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New Halo Nitrosyl Complexes of Chromium Resulting from the Reactions of Halogens with $(\eta^5\text{-}C_5R_5)Cr(CO)(NO)L$ (R = H, Me; L = CO, PPh_3)[1]

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Treatment of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ with iodine in a 2:1 molar ratio in CH_2Cl_2 affords $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ in excellent yield. The dimer reacts further with excess I_2 to produce $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$ as the ultimate nitrosyl-containing product. Intermediate nitrosyl complexes can be detected by IR spectroscopy during the progress of both transformations. In contrast, $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ rapidly converts to $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$ (X = Cl, Br) in the presence of Cl_2 and Br_2, respectively, in CH_2Cl_2, transient species not being detectable spectroscopically. The iodo nitrosyl dimer $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ does not appear to contain a conventional two-center, two-electron Cr–Cr linkage since it is moderately paramagnetic both in solutions and in the solid state. Its putative iodide bridges are cleaved by Lewis bases, L, to give the monomeric, 17-electron complexes $(\eta^5\text{-}C_5H_5)Cr(NO)(L)I$ (L = PPh_3, $P(OPh)_3$, $P(OEt)_3$). When L = PPh_3, analogous halo nitrosyl complexes can be obtained in good yields by treatment of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3)$ with 0.5 equiv of X_2 (X = Cl, Br, I) in CH_2Cl_2. All these 17-electron species are paramagnetic, having molar magnetic susceptibilities, permanent moments, and ESR spectra indicative of one unpaired electron. The reactivity of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ toward I_2 and Br_2 generally resembles that exhibited by its C_5H_5 analogue, the presence of the $\eta^5\text{-}C_5Me_5$ group not imparting enhanced stability to the intermediate complexes. The physical properties of all new complexes synthesized are presented.

Introduction

We recently described the synthesis of $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ by the treatment of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$ with iodine.[2] This iodo nitrosyl complex, like its molybdenum congener,[3-7] has proven to be a useful precursor to a variety of new organometallic compounds, e.g.

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 2L \xrightarrow{CH_2Cl_2{}^2} 2(\eta^5\text{-}C_5H_5)W(NO)(L)I_2 \quad (1)$$

where L = PPh_3, $P(OPh)_3$, or $SbPh_3$

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 4M(C_5H_5) \xrightarrow{THF^2} 2(C_5H_5)_3W(NO) + 4MI \quad (2)$$

where M = Tl or Na, and

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 \xrightarrow[THF]{Sn(C_3H_5)_4{}^8} 2(\eta^5\text{-}C_5H_5)W(NO)(\eta^3\text{-}C_3H_5)I \quad (3)$$

$$[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2 + 4H^- \xrightarrow{C_6H_6{}^9} [(\eta^5\text{-}C_5H_5)W(NO)H_2]_2 + 4I^- \quad (4)$$

In the light of these facts, we were naturally curious as to whether the chromium analogue, $[(\eta^5\text{-}C_5H_5)Cr(NO)I_2]_2$, could be prepared similarly and whether it too would exhibit an equally rich derivative chemistry. Consequently, we undertook a general investigation of the reactions of $(\eta^5\text{-}C_5R_5)Cr(CO)(NO)L$ (R = H, Me; L = CO, PPh_3) with halogens, and in this paper we wish to present the complete results of these studies.

Experimental Section

The general experimental procedures routinely employed in these laboratories have been described in detail previously.[10] Solution magnetic susceptibility measurements were effected by Evans' method using an 8% solution of $(CH_3)_3COH$ in $CHCl_3$ as the solvent.[11] Pascal's constants were used to correct the measured molar susceptibilities for the diamagnetic contributions of the ligands.[12] Solid-state magnetic susceptibilities were measured by the Gouy method[13] with the assistance of K. Oliver. X-Band ESR spectra of $\sim 10^{-3}$ M toluene solutions were recorded on a Varian E-3 spectrometer at ambient temperatures.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ with I_2. To a stirred orange solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[14] (2.03 g, 10.0 mmol) in CH_2Cl_2 (80 mL) was added solid I_2 (1.24 g, 4.90 mmol). Reaction occurred after ~5 min as evidenced by gas evolution and a color range of the reaction mixture to green-brown. After being stirred for 1 h to ensure completion of the reaction, the mixture was taken to dryness under reduced pressure. Crystallization of the residue from CH_2Cl_2–hexanes afforded 2.35 g (88% yield) of dark green $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$; mp (in air) 119 °C dec.

Anal. Calcd for $C_{10}H_{10}Cr_2N_2O_2I_2$: C 21.92; H, 1.84; N, 5.11; I, 46.33. Found: C 22.00; H, 1.77; N, 5.00; I, 46.08. IR(CH_2Cl_2): ν_{NO} 1673 cm^{-1}.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ with Br_2. A bright red solution of Br_2 in CH_2Cl_2 was added dropwise to a rapidly stirred orange solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (0.50 g, 2.5 mmol) in CH_2Cl_2 (30 mL). Immediately the latter solution became blue-green, and gas was evolved. The addition of bromine was continued until IR monitoring of the reaction mixture indicated that the organometallic reactant had been completely consumed. The final mixture was then concentrated in vacuo to ~5 mL and was transferred to the top of a Florisil column (2 × 6 cm). Elution of the column with CH_2Cl_2 developed a golden yellow band, which was collected and taken to dryness in vacuo to obtain 0.13 g (42% yield based on NO) of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$. The product was readily identifiable by its characteristic spectroscopic properties.[15] IR (CH_2Cl_2): ν_{NO} 1819, 1711 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.74.

The reaction was also performed in an identical manner in THF. Solvent was removed from the final mixture under reduced pressure, the residue was extracted with CH_2Cl_2 (5 mL), and the extracts were filtered through a Florisil column (2 × 4 cm) supported on a medium-porosity frit. Removal of all volatiles from the filtrate in vacuo afforded microcrystalline $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$ (0.27 g, 86% yield based on NO).

Thermal Decomposition of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ in CH_2Cl_2 and THF. The two experiments were performed similarly. A sample (0.27 g, 0.50 mmol) of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ was dissolved in 25 mL of the solvent, and the resulting solution was stirred at room temperature. The decomposition of the organometallic complex was monitored by the disappearance of its characteristic ν_{NO} absorption in the IR spectrum of the solution. After decomposition was judged to be complete (45 h in CH_2Cl_2, 200 h in THF), the solution was taken to dryness in vacuo. The residue was extracted with CH_2Cl_2 (~20 mL), and the extracts were

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Table I. Physical Properties of the Complexes $(\eta^5\text{-}C_5H_5)Cr(NO)(L)X$ (X = Cl, Br, I; L = PPh_3, $P(OPh)_3$, $P(OEt)_3$)

complex	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	color	mp, °C (in air)	IR ν_{NO}, cm^{-1} (in CH_2Cl_2)
$(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Cl$	62.10	61.90	4.53	4.56	3.15	3.09	green	157 dec	1664
$(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Br$	56.46	56.44	4.12	4.19	2.86	2.88	green	162 dec	1664
$(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)I$	51.51	51.21	3.76	3.77	2.61	2.59	lime green	158 dec	1666
$(\eta^5\text{-}C_5H_5)Cr(NO)[P(OPh)_3]I$	47.26	47.15	3.42	3.39	2.40	2.40	lime green	132 dec	1686
$(\eta^5\text{-}C_5H_5)Cr(NO)[P(OEt)_3]I$	30.00	29.87	4.55	4.57	3.18	3.30	dark green	49–50	1670

filtered through a Florisil column (2 × 4 cm). Addition of hexanes to the filtrate and slow concentration of the resulting solution under reduced pressure induced the crystallization of golden brown needles of $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$. Both conversions produced 0.06 g (40% yield based on NO) of this complex, which was identified by its characteristic IR spectrum.[16] IR (CH_2Cl_2): ν_{NO} 1817, 1713 cm^{-1}.

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ with Excess I_2. Solid I_2 (0.25 g, 1.0 mmol) was added to a rapidly stirred solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ (0.27 g, 0.50 mmol) in CH_2Cl_2 (25 mL). The progress of the reaction was monitored by IR spectroscopy, which revealed that the transformation was complete after 15 min and that the only nitrosyl-containing product formed was $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$.[16]

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ with NO. A dark green solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ (0.25 g, 0.46 mmol) in CH_2Cl_2 (15 mL) was treated with a stream of NO gas for 10 min at room temperature. The solution rapidly became golden brown. The final reaction mixture was filtered through a Florisil column (3 × 3 cm) supported on a medium-porosity frit, and the filtrate was concentrated in vacuo to induce the crystallization of 0.25 g (89% yield) of golden $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$.[16]

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ with CO. Carbon monoxide was bubbled through a solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ (0.27 g, 0.50 mmol) in CH_2Cl_2 (25 mL) for a period of 1 h. At the end of this time, an IR spectrum of the dark green solution revealed ~10% conversion of the organometallic reactant to a new carbonyl nitrosyl species (ν_{CO} = 2096 cm^{-1}, ν_{NO} = 1706 cm^{-1}). Further exposure of the solution to CO did not, however, increase the amount of this complex produced.

Reactions of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ with NaOR (R = Et, Me). An excess (0.22 g, 3.2 mmol) of solid NaOEt was added to a rapidly stirred THF solution (50 mL) of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ (0.82 g, 1.5 mmol). After 3 h, removal of volatiles from the reactiom mixture in vacuo afforded a green-brown oil. This oil was extracted with CH_2Cl_2 (3 × 15 mL), and the combined extracts were filtered through a Florisil column (2 × 4 cm) supported on a medium-porosity frit. The column was washed with CH_2Cl_2 until the washings were colorless, and the volume of the filtrate was reduced to ~25 mL under reduced pressure. The addition of hexanes (40 mL) and the slow concentration of the resulting solution in vacuo resulted in the crystallization of dark green $[(\eta^5\text{-}C_5H_5)Cr(NO)(OEt)]_2$ (0.10 g, 18% yield). The isolated product was identified by its characteristic physical properties,[17] e.g.: mp (under N_2) 230 °C dec; IR (CH_2Cl_2) ν_{NO} 1660 cm^{-1}.

Bright green microcrystals of $[(\eta^5\text{-}C_5H_5)Cr(NO)(OMe)]_2$ were obtained in a similar manner in 15% yield from the reaction of NaOMe with the iodo nitrosyl dimer; mp (in air) 172 °C dec.

Anal. Calcd for $C_{12}H_{16}Cr_2N_2O_4$: C, 40.45; H, 4.53; N, 7.86. Found: C, 40.30; H, 4.48; N, 7.73. IR (CH_2Cl_2): ν_{NO} 1661 cm^{-1}.

Reactions of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ with Lewis Bases, L (L = PPh_3, $P(OPh)_3$, $P(OEt)_3$). The experimental procedure, with the reaction with L = $P(OPh)_3$ as a representative example, was as follows.

Neat triphenyl phosphite (0.13 mL, 0.16 g, 0.50 mmol) was added to the stirred CH_2Cl_2 (25 mL) solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ (0.14 g, 0.25 mmol), and the mixture was stirred for 1 h to ensure complete reaction. The final blue-green solution was filtered through a Florisil column (2 × 4 cm) supported on a medium-porosity frit. Hexanes (30 mL) were added to the filtrate, and the resulting solution was concentrated under reduced pressure to obtain green crystals of $(\eta^5\text{-}C_5H_5)Cr(NO)[P(OPh)_3]I$ (0.20 g, 68% yield). Green microcrystals of $(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)I$ were isolated similarly in 64% yield.

The reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ and $P(OEt)_3$ was effected identically. However, the $(\eta^5\text{-}C_5H_5)Cr(NO)[P(OEt)_3]I$ product was obtained analytically pure (32% yield) by chromatography of the final reaction mixture on a Florisil column (2 × 6 cm) with CH_2Cl_2 as eluant and subsequent recrystallization of the material thus isolated from hexanes.

The physical properties of all three compounds are summarized in Table I.

Reactions of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3)$ with the Halogens Cl_2, Br_2, and I_2. These reactions were all performed similarly, and the reaction with Cl_2 is described in detail as a representative example.

A saturated solution of chlorine in CH_2Cl_2 was prepared by purging 20 mL of CH_2Cl_2 with a stream of Cl_2 gas for 10 min. An aliquot (1 mL) of this solution was transferred by syringe into a dropping funnel containing CH_2Cl_2 (10 mL). This diluted solution of Cl_2 was then added dropwise to a rapidly stirred, yellow-brown solution of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3)$[18] (0.58 g, 1.33 mmol) in CH_2Cl_2 (30 mL). The solution immediately became dark green, and gas was evolved. Just enough chlorine was added to consume all the organometallic reactant, as monitored by the disappearance of its characteristic carbonyl absorption in the IR spectrum of the reaction mixture. The final green solution was concentrated under reduced pressure to a volume of ~10 mL and was filtered through a Florisil column (2 × 5 cm) supported on a medium-porosity frit. The column was washed with CH_2Cl_2 (~60 mL) until the washings were colorless. Hexanes (60 mL) were added to the filtrate, and the resulting solution was concentrated in vacuo to induce the crystallization of 0.34 g (57% yield) of bright green, analytically pure $(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Cl$.

The analogous bromide and iodide complexes were prepared in a similar manner (in isolated yields of 43% and 41%, respectively) by the dropwise addition of a solution of Br_2 in CH_2Cl_2 or by the addition of a stoichiometric amount of solid I_2 to a CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3)$.

The physical properties of all three compounds are summarized in Table I.

Reaction of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ with I_2. Solid iodine (0.13 g, 0.5 mmol) was added to a stirred, red solution of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$[19] (0.27 g, 1.0 mmol) in CH_2Cl_2 (25 mL). Gas evolution occurred, and the solution became purple-red initially and then brown. After being stirred for 24 h, the solution was concentrated in vacuo to ~1 mL and was transferred by syringe to the top of a Florisil column (2 × 5 cm) made up in CH_2Cl_2. Elution of the column with CH_2Cl_2 developed an orange-brown band, which was eluted from the column and collected. Hexanes (75 mL) were added to the eluate, and the resulting solution was concentrated to ~20 mL under reduced pressure whereupon a small amount of an orange-brown solid precipitated. The mixture was then warmed gently to redissolve this solid, and the warm solution was cooled overnight to −10 °C to obtain golden brown crystals of $(\eta^5\text{-}C_5Me_5)Cr(NO)_2I$ (0.08 g, 42% yield based on NO); mp (in air) 119 °C dec.

Anal. Calcd for $C_{10}H_{15}CrN_2O_2I$: C, 32.10; H, 4.04; N, 7.49. Found: C, 31.83; H, 3.91; N, 7.19. IR (CH_2Cl_2): ν_{NO} 1786, 1687 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.91 (s). Low-resolution mass spectrum (probe temperature 60 °C): *m/z* 374 (P^+), 344 ($[P - NO]^+$), 314 ($[P - 2\,NO]^+$).

Sequential Reaction of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ with Br_2 and NO. A red solution of Br_2 in CH_2Cl_2 was added dropwise to a stirred red solution of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ (0.55 g, 2.0 mmol) in CH_2Cl_2 (30 mL). Gas was evolved, and the solution became bright green in color. The addition of Br_2 was stopped when the characteristic carbonyl absorptions of the organometallic reactant had just disappeared from the IR spectrum of the reaction mixture. At this point, the spectrum exhibited three ν_{NO} bands at 1784, 1730, and 1685 cm^{-1} whose relative intensities did not change even upon stirring of this mixture for 24 h at ambient temperatures. This solution was then treated with NO gas for 15 min, whereupon it became golden brown, and its IR spectrum revealed a diminution in intensity of the band at 1730 cm^{-1} and a concomitant increase in intensity of the other two nitrosyl absorptions. Chromatography of the final solution on a 2 × 6 cm Florisil column using CH_2Cl_2 as eluant developed a single golden brown band. This band was eluted, and the collected eluate was taken to dryness under reduced pressure. Recrystallization of the resulting residue from CH_2Cl_2–hexanes produced 0.29 g (53% yield

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with respect to Cr) of golden, microcrystalline (η^5-C_5Me_5)Cr(NO)$_2$Br; mp (in air) 149 °C dec.

Anal. Calcd for $C_{10}H_{15}CrN_2O_2Br$: C, 36.71; H, 4.62; N, 8.57. Found: C, 36.77; H, 4.84; N, 8.47. IR (CH_2Cl_2): ν_{NO} 1784, 1685 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.82 (s). ^{13}C NMR ($CDCl_3$): δ 112.2 (CCH_3), 9.7 (CH_3). Low-resolution mass spectrum (probe temperature 60 °C): *m/z* 326 (P$^+$), 296 ([P − NO]$^+$), 266 ([P − 2 NO]$^+$).

Results and Discussion

Reactions of (η^5-C_5H_5)Cr(CO)$_2$(NO) with Halogens. The products resulting from the treatment of (η^5-C_5H_5)Cr(CO)$_2$(NO) with halogens do not resemble those produced by the congeneric molybdenum and tungsten compounds. The addition of halogens to the latter compounds in 1:1 stoichiometry results in the production of the halogen-bridged dimers [(η^5-C_5H_5)M(NO)X_2]$_2$ (M = Mo, X = Cl,[20] Br,[20] I;[3,20] M = W, X = I[2]), which can be isolated in good yields; i.e.

$$2(\eta^5\text{-}C_5H_5)M(CO)_2(NO) + 2X_2 \xrightarrow[\text{or } CCl_4]{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)M(NO)X_2]_2 + 4CO\uparrow \quad (5)$$

where M = Mo, W and X = Cl, Br, I. In contrast, the reactions of (η^5-C_5H_5)Cr(CO)$_2$(NO) with Cl_2[17] and Br_2 in CH_2Cl_2 result in the rapid formation in moderate yields of (η^5-C_5H_5)Cr(NO)$_2$X (X = Cl and Br, respectively) as the only nitrosyl-containing products. In neither case have we been able to obtain any spectroscopic evidence for the formation of an intermediate carbonyl nitrosyl or nitrosyl complex.

More interestingly, we have discovered that treatment of (η^5-C_5H_5)Cr(CO)$_2$(NO) with iodine in a 2:1 molar ratio produces the new dimeric complex [(η^5-C_5H_5)Cr(NO)I]$_2$ in excellent yield; i.e.

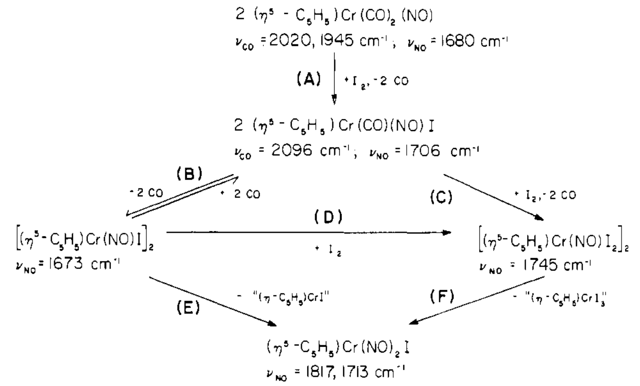
$$2(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + I_2 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Cr(NO)I]_2 + 4CO\uparrow \quad (6)$$

This stoichiometry of the reactants is essential for the formation of the dimeric product in optimum yields, since the dimer reacts further with excess I_2 to yield (η^5-C_5H_5)Cr(NO)$_2$I as the ultimate nitrosyl-containing product. A more detailed analysis of these transformations can be effected by careful monitoring of their progress by IR spectroscopy. Thus, upon the addition of 0.5 equiv of solid I_2 to a CH_2Cl_2 solution containing 1 equiv of (η^5-C_5H_5)Cr(CO)$_2$(NO), the characteristic absorptions of the organometallic reactant (i.e. ν_{CO} = 2020, 1945 cm^{-1}; ν_{NO} = 1680 cm^{-1}) disappear rapidly, and three new absorbances appear in the carbonyl–nitrosyl region of the spectrum (i.e. ν_{CO} = 2096 cm^{-1}; ν_{NO} = 1706, 1673 cm^{-1}). The carbonyl and higher energy nitrosyl absorptions then gradually diminish in intensity, until after 10 min only the 1673-cm^{-1} band due to [(η^5-C_5H_5)Cr(NO)I]$_2$ remains.

Alternatively, if an excess of I_2 is added to the original dicarbonyl nitrosyl reactant, the initial IR spectral changes are as described in the preceding paragraph for the stoichiometric reaction. However, a new nitrosyl absorption at 1745 cm^{-1} appears before the bands at 2096 and 1706 cm^{-1} have completely vanished, and it attains maximum intensity after ~2 h. Concomitantly, absorptions at 1817 and 1713 cm^{-1} (diagnostic of (η^5-C_5H_5)Cr(NO)$_2$I) appear and slowly increase in intensity at the expense of the bands at 1745 and 1673 cm^{-1}. After 18 h, the iodo dinitrosyl complex is the only nitrosyl-containing species detectable in solution. To account for these observed spectral changes in CH_2Cl_2, we propose the reaction sequence presented in Scheme I.

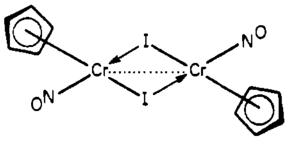
It seems likely that Cl_2 and Br_2 react with (η^5-C_5H_5)Cr(CO)$_2$(NO) in an analogous manner to produce (η^5-C_5H_5)Cr(NO)$_2$X (X = Cl, Br) ultimately, but spectroscopic evidence to support this hypothesis is lacking. Nevertheless, it may be noted that [(η^5-C_5H_5)Cr(NO)Cl]$_2$, one of the intermediate complexes in the sequence of reactions involving Cl_2, has been previously prepared by a different synthetic route.[17] In solution, even in the absence of excess Cl_2, this complex converts over a period of ~48 h to (η^5-C_5H_5)Cr(NO)$_2$Cl.[21] We find that a similar decomposition mode is also displayed by the isolable iodo intermediate, [(η^5-C_5H_5)Cr(NO)I]$_2$. In CH_2Cl_2 or THF, it eventually transforms to (η^5-C_5H_5)Cr(NO)$_2$I, but at a rate substantially slower than in the presence of excess I_2. Again, the ν_{NO} band at 1745 cm^{-1}, which we attribute to the [(η^5-C_5H_5)Cr(NO)I_2]$_2$ species, can be detected during the course of the decomposition reaction.

Scheme I



The lability of the carbonyl ligand in the proposed (η^5-C_5H_5)Cr(CO)(NO)I intermediate formed in reaction A of Scheme I is not without precedent, having been reported for many carbonyl halo nitrosyl complexes.[2,17,22,23] Furthermore, we have verified independently that conversion B of Scheme I is reversible, the iodo nitrosyl dimer being cleaved by carbon monoxide. However, IR spectroscopy indicates that (η^5-C_5H_5)Cr(CO)(NO)I[24] is generated in only 10–20% yield in this manner and that it rapidly decarbonylates in the absence of a CO atmosphere. It should also be noted that the transformation analogous to reaction D of Scheme I has been previously observed for the congeneric molybdenum complexes.[6a]

The new bis[(η^5-cyclopentadienyl)iodonitrosylchromium] complex is a dark green solid (mp 119 °C dec) that is freely soluble in benzene, CH_2Cl_2, and all organic donor solvents, less soluble in $CHCl_3$, and only very sparingly soluble in paraffin hydrocarbons. Although its solutions are air-sensitive and (as discussed above) thermally unstable, the solid itself is stable in air at ambient temperatures for short periods of time and can be stored unchanged indefinitely under an inert atmosphere. An IR spectrum of a fresh CH_2Cl_2 solution of the complex exhibits a single strong absorption at 1673 cm^{-1} attributable to a terminal, linear nitrosyl ligand.[25] The compound is best formulated as the iodo-bridged dimer (either cis or trans), e.g.



since a monomeric formulation would leave the chromium atom with three electrons less than the favored 18-electron configuration. The dimeric nature of the complex is also suggested by its mass

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[24] In the absence of definitive evidence, it is a matter of preference whether the carbonyl halo nitrosyl complexes are formulated as the 17-electron monomers (η^5-C_5H_5)(Cr(CO)(NO)X or the 18-electron dimers [(η^5-C_5H_5)Cr(CO)(NO)X]$_2$.

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Table II. Low-Resolution Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)Cr(NO)X]_2$ (X = I, OMe)

$[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$[a]			$[(\eta^5\text{-}C_5H_5)Cr(NO)(OMe)]_2$[b]		
m/z	rel abund	assignt[c]	*m/z*	rel abund	assignt[c]
548	7	$(C_5H_5)_2Cr_2(NO)_2I_2^+$	356	5	$(C_5H_5)_2Cr_2(NO)_2(OMe)_2^+$
518	42	$(C_5H_5)_2Cr(NO)I_2^+$	326	36	$(C_5H_5)_2Cr_2(NO)(OMe)_2^+$
488	21	$(C_5H_5)_2Cr_2I_2^+$	296	52	$(C_5H_5)_2Cr_2(OMe)_2^+$
371	13	$(C_5H_5)CrI_2^+$	281	20	$(C_5H_5)_2Cr_2(OMe)O^+$
304	9	$(C_5H_5)Cr(NO)_2I^+$	266	10	$(C_5H_5)_2Cr_2O_2^+$
274	12	$(C_5H_5)Cr(NO)I^+$	251	10	$(C_5H_5)_2Cr_2OH^+$
244	67	$(C_5H_5)CrI^+$	182	100	$(C_5H_5)_2Cr^+$
182	100	$(C_5H_5)_2Cr^+$	148	20	$(C_5H_5)Cr(OMe)^+$
117	96	$(C_5H_5)Cr^+$	117	20	$(C_5H_5)Cr^+$
52	73	Cr^+	52	49	Cr^+

[a] Probe temperature ~150 °C. [b] Probe temperature ~160 °C. [c] The assignments involve the most abundant naturally occurring isotopes, e.g., ^{52}Cr, in each fragment.

Table III. Magnetic Susceptibility Data

complex	method	$10^3\chi_M^{cor}$, cgsu/mol	μ_{eff}, μ_B
$[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$	Faraday	0.349 ± 0.014^a	0.91 ± 0.02^b
$[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$	Gouy (solid)	0.329 ± 0.006	0.90 ± 0.02^c
	Evans	1.51 ± 0.06	1.94 ± 0.03^c
$(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Cl$	Evans	1.38^d	1.86
$(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Br$	Evans	1.31 ± 0.19	1.80 ± 0.13^c
$(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)I$	Evans	1.44 ± 0.10	1.89 ± 0.07^c
$(\eta^5\text{-}C_5H_5)Cr(NO)[P(OPh)_3]I$	Evans	1.36 ± 0.09	1.84 ± 0.06^c
$(\eta^5\text{-}C_5H_5)Cr(NO)[P(OEt)_3]I$	Evans	1.23 ± 0.08	1.74 ± 0.06^c

[a] Taken from ref 26. [b] Measured at 292 K. [c] Measured at 305 K. [d] Taken from ref 27.

spectrum (Table II), which displays peaks due to the parent ion (m/z = 548) and other Cr_2-containing ions, which together contribute a significant percentage of the total ion current. However, the greater relative abundances of monometallic ions such as $(C_5H_5)Cr(NO)I^+$, $(C_5H_5)CrI^+$, and $(C_5H_5)_2Cr^+$ indicate that the dimer is readily cleaved on vaporization or electron impact. Interestingly, $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ exhibits significant paramagnetism both in solution and in the solid state (Table III), a feature that precludes the routine measurement of its ^1H and ^{13}C NMR spectra. This paramagnetism indicates either that the complex does not possess a conventional two-center, two-electron Cr–Cr linkage or that it undergoes partial dissociation into monomeric fragments; i.e.

$$[(\eta\text{-}C_5H_5)Cr(NO)I]_2 \rightleftharpoons 2(\eta^5\text{-}C_5H_5)Cr(NO)I \quad (7)$$

a process that should be more facile in solution. Since in the total absence of any Cr–Cr interaction a value of μ_{so} = 2.83 μ_B would be expected, it is evident that some spin pairing must be occurring in the monoiodide dimer. Such pairing, however, could occur by indirect coupling through the iodide bridges as well as by a direct metal–metal interaction. The valence isoelectronic complex $[(\eta^5\text{-}C_5H_5)Cr(NO)(OMe)]_2$ also does not contain a chromium–chromium bond as judged by its solid-state molecular structure.[28] Not surprisingly, the latter complex may also be synthesized, albeit in moderate yields, by the metathesis reaction

$$[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2 + 2NaOR \xrightarrow{THF} [(\eta^5\text{-}C_5H_5)Cr(NO)(OR)]_2 + 2NaI \quad (8)$$

where R = Me, Et, and its mass spectrum (Table II) confirms its bimetallic nature.

The final transformations presented in Scheme I involve $[(\eta^5\text{-}C_5H_5)Cr(NO)I_2]_2$ in either the presence (reactions D and F) or absence (reaction E) of excess iodine, processes that involve the transfer of NO groups between the two chromium atoms. Such transfer could occur either via transient formation of bridging nitrosyl linkages[29,30] or by initial dissociation of bound NO.[34] The latter pathway seems most likely for this system even though the presence of free NO is not detectable spectroscopically. The first step in reaction F probably involves the slow process

$$[(\eta^5\text{-}C_5H_5)Cr(NO)I_2]_2 \rightarrow [(\eta^5\text{-}C_5H_5)CrI_2]_2 + 2NO \quad (9)$$

which is followed by rapid reaction of the liberated NO with any of the three dimeric species $[(\eta^5\text{-}C_5H_5)CrI_2]_2$, $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$, or $[(\eta^5\text{-}C_5H_5)Cr(NO)I_2]_2$. Support for this view comes from the fact that it can be independently demonstrated that $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ is cleanly converted to $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$ in virtually quantitative yields by the action of NO gas; i.e.

$$[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2 + 2NO \xrightarrow{CH_2Cl_2} 2(\eta^5\text{-}C_5H_5)Cr(NO)_2I \quad (10)$$

Furthermore, analogous halo dinitrosyl products are known to result from the reactions of nitric oxide with $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$,[17] $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$,[17] and $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$.[2]

Reactions of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3)$ with Halogens. The reactions of $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3)$ with halogens are much simpler than those of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ (Scheme I). Indeed, only the transformations analogous to reaction A of Scheme I occur when the phospine-containing reactant is treated with chlorine, bromine, and iodine; i.e.

$$2(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3) + X_2 \xrightarrow{CH_2Cl_2} 2(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)X + 2CO\uparrow \quad (11)$$

where X = Cl, Br, I, a feature that reflects the inertness of the triphenylphosphine ligand in the product complexes. For the case when X = I, such complexes may also be obtained by cleavage of the iodide bridges in $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ with a Lewis base, L; i.e.

$$[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2 + 2L \xrightarrow{CH_2Cl_2} 2(\eta^5\text{-}C_5H_5)Cr(NO)(L)I \quad (12)$$

where L = PPh_3, $P(OPh)_3$, $P(OEt)_3$, conversions that are analogous to the reverse of reaction B in Scheme I. Of the monomeric complexes produced in reactions 11 and 12, only the chloro derivative, $(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Cl$, has been reported previously,

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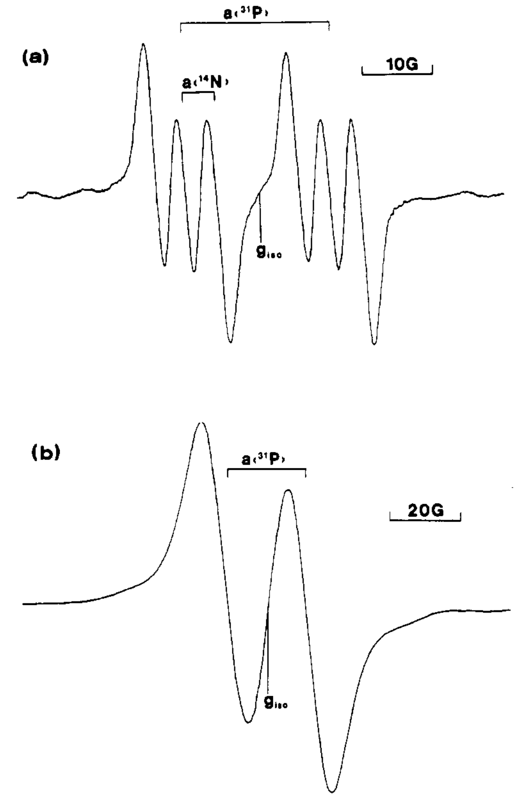


Figure 1. Electron paramagnetic resonance spectra (X-band) of dilute toluene solutions of (a) (η^5-C_5H_5)Cr(NO)(PPh_3)Cl and (b) (η^5-C_5H_5)-Cr(NO)(PPh_3)I.

having been isolated in low yield from the reaction of (η^5-C_5H_5)Cr$(NO)_2$Cl with PPh_3.[27] Reactions 11 or 12, as appropriate, are thus the preparative methods of choice for these organometallic compounds.

The (η^5-C_5H_5)Cr(NO)(L)X species are green, fairly air-stable microcrystalline solids whose physical properties are summarized in Table I. Their solubilities depend on the nature of L and X. Thus, when L = PPh_3, the solubilities vary in the order X = Cl > Br > I, (η^5-C_5H_5)Cr(NO)(PPh_3)I being only moderately soluble in CH_2Cl_2, less so in $CHCl_3$ and organic donor solvents, and virtually insoluble in paraffin hydrocarbons. For X = I, the solubilities in the above solvents diminish as L = $P(OEt)_3$ >> $P(OPh)_3$ > PPh_3, the triethyl phosphite complex being very soluble in all organic solvents including hexanes.

All these 17-electron compounds are paramagnetic, having molar magnetic susceptibilities and permanent moments (μ_{eff}) indicative of one unpaired electron (Table III). Toluene solutions of the complexes at ambient temperature exhibit ESR spectra that consist of a simple two-line pattern except for (η^5-C_5H_5)Cr-(NO)(PPh_3)Cl, which shows a six-line pattern with approximately equal intensities (Table IV and Figure 1). The two-line patterns arise from the hyperfine splitting of the signal due to interaction of the odd electron with the ^{31}P ($I = {}^1/_2$) nucleus in each molecule, whereas the six-line pattern (a doublet of triplets) results from coupling to both the ^{31}P and ^{14}N ($I = 1$) nuclei. Coupling constants to ^{31}P are in the range 20–33 G while the observed coupling constant to ^{14}N is 4.6 G. ESR spectra of the pure solids (Table IV) display fairly isotropic g tensors, the g values both in solution and in the solid state being in the range 1.99–2.10.

The monomeric natures of the new (η^5-C_5H_5)Cr(NO)(L)X complexes are confirmed by their low-resolution mass spectra, which display peaks due to the parent ions and ions resulting from the successive loss of ligands or ion–molecule reactions. The IR spectra of these compounds exhibited single, sharp nitrosyl-stretching absorptions in the range 1660–1690 cm^{-1}, which are 20–40 cm^{-1} lower than that displayed by (η^5-C_5H_5)Cr(CO)(NO)I. The decrease in ν_{NO} as L varies in the order CO > $P(OPh)_3$ > $P(OEt)_3$ > PPh_3 is consistent with the documented electron-donating and -accepting properties of these ligands.[33] The ν_{NO} values of the 17-electron chromium species also occur at considerably lower frequencies than those of the analogous 18-electron manganese compounds. A similar phenomenon has recently been reported for the related [(η^5-C_5H_5)M(NO)(L-L)]$^+$ (M = Cr, Mn) ctaions.[34] These physical properties are conistent with the (η^5-C_5H_5)Cr(NO)(L)X compounds possessing the familiar "three-legged piano stool" molecular structures, i.e.

Table IV. Electron Paramagnetic Resonance Data

complex	solid state g	toluene soln g_{iso}	toluene soln a(^{31}P), G
(η^5-C_5H_5)Cr(NO)(PPh_3)Cl	1.996[a]	1.994[b]	20.4
(η^5-C_5H_5)Cr(NO)(PPh_3)Br	2.012[a]	2.014	24
(η^5-C_5H_5)Cr(NO)(PPh_3)I	2.036[a]	2.046	24.5
(η^5-C_5H_5)Cr(NO)[$P(OPh)_3$]I	1.992, 2.111[c]	2.006	29
(η^5-C_5H_5)Cr(NO)[$P(OEt)_3$]I	2.021, 2.091[c]	2.052	32.5
(η^5-C_5H_5)Cr$(CO)_3$·	...	2.014	

[a] Exhibits only one resolvable resonance. [b] a(^{14}N) = 4.6 G. [c] Values obtained by the deconvolution procedure of Kneubühl.[32]

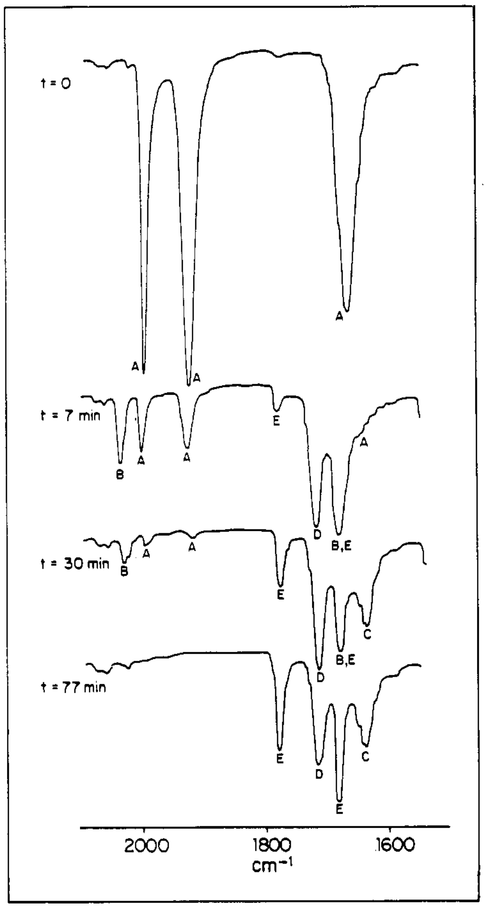
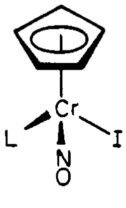


Figure 2. IR spectral changes accompanying the reaction of (η^5-C_5Me_5)Cr$(CO)_2$(NO) with 0.5 equiv of I_2. Assignments of absorptions: (A) (η^5-C_5Me_5)Cr$(CO)_2$(NO); (B) (η^5-C_5Me_5)Cr(CO)(NO)I; (C) [(η^5-C_5Me_5)Cr(NO)I]$_2$; (D) [(η^5-C_5Me_5)Cr(NO)I_2]$_2$; (E) (η^5-C_5Me_5)-Cr$(NO)_2$I.



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even though they are formally valence isoelectronic with the carbonyl complexes $[(\eta^5\text{-}C_5H_5)Cr(CO)_2L]_2$ (L = CO,[35,36] PPh_3,[37] $P(OMe)_3$[38]), which are diamagnetic. It must be noted, however, that the Cr–Cr linkages in the carbonyl dimers are not particularly strong,[35,38] and hence they are prone to undergo some dissociation into paramagnetic monomers upon vaporization or dissolution.[35,39]

Reactions of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ with Halogens. Due to its increased basicity and steric requirements, the pentamethylcyclopentadienyl ligand has been employed successfully in recent years to prepare stable analogues of unstable or transient cyclopentadienyl–transition-metal complexes.[40] We therefore decided to investigate the reactivity of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ toward halogens with a view to isolating C_5Me_5 analogues of the various intermediate species formed during the similar reactions of the cyclopentadienyl reactant (cf. Scheme I). Specifically, we hoped to obtain $(\eta^5\text{-}C_5Me_5)Cr(CO)(NO)I$. Unfortunately, our expectations were not realized.

The only nitrosyl-containing compound isolable after treatment of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ with I_2 in CH_2Cl_2 is $(\eta^5\text{-}C_5Me_5)Cr(NO)_2I$ even if the stoichiometry of the reactants is carefully controlled at 2:1 (cf. eq 6); i.e.

$$(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO) \xrightarrow[CH_2Cl_2]{{}^1/_2I_2} (\eta^5\text{-}C_5Me_5)Cr(NO)_2I\ (42\%) \quad (13)$$

During the progres of the transformation represented by eq 13, however, C_5Me_5 analogues of all the intermediates proposed for the C_5H_5 reactant (Scheme I) are detectable in solution by IR spectroscopy (Figure 2), but they cannot be isolated by conventional techniques. In this system, at least, the presence of the pentamethylcyclopentadienyl ligand does not seem to impart any enhanced stability to the intermediate complexes. If anything, it increases the susceptibility of these complexes to electrophilic attack by iodine.

Finally, the reaction of $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$ with Br_2 was investigated. Addition of just enough Br_2 to consume the organometallic reactant produces a mixture of $[(\eta^5\text{-}C_5Me_5)Cr(NO)Br_2]_2$ and $(\eta^5\text{-}C_5Me_5)Cr(NO)_2Br$. An unusual feature of this conversion is that the dimeric product does not transform into the monomeric dinitrosyl product at an appreciable rate in the absence of NO. The physical properties of the new $(\eta^5\text{-}C_5Me_5)Cr(NO)_2X$ (X = Br, I) complexes are similar to those exhibited by their C_5H_5 analogues.[15,16]

Summary

This work has established that the isolable, nitrosyl-containing products resulting from the treatment of $(\eta^5\text{-}C_5R_5)Cr(CO)(NO)L$ (R = H, Me; L = CO, PPh_3) with halogens, X_2 (X = Cl, Br, I), do not resemble those produced by the congeneric molybdenum and tungsten reactants under identical experimental conditions. Specifically, it has shown that when L = CO in the chromium reactant, the originally anticipated dimeric products, $[(\eta^5\text{-}C_5R_5)Cr(NO)X]_2$ and $[(\eta^5\text{-}C_5R_5)Cr(NO)X_2]_2$, are formed only transiently and do not generally persist in solution. Instead, they undergo disproportionation to produce the thermodynamically more stable $(\eta^5\text{-}C_5R_5)Cr(NO)_2X$ as the ultimate nitrosyl products. Furthermore, it has been demonstrated that when L = PPh_3 in the chromium reactant, the reactions with X_2 afford the novel, paramagnetic species $(\eta^5\text{-}C_5R_5)Cr(NO)(PPh_3)X$ when R = H. As to the derivative chemistry of the new compounds synthesized during this work, we can only report that our attempts to utilize $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$ and $(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)I$ as precursors for the preparation of novel organic derivatives by metathesis have thus far been unsuccessful.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of a grant (A5885) to P.L. and to the University of British Columbia for the award of a University Graduate Fellowship to C.R.N. We also thank K. Oliver for assistance during the measurements of magnetic susceptibility by the Gouy method.

Registry No. $(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Cl$, 12303-12-7; $(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)Br$, 94090-61-6; $(\eta^5\text{-}C_5H_5)Cr(NO)(PPh_3)I$, 94090-62-7; $(\eta^5\text{-}C_5H_5)Cr(NO)[P(OPh)_3]I$, 94090-63-8; $(\eta^5\text{-}C_5H_5)Cr(NO)[P(OEt)_3]I$, 94090-64-9; $[(\eta^5\text{-}C_5H_5)Cr(NO)I]_2$, 94090-65-0; $[(\eta^5\text{-}C_5H_5)Cr(NO)(OMe)]_2$, 70953-79-6; $(\eta^5\text{-}C_5H_5)Cr(CO)_3\cdot$, 12079-91-3; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Br$, 77662-15-8; $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$, 53504-57-7; $[(\eta^5\text{-}C_5H_5)Cr(NO)(OEt)]_2$, 64024-34-6; $(\eta^5\text{-}C_5Me_5)Cr(NO)_2I$, 94090-66-1; $(\eta^5\text{-}C_5Me_5)Cr(NO)_2Br$, 94090-67-2; $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)I$, 94090-68-3; $[(\eta^5\text{-}C_5Me_5)Cr(NO)Br_2]_2$, 94090-69-4; $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, 36312-04-6; $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(PPh_3)$, 32660-67-6; $(\eta^5\text{-}C_5Me_5)Cr(CO)_2(NO)$, 34808-36-1; $[(\eta^5\text{-}C_5H_5)Cr(NO)I_2]_2$, 94090-70-7.

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