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Organometallic Nitrosyl Chemistry. 6.[1] Cyclopentadienylnitrosyl Complexes of Chromium

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The photoinduced reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ with gaseous nitric oxide in hexanes produces a mixture of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ (major product). The same organometallic compounds can be obtained more conveniently, in better overall yields, by treating photogenerated $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O)$ with NO in tetrahydrofuran. They also occur as minor products when $(\eta^5\text{-}C_5H_5)_2Cr$ reacts with NO in hexanes, the principal product being $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$ which can be isolated in 35% yield. Their formation in these conversions can be rationalized in terms of the reactive intermediate $(\eta^5\text{-}C_5H_5)Cr(NO)_2\cdot$.

Introduction

In previous papers in this series we have outlined several general preparative routes that lead to neutral organometallic nitrosyl compounds in high yields. The principal pathways involve the treatment of anionic[2] or neutral[2,3] carbonyl complexes with nitrosyl chloride. Another potentially general method for the synthesis of these nitrosyl complexes is the reaction of nitric oxide with electron-deficient or coordinatively unsaturated organometallic compounds. The latter classification of reactants encompasses those species in which the metal attains coordinative unsaturation during thermolysis or photolysis. Some reactions of this type have been individually reported previously,[4] but a systematic study of these transformations has not yet been carried out.

We have now initiated such a study, and in this paper we describe new reactions between nitric oxide and the cyclopentadienylchromium complexes $(\eta^5\text{-}C_5H_5)_2Cr$ and $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. The chromium systems were chosen as a convenient starting point because of our familiarity with cyclopentadienylchromium nitrosyls acquired during our earlier work.[2,3,5]

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to published procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Nitric oxide (Matheson CP grade, 99.0% minimum) was further purified by passing it through a column of activated silica gel maintained at −78 °C. A mass spectrum of the effluent gas exhibited only a sharp peak at m/e 30 assignable to NO^+; it did not exhibit peaks attributable to ions such as NO_2^+ or N_2O^+. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton and carbon-13 magnetic resonance spectra were recorded on Varian Associates T60 and CFT20 spectrometers, respectively, with tetramethylsilane being employed as an internal standard. The low-resolution mass spectra were taken at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method with the assistance of Dr. G. K. Eigendorf and Mr. J. W. Nip. Elemental analyses were carried out by Mr. P. Borda of this department.

Reaction of Nitric Oxide with $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O)$. A stirred orange solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[6] (1.02 g, 5.03 mmol) in tetrahydrofuran (250 mL) was irradiated for 0.5 h in a photoreactor using a medium-pressure mercury lamp (Hanovia L-450W) housed in a water-cooled Pyrex immersion well. [Monitoring of several runs by infrared spectroscopy indicated these to be the most efficient conditions for generation of the desired reactive intermediate.] Prepurified nitric oxide was gently bubbled through the resulting red-black solution for 1 h at room temperature, and the solvent was removed from the reaction mixture in vacuo. The remaining dark green residue was redissolved in a minimum of dichloromethane (~10 mL), and the solution was transferred by syringe onto a short (3 × 5 cm) Florisil column. Elution of the column with dichloromethane developed a red-orange band that was collected and taken to dryness in vacuo. Sublimation of the residue at room temperature (5×10^{-3} mm) onto a dry ice cooled probe afforded 0.20 g of unreacted $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. The involatile red-violet solid remaining (~0.01 g) was identified by its infrared spectrum as $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$.[7]

The Florisil column was then eluted with tetrahydrofuran to produce a dark green band which was also collected and taken to dryness in vacuo. Crystallization of the resulting solid from dichloromethane–hexane yielded green crystals (0.38 g, 42% yield based on unrecovered starting material) of analytically pure $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$: ν_{NO} (in CH_2Cl_2) 1825, 1719 cm^{-1}; proton NMR δ (in $CDCl_3$) 5.78 (s); mp (in air) 86–87 °C. Anal. Calcd for $C_5H_5CrN_3O_4$: C, 26.92; H, 2.26; N, 18.83. Found: C, 27.21; H, 2.15; N, 18.76.

The Photonitrosylation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. A stirred solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (1.50 g, 7.39 mmol) in hexanes (200 mL) was irradiated as described above while a slow stream of prepurified nitric oxide was passed through the reaction mixture. After 1 h the color of the solution had changed to brown-red, and a green-brown precipitate had formed. An infrared spectrum of the solution showed an ~40% decrease in intensity of the carbonyl and nitrosyl absorptions due to the initial reactant. Irradiation for an additional 1 h diminished the amount of starting material by a further 10%, and at this point the reaction was stopped. The reaction mixture was purged with N_2, and the solid was allowed to settle. The supernatant hexane solution was decanted and taken to dryness in vacuo to obtain a red-brown residue. This residue was chromatographed

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Table I. Low-Resolution Mass Spectral Data for $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$ and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$[a]

m/e	rel abund	assignment
	$(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$	
242	13	$(C_5H_5)_2Cr(NO)_2^+$
182	100	$(C_5H_5)_2Cr^+$
177	8	$C_5H_5Cr(NO)_2^+$
147	7	$C_5H_5Cr(NO)^+$
117	36	$C_5H_5Cr^+$
65	5	$C_5H_5^+$
52	31	Cr^+
	$(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$	
223	18	$C_5H_5Cr(NO)_2(NO_2)^+$
193	7	$C_5H_5Cr(NO)(NO_2)^+$
177	49	$C_5H_5Cr(NO)_2^+$
163	39	$C_5H_5Cr(NO_2)^+$
147	5	$C_5H_5Cr(NO)^+$
133	100	$C_5H_5CrO^+$
117	12	$C_5H_5Cr^+$
105	29	$C_4H_5Cr^+$
65	3	$C_5H_5^+$
52	27	Cr^+

[a] The assignments involve the most abundant naturally occurring isotopes in each fragment.

on Florisil as outlined above, and the complexes isolated were unreacted $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (0.25 g, 17%), $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (0.10 g, 7.6%), and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ (0.20 g, 12%). The original precipitate from the photonitrosylation reaction was extracted with dichloromethane (50 mL) to obtain a yellow-green solution. Addition of hexanes (30 mL) and concentration of the solution under reduced pressure afforded 0.31 g of analytically pure microcrystalline $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$. The total yield of the nitrite complex based on unrecovered starting material was 37%.

The Photonitrosylation of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$. While prepurified nitric oxide was gently bubbled through the reaction mixture, a stirred red-brown solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (0.10 g, 0.28 mmol) in hexanes (200 mL) was irradiated as described above for 1 h. At the end of this time the reaction mixture consisted of a brown precipitate and an olive green supernatant solution whose infrared spectrum did not exhibit the nitrosyl absorptions characteristic of the dimeric reactant. The solvent was removed in vacuo, and the resulting solid was sublimed at 40 °C (5×10^{-3} mm) onto a water-cooled probe to obtain ~0.1 g of analytically pure $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ (vide supra).

Reaction of Nitric Oxide with Chromocene. (a) In Hexanes. A slow stream of prepurified nitric oxide was passed over a rapidly stirred, red solution of $(\eta^5\text{-}C_5H_5)_2Cr$[8] (0.91 g, 5.0 mmol) in hexanes (150 mL) at 0 °C. Immediately the solution developed a dark brown coloration and a brown precipitate was formed. The nitric oxide atmosphere was maintained over the reaction mixture for 15 min to ensure complete reaction. The volume of the solvent was reduced to ~15 mL in vacuo, and the reaction mixture was then transferred to the top of a 2 × 15 cm column of alumina (Woelm neutral, activity grade IV). Elution of the column with hexanes developed two bands. The first band, golden brown, was collected, and the solvent was removed from the eluate in vacuo to obtain $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$ as a dark brown solid: ν_{NO} (in CH_2Cl_2) 1785, 1686 cm^{-1}; proton NMR δ (in $CDCl_3$) 6.01 (s), 4.99 (s); carbon-13 NMR δ (in $CDCl_3$) 113.89 (s), 101.41 (s); mp (in air) 64–65 °C. Anal. Calcd for $C_{10}H_{10}CrN_2O_2$: C, 49.59; H, 4.16; N, 11.56. Found: C, 49.75; H, 4.31; N, 11.20. Its mass spectrum is summarized in Table I.

Elution of the second band from the column with hexanes produced a purple solution which contained $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, identified by its infrared spectrum.[7] This dimeric product was isolated as a red-violet solid by taking the eluate to dryness in vacuo, and its identity was confirmed by its characteristic mass spectrum.[5]

A third band was then eluted from the alumina column with dichloromethane as eluant, thereby producing a green solution which contained $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$, identified by its infrared and proton NMR spectra (vide supra).

Finally, elution of the column with tetrahydrofuran produced an orange-brown solution which was taken to dryness under reduced pressure. Proton NMR and mass spectroscopy indicated that the remaining brown solid [ν_{NO} (in CH_2Cl_2) 1640–1660 cm^{-1}] was an aggregated species. For instance, its mass spectrum at 200 °C exhibited the highest m/e peak at 466 which could be assigned to the $(C_5H_5)_2Cr_3(NO)_6^+$ ion. Unfortunately, this solid could not be rendered pure by chromatography, sublimation, or recrystallization.

(b) In Benzene or Tetrahydrofuran. These reactions were performed in a manner similar to that described in part (a) except that the benzene reaction mixture was maintained at ~6 °C, and the reaction time was extended to 30 min for both conversions. In both cases, the final reaction mixture consisted of a very dark solution with no precipitate being present. Separation of the products was effected as in (a), but $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ was not detected in either solvent.

In all three solvents, the yields of the nitrosyl products were somewhat variable, appearing to depend both on the rate of introduction of NO and on the reaction time. Typical yields are tabulated here.

solvent	$(C_5H_5)_2Cr(NO)_2$	$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$	$(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$
hexanes	35%	6%	4%
benzene	25%	0%	10%
tetrahydrofuran	13%	0%	10%

Reaction of Nitric Oxide with $(C_5H_5)_2Cr(NO)_2$. A slow stream of prepurified nitric oxide was passed over a stirred brown solution of $(C_5H_5)_2Cr(NO)_2$ (18 mg, 0.1 mmol) in hexanes (25 mL) at ambient temperature for 1 h, during which time a dark brown precipitate was gradually formed. The solvent was removed from the reaction mixture in vacuo, and the residue was redissolved in a small amount (~5 mL) of dichloromethane. An infrared spectrum of the dichloromethane solution revealed that ~35% of the organometallic reactant had been consumed and that the only other nitrosyl-containing complex present was $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$. Treatment of a hexane solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ with nitric oxide in an identical manner resulted in the formation of the nitrite species in low yields (<10%).

Reaction of Nitrosyl Chloride with Chromocene. To a stirred solution of $(\eta^5\text{-}C_5H_5)_2Cr$ (0.27 g, 1.5 mmol) in dichloromethane (50 mL) at 0 °C was added an excess of ClNO[6] dissolved in dichloromethane. Immediately the solution developed a blue-green coloration, but no precipitate was formed. The solution was stirred for 30 min while it was permitted to slowly warm to room temperature. It was then concentrated at reduced pressure to ~15 mL and was transferred by syringe onto a 2 × 7 cm Florisil column. Elution of the column with dichloromethane developed a green band which was collected. The olive green eluate contained only $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, identified by its characteristic infrared and proton NMR spectra.[2]

Reaction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $(C_5H_5)_3Al$. To a stirred green solution of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$[2] (1.00 g, 4.71 mmol) in toluene (30 mL) at room temperature was added dropwise a yellow toluene solution of $(C_5H_5)_3Al$[9] (typically 0.087 M). A red-brown color developed immediately and a brown solid precipitated. The $(C_5H_5)_3Al$ solution was added until the nitrosyl absorptions due to the initial reactant had disappeared from the infrared spectrum of the reaction mixture's supernatant liquid. The final mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure to ~5 mL. Chromatography of this solution on a 2 × 15 cm column of alumina (vide supra) afforded 0.20 g (17% yield) of analytically pure $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$.

Results and Discussion

Reactions of Nitric Oxide with $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. No reaction occurs when a slow stream of prepurified NO is bubbled through a hexane solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ at ambient temperature. However, when the reaction mixture is subjected to ultraviolet irradiation, the organometallic reactant is gradually converted to a mixture of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ as the only nitrosyl-containing products, i.e.

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + \text{excess NO} \xrightarrow[\text{hexanes}]{h\nu} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 + (\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2) \quad (1)$$

This conversion is hampered by the fact that the products are only sparingly soluble in hexanes. Consequently, they (along with some decomposed matter) are deposited on the walls of the reaction vessel where they block an increasingly greater amount of the incident radiation as the reaction progresses. This difficulty can be overcome by carrying out the desired reaction in the sequential manner shown in eq 2 and 3. The

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + C_4H_8O \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O) + CO \tag{2}$$

$$(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O) + \text{excess } NO \rightarrow [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 + (\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2) \tag{3}$$

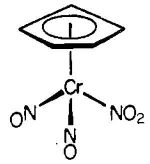
first step in this sequence exploits the well-documented[10] ability of carbonyl complexes to undergo CO substitution reactions when irradiated in the presence of donor molecules. Specifically, it parallels the previously reported conversions[11]

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + L \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Cr(CO)(NO)L + CO \tag{4}$$

where L = a phosphine or an olefin. By analogy, we formulate the organometallic product of reaction 2 as $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O)$. It is an air-sensitive species that is stable only in tetrahydrofuran solution, and its infrared spectrum in solution exhibits strong carbonyl and nitrosyl stretching absorptions at 1905 and 1642 cm^{-1}, respectively. These absorptions occur at frequencies lower than those exhibited by $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ in tetrahydrofuran (i.e., ν_{CO} 2008 (s), 1944 (s) cm^{-1}; ν_{NO} 1699 (s) cm^{-1}) and are consistent with the replacement of a carbonyl ligand on the reactant by the better electron-donating group C_4H_8O.

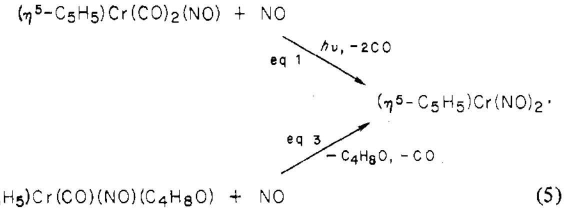
More importantly, reaction 2 provides a convenient means of selectively enhancing the reactivity of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ toward NO.[12] The photogenerated intermediate reacts readily with NO (eq 3) to form two complexes, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$, neither of which bears a coordinated CO or C_4H_8O group. Hence, when the photoactivation and nitrosylation steps are performed separately, well-defined products can be isolated. This is in marked contrast to the ill-defined and uncharacterizable species that often result from direct photonitrosylation reactions in donor solvents such as tetrahydrofuran.[13]

The products obtained by both reaction pathways (i.e., either eq 1 or eq 2 and 3) are compounds that have been synthesized previously as derivatives of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.[7,14] In either reaction the dimeric $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ complex is the minor product and the $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ complex is the major product, being isolable in 42% yield when the reaction is carried out in tetrahydrofuran. Since this nitrite complex has been mentioned only in passing in the literature,[14] its physical properties merit delineation. $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ is an olive green, diamagnetic solid (mp 86–87 °C) which can be handled in air for short periods of time without noticeable decomposition occurring. It is freely soluble in common organic solvents (except paraffin hydrocarbons) to give air-sensitive, green solutions, and it sublimes at 40 °C (5×10^{-3} mm) with concomitant decomposition. The proton NMR spectrum of the complex in $CDCl_3$ exhibits a sharp resonance at δ 5.78 characteristic of a η^5-cyclopentadienyl ring. The infrared spectrum of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ in CH_2Cl_2, which shows two strong bands at 1825 and 1719 cm^{-1} attributable to terminal nitrosyl groups, is also consistent with the compound having the molecular structure



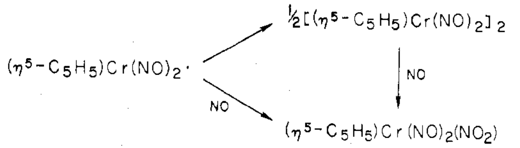
Its mass spectrum (summarized in Table I) exhibits the parent ion and the expected fragmentation pattern, namely, the sequential loss of ligands from the metal center. Interestingly, the base peak is due to the $(C_5H_5)CrO^+$ ion; similar oxo ions have been previously detected in the mass spectra of other organometallic nitrosyl compounds.[15]

The formation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ as the principal product in these reactions can be rationalized in the manner depicted by



(5)

followed by



(6)

Initially the incoming nitric oxide could replace two labile (or dissociated) ligands capable of donating two electrons each to the metal to form the 17-electron species $(\eta^5\text{-}C_5H_5)Cr(NO)_2\cdot$. This entity could then either dimerize to $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ or react further with NO to produce the nitrite. The latter complex could also result, in part, from the reaction of the dimer with nitric oxide. The following experimental facts are in accord with this rationale.

(1) $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ is indeed converted to $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$ by NO but only slowly at ambient temperature in solvents such as tetrahydrofuran or hexanes. The rate of the reaction in hexanes can be enhanced significantly by irradiation of the reaction mixture, an increase that probably reflects the effect of the photodissociation of the dimer, i.e.

$$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \xrightarrow{h\nu} 2(\eta^5\text{-}C_5H_5)Cr(NO)_2\cdot \tag{7}$$

(2) The photonitrosylation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ in either $CHCl_3$ or CCl_4 results in complete decarbonylation and formation of a homogeneous yellow-brown solution containing $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.[16] This transformation can also be understood in terms of the reactive intermediate $(\eta^5\text{-}C_5H_5)Cr(NO)_2\cdot$ which, once formed, could abstract halogen from the solvent to give the final product. Such halogen-abstraction reactions are well-known for a variety of organometallic carbonyl radicals.[17]

(3) The isolation of a nitrite-containing species from reactions involving transition-metal complexes and nitric oxide has several precedents in the literature.[4,18] Generally, such complexes are believed to arise from the oxidation of a coordinated nitrosyl ligand by nitric oxide. A similar mechanism may well be operative in our system.

Reactions of Nitric Oxide with $(\eta^5\text{-}C_5H_5)_2Cr$. When a hexane solution of $(\eta^5\text{-}C_5H_5)_2Cr$ at 0 °C is exposed to an atmosphere of prepurified NO, the organometallic reactant is rapidly consumed in the reaction

$$(\eta^5\text{-}C_5H_5)_2Cr + \text{excess } NO \xrightarrow{\text{hexanes}} (\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5) + (\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2) + [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \tag{8}$$

(A principal product in this reaction is a red-brown cluster compound whose exact formulation has yet to be determined.)

These reaction conditions are much less stringent than those required to carbonylate the metallocene,[19] the latter process requiring both high temperatures and high pressures of CO to bring about the displacement of a cyclopentadienyl ring. Indeed, the ease with which nitric oxide reacts with chromocene resembles its ready reactivity with manganocene[14] and nickelocene[20] at room temperature and pressure. The major isolable product of the reaction is $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$ which can be obtained in ~35% yield. This complex has been prepared previously by the metathetical reactions of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with C_5H_5Tl[21] or $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$ with C_5H_5Na[22] in yields of 16 and 20%, respectively. We find that even when the gentle alkylating agent[23] $(C_5H_5)_3Al$ is employed in such metatheses, the desired complex can only be obtained in 17% yield. Hence, reaction 8 represents the most convenient and highest yield preparative route to the bis(cyclopentadienyl) species.

$(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$ is a dark brown, volatile, air-sensitive solid that is known[21] to be stereochemically nonrigid in solution at room temperature. Its formation in reaction 8 can be viewed as resulting from the sequential addition of NO groups to chromocene, a process in which coordination of even the first nitrosyl ligand as a three-electron donor to the electron-deficient chromium atom requires a change in the bonding mode of one of the cyclopentadienyl rings if the inert gas formalism is to be satisfied. The $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$ so formed can then react further with excess NO to give the ubiquitous nitrite complex, i.e.

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5) + \text{excess } NO \rightarrow (\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2) \quad (9)$$

but we have demonstrated that this conversion proceeds rather slowly under the experimental conditions employed. This latter reaction could proceed via the $(\eta^5\text{-}C_5H_5)Cr(NO)_2\cdot$ intermediate invoked previously (eq 5), and, indeed, the isolation of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ from reaction 8 is consistent with the involvement of such a transient species (see eq 6). The fact that the dimer is not detected when the same reaction is performed in tetrahydrofuran or benzene probably reflects the longer lifetime of $(\eta^5\text{-}C_5H_5)Cr(NO)_2\cdot$ in these solvents, a longevity that increases the likelihood of its reaction with NO as depicted in eq 6.

In contrast to its behavior toward NO, chromocene reacts only slowly with ClNO in CH_2Cl_2 at 0 °C to yield $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ as the only nitrosyl-containing product. Infrared monitoring of the reaction fails to detect any of the products from reaction 8 as intermediates even though some reactions of ClNO can be understood[2] in terms of the equilibrium

$$2ClNO \rightleftharpoons 2NO + Cl_2$$

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Registry No. $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(C_4H_8O)$, 68013-61-6; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$, 68013-60-5; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$, 68013-59-2; $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, 36312-04-6; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, 36607-01-9; $(\eta^5\text{-}C_5H_5)_2Cr$, 1271-24-5; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $(C_5H_5)_3Al$, 20302-34-5; NO, 10102-43-9; ClNO, 2696-92-6.

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