Alkyl-for-Iodide Metathesis Initiated by Dissociation of the Phosphine Ligand from $CpCr(NO)(PPh_3)I$

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Abstract: The alkyl-for-iodide metathesis reaction that occurs when $CpCr(NO)(PPh_3)I$ (**1**) is treated with 2 equiv of Me_3SiCH_2MgCl in THF to form $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ (**6**) has been investigated in some detail. The conversion is initiated by loss of the phosphine ligand from the chromium atom's coordination sphere, the most compelling evidence for this step being that addition of excess phosphine (e.g. 4 equiv) to the initial reaction mixture completely inhibits the reaction. Four intermediate complexes which are formed sequentially on the reaction path from **1** to **6** have been detected by IR and ESR spectroscopy. These complexes have been identified as $CpCr(NO)(THF)I$ (**2**), $CpCr(NO{\rightarrow}Mg\{CH_2SiMe_3\}Cl)(THF)I$ (**3**), $CpCr(NO{\rightarrow}Mg\{CH_2SiMe_3\}Cl)(THF)(CH_2SiMe_3)$ (**4**), and $CpCr(NO)(THF)(CH_2SiMe_3)$ (**5**). Complexes **3** and **4** have also been detected spectroscopically during the reaction of $CpCr(NO)(THF)I$ (**2**) with Me_3SiCH_2MgCl which produces $CpCr(NO)(THF)(CH_2SiMe_3)$ (**5**). This understanding of the mechanistic pathway has resulted in the development of a general synthetic route to previously inaccessible 17-valence-electron $CpCr(NO)(L)R$ complexes ($L = C_5H_{11}N$ or NH_2CMe_3, $R = CH_2SiMe_3$; $L = C_5H_{11}N$, $R = CH_2Ph$).

Introduction

Ligand-dissociation processes play a fundamental role in contemporary organotransition-metal chemistry.[1,2] For instance, such processes have been demonstrated to be essential for the subsequent occurrence of some oxidative addition, migratory insertion, and reductive elimination reactions at transition-metal centers.[1,2] In turn, the latter reactions are frequently invoked to account for the catalytic or stoichiometric conversions mediated by complexes containing such centers, the classic example being Wilkinson's catalyst.[2] In this paper we report the first documented example of an apparently simple metathesis reaction (eq 1) which we have established proceeds via initial dissociation of the phosphine ligand from the metal center.

$$CpCr(NO)(PPh_3)I \xrightarrow{2Me_3SiCH_2MgCl,\ THF} CpCr(NO)(PPh_3)(CH_2SiMe_3) \quad (1)$$

We discovered the synthesis of the unusual 17-electron $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ complex by reaction 1 some two years ago.[3] However, as our studies with these systems progressed, we soon discovered that similar reactions could not be utilized to prepare a range of related $CpCr(NO)(L)(CH_2SiMe_3)$ (L = Lewis base) complexes. We were also intrigued by the fact that 2 equiv of Grignard reagent are required to consume completely the $CpCr(NO)(PPh_3)I$ reactant during conversion 1. We thus decided to effect a more detailed investigation of the chemical processes operative during the iodide-for-alkyl metathesis that occurs during this synthesis of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$. This paper presents the results of this investigation, the most remarkable of which (as noted above) is that the process is initiated by loss of the phosphine ligand from the chromium's coordination sphere.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen.[4,5] General procedures routinely employed in these laboratories have been described previously.[6] All reagents were purchased from commercial suppliers or were prepared according to literature methods. Thus, $[CpCr(NO)I]_2$,[7] $CpCr(NO)(PPh_3)I$,[7] $CpCr(NO)[P(OMe)_3]I$,[7] $CpCr(NO)(C_5H_{11}N)I$,[8] $(Me_3SiCH_2)_2Mg{\cdot}X$(dioxane),[6] $(PhCH_2)_2Mg{\cdot}X$(dioxane),[6] and Cp_3Sm[9] were prepared by published procedures. All Grignard reagents and piperidine (pip, $C_5H_{11}N$) were purchased from Aldrich Chemical Co. and were used as received.

IR Monitoring. A flow system for in situ IR monitoring of reactions was constructed using a Teflon diaphragm pump (Cole-Parmer 0700-62) and a NaCl IR flow cell (Wilmad 105A10-5, 0.2-mm path length).

ESR Measurements. Ambient-temperature X-band ESR spectra of $\approx 10^{-3}$ M solutions were recorded using a Varian E-3 spectrometer or with the spectrometer and interfaced computer system described by Phillips and Herring.[10] Spectral data thus obtained are collected in Table 1.

Synthesis of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$. Lime-green $CpCr(NO)(PPh_3)I$ (0.53 g, 1.00 mmol) was suspended in THF (15 mL). To the stirred suspension was added Me_3SiCH_2MgCl (2.0 mL, 1.0 M in Et_2O, 2.0 mmol). The stirred mixture became dark brown over 1 h as the organometallic reactant completely dissolved. This solution was stirred for a further 18 h, whereupon it became dark green and a voluminous white precipitate formed. The solvent was removed in vacuo, and Et_2O (20 mL) was added. The resulting mixture was filtered through a column of basic alumina (2×5 cm^2) supported on a glass frit. This column was washed with Et_2O (50 mL) until the washings became colorless. Solvent was removed from the filtrate in vacuo, the resulting oily green residue was extracted with hexanes (50 mL), and the extracts were filter-cannulated into another vessel. The volume of this solution was reduced in vacuo until incipient precipitation. Cooling of this mixture to -30 °C overnight resulted in the deposition of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ (0.30 g, 60% yield) as analytically pure, emerald-green microcrystals.

Anal. Calcd for $C_{27}H_{31}NOSiPCr$:[11] C, 65.30; H, 6.29; N, 2.82. Found: C, 65.09; H, 6.27; N, 2.67. IR (KBr): ν_{NO} 1611 cm^{-1}. IR

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(2) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley Interscience: New York, 1988; Chapters 27-29.

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(10) Phillips, P. S.; Herring, F. G. *J. Magn. Reson.* **1984**, *57*, 43.

(11) The analytical data originally reported[3] for this complex are actually those for $CpCr(NO)(PPh_3)I$.

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Table 1. IR and ESR Data for Complexes 1–6 in THF

complex	ν_{NO} (cm^{-1})	*g* value	hyperfine coupling constants (G)
$CpCr(NO)(PPh_3)I$ (**1**)	1672	2.046	$a(^{31}P) = 24.5$
$CpCr(NO)(THF)I$ (**2**)	1674	2.017	$a(^{14}N) = 5$
			$a(^{127}I) = 4$
$CpCr(NO{\rightarrow}Mg\{CH_2SiMe_3\}Cl)(THF)I$ (**3**)	1583	2.032	
$CpCr(NO{\rightarrow}Mg\{CH_2SiMe_3\}Cl)(THF)(CH_2SiMe_3)$ (**4**)	1525	2.016	
$CpCr(NO)(THF)(CH_2SiMe_3)$ (**5**)	1631	1.994	$a(^{14}N) = 10$
			$a(C_5H_5) = 3$
$CpCr(NO)(PPh_3)(CH_2SiMe_3)$ (**6**)	1624	1.998	$a(^{31}P) = 27.1$
			$a(CHHSi) = 11.5$
			$a(^{14}N) = 4.1$

(hexanes): ν_{NO} 1631 cm^{-1}. IR (THF): ν_{NO} 1624 cm^{-1}. ^1H NMR (C_6D_6) δ 8.5–7.1 (br m, 15H, $P(C_6H_5)_3$), 7.0 (br s, 5H, C_5H_5), 1.5–0.9 (br m, 2H, CH_2), 0.1 (br s, 9H, $Si(CH_3)_3$). FAB mass spectrum: *m/z* 496 [P^+], 409 [$P^+ - CH_2SiMe_3$].

Reaction of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ with Cp_3Sm. To a stirred orange slurry of Cp_3Sm (0.19 g, 0.55 mmol) in toluene (20 mL) was added $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ (0.27 g, 0.55 mmol). The mixture was stirred overnight, whereupon the orange solid was consumed and a clear green solution was formed. This solution was filtered through a plug of Celite (1.0 × 1.5 cm^2) supported on a glass frit. The filtrate was concentrated in vacuo to 5 mL and cooled to −30 °C for 1 week to induce crystallization. The precipitated green solid was collected by filtration, washed with hexanes (4 × 20 mL), and dried in vacuo to obtain $CpCr(NO{\rightarrow}SmCp_3)(PPh_3)(CH_2SiMe_3)\cdot{}^1/_2C_7H_8$ (0.20 g, 41% yield).

Anal. Calcd for $C_{45.5}H_{50}NOSiPCrSm$: C, 61.52; H, 5.67; N, 1.58. Found: C, 61.40; H, 5.82; N, 1.25. IR (Nujol mull): ν_{NO} 1550 cm^{-1}. FAB mass spectrum: *m/z* 843 [P^+], 91 [$C_6H_5Me - H$].

Similar treatment of $CpCr(NO)(PPh_3)I$ with Cp_3Sm in toluene at room temperature overnight resulted in no reaction.

Reaction of $CpCr(NO)[P(OMe)_3]I$ with Me_3SiCH_2MgCl. To a stirred THF (10 mL) solution of $CpCr(NO)[P(OMe)_3]I$ (0.40 g, 1.0 mmol) was added Me_3SiCH_2MgCl (2.0 mL, 1.0 M in Et_2O, 2.0 mmol). The green solution immediately became red brown. Stirring was continued overnight, and solvent was then removed in vacuo. The residue was extracted with Et_2O (20 mL), and the extracts were filtered through a column (3 × 1.5 cm^2) of alumina I supported on a medium-porosity frit to obtain an orange filtrate. The column was washed with Et_2O (20 mL), and the combined filtrates were concentrated in vacuo to incipient precipitation. The resulting mixture was maintained at −30 °C overnight to complete the deposition of $CpCr(NO)[P(OMe)_3]_2$ (0.15 g, 80% yield based on $P(OMe)_3$) as orange crystals. This material was identified by comparison of its spectroscopic properties with those exhibited by an authentic sample.[12]

IR (Nujol mull): ν_{NO} 1634 cm^{-1}. 200 MHz ^1H NMR (C_6D_6): δ 4.73 (t, 5H, $^3J_{P-H}$ = 3.00 Hz, C_5H_5), 3.52 (d, $^2J_{P-H}$ = 11.00 Hz, CH_3). FAB mass spectrum: *m/z* 395 [P^+], 364 [$P^+ - NO$].

Similar treatment of $CpCr(NO)[P(OPh)_3]I$ with Me_3SiCH_2MgCl afforded similar yields of the known[12] $CpCr(NO)[P(OPh)_3]_2$.

Treatment of $CpCr(NO)(pip)I$ with Me_3SiCH_2MgCl. To a stirred THF (10 mL) solution of $CpCr(NO)(pip)I$ (0.10 g, 0.28 mmol) was added Me_3SiCH_2MgCl (0.56 mL, <0.56 mmol). The green solution turned red brown within 1 h. The reaction mixture was stirred overnight, after which time the IR spectrum revealed strong bands at 1655 cm^{-1} due to $CpCr(NO)(pip)I$ and 1631 cm^{-1} due to $CpCr(NO)(THF)(CH_2SiMe_3)$. The solvent was removed under reduced pressure, and the residue was extracted with Et_2O (20 mL). The extracts were filtered through acidic alumina I (3 × 1.5 cm^2) supported on a medium-porosity glass frit. This operation afforded a clear filtrate displaying no bands in its IR spectrum in the region of 1550–1700 cm^{-1} and a brown band which could not be eluted with THF (30 mL).

Reactions of these and other $CpCr(NO)(L)I$ complexes (e.g. L = $PMePh_2$) with other Grignard reagents, RMgCl (e.g. R = Me, Et, Ph, *o*-C_6H_4Me, CH_2Ph, and C≡CH), also did not result in the production of tractable alkylated products.

Reaction of $CpCr(NO)(PPh_3)I$ with $(Me_3SiCH_2)_2Mg\cdot X$(dioxane). To a stirred solution of $CpCr(NO)(PPh_3)I$ (0.20 g, 0.37 mmol) in THF (10 mL) was added $(Me_3SiCH_2)_2Mg\cdot X$(dioxane) (titrated as 0.74 mmol of $Me_3SiCH_2^-$). The solution changed color from dark green to red brown over a period of 4 h. Stirring was continued overnight, and the final solution displayed ν_{NO} bands in its IR spectrum of equal intensity at 1672 and 1624 cm^{-1}. Addition of another 1.00 equiv of $(Me_3SiCH_2)_2Mg\cdot X$(dioxane) resulted in complete consumption of the starting material. Workup of the final mixture as outlined above for the synthesis of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ afforded 0.10 g (ca. 55% yield) of crude $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ which was identified by comparison of its characteristic IR and ESR spectra to those exhibited by an authentic sample (vide supra).

Treatment of $CpCr(NO)(PPh_3)I$ with $(PhCH_2)_2Mg\cdot X$(dioxane). To a stirred green solution of $CpCr(NO)(PPh_3)I$ (0.53 g, 1.0 mmol) in THF (30 mL) was added $(PhCH_2)_2Mg\cdot X$(dioxane) (0.32 g, 2.0 mmol of $PhCH_2^-$), whereupon the solution became dark red within 30 min. After being stirred for 18 h, the solution was still dark red, and its IR spectrum exhibited ν_{NO} bands at 1672, 1631, and 1535 cm^{-1}. Addition of another equiv of $(PhCH_2)_2Mg\cdot X$(dioxane) resulted in the complete disappearance of the band due to starting material at 1672 cm^{-1} within 12 h. Solvent was removed in vacuo from the final red solution. The residue was extracted with Et_2O (3 × 15 mL), and the combined extracts were filtered through alumina (2 × 5 cm^2) supported on a frit. This filtration resulted in a red-brown band which remained at the top of the column of alumina even when eluted with THF (30 mL).

Synthesis of $CpCr(NO)(L)R$ (L = pip or NH_2CMe_3, R = CH_2SiMe_3; L = pip, R = CH_2Ph). These compounds were prepared similarly, and the preparation of $CpCr(NO)(pip)(CH_2SiMe_3)$ is described in detail.

To an orange-brown solution of $[CpCr(NO)I]_2$ (0.27 g, 0.50 mmol) in THF (15 mL) was added Me_3SiCH_2MgCl (2.00 mL, 1.0 M in Et_2O, 2.00 mmol). The solution changed color from orange brown to dark red immediately. The reaction mixture was stirred overnight, whereupon a white precipitate formed. An IR spectrum of the supernatant solution displayed ν_{NO} bands at 1631 and 1525 cm^{-1}. To this mixture was added CH_3I (62 μL, 1.0 mmol), and stirring was continued. After 1 h, $C_5H_{11}N$ (pip, 0.20 mL, 2.0 mmol) was added, and the solution was stirred at ambient temperature for another 2 h, during which time the color changed to dark green. The THF was removed in vacuo, and the residue was extracted with Et_2O (30 mL). The Et_2O extract was filtered through alumina (2 × 4 cm^2) supported on a frit, and the column was washed with Et_2O (50 mL) to obtain a bright-green filtrate. The Et_2O was removed from the filtrate under reduced pressure, and the residue was recrystallized from pentane to obtain 0.11 g (30% yield) of $CpCr(NO)(pip)(CH_2SiMe_3)$ as dark-green needles.

Anal. Calcd for $C_{14}H_{27}N_2OSiCr$: C, 52.63; H, 8.52; N, 8.77. Found: C, 52.55; H, 8.70; N, 8.90. IR (Nujol mull): ν_{NO} 1606 cm^{-1}. FAB mass spectrum: *m/z* 319 [P^+].

Data for $CpCr(NO)(NH_2CMe_3)(CH_2SiMe_3)$: 0.09 g, 29% yield. Anal. Calcd for $C_{13}H_{27}N_2OSiCr$: C, 50.79; H, 8.85; N, 9.11. Found: C, 50.45; H, 8.66; N, 8.88. IR (Nujol mull): ν_{NO} 1601, δ_{NH} 1578 cm^{-1}. FAB mass spectrum: *m/z* 307 [P^+].

Data for $CpCr(NO)(pip)(CH_2Ph)$: 0.10 g, 31% yield. Anal. Calcd for $C_{17}H_{23}N_2OCr$: C, 63.14; H, 7.17; N, 8.66. Found: C, 62.76; H, 7.04; N, 8.48. IR (Nujol mull): 1596, 1585, 1574 cm^{-1}. FAB mass spectrum: *m/z* 323 [P^+].

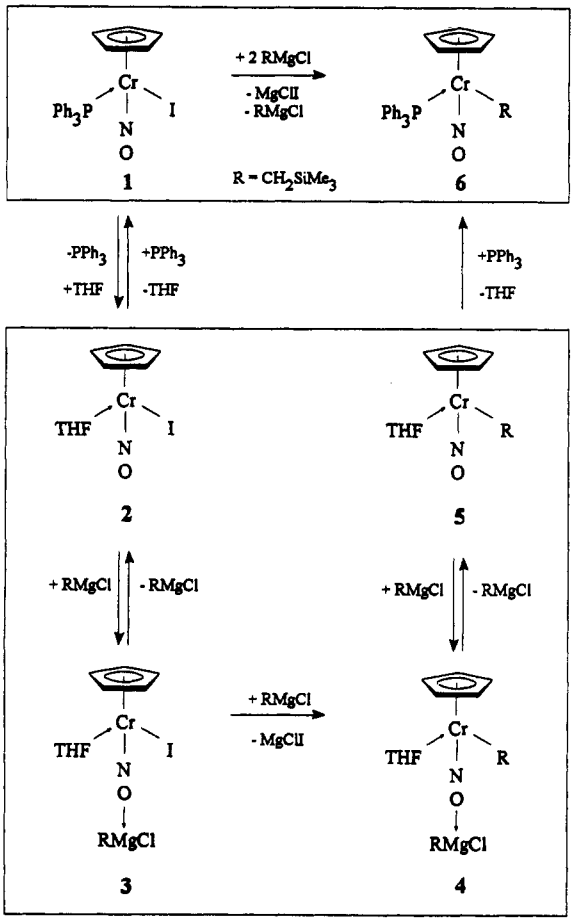
Results and Discussion

General Observations. As shown in eq 1, treatment of $CpCr(NO)(PPh_3)I$ with excess Me_3SiCH_2MgCl in THF yields the expected metathesis product, $CpCr(NO)(PPh_3)(CH_2SiMe_3)$. This

$$CpCr(NO)(PPh_3)I \xrightarrow{2Me_3SiCH_2MgCl,\ THF} CpCr(NO)(PPh_3)(CH_2SiMe_3) \quad (1)$$

(12) Hunter, A. D.; Legzdins, P. *Organometallics* **1986**, *5*, 1001.

Scheme 1



reaction is not as straightforward as it first seems. The starting mixture is a green slurry which changes into a red-brown solution within minutes of the addition of the Grignard reagent. Continued stirring for 18 h results in a gradual change back to a rich green due to the $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ product with concomitant precipitation of magnesium salts. No tractable products have yet been isolated from the red-brown solution.

Attempts to synthesize alkyl derivatives of other CpCr(NO)(L)I complexes (e.g. L = $PMePh_2$, $P(OMe)_3$, $P(OPh)_3$, and $C_5H_{11}N$ (pip)) by similar methodology meet with no success. These latter reactions are similar to conversion 1 in that red-brown solutions form upon addition of the Grignard reagent, but no further changes occur. These solutions exhibit several strong bands in the 1520–1670-cm^{-1} region of their solution IR spectra and one or more signals in their ESR spectra. Other Grignard reagents, RMgCl (R = Me, Et, Ph, *o*-C_6H_4Me, CH_2Ph, and C≡CH) react with the CpCr(NO)(L)I complexes (including L = PPh_3 and py), but again without the formation of tractable alkylated products. As described in the Experimental Section, 18-valence-electron $CpCr(NO)(L)_2$ (L = $P(OMe)_3$, $P(OPh)_3$) complexes can be isolated in some cases, a fact which indicates that the Grignard reagent is probably functioning as a reducing agent in these instances.[8,13] Monitoring of these reactions by IR spectroscopy and the use of dialkylmagnesium reagents such as $(PhCH_2)_2Mg{\cdot}X$(dioxane) and $(Me_3SiCH_2)_2Mg{\cdot}X$(dioxane) reveal that 2 equiv of the Mg-containing reagent are necessary to consume all the starting material. This observation is true regardless of whether the organomagnesium reagent possesses one or two alkyl groups or whether a tractable CpCr(NO)(L)R product is ultimately formed.

Given these observations, we thus decided to undertake a detailed investigation of reaction 1 with two specific goals in mind. First, we wanted to discover the reason underlying the fact that 2 equiv of organomagnesium reagents are necessary to effect complete consumption of the starting material. Second, we wanted to determine how the reaction differs when the identity of L in the CpCr(NO)(L)I complex is varied.

Overall Reaction Pathway for the Alkylation of CpCr(NO)(PPh_3)I. The overall alkylation reaction of $CpCr(NO)(PPh_3)I$ (shown in the top box of Scheme 1) proceeds through four detectable intermediates (shown in the lower box of Scheme 1). The diagnostic spectral data for complexes **1**–**6** are collected in Table 1. We preclude the assignment of these observed intermediates as dinuclear species, since we would not expect them to persist in THF given that $[CpCr(NO)I]_2$ is cleaved very quickly by THF.[8] Secondly, dimeric complexes would be likely to undergo antiferromagnetic interactions between the unpaired electrons, thereby making it unlikely that room-temperature solution ESR spectra of these complexes would be observable. Indeed, such is the case for $[CpCr(NO)I]_2$ in C_6H_6 and CH_2Cl_2.[8] Finally, the ν_{NO} values of complexes having bridging nitrosyl ligands would be much lower in energy than those evident in the IR spectra of these intermediate complexes.

The key first step in the process illustrated in Scheme 1 is that the phosphine ligand is replaced by a solvent molecule,[8] thereby generating the CpCr(NO)(THF)I complex (**2**), which in turn undergoes subsequent alkylation. The resulting CpCr(NO)(THF)(CH_2SiMe_3) complex (**5**) undergoes ligand substitution again to form the corresponding $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ species (**6**). Reaction of authentic **2**[14] with Me_3SiCH_2MgCl proceeds in much the same manner as the reaction of **1**, the ultimate product in the latter case being the solvated alkyl complex **5** (eq 2). There is considerable evidence supporting the overall

$$CpCr(NO)(THF)I \xrightarrow{2Me_3SiCH_2MgCl} CpCr(NO)(THF)(CH_2SiMe_3) \quad (2)$$

pathway outlined for these two related reactions in Scheme 1. In the next sections we present this evidence.

First Step: Dissociation of the Phosphine Ligand. The most compelling evidence for this step is that addition of excess PPh_3 (e.g. 4 equiv) completely inhibits reaction 1. None of the other intermediates are observed when excess phosphine is present, thereby implying that ligand dissociation occurs early in the process of formation of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$. This observation also reveals that under normal reaction conditions **1** does not form **6** directly. Furthermore, it implies that the initial ligand substitution resulting in the formation of **2** (eq 3) is a vital

$$CpCr(NO)(PPh_3)I \xrightarrow{THF} CpCr(NO)(THF)I + PPh_3 \quad (3)$$

step in the overall reaction. Reaction 3 probably occurs associatively, since we have established that $\Delta S^{\ddagger} = -71$ J mol^{-1} K^{-1} for its reverse reaction.[8] This mode of substitution is common for 17-electron organometallic radicals.[15] The driving force for the occurrence of reaction 3 may well be steric in origin, but there is also a key electronic factor operative in that the CpCr(NO)(THF)I product [ν_{NO}(THF) 1674 cm^{-1}] contains a nitrosyl ligand that is just as electron rich as the one in its $CpCr(NO)(PPh_3)I$ precursor [ν_{NO}(THF) 1672 cm^{-1}]. This feature is essential for the occurrence of the next step, namely the formation of the isonitrosyl linkage in complex **3**. Evidently, steric factors preclude formation of the analogous adduct between $CpCr(NO)(PPh_3)I$ and the Grignard reagent.

IR Spectroscopic Monitoring of the Overall Reactions of 1 to 6 and 2 to 5. IR spectroscopic monitoring of reaction 1 reveals

(13) Psarras, T.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 5132.

(14) Complex **2** can be generated simply by dissolving $[CpCr(NO)I]_2$ in THF.[8]

(15) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

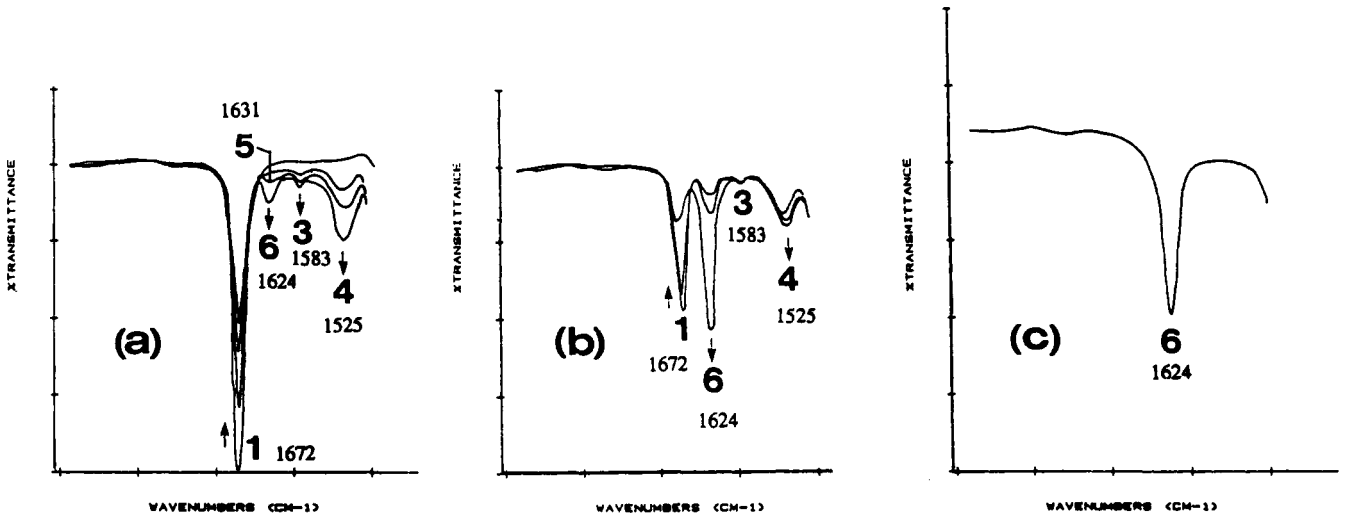


Figure 1. IR spectra accompanying conversion of **1** to **6** in THF: (a) 0–20 min; (b) 20 min–1 h; (c) 20 h.

the presence of ν_{NO} bands due to complexes **1** and **3–6**. As shown in Figure 1, the first intermediate observed is complex **3**. The ν_{NO} band for this species quickly increases and then decreases in intensity. This is followed by the growth of the ν_{NO} band attributed to complex **4**, which starts its decline after reaching a maximum intensity after 60 min. The ν_{NO} band due to complex **5** appears after 40 min but is soon thereafter hidden under the band which develops for complex **6**.

The intermediacy of **2** in reaction 1 is substantiated by IR spectroscopic monitoring of the reaction of authentic CpCr(NO)(THF)I with 2 equiv of Me_3SiCH_2MgCl, the resulting spectra being presented in Figure 2. These spectra exhibit ν_{NO} IR bands that are attributable to **3–5**. These bands appear in the same relative order and in the same positions as for the reaction of **1**, but in the absence of free PPh_3 this reaction stops at complex **5**.

Intermediate complexes **3** and **4** exhibit ν_{NO} bands in their IR spectra at unusually low frequencies for chromium nitrosyl complexes. These low-energy ν_{NO} bands (Table 1) indicate the existence of isonitrosyl linkages in these two intermediate species. Thus, **3** and **4** are assigned the formulations $CpCr\{NO\rightarrow Mg(CH_2SiMe_3)Cl\}(THF)I$ and $CpCr\{NO\rightarrow Mg(CH_2SiMe_3)Cl\}(THF)CH_2SiMe_3$, respectively. The isonitrosyl-stretching frequencies resemble those exhibited by isolable $CpCr(NO\rightarrow SmCp_3)(PPh_3)(CH_2SiMe_3)\cdot{}^1/_2C_7H_8$ [ν_{NO} (Nujol mull) = 1550 cm^{-1}] and are consistent with those displayed by other isonitrosyl complexes.[9,16]

The IR spectral data exhibit several other interesting features. The nitrosyl band due to **4** is 58 cm^{-1} lower than that due to **3**. This difference is similar to the 48-cm^{-1} difference observed between $CpCr(NO)(PPh_3)I$ and $CpCr(NO)(PPh_3)(CH_2SiMe_3)$, thereby suggesting that **4** arises from the alkylation of **3**. Also, the fact that the nitrosyl absorption due to **3** originates before those of **4** or **5** indicates that the preferred mode of reactivity of CpCr(NO)(THF)I with Grignard reagents is via isonitrosyl adduct formation and not metathesis.

ESR Spectroscopic Monitoring of the Overall Reactions of 1 to 6 and 2 to 5. The progress of the reactions of **1** and **2** with Me_3SiCH_2MgCl can also be monitored by ESR spectroscopy. These monitoring studies effectively demonstrate the complexity of the reaction pathway for these transformations. A representative series of ESR spectra accompanying the alkylation of complex **1** is displayed in Figure 3. In this series of ESR spectra, the first intermediate to be observed is complex **4**, which is generated within minutes of the addition of the Grignard reagent. The next feature to appear is due to the $CpCr(NO)(THF)(CH_2SiMe_3)$ complex (**5**), and this signal persists for several hours before being totally replaced by the signal due to the $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ complex (**6**). The ESR signals of complexes **4** and **5** do not display hyperfine coupling to the ^{31}P nucleus; this evidence again indicates that the PPh_3 ligand is lost early on during the reaction. Intermediate species **2** and **3** are not evident under these experimental conditions, but **3** is detectable by IR spectroscopy and complex **2** is known to be present before the addition of the Grignard reagent.[8] After 24 h at ambient temperatures, only signals characteristic of **6** are evident in the ESR spectrum of the final reaction mixture.

When the corresponding reaction of **2** (eq 2) is monitored by ESR spectroscopy, signals due to complexes **3–5** are observed (Figure 4). Complex **3** is produced immediately but is rapidly consumed as **4** is formed. As evidenced by the low intensity of its signal, complex **3** does not achieve very high concentrations during the conversion of **2** to **5**. This fact explains why the signals due to this complex are not observed in the ESR spectra of the conversion of **1** to **6**, especially since the concentration of its immediate precursor (**2**) is known to be very small. It should be reemphasized at this point that, during the conversion of **1** to **6**, the ν_{NO} attributed to complex **3** is clearly evident in the IR spectra.

Once formed, complex **4** persists for several hours at room temperature before fully converting to **5**. Since complexes **2** and **4** possess similar g values, ESR monitoring cannot easily distinguish between them. Nevertheless, IR spectroscopy can make this distinction (Table 1), and after 2 h the IR spectrum of the reaction solution is devoid of signals due to **2**. The ESR signal due to **5** is initially broadened by the precipitation of magnesium salts in the reaction mixture contained in the ESR tube. After 24 h, these salts have settled out, and the spectrum of **5** sharpens, thereafter appearing identical to the signal attributed to **5** in the conversion of **1** to **6**. It is significant that addition of PPh_3 to the final solution of **5** cleanly forms complex **6**. This observation conclusively establishes that the intermediates observed during the transformation of **2** to **5** are the same as those observed during the conversion of **1** to **6**.

Differing Reaction Conditions. Under the original conditions used to effect and monitor the reactions of **1** and **2** with the organomagnesium reagent, the starting material cleanly converts to its ultimate product. However, when the reaction conditions are changed, different product distributions result. For example, treatment of **1** with 1 equiv of Me_3SiCH_2MgCl results in only half of the starting material converting to complex **6** after 3 days of reaction at room temperature. Similar treatment of **2** results in solutions containing equal amounts of **2** and **5**. When **1** is treated with 1 equiv of $(Me_3SiCH_2)_2Mg\cdot X(dioxane)$ or $(PhCH_2)_2$-

(16) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41.

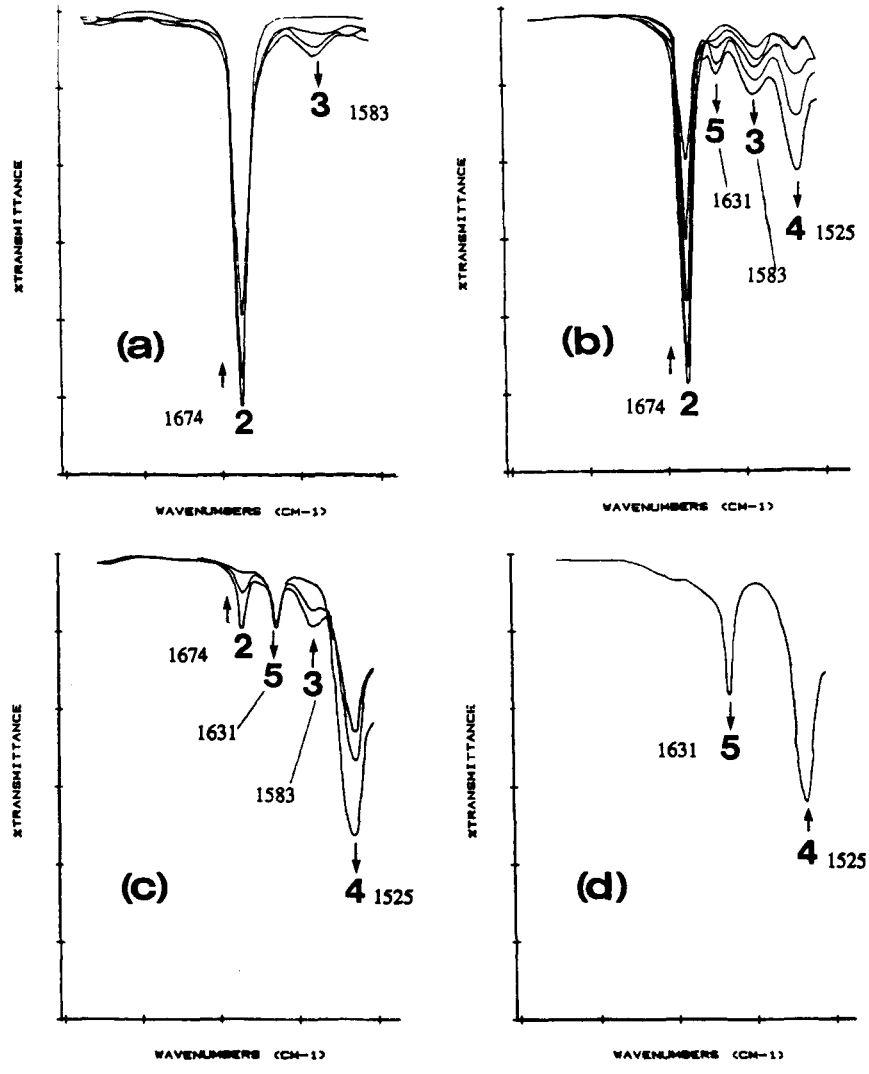


Figure 2. IR spectra accompanying conversion of **2** to **5** in THF: (a) 0–10 min; (b) 15 min–1 h; (c) 1–3 h; (d) 5 h.

Mg·X(dioxane), approximately half of the starting material is again consumed. This series of experiments establishes that 2 equiv of the dialkylmagnesium reagent (rather than 2 equiv of R^-) is required to consume completely the starting halide complex. Furthermore, these results also indicate that the second equivalent of the Grignard or the dialkylmagnesium reagent is not free at the end of the reaction but rather is chemically combined. Since the IR and ESR data rule out combination with an organochromium complex, it probably occurs with the MgBrI-containing byproduct.

Raising the temperature results in yet another product distribution. When refluxing THF solutions of complex **2** are treated with 1 equiv of the Grignard reagent, IR and ESR spectroscopic signals indicative of the presence of large amounts of complex **3** are observed. Although signals due to small amounts of **2** and **5** can also be observed, there is no indication of any further change in the ESR spectrum even after 24 h. Treatment of this solution with additional Me_3SiCH_2MgCl results in the immediate generation of **4** and **5** at the expense of **3**. These observations are consistent with the view that the actual alkyl-for-halide metathesis step occurs via the isonitrosyl complexes **3** and **4** and that **5** is not generated directly from **2**. The isonitrosyl complex **3** is therefore stable in the absence of excess Grignard reagent, a feature which suggests that the Cr–I bond in **3** is activated toward halide metathesis reactions.

Alkyl-for-Iodide Metathesis Step. Taken together, then, the IR and ESR spectral evidence accumulated during the various reactions investigated indicate that the alkylation of $CpCr(NO)(PPh_3)I$ proceeds as shown in Scheme 1. It is noteworthy that the need for 2 equiv of the organomagnesium reagent arises because intermolecular halide metathesis occurs on a complex which already incorporates 1 equiv of Grignard reagent (eq 4).

$$CpCr\{NO\rightarrow Mg(CH_2SiMe_3)Cl\}I \xrightarrow{Me_3SiCH_2MgCl} CpCr\{NO\rightarrow Mg(CH_2SiMe_3)Cl\}(CH_2SiMe_3) \quad (4)$$

This requirement of 2 equiv of the alkylating agent has also been observed recently during the alkylation reactions of various Tp* oxo complexes of group 5[17] and 6[18] metals, e.g.

$$Tp^*Nb(=O)Cl_2 \xrightarrow{\text{(a) } 2Me_3Al,\ \text{(b) } 2py} Tp^*Nb(=O)(Cl)(Me) \quad (5)$$

where Tp* = $[HB(3,5\text{-}Me_2pz_3)]^-$. Just as invoked for the Grignard reagent in Scheme 1, 1 equiv of Me_3Al in conversion 5 is believed to function as a Lewis acid at the Nb=O link, thereby activating a Nb–Cl bond for metathesis by the second equivalent of Me_3Al.[17] As shown in eq 5, pyridine is required both to break up the Lewis acid–base adduct as well as to complex the Me_2AlCl byproduct. The type of reactivity exhibited by the alkylating agents in conversions 4 and 5 is reminiscent of that displayed by Grignard reagents toward organic functional groups

(17) Foth, M. Diplomarbeit, Universität Würzburg, Germany, 1993.
(18) Sundermeyer, J.; Putterlik, J.; Pritzkow, H. *Chem. Ber.* **1993**, *126*, 289.

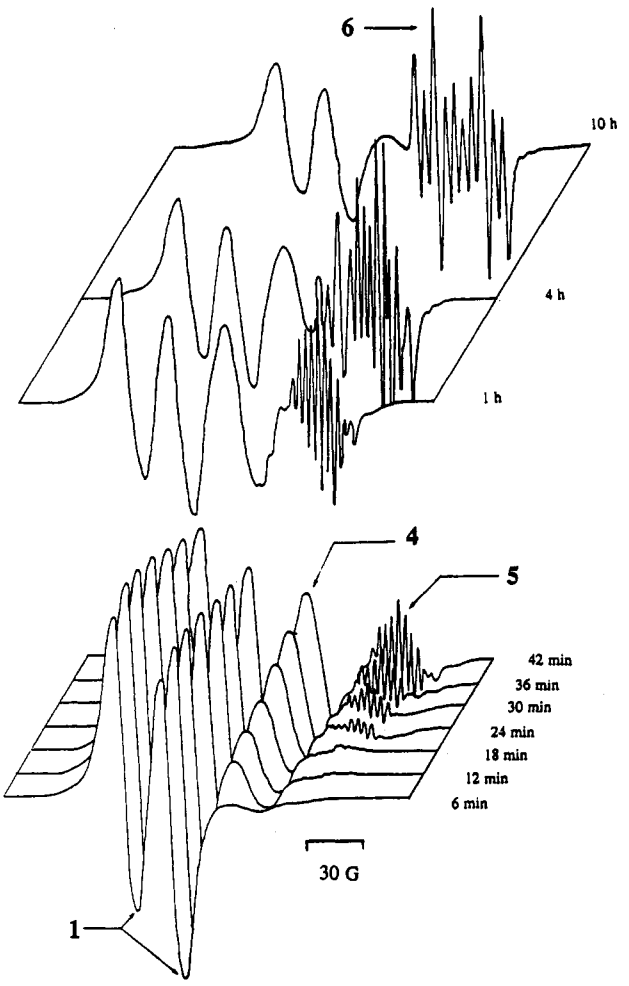


Figure 3. ESR spectra accompanying conversion of **1** to **6** in THF.

such as ketones which can act as Lewis bases.[19] In this latter case 2 equiv of RMgX is again required to effect complete conversion of the ketene functionality into a tertiary alcohol.

Our attempts to effect conversions analogous to reaction 4 with other isonitrosyl-forming Lewis acids have to date been unsuccessful simply because we have not yet discovered the requisite "innocent" Lewis acid. We find that usually the THF solvent reacts first with acids such as Cp_3Sm, Et_3B, $PbCl_2$, or $MgCl_2$. With $AlCl_3$, small amounts of isonitrosyl adduct are formed initially, but longer reaction times result in the production of dinitrosyl complexes.

Attempted Alkylation of Other CpCr(NO)(L)I Complexes. When treated with Me_3SiCH_2MgCl, the other CpCr(NO)(L)I complexes seem to follow the same general pathway outlined above for $CpCr(NO)(PPh_3)I$. Unfortunately, in these cases the ligand L does not seem to recoordinate to the metal center once complex **5** has been formed. For example, ESR monitoring of the reaction of CpCr(NO)(pip)I with 2 equiv of Me_3SiCH_2MgCl reveals that complex **4** forms very quickly. Complex **5** then slowly forms under the conditions employed until it is the sole product species in solution. No further change occurs in the next 3 days. The speed with which complex **4** is formed (i.e. within 2 min after the addition of the Grignard reagent) suggests that the dissociation of the piperidine ligand is aided by the presence of the Grignard reagent.

All of this mechanistic knowledge taken together then suggests that a general synthetic route to the desired (and previously inaccessible) 17-valence-electron $CpCr(NO)(L)(CH_2SiMe_3)$ (L = Lewis base) complexes involves effecting the conversion from

(19) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

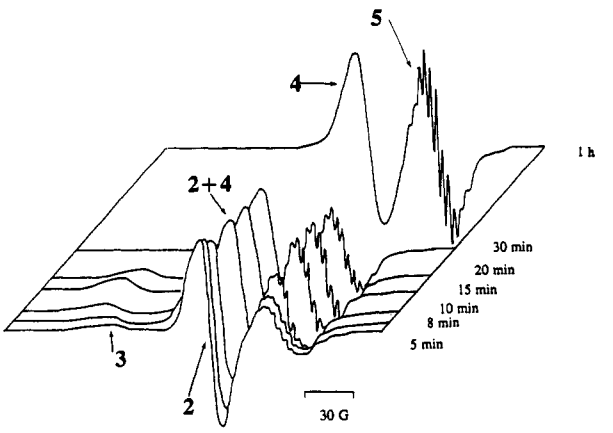


Figure 4. ESR spectra for conversion of **2** to **5** in THF.

2 to **5** as outlined in Scheme 1, destroying the 1 equiv of Me_3SiCH_2–Mg-containing species remaining, and then introducing L to displace THF from the coordination sphere of the intermediate $CpCr(NO)(THF)(CH_2SiMe_3)$ complex (eq 6). By

$$CpCr(NO)(THF)(CH_2SiMe_3) + L \rightarrow CpCr(NO)(L)(CH_2SiMe_3) + THF \quad (6)$$

employing CH_3I as the agent to consume the excess Me_3SiCH_2–Mg-containing complex, we have synthesized (and isolated) in just this way the novel 17-valence-electron complexes $CpCr(NO)(pip)(CH_2SiMe_3)$ and $CpCr(NO)(NH_2CMe_3)(CH_2SiMe_3)$. We have also extended this methodology to encompass a related benzyl complex, namely $CpCr(NO)(pip)(CH_2Ph)$. We are continuing our investigations of these fascinating radical complexes, and we shall report the characteristic chemical properties of these and related compounds in a separate manuscript.

Conclusion

It is well-known that 17-electron complexes usually react several orders of magnitude faster than their diamagnetic analogues and that ligand substitution on these complexes generally proceeds associatively via 19-electron intermediates.[20] It is almost certain that the individual transformations presented in Scheme 1 proceed associatively. This is especially true given that we have established that the reverse of the initial dissociation reaction converting **1** to **2** occurs in a bimolecular fashion.[8] However, our observation that the initial replacement of a two-electron ligand is necessary to initiate the desired reactivity of a paramagnetic compound is without precedent.[21] To the best of our knowledge, initial ligand exchange preceding alkyl-for-halide metathesis is also unprecedented in diamagnetic systems where ligand dissociation reactions are known to precede oxidative addition, reductive elimination, or migratory insertion processes.[2]

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(20) Trogler, W. C. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Chapter 4.

(21) Paramagnetic complexes usually undergo ligand substitution processes quite spontaneously; see, for example: Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61.