 min, followed by hydrolysis with 10 mL of water and 3 drops of concentrated hydrochloric acid. The ether layer was separated and washed twice with water and then dried with anhydrous magnesium sulfate, and the solvent was removed under aspirator vacuum to give 0.2643 g (55%) of **24**, identical with the product described above.

[η^5-(2-Phenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (25). In a manner similar to that described above, lithium aluminum hydride (0.0613 g, 1.62 mmol) in 3 mL of ethyl ether, aluminum chloride (0.2120 g, 1.59 mmol), and [η^5-(1-hydroxy-2-phenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (0.5270 g, 1.63 mmol) in 10 mL of ethyl ether were allowed to react to give 0.3056 g (61%) of **25** as a red liquid: bp 80 °C (0.01 torr); IR (neat) 3040 (w), 2940 (w), 2020 (vs), 1945 (vs), 1690 (vs), 1600 (w), 1490 (m), 1445 (m), 1170 (w), 1065 (w), 1020 (m), 955 (m), 820 (s), 745 (s), 690 (s), 660 (s), 635 (vs) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.60 (4 H, m, CH$_2$CH$_2$), 4.82 (4 H, s, H$_{2-5}$), 7.20 (5 H, s, Ph); mass spectrum, *m/e* 307 (M$^+$).

Anal. Calcd for $C_{15}H_{13}CrNO_3$: C, 58.63; H, 4.23; N, 4.56. Found: C, 58.82; H, 4.26; N, 4.43.

[η^5-(1-Hydroxy-1-methylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (14). A solution of methylmagnesium iodide was prepared from magnesium (0.098 g, 4.0 mmol) and excess methyl iodide in 6 mL of ethyl ether. To this solution was added rapidly (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (0.4995 g, 2.0 mmol) in 5 mL of ethyl ether, and the solution was stirred at room temperature for 1 h. The reaction mixture was hydrolyzed with 10 mL of water, the aqueous and organic layers were separated, and the aqueous layer was extracted with 10 mL of ether. The combined organic layers were washed with water and then dried with anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 0.50 g (94%) of **14**: IR (neat) 3400 (s), 2975 (m), 2025 (s), 1945 (s), 1815 (w), 1675 (s), 1450 (w), 1370 (w), 1260 (m), 1160 (w), 1100 (m), 1030 (m), 950 (w), 790 (m), 640 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.39 (6 H, s, Me), 2.24 (1 H, s, OH), 4.80 (2 H, t, H$_{3,4}$), 5.14 (2 H, t, H$_{2,5}$); mass spectrum, *m/e* 261 (M$^+$).

Anal. Calcd for $C_{10}H_{11}CrNO_4$: mol wt, 261.0093. Found: mol wt, 261.0162.

[η^5-(1-Hydroxy-1-phenylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (15). Method A. In a manner similar to that described above, methylmagnesium bromide in 6 mL of ethyl ether was allowed to react with (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (0.5015 g, 1.63 mmol) in 6 mL of ethyl ether to give upon the usual workup 0.48 g (89%) of **15**. Treatment of **6** as above with methylmagnesium chloride or iodide in the place of methylmagnesium bromide gave **15** in yields of 75% and 95%, respectively: IR (neat) 3500 (m), 2025 (vs), 1950 (vs), 1695 (vs), 1495 (m), 1450 (m), 1410 (w), 1380 (m), 1330 (w), 1170 (m), 1020 (m), 1000 (m), 930 (w), 895 (w), 820 (m), 785 (m), 760 (m), 695 (s), 650 (m), 635 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.76 (3 H, s, Me), 2.20 (1 H, s, OH), 4.83 (2 H, t, H$_{3,4}$), 5.15 (1 H, q, H$_2$ or H$_5$), 5.24 (1 H, t, H$_2$ or H$_5$), 7.15–7.60 (5 H, m, Ph); mass spectrum, *m/e* 323 (M$^+$).

Anal. Calcd for $C_{15}H_{13}CrNO_4$: mol wt, 323.0249. Found: mol wt, 323.0256.

Method B. In a manner similar to that described above, a solution of phenylmagnesium bromide prepared from magnesium (0.0989 g, 4.11 mmol) and bromobenzene (0.6459 g, 4.1 mmol) in 6 mL of ethyl ether was allowed to react with (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (0.4009 g, 1.64 mmol) in 5 mL of ethyl ether to give, upon the usual workup, 0.48 g (89%) of **15** identical with the product obtained above. Treatment of **10** with phenylmagnesium iodide as above gave **15** in 94% yield.

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[η^5-(Hydroxydiphenylmethyl)cyclopentadienyl]dicarbonylnitrosylchromium (16). In a manner similar to that described above, phenylmagnesium bromide, prepared from magnesium (0.078 g, 3.2 mmol) and bromobenzene (0.53 g, 3.3 mmol) in 6 mL of ethyl ether, was allowed to react with (η^5-benzoylcyclopentadienyl)dicarbonylnitrosylchromium (0.500 g, 1.6 mmol) in 6 mL of ethyl ether to give, after the usual workup, 0.395 g (64%) of **16** as a red, crystalline solid. An analytical sample was obtained by sublimation under high vacuum at 100 °C: mp 115–116 °C; IR (KBr) 3575 (m), 3400 (m), 2015 (vs), 1935 (vs), 1695 (vs), 1480 (m), 1440 (w), 1315 (m), 1225 (w), 1160 (m), 1080 (m), 1025 (m), 1005 (m), 945 (w), 920 (w), 885 (w), 830 (m), 760 (s), 745 (s), 698 (vs), 664 (m), 625 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.56 (1 H, s, OH), 4.88 (2 H, t, $H_{3,4}$), 5.08 (2 H, t, $H_{2,5}$), 7.22 (10 H, s, Ph); mass spectrum, *m/e* 385 (M^+).

Anal. Calcd for $C_{20}H_{15}CrNO_4$: C, 62.33; H, 3.92. Found: C, 62.44; H, 4.11.

(η^5-Isopropenylcyclopentadienyl)dicarbonylnitrosylchromium (18). [η^5-(1-Hydroxy-1-methylethyl)cyclopentadienyl]dicarbonylnitrosylchromium (3.31 g, 12.7 mmol), *p*-toluenesulfonic acid (0.60 g, 3.2 mmol), and 10 mg of hydroquinone were dissolved in 100 mL of benzene. The mixture was refluxed for 2 h with continual removal of water, and then the solvent was removed under vacuum. The resulting oil was extracted with hexane and filtered through silica gel by eluting with hexane and then hexane–ether 5:1. The solvent was removed under vacuum to give 2.5 g (81%) of **18** as a red liquid: bp 90–92 °C (0.5 torr); IR (neat) 3100 (w), 2950 (w), 2020 (vs), 1945 (vs), 1695 (vs), 1475 (w), 1440 (w), 1380 (w), 1300 (w), 1160 (w), 1040 (w), 895 (m), 825 (m), 678 (m), 640 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.80 (3 H, d, CH_3), 4.8–5.0 (3 H, m, $H_{3,4}$ and vinyl), 5.1–5.25 (3 H, m, $H_{2,5}$ and vinyl); mass spectrum, *m/e* 243 (M^+).

Anal. Calcd for $C_{10}H_9CrNO_3$: C, 49.39; H, 3.73; N, 5.76. Found: C, 49.31; H, 3.90; N, 5.94.

[η^5-(2-Formyl-1-chlorovinyl)cyclopentadienyl]dicarbonylnitrosylchromium (26). Phosphorus oxychloride (3.3 mL, 35.5 mmol) was added dropwise to 20 mL of dimethylformamide cooled to 0 °C. To this mixture was added dropwise (η^5-acetylcyclopentadienyl)dicarbonylnitrosylchromium (2.90 g, 11.8 mmol) dissolved in 10 mL of dimethylformamide. The solution was stirred at 0 °C for 15 min and 25 °C for 5 h and then poured into cold sodium acetate solution (20%, 100 mL) and stirred for another 2 h. The mixture was poured into water and extracted thoroughly with methylene chloride. The combined extracts were washed well with water and dried over magnesium sulfate. The solution was filtered, 20 g of silica gel was added, and the solvent was removed under vacuum. The residue was added to a dry-packed column (4 × 8 cm) of silica gel. Elution of the column with ethyl ether gave a red band which upon removal of the solvent under vacuum gave 1.3 g (38%) of **26**. An analytical sample was obtained by several recrystallizations from ethyl ether–hexane to give red plates: mp 106–107.5 °C; IR (KBr) 2020 (s), 1950 (s), 1700 (s), 1650 (s), 1600 (w), 1265 (w), 1115 (m), 930 (w), 820 (w), 615 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.25 (2 H, t, $H_{3,4}$), 5.74 (2 H, t, $H_{2,5}$), 6.45 (1 H, d, olefin), 10.19 (1 H, d, aldehyde).

Anal. Calcd for $C_{10}H_6CrClNO_4$: C, 41.20; H, 2.07; N, 4.80. Found: C, 41.60; H, 2.21; N, 4.63.

(η^5-Ethynylcyclopentadienyl)dicarbonylnitrosylchromium (27). [η^5-(2-Formyl-1-chlorovinyl)cyclopentadienyl]dicarbonylnitrosylchromium (1.0 g, 3.4 mmol) was dissolved in 20 mL of dioxane and heated to reflux. To the refluxing solution was added 20 mL of hot 0.5 N sodium hydroxide solution, and refluxing was continued for an additional 30 min. The solution was poured into ice water, acidified with dilute hydrochloric acid, and extracted into ether. The ether extracts were combined, washed well with water, dried over magnesium sulfate, and filtered. The ether was removed under vacuum to give 0.6 g (77%) of **27** as a red oil: bp 72–75 °C (0.5 torr); IR (neat) 3305 (m), 3020 (w), 2960 (w), 2010 (s), 1975 (s), 1715 (s), 1470 (w), 1255 (w), 830 (m), 640 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.80 (1 H, s, ethynyl), 4.94 (2 H, t, $H_{3,4}$), 5.28 (2 H, t, $H_{2,5}$).

Anal. Calcd for $C_9H_5CrNO_3$: C, 47.57; H, 2.22; N, 6.17. Found: C, 47.55; H, 2.46; N, 5.87.

Determination of the pK_a of (η^5-Carboxycyclopentadienyl)dicarbonylnitrosylchromium (9). Ten-milliliter solutions of 0.003 M (η^5-carboxycyclopentadienyl)dicarbonylnitrosylchromium in water were titrated with 0.5 N sodium hydroxide at 23 °C. The pK_a was obtained experimentally from the titration curve by determining the pH at half-neutralization. The titrations were made on a Radiometer Titrigraph, Type SBR2c, Copenhagen (U.S. distributor, The London Co., Westlake, Ohio) coupled with the Radiometer Titrator II and pH Meter 25 with a combination glass electrode. It was necessary to connect a ground wire from the chassis of the Titrigraph to that of the Titrator II. The Titrigraph was coupled by its flexible drive shaft to a 0.5-mL syringe which delivered the titrant into the stirred sample. The pK_a was determined to be 5.1 ± 0.15.

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Transition-Metal-Catalyzed Reactions of Diazo Compounds. 1. Cyclopropanation of Double Bonds

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Rhodium(II) and palladium(II) carboxylates are efficient catalysts for the cyclopropanation of olefins by diazo esters. Intramolecular competitions within diolefins and intermolecular competitions between pairs of monoolefins showed quite different cyclopropanation selectivities with the above-mentioned metal derivatives. Rhodium essentially promotes a carbenoid mechanism involving an electrophilic attack of uncomplexed olefins, while a determinant olefin coordination is observed with palladium. By comparison, the classical copper derivatives are essentially borderline cases: most often they behave as carbenoid catalysts, except when associated with very weak ligands such as in copper triflate. The synthetic usefulness of these reactions is emphasized in terms of their high efficiency and regioselectivity.

The reactions of carbenes or carbenoids generated by metal-catalyzed decomposition of diazo compounds are now of major synthetic importance. The historical significance of copper catalysis in this field needs no em-

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