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Organometallic Nitrosyl Chemistry. I. Reactions of Nitrosyl Chloride with Some Anionic and Neutral Carbonyl Complexes

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The stoichiometric reaction of nitrosyl chloride with weakly nucleophilic metal carbonyl anions such as $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3^-$ ($\text{M} = \text{Cr, Mo, or W}$), $\text{W}(\text{CO})_5\text{Cl}^-$, $\text{Mn}(\text{CO})_5^-$, and $\text{Fe}(\text{CO})_4^{2-}$ is a new and convenient means of preparing the neutral nitrosyl compounds $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ ($\text{M} = \text{Cr, Mo, or W}$), $\text{W}(\text{CO})_4(\text{NO})\text{Cl}$, $\text{Mn}(\text{CO})_4(\text{NO})$, and $\text{Fe}(\text{CO})_2(\text{NO})_2$. More nucleophilic anions are oxidized rapidly by ClNO . Treatment of the neutral compounds $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ ($\text{M} = \text{Cr, Mo, or W}$) and $\text{Fe}(\text{CO})_2(\text{NO})_2$ with nitrosyl chloride provides a new and high-yield synthetic route to the chloronitrosyl compounds $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{Cl}$ ($\text{M} = \text{Cr, Mo, or W}$) and $\text{Fe}(\text{NO})_3\text{Cl}$. Some reactions of compounds containing metal-metal bonds with ClNO are also described.

Introduction

Nitrosyl chloride has previously been utilized to introduce the nitrosyl functionality into organometallic complexes. Typically, it may oxidatively add to coordinatively unsaturated substrates, or, when reaction occurs with coordinatively saturated compounds, each ClNO added may displace ligands capable of donating a total of four electrons to the metal.¹ However, previous attention has been focused almost exclusively on the interaction of nitrosyl chloride with neutral complexes. This paper describes the reactions of this versatile synthetic reagent with a variety of organometallic anions and outlines some new reactions between ClNO and neutral carbonyl-containing entities that readily lead to neutral chloronitrosyl compounds.

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to reported procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried (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 magnetic resonance spectra were recorded on a Varian Associates T60 spectrometer 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, and the high-resolution mass spectrum was obtained on an MS902 spectrometer with the assistance of Mr. G. Eigendorf and Mr. G. Gunn. Elemental analyses were carried out by Mr. P. Borda of this department.

Reaction of Nitrosyl Chloride with $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]$ ($\text{M} = \text{Cr, Mo, W}$). All three of these reactions were carried out in a similar manner. The experimental procedure, using the chromium complex as a typical example, was as follows. To a solution of $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ (4.89 g, 21.8 mmol) in tetrahydrofuran (90 ml) at room temperature was added dropwise with rapid stirring a solution of ClNO (1.4 g, 21 mmol) in tetrahydrofuran (20 ml). Gas evolution occurred throughout the course of the reaction and a dark solid precipitated. After addition of the ClNO was completed, a solution

infrared spectrum revealed the final reaction mixture to contain $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ as the principal carbonyl-bearing compounds. The reaction mixture was taken to dryness in vacuo and sublimation of the dried residue at 60° (5×10^{-3} mm) onto a water-cooled probe produced 1.01 g (5.0 mmol, 23% yield) of the bright orange-red $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ which was identified by its infrared spectrum. The reactions involving the molybdenum and tungsten anions proceeded comparably, but it should be noted that if an excess of ClNO is employed in the above synthesis, significant amounts of the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{Cl}$ compounds are also formed. The physical and chemical properties of the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ complexes have been extensively described.⁴

The treatment of other transition metal compounds with nitrosyl chloride was effected similarly and the experimental procedures are summarized in Table I.

Reaction of Nitrosyl Chloride with $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ [$\text{M} = \text{Cr, W}$]. Both of these reactions were performed in the same manner. The experimental procedure, using the chromium compound as a particular example, was as follows. To a solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$ ¹⁷ (4.70 g, 23.2 mmol) in dichloromethane (30 ml) at -78° was added dropwise with rapid stirring a dichloromethane solution of ClNO (containing 2.0 g of ClNO in 30 ml of CH_2Cl_2). Gas evolution occurred and a small quantity of a dark solid precipitated. The reaction was monitored by infrared spectroscopy and the ClNO solution was added until the carbonyl absorptions due to the initial reactant had disappeared. The final reaction mixture was concentrated in vacuo to approximately 15 ml in total volume and it was then filtered through a short (30 \times 40 mm) Florisil column. Addition of hexane to the filtrate induced the crystallization of golden needles of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}$ (3.80 g, 17.9 mmol, 77% yield) which were collected by filtration. The analogous bright green tungsten compound was prepared similarly in 72% yield. The physical properties of both compounds are summarized in Table II.

Reaction of Nitrosyl Chloride with $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})$. A stirred, orange solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})$ ¹⁷ (6.50 g, 26.3 mmol) in dichloromethane (100 ml) at room temperature was treated dropwise with a dichloromethane solution of ClNO . Gas was evolved, the reaction mixture developed a green coloration, and a small quantity of a red precipitate was formed. Again, the ClNO solution was added until the carbonyl absorptions due to the initial reactant had disappeared from the infrared spectrum of the reaction mixture's supernatant liquid. Hexane (50 ml) was then added and the volume of the reaction mixture was reduced in vacuo to approximately 60 ml at which point the red solid was removed by filtration. Further concentration of the filtrate in vacuo resulted in the formation of green

Table I. Reactions of Nitrosyl Chloride with Some Transition Metal Compounds

Transition metal compd (amt, mmol)	Amt of ClNO, mmol	Solvent (vol, ml)	Temp and time of mixing	Products (yields)	Isolation and identification
(C ₆ H ₅) ₄ N[W(CO) ₅ Cl] ⁵ (6.9)	8.0	THF (130)	Room temp, 30 min	W(CO) ₄ (NO)Cl (~8%)	Sublimation at 45– 65° (5 × 10 ⁻³ mm); infrared spectrum ⁶
[(C ₆ H ₅) ₃ P] ₂ N[W(CO) ₅ Cl] ^a (2.0)	2.0	CH ₂ Cl ₂ (30)	-78°, 30 min	W(CO) ₄ (NO)Cl (28%)	Sublimation at 60° (5 × 10 ⁻³ mm); elemental analysis
[(C ₆ H ₅) ₃ P] ₂ N[Mn(CO) ₅] ^b (1.1)	1.1	CH ₂ Cl ₂ (30)	Room temp, 15 min	Mn(CO) ₄ (NO) (~70%)	Vacuum distillation; infrared spectrum ⁹
Na[Re(CO) ₅] ⁸ (4.0)	4.0	THF (60)	0°, 15 min	Re ₂ (CO) ₁₀	Sublimation at 40– 60° (5 × 10 ⁻³ mm); infrared spectrum ^c
Na[(η ⁵ -C ₅ H ₅)Fe(CO) ₂] ¹⁰ (15)	15	THF (60)	0°, 20 min	[(η ⁵ -C ₅ H ₅)Fe(CO) ₂] ₂	Identification in solution by infrared spectroscopy ^c
(C ₆ H ₅) ₃ SnFe(η ⁵ -C ₅ H ₅)(CO) ₂ ¹⁰ (2.0)	3.0	CH ₂ Cl ₂ (15)	Room temp, 15 min	(C ₆ H ₅) _{3-n} Cl _n SnFe- (η ⁵ -C ₅ H ₅)(CO) ₂ (n = 0, 1, 2, 3)	THF extracts; infrared spectrum ¹²
(C ₆ H ₅) ₃ SnRe(CO) ₅ ¹³ (1.5)	2.0	CH ₂ Cl ₂ (10)	Room temp, 15 min	(C ₆ H ₅) _{3-n} Cl _n SnRe- (CO) ₅ (n = 0, 1, 2, 3)	<i>d</i>
Na ₂ [Fe(CO) ₄] ¹⁵ (10.0)	20	(C ₂ H ₅) ₂ O (150)	-78°, 30 min	Fe(CO) ₂ (NO) ₂ (30%)	Vacuum distillation; infrared spectrum ¹⁶
[(η ⁵ -C ₅ H ₅)Fe(CO) ₂] ₂ (1.4)	4.0	CH ₂ Cl ₂ (30)	Room temp, 20 min	(η ⁵ -C ₅ H ₅)Fe(CO) ₂ Cl (51%)	Sublimation at 50– 60° (5 × 10 ⁻³ mm); infrared spectrum ^{18,19}

^a Prepared from [(C₆H₅)₃P]₂NCl⁷ and W(CO)₆ in diglyme at 130° and recrystallized from CH₂Cl₂-hexane; ν(CO) (in diglyme) 1950 (m), 1905 (vs), and 1838 (s) cm⁻¹. ^b Prepared from Na[Mn(CO)₅]⁸ and [(C₆H₅)₃P]₂NCl in THF-CH₂Cl₂ and recrystallized from CH₂Cl₂-ethyl acetate. ^c By comparison with an authentic infrared spectrum of the compound. ^d Inferred from the characteristic shift of the carbonyl absorptions to higher wave numbers during the course of the reaction.¹⁴

Table II. Physical properties of (η⁵-C₅H₅)M(NO)₂Cl (M = Cr, Mo, W)

Compd	Color	Mp, °C	Analyses, %								Proton NMR, τ (in C ₆ - D ₆), η ⁵ - C ₅ H ₅	ν(NO), cm ⁻¹ (in CH ₂ Cl ₂)
			C		H		N		Cl			
(η ⁵ -C ₅ H ₅)Cr(NO) ₂ Cl	Gold	144 dec	28.26	28.29	2.37	2.55	13.18	12.86	16.68	16.99	5.22	1816 s, 1711 s
(η ⁵ -C ₅ H ₅)Mo(NO) ₂ Cl	Green	116	23.42	23.53	1.96	1.90	10.92	10.70			4.93	1759 s, 1665 s
(η ⁵ -C ₅ H ₅)W(NO) ₂ Cl	Green	127 dec	17.44	17.68	1.46	1.62	8.13	8.10	10.29	10.26	5.02	1733 s, 1650 s

crystals of (η⁵-C₅H₅)Mo(NO)₂Cl (6.00 g, 23.4 mmol, 89% yield) which were collected by filtration. The physical properties of this compound are summarized in Table II.

Subsequent recrystallization of the red by-product from dichloromethane-hexane yielded ~0.3 g of [(η⁵-C₅H₅)Mo(NO)Cl]₂.

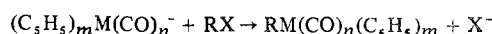
Anal. Calcd for C₁₀H₁₀Mo₂N₂O₂Cl₄: C, 22.93; H, 1.92; N, 5.35; Cl, 27.07. Found: C, 23.08; H, 1.95; N, 5.30; Cl, 27.23.

Reaction of Nitrosyl Chloride with Fe(CO)₅. A stirred solution of Fe(CO)₅ (7.5 ml, 58 mmol) in dichloromethane (30 ml) at room temperature was treated dropwise with a solution of ClNO (7.37 g, 112 mmol) in dichloromethane (50 ml). Vigorous gas evolution occurred and the reaction mixture became purple black. The final reaction mixture was taken to dryness in vacuo and the residue was extracted into hexane (150 ml). Cooling of the extract to -78° resulted in the precipitation of a dark red-brown solid which was collected by filtration. In this manner 3.0 g (16.6 mmol, 29% yield) of Fe(NO)₃Cl was isolated. The product, identified by its infrared spectrum,^{20,21} readily lost nitric oxide, especially under vacuum, and so an acceptable elemental analysis could not be obtained.

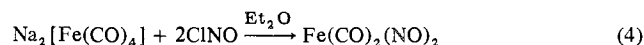
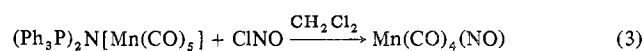
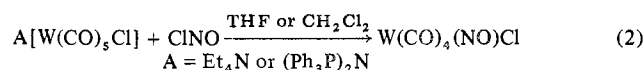
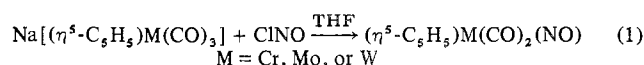
Reaction of Nitrosyl Chloride with Fe(CO)₂(NO)₂. To a solution of Fe(CO)₂(NO)₂²² (4.96 g, 28.8 mmol) in pentane (20 ml) at room temperature was added dropwise with stirring a solution of ClNO (2.6 g, 40 mmol) in pentane (30 ml). Vigorous gas evolution occurred and a red-brown solid was formed. The final reaction mixture was distilled in a vacuum system from a room temperature to a -78° trap. The distillate was merely a pentane solution of unreacted Fe(CO)₂(NO)₂. The reaction residue (1.63 g, 9.0 mmol, 31% yield) was identified as Fe(NO)₃Cl by its characteristic infrared spectrum and it dissolved completely in tetrahydrofuran and dichloromethane to give deep red solutions.

Results and Discussion

Reactions of Nitrosyl Chloride with Anionic Carbonyl Complexes. This class of reactions has been ignored except in the preparation of (RB(pz)₃)M(CO)₂(NO) (where RB(pz)₃ = tris(pyrazolyl) borate, R = H or pz, and M = Cr, Mo, or W) from [(RB(pz)₃)M(CO)₃]⁻.²³ A characteristic reaction of metal carbonyl anions and cyclopentadienylmetal carbonyl anions is the nucleophilic displacement of halide from both organic and inorganic halides, according to the general scheme²⁴



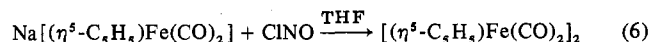
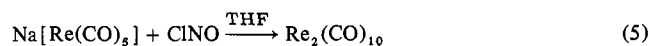
m = 0 or 1; *n* = 1–5 depending on M. We find that some of these anions also displace the chloride from nitrosyl chloride in a somewhat analogous manner, thereby providing a convenient synthetic route to neutral nitrosyl compounds. Typical examples of such reactions are summarized in eq 1–4. All



of these conversions are accompanied by the evolution of gas and they proceed readily and in reasonable yields. Even though nitrosyl chloride is a covalent, bent molecule, the chlorine-nitrogen bond is somewhat ionic in character.²⁵ Consequently, in its reactions with metal carbonyl anions CINO appears to behave analogously to a nitrosonium salt, and the concomitant formation of a metal chloride provides a strong thermodynamic driving force for these reactions.

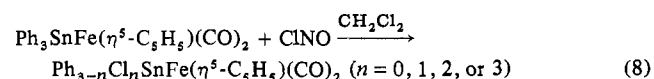
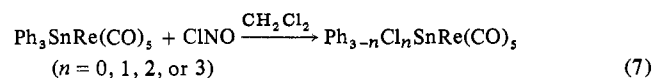
One aspect of reaction 2 deserves special comment. When the tetraethylammonium salt of $W(CO)_5Cl^-$ is treated with CINO in either of the indicated solvents, some $W(CO)_6$ is formed as a by-product. Similar results are obtained when nitrosylsulfuric acid is employed as a nitrosylating agent.⁶ However, we find that the bis(triphenylphosphine)iminium salt can be nitrosylated with CINO in CH_2Cl_2 to produce $W(CO)_4(NO)Cl$ without concurrent formation of the hexacarbonyl, thereby permitting isolation of the desired product much more conveniently than was previously possible.⁶

More nucleophilic carbonyl anions²⁴ cannot be nitrosylated with nitrosyl chloride. The stronger nucleophiles apparently act as reducing agents and are oxidized rapidly when treated with CINO, e.g.



Consequently, some $[(\eta^5-C_5H_5)M(CO)_3]_2$ is formed as a by-product in reaction 1 when $M = Cr, Mo,$ or W . However, nucleophilicity is obviously not the only factor influencing the outcome of these reactions as evidenced by the fact that treatment of $Mn(CO)_5^-$ (an anion of slightly greater nucleophilicity than $(\eta^5-C_5H_5)Mo(CO)_3^-$) with CINO does not produce any detectable amount of $Mn_2(CO)_{10}$ in reaction 3.

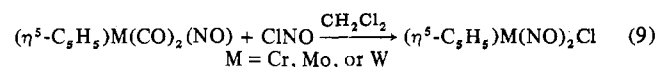
The triphenyltin derivatives of the anions in reactions 5 and 6 (which presumably contain less nucleophilic transition metal centers than the anions themselves) also react at ambient temperatures with nitrosyl chloride. Nitrosyl complexes are not formed, however, as the metal-metal bonds remain intact and only the tin-carbon bonds are cleaved, i.e.



This behavior is similar to that observed²⁶ when the iron-containing reactant is treated with HCl.

Finally, it should be noted that an excess of nitrosyl chloride must be avoided during reactions of the type (1)–(4) since the possibility exists that two carbonyl ligands can be readily displaced from the coordinatively saturated products. Indeed, just such a displacement forms the basis for a convenient synthetic route to some chloronitrosyl compounds as discussed in the next section.

Reaction of Nitrosyl Chloride with Neutral Carbonyl Complexes. The chemical transformations



proceed smoothly, but in order to achieve maximum yields of the chromium and tungsten compounds, the reactions must be effected at -78° . The molybdenum complex, on the other hand, can be prepared in excellent yields even at room temperature, but a small amount of $[(\eta^5-C_5H_5)Mo(NO)Cl_2]_2$ is formed as a by-product. Since the latter compound can be formed by the direct treatment of $(\eta^5-C_5H_5)Mo(CO)_2(NO)$ with Cl_2 ,²⁷ its appearance simply reflects the fact that CINO

Table III. High-Resolution Mass Spectral Data for $(\eta^5-C_5H_5)Cr(NO)_2Cl$

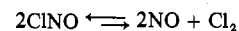
<i>m/e</i>		Rel abund	Assignment
Measd	Calcd		
213.9423	213.9414	11.9	$C_5H_5Cr(NO)_2^{37}Cl^+$
211.9440	211.9444	32.6	$C_5H_5Cr(NO)_2^{35}Cl^+$
183.9447	183.9434	13.8	$C_5H_5Cr(NO)^{37}Cl^+$
181.9476	181.9464	36.6	$C_5H_5Cr(NO)^{35}Cl^+$
153.9459	153.9455	36.6	$C_5H_5Cr^{37}Cl^+$
151.9481	151.9484	100	$C_5H_5Cr^{35}Cl^+$
176.9796	176.9756	5.3	$C_5H_5Cr(NO)_2^+$
146.9818	146.9776	3.4	$C_5H_5Cr(NO)^+$
116.9784	116.9796	18.0	$C_5H_5Cr^+$
88.9050	88.9063	10.6	$Cr^{37}Cl^+$
86.9089	86.9093	23.9	$Cr^{35}Cl^+$
65.0396	65.0391	13.3	$C_5H_5^+$
51.9412	51.9404	13.8	Cr^+

Table IV. Low-Resolution Mass Spectral Data for $(\eta^5-C_5H_5)M(NO)_2Cl^a$ ($M = Mo, W$)

$(\eta^5-C_5H_5)Mo(NO)_2Cl$			$(\eta^5-C_5H_5)W(NO)_2Cl$		
<i>m/e</i>	Rel abund	Assignment	<i>m/e</i>	Rel abund	Assignment
258	43.7	$C_5H_5Mo(NO)_2Cl^+$	344	100	$C_5H_5W(NO)_2Cl^+$
228	33.5	$C_5H_5Mo(NO)Cl^+$	314	81.0	$C_5H_5W(NO)Cl^+$
198	100	$C_5H_5MoCl^+$	284	53.7	$C_5H_5WCl^+$
172	30.4	$C_3H_3MoCl^+$	258	71.4	$C_3H_3WCl^+$
163	7.5	$C_5H_5Mo^+$	249	28.1	$C_5H_5W^+$
137	12.4	$C_3H_3Mo^+$	223	13.0	$C_3H_3W^+$
133	24.2	$MoCl^+$	219	16.0	WCl^+
98	10.4	Mo^+	184	2.1	W^+
65	3.7	$C_5H_5^+$	65	6.8	$C_5H_5^+$

^a The assignments involve the most abundant naturally occurring isotopes, i.e., ⁹⁸Mo, ¹⁸⁴W, and ³⁵Cl, in each fragment.

exists in solution as part of the equilibrium



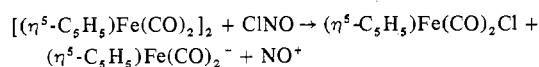
In any event, reaction 9 is, by far, the best and most convenient preparative route to all of the $(\eta^5-C_5H_5)M(NO)_2Cl$ complexes.

The chromium complex $(\eta^5-C_5H_5)Cr(NO)_2Cl$ has already been well characterized.²⁸ However, contrary to the first report of its preparation,²⁹ we find the molybdenum analog to be air stable in the solid state for at least 1 week and in dichloromethane solution for at least several hours. The tungsten complex, only very recently prepared by another synthetic route,³⁰ exhibits similar properties. All three compounds possess reasonable thermal stability and can be sublimed in vacuo at $40-50^\circ$ with only slight decomposition. Their mass spectra, summarized in Tables III and IV, exhibit the expected fragmentation patterns, namely, the loss of ligands from the metal center. Of particular interest is the fact that the fragments $C_3H_3MCl^+$ and $C_3H_3M^+$ are not observed for the chromium complex but become increasingly abundant for the molybdenum and tungsten compounds. Furthermore, the relative abundance of fragments containing the nitrosyl ligand varies considerably with the metal thereby indicating differences in the metal-nitrosyl bond strength. Chemically, the $(\eta^5-C_5H_5)M(NO)_2Cl$ species are useful precursors for the synthesis of a wide variety of thermally stable alkyl and aryl complexes, $(\eta^5-C_5H_5)M(NO)_2R$.³¹ All of these physical and chemical facts are in direct contrast to previously reported observations²⁹ on the molybdenum system.

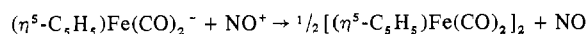
The products obtained from the reaction of CINO with neutral carbonyl complexes may vary with differing reaction conditions. For example, nitrosyl chloride in the gas phase converts $Fe(CO)_5$ to $Fe(CO)_2(NO)_2$ in a maximum yield of 50%.³² The yields decrease with increasing proportions of CINO until none of the carbonylnitrosyl is found when the molar ratio of CINO to $Fe(CO)_5$ is 2.7:1. We find that the

same reaction in dichloromethane produces $\text{Fe}(\text{NO})_3\text{Cl}$ with maximum yields being obtained when the molar ratio of ClNO to $\text{Fe}(\text{CO})_5$ is 2:1. $\text{Fe}(\text{CO})_2(\text{NO})_2$ may be an intermediate in this reaction since the direct treatment of $\text{Fe}(\text{CO})_2(\text{NO})_2$ with ClNO also produces $\text{Fe}(\text{NO})_3\text{Cl}$. This synthetic route to the chloronitrosyl compound is much more convenient than the previously reported procedure.³³

Nitrosyl chloride is also known to react with dimeric carbonyl compounds to produce polymeric or dimeric nitrosyl complexes. For example, $\text{M}_2(\text{CO})_8\text{Cl}_4$ (where $\text{M} = \text{Mo}$ or W) is converted to a mixture of $[\text{M}(\text{NO})\text{Cl}_3]_n$ and $[\text{M}(\text{NO})_2\text{Cl}_2]_n$,³⁴ and $[\text{Re}(\text{CO})_4\text{Cl}]_2$ is converted to $[\text{Re}(\text{CO})_2(\text{NO})\text{Cl}_2]_2$ ³⁵ by nitrosyl chloride. In contrast, we find that ClNO cleaves the dimeric $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ to give $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$ and no nitrosyl-containing compound. This transformation resembles the known oxidation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ in the presence of HCl .¹⁸ A plausible reaction sequence is



followed by



with the second step being identical with that described in reaction 6. We also have observed³⁶ that the compounds $\text{M}_2(\text{CO})_{10}$ (where $\text{M} = \text{Mn}$ or Re) are cleaved in a similar manner by ClNO to yield the well-known $\text{M}(\text{CO})_5\text{Cl}$ species.

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Registry No. $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]$, 12203-12-2; $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]$, 12107-35-6; $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]$, 12107-36-7; $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})$, 12192-94-8; $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{NO})$, 12128-13-1; $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{NO})$, 12128-14-2; $\text{Fe}(\text{CO})_5$, 13463-40-6; $\text{Fe}(\text{CO})_2(\text{NO})_2$, 13682-74-1; ClNO , 2696-92-6; $(\text{C}_2\text{H}_5)_4\text{N}[\text{W}(\text{CO})_5\text{Cl}]$, 14780-97-3; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}[\text{W}(\text{CO})_5\text{Cl}]$, 39048-34-5; $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}[\text{Mn}(\text{CO})_5]$, 52542-59-3; $\text{Na}[\text{Re}(\text{CO})_5]$, 33634-75-2; $\text{Na}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$, 12152-20-4; $(\text{C}_6\text{H}_5)_3\text{SnFe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$, 12132-09-1; $(\text{C}_6\text{H}_5)_3\text{SnRe}(\text{CO})_5$, 15614-21-8; $\text{Na}_2[\text{Fe}(\text{CO})_4]$, 14878-31-0; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, 12132-86-4; $\text{W}(\text{CO})_4(\text{NO})\text{Cl}$, 55057-86-8; $\text{Mn}(\text{CO})_4(\text{NO})$, 16104-17-9; $\text{Re}_2(\text{CO})_{10}$, 14285-68-8; $(\text{C}_6\text{H}_5)_2\text{ClSnFe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$, 32610-36-9; $(\text{C}_6\text{H}_5)\text{Cl}_2\text{SnFe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$, 31781-21-2; $\text{Cl}_3\text{SnFe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$, 12192-93-7; $(\text{C}_6\text{H}_5)_2\text{ClSnRe}(\text{CO})_5$, 55029-94-2; (C_6H_5) -

$\text{Cl}_2\text{SnRe}(\text{CO})_5$, 55029-95-3; $\text{Cl}_3\text{SnRe}(\text{CO})_5$, 15556-16-8; $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$, 12107-04-9; $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})_2\text{Cl}$, 12071-51-1; $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{Cl}$, 53419-14-0; $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})_2\text{Cl}$, 12305-00-9; $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{Cl}_2]_2$, 41395-41-9; $\text{Fe}(\text{NO})_3\text{Cl}$, 14972-71-5.

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Kinetics of Solvent Exchange of Hexakis(*N,N*-dimethylformamide)chromium(III) Ion in *N,N*-Dimethylformamide. Temperature and Pressure Effects and Mechanism

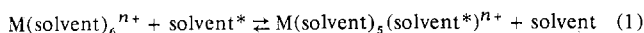
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The exchange of *N,N*-dimethylformamide (DMF) between $\text{Cr}(\text{DMF})_6^{3+}$ and solvent DMF proceeds according to pseudo-first-order kinetics with rate coefficient $k_{\text{ex}} = 7.4 \times 10^{-5} \text{ sec}^{-1}$ at 344.5 K and 0.1 MPa for the exchange of all six ligands, the activation parameters being $\Delta H^* = 97.1 \text{ kJ mol}^{-1}$, $\Delta S^* = -43.5 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta V^* = -6.3 \text{ cm}^3 \text{ mol}^{-1}$ (independent of pressure to 400 MPa at least). These and other data provide evidence for an associative interchange (i_a) mechanism. Perchlorate ion reduces the rate of solvent exchange slightly, apparently through formation of $\{\text{Cr}(\text{DMF})_6^{3+}, \text{ClO}_4^-\}$ ion pairs (formation constant $\sim 6 \text{ dm}^3 \text{ mol}^{-1}$ at 344.5 K, 0.1 MPa) in which k_{ex} is $\sim 40\%$ of its value in free $\text{Cr}(\text{DMF})_6^{3+}$.

The study of the kinetics of solvent-exchange reactions of metal ion-solvent complexes



offers unique opportunities for the assignment of reaction mechanism from activation parameters (especially the volume of activation, ΔV^*) because there is no net chemical change and no significant development of charge on going to the