same reaction in dichloromethane produces $Fe(NO)_3Cl$ with maximum yields being obtained when the molar ratio of ClNO to $Fe(CO)_5$ is 2:1. $Fe(CO)_2(NO)_2$ may be an intermediate in this reaction since the direct treatment of $Fe(CO)_2(NO)_2$ with ClNO also produces $Fe(NO)_3Cl$. 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, $M_2(CO)_8Cl_4$ (where M = Mo or W) is converted to a mixture of $[M(NO)Cl_3]_n$ and $[M(NO)_2Cl_2]_n$,[34] and $[Re(CO)_4Cl]_2$ is converted to $[Re(CO)_2(NO)Cl_2]_2$[35] by nitrosyl chloride. In contrast, we find that ClNO cleaves the dimeric $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to give $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ and no nitrosyl-containing compound. This transformation resembles the known oxidation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in the presence of HCl.[18] A plausible reaction sequence is

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + ClNO \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)_2Cl + (\eta^5\text{-}C_5H_5)Fe(CO)_2^- + NO^+$$

followed by

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2^- + NO^+ \rightarrow {}^1/_2[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + NO$$

with the second step being identical with that described in reaction 6. We also have observed[36] that the compounds $M_2(CO)_{10}$ (where M = Mn or Re) are cleaved in a similar manner by ClNO to yield the well-known $M(CO)_5Cl$ species.

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Registry No. $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$, 12203-12-2; $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$, 12107-35-6; $Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$, 12107-36-7; $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, 12192-94-8; $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$, 12128-13-1; $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, 12128-14-2; $Fe(CO)_5$, 13463-40-6; $Fe(CO)_2(NO)_2$, 13682-74-1; ClNO, 2696-92-6; $(C_2H_5)_4N[W(CO)_5Cl]$, 14780-97-3; $[(C_6H_5)_3P]_2N[W(CO)_5Cl]$, 39048-34-5; $[(C_6H_5)_3P]_2N[Mn(CO)_5]$, 52542-59-3; $Na[Re(CO)_5]$, 33634-75-2; $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, 12152-20-4; $(C_6H_5)_3SnFe(\eta^5\text{-}C_5H_5)(CO)_2$, 12132-09-1; $(C_6H_5)_3SnRe(CO)_5$, 15614-21-8; $Na_2[Fe(CO)_4]$, 14878-31-0; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12132-86-4; $W(CO)_4(NO)Cl$, 55057-86-8; $Mn(CO)_4(NO)$, 16104-17-9; $Re_2(CO)_{10}$, 14285-68-8; $(C_6H_5)_2ClSnFe(\eta^5\text{-}C_5H_5)(CO)_2$, 32610-36-9; $(C_6H_5)Cl_2SnFe(\eta^5\text{-}C_5H_5)(CO)_2$, 31781-21-2; $Cl_3SnFe(\eta^5\text{-}C_5H_5)(CO)_2$, 12192-93-7; $(C_6H_5)_2ClSnRe(CO)_5$, 55029-94-2; $(C_6H_5)Cl_2SnRe(CO)_5$, 55029-95-3; $Cl_3SnRe(CO)_5$, 15556-16-8; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, 12107-04-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$, 53419-14-0; $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$, 12305-00-9; $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl_2]_2$, 41395-41-9; $Fe(NO)_3Cl$, 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 $Cr(DMF)_6^{3+}$ and solvent DMF proceeds according to pseudo-first-order kinetics with rate coefficient $k_{ex} = 7.4 \times 10^{-5}$ sec^{-1} at 344.5 K and 0.1 MPa for the exchange of all six ligands, the activation parameters being $\Delta H^* = 97.1$ kJ mol^{-1}, $\Delta S^* = -43.5$ J K^{-1} mol^{-1}, and $\Delta V^* = -6.3$ cm^3 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 $\{Cr(DMF)_6^{3+},ClO_4^-\}$ ion pairs (formation constant ~6 dm^3 mol^{-1} at 344.5 K, 0.1 MPa) in which k_{ex} is ~40% of its value in free $Cr(DMF)_6^{3+}$.

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

$$M(solvent)_6^{n+} + solvent^* \rightleftarrows M(solvent)_5(solvent^*)^{n+} + solvent \quad (1)$$

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 transition state.[1] Furthermore, since all the ligands involved are chemically identical, direct experimental assessment of the various theories of ligand field effects on substitution kinetics[1] is facilitated. Finally, a distinction between the associative (I_a) and dissociative (I_d) interchange mechanisms[2] for reactions of the type

$$\mathrm{M(solvent)_6}^{n+} + \mathrm{X}^- \overset{K_{ip}}{\rightleftharpoons} \{\mathrm{M(solvent)_6}^{n+},\mathrm{X}^-\} \xrightarrow{k_i} \mathrm{M(solvent)_5X}^{(n-1)+} + \text{solvent} \qquad (2)$$

can be made if the solvent-exchange rate coefficient k_{ex} is known; for I_d, k_i should be less than k_{ex} and insensitive to the nature of X^-, whereas for I_a k_i should vary markedly with the nucleophilic power of X^- toward M^{n+} and, where this power is high, may actually exceed k_{ex}.

We have previously applied the above criteria in assigning an I_a mechanism to reactions 1 and 2 where $M^{n+} = Cr^{3+}$ and solvent = dimethyl sulfoxide (DMSO).[3] The present paper reports a similar but more detailed study of the system in which $M^{n+} = Cr^{3+}$ and solvent = *N,N*-dimethylformamide (DMF). The above mechanistic criteria are more readily applied to nonprotonic solvent systems such as DMSO and DMF than to water, since the lower dielectric constants lead to extensive ion pairing and hence more accurate values of k_i in reaction 2, and the absence of protonic acid–base equilibria solves the problems of cation hydrolysis and protonation of basic nucleophiles X^- in water. Furthermore, in this study with DMF as solvent, unusually good precision in k_{ex} has been attained by mass spectrometry using $(CD_3)_2NCDO$ as the labeled form of the solvent, the isotopic contamination which plagues aqueous studies using $H_2{}^{18}O$ being absent.

Experimental Section

Materials. *N,N*-Dimethylformamide (reagent grade, Baker Chemical Co.) was dried over a 4A molecular sieve (Guild Corp.) and fractionally distilled under vacuum as described previously.[4] Tetraethylammonium perchlorate was prepared by a published method.[5]

Preparation of Hexakis(*N,N*-dimethylformamide)chromium(III) Perchlorate. Hydrated hexaaquochromium(III) perchlorate (10 g) was dissolved in DMF (100 cm^3) and kept at 90° for 10 hr. On cooling, ethanol (100 cm^3) was added followed by ether (100 cm^3). After the mixture was allowed to stand at 0° for 0.5 hr, the blue precipitate was collected and washed thoroughly with ethanol and then ether; yield 13 g. The crude product was dissolved in DMF (100 cm^3), kept at 90° for 10 hr, and reprecipitated with an equal volume of ether; yield 12 g. This compound was finally recrystallized from cold DMF (100 cm^3) by slow addition of ether (100 cm^3); yield 11.5 g. The spectrum of the complex in DMF exhibited absorption maxima at 591 and 422 nm (molar absorptivity 57.9 and 45.1 $dm^3\ cm^{-1}\ mol^{-1}$ respectively). Anal. Calcd for $[Cr(DMF)_6](ClO_4)_3$: C, 27.4; H, 5.4; N, 10.7; Cl, 13.5. Found: C, 27.1; H, 5.2; N, 10.1; Cl, 13.6.

The coordinated solvent molecules of $[Cr(DMF)_6](ClO_4)_3$ were partially labeled (~6%) with DMF-d_7 by dissolving the salt (5 g) in 8% DMF-d_7 (30 cm^3) and maintaining the solution at 90° for 10 hr. The salt was reprecipitated with ether (30 cm^3); yield 4.5 g.

Preparation of Hexakis(*N,N*-dimethylformamide)chromium(III) Tetraphenylborate. Aqueous sodium tetraphenylborate (2.4 g in 50 cm^3) was added dropwise to a well-stirred solution of $[Cr(DMF)_6](ClO_4)_3$ (2 g) in DMF (50 cm^3). Following the addition, water (100 cm^3) was immediately added and the mixture was stirred for 0.5 hr and filtered. The blue precipitate was washed thoroughly with water, methanol, and ether and recrystallized from DMF (25 cm^3) by adding ether (150 cm^3); yield 3.6 g. Anal. Calcd for $[Cr(DMF)_6](BPh_4)_3$: C, 75.2; H, 7.2; N, 5.9. Found: C, 74.6; H, 7.4; N, 5.9. The partially labeled complex was prepared from the corresponding labeled perchlorate salt in the same way.

Preparation of Tetraethylammonium Hexakis(thiocyanato-*N*)-chromate(III). This salt was precipitated from an aqueous solution of $K_3[Cr(NCS)_6]$[6] by adding an appropriate amount of aqueous tetraethylammonium bromide solution. It was recrystallized from DMF by the addition of ether. Anal. Calcd for $(Et_4N)_3[Cr(NCS)_6]$: C, 45.5; H, 7.6; N, 15.9; S, 24.3. Found: C, 45.5; H, 7.6; N, 15.2; S, 24.4.

Table I. Effects of Perchlorate Ion on the Exchange of All Six *N,N*-Dimethylformamide Ligands in $Cr(DMF)_6{}^{3+}$ with DMF Solvent at 71.3° and 0.1 MPa

[Cr(III)], mol dm^{-3}	Total $[ClO_4^-]$, mol dm^{-3}	$10^5 k_{ex}$, sec^{-1}
0.00266–0.0115[a]	0	7.37 ± 0.05
0.00574[b]	0.0172	6.8 ± 0.2
0.0117[b]	0.0351	6.5 ± 0.2
0.0230[b]	0.0690	6.2 ± 0.2
0.00587[c]	0.118	5.74 ± 0.17
0.00608[c]	0.221	4.57 ± 0.14

[a] $[Cr(DMF)_6](BPh_4)_3$ salt. [b] $[Cr(DMF)_6](ClO_4)_3$ salt. [c] $[Cr(DMF)_6](ClO_4)_3$ salt with added Et_4NClO_4.

Table II. Kinetics of Exchange of All Six *N,N*-Dimethylformamide Ligands in $[Cr(DMF)_6](BPh_4)_3$ with DMF Solvent

Temp, °C	Pressure, MPa	[Cr(III)], mol dm^{-3}	$10^5 k_{ex}$, sec^{-1}
40.3	0.1	0.00348	0.238 ± 0.007
56.3	0.1	0.00341	1.44 ± 0.04
65.1	0.1	0.00350	3.99 ± 0.12
	50.0	0.00473	4.77 ± 0.12
	98.5	0.00465	5.02 ± 0.13
	150.0	0.00473	5.67 ± 0.14
	198.0	0.00474	6.4 ± 0.2
	250.0	0.00396	7.2 ± 0.2
	327.5	0.00395	8.2 ± 0.3
	400.0	0.00395	10.2 ± 0.3
71.3	0.1	0.00266	7.4 ± 0.2
		0.00581	7.3 ± 0.2
		0.0115	7.4 ± 0.2
80.0	0.1	0.00326	17.4 ± 0.5

Kinetics. Typically, a solution of labeled $[Cr(DMF)_6](ClO_4)_3$ or $[Cr(DMF)_6](BPh_4)_3$ in freshly distilled DMF was brought to the temperature of the thermostat bath (±0.1°) in a stoppered light-proof flask. The progress of the reaction at atmospheric pressure was followed by removing samples at appropriate intervals and cooling them immediately to 0°. The complex cation was precipitated with a stoichiometric amount of $Cr(NCS)_6{}^{3-}$ in DMF, and the filtered precipitate was washed thoroughly with methanol and dried under vacuum. The coordinated solvent was quantitatively driven off by fusing the precipitate with KNCS at 200° on a vacuum line, collected in a preevacuated tube chilled in liquid nitrogen, and analyzed for DMF-d_7 of mass 80 and DMF-^{13}C, DMF-^{15}N, and DMF-d_1 of mass 74 using a Varian-MAT CH5 mass spectrometer. The 80:74 mass ratios ranged conveniently on either side of unity (measurement of the much smaller 80:73 ratios would have introduced range-switching errors), and the values adopted were the mean of at least ten measurements, the standard deviations being ±1.5%.

The pressure dependence of the reaction rate was measured by removing samples from a pressurized syringe as described previously.[7]

Results

The rate of replacement of DMF-d_7 in $Cr(DMF\text{-}d_7)_6{}^{3+}$ by DMF-h_7 solvent was accurately first order over at least 80% completion of reaction, whether the anion present was tetraphenylborate or perchlorate, and the corresponding rate coefficients k_{ex} for the exchange of all six ligands are listed with their standard errors in Tables I and II. Perchlorate ion was found to depress the rate of exchange slightly (Table I) but tetraphenylborate had no discernible effect on k_{ex}. If the perchlorate effect is ascribed to ion pairing with a formation constant K_{ClO_4}, then

$$k_{ex} = (k_1 K_{ClO_4}[ClO_4^-] + k_2)/(1 + K_{ClO_4}[ClO_4^-]) \qquad (3)$$

where k_1 and k_2 are the first-order exchange rate coefficients associated with the ion pair and the free complex ion, respectively. If ionic strength effects and the possibility of ion triplet formation are ignored, then graphical examination of the data of Table I shows the extreme possible values of the limiting rate coefficient k_1 to be 1.0×10^{-5} and 4.0×10^{-5} sec^{-1} (corresponding to K_{ClO_4} = 4 and 10 $dm^3\ mol^{-1}$), so that

Table III. Kinetic Parameters for Reaction 2 Where M = Cr(III), Solvent = DMF, and $X^- = Cl^-$

	k_i or k_{ex} (sec^{-1}, $\times 10^5$)				ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}
	65.1°	71.1°	76.0°	81.0°		
DMF exchange[a]	3.99	7.2[b]	11.7[b]	19.1[b]	97.1	−43.5
Cl^- anation[c]	3.11[b]	7.0	13.4	26.5	131.1	55.1

[a] This work. [b] Calculated value. [c] References 5 and 10.

Table IV. Kinetic Parameters for the Exchange of All Six Solvent Ligands between $M(solvent)_6^{3+}$ and Bulk Solvent

M	Solvent	ΔH^*, kJ mol^{-1}	Dq, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	k_{ex}(298.2 K, 0.1 MPa), sec^{-1}
Cr	DMSO[a]	97	19.0	−49	1.9×10^{-7}
	DMF[b]	97	20.2	−43	3.3×10^{-7}
	H_2O[c]	110	20.8	+16	2.8×10^{-6}
	NH_3[d]	132	25.9		4.4×10^{-5}
Al	DMF[e]	74	0	+5	1.23
Fe	DMF[f]	52	0	−42	33
	DMF[g]	42	0	−69	61
Ga	DMF[h]	61	0	−35	1.7
Al	DMSO[i]	84	0	+13	5.7×10^{-2}
Fe	DMSO[j]	~42	0	~−74	~40
Al	H_2O[k]	112	0	+117	0.13
Ga	H_2O[k]	26	0	−95	1.8×10^3
Ti	H_2O[k]	26	24.0	−62	1.0×10^5

[a] Reference 3. [b] This work. [c] Reference 9. [d] T. W. Swaddle, L. F. Coleman, and J. P. Hunt, *Inorg. Chem.*, **2**, 950 (1963). [e] W. G. Movius and N. A. Matwiyoff, *ibid.*, **6**, 847 (1967). [f] F. Breivogel, *J. Phys. Chem.*, **73**, 4203 (1969). [g] Reference 8. [h] W. G. Movius and N. A. Matwiyoff, *Inorg. Chem.*, **8**, 925 (1969). [i] S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **44**, 3148 (1966). [j] C. H. Langford and H. F. M. Chung, *J. Am. Chem. Soc.*, **90**, 4485 (1968). [k] D. Fiat and R. E. Connick, *ibid.*, **90**, 608 (1968).

the most likely values are $K_{ClO_4} = 6$ dm^3 mol^{-1}, $k_1 = 3 \times 10^{-5}$ sec^{-1} and $k_2 = 7.3_7 \times 10^{-5}$ sec^{-1} at 71.3° and 0.1 MPa.

The data of Table II give excellent linear plots of ln (k_{ex}/T) vs. temperature T and of ln k_{ex} vs. pressure P. Least-squares data reduction yielded the following kinetic parameters: $\Delta H^* = 97.1 \pm 0.9$ kJ mol^{-1}, $\Delta S^* = -43.5 \pm 2.8$ J K^{-1} mol^{-1} (for the exchange of all six DMF ligands) or -58.4 ± 2.8 J K^{-1} mol^{-1} (for the exchange of one DMF ligand), $\Delta V^* = -6.3 \pm 0.2$ cm^3 mol^{-1}, $|(\partial V^*/\partial P)_T| < 3 \times 10^{-3}$ cm^3 mol^{-1} MPa^{-1} (i.e., ΔV^* is independent of P within the experimental uncertainty), and, at 298.2 K and 0.1 MPa, $k_{ex} = 3.3 \times 10^{-7}$ sec^{-1} (all six ligands) or $k_{ex}' = k_{ex}/6 = 5.5 \times 10^{-8}$ sec^{-1} (one ligand exchanging).

Discussion

The negative value and pressure independence of ΔV^* provide strong evidence for an associative interchange (I_a) mechanism for the $Cr(DMF)_6^{3+}$–DMF solvent exchange reaction,[1] although an associative (A) mechanism cannot be rigorously excluded. The numerical value of ΔV^* (−6.3 cm^3 mol^{-1}) cannot at present be rationalized in detail but is 5 cm^3 mol^{-1} more positive than for the $Cr(DMSO)_6^{3+}$–DMSO system presumably because steric compression of the first coordination sphere is likely to be more important for DMSO ligands[3] than for DMF, since a DMF ligand may be regarded as being flat in the immediate vicinity of the central metal ion.[8] For the $Cr(H_2O)_6^{3+}$–H_2O exchange, ΔV^* is 3 cm^3 mol^{-1} more negative than for $Cr(DMF)_6^{3+}$–DMF, presumably because of the relatively open hydrogen-bonded structure of the second coordination sphere in the aqueous system.[9] In all the Cr(III) solvent-exchange systems, the ΔV^* values indicate an I_a or possibly an A mechanism, whereas I_d processes prevail at low-spin Co(III) centers in aqueous and nonaqueous solvents,[1] so that the identity of the central metal ion would seem to be more important than the nature of the ligands or the solvent in determining the intimate mechanism of ligand substitution.

Support for the assignment of an I_a mechanism for substitution of $Cr(DMF)_6^{3+}$ in DMF comes from consideration of values of k_i (eq 2) for $X^- = Cl^-$ [5,10] relative to k_{ex} (Table III). Although solvent exchange is slightly faster than Cl^- entry at 65°, chloride anation outpaces DMF exchange above 72° because ΔH^* is 34 kJ mol^{-1} higher for the anation reaction within the ion pair. Although it may be conceded that ion pairing can affect k_{ex}, it seems unreasonable to attribute the large difference in ΔH^* to this effect in defense of an I_d mechanism. In any event, the data on the perchlorate ion effect (Table I) suggest that k_{ex} would in general be *reduced* by ion pairing, which is perhaps to be expected since some of the solvent molecules available for exchange in the second coordination sphere of the free complex would be displaced to bulk solvent in the ion pair.

Data pertaining to reaction 1 for various solvents and trivalent metal ions are collected in Table IV, in which the close kinetic similarity of the corresponding $M(DMF)_6^{3+}$–DMF and $M(DMSO)_6^{3+}$–DMSO systems is readily seen. If it is accepted that an I_a mechanism operates in $Cr(DMSO)_6^{3+}$ [3] and $Cr(DMF)_6^{3+}$, the ΔS^* values indicate that substitution in the corresponding iron(III) complexes and in $Ga(DMF)_6^{3+}$ in their respective solvents is I_a but that substitution in the Al(III) systems is I_d or D.[11] The anomaly of Al(III) can be ascribed to steric inhibition of I_a and facilitation of I_d or D because of the unusually small ionic radius of Al^{3+}; the prevalence of I_d mechanisms in spin-paired Co(III) complexes can be similarly rationalized[12] (ionic radii of octahedral spin-paired Co^{3+}, Al^{3+}, Cr^{3+}, Ga^{3+}, and high-spin Fe^{3+} are 52.5, 53.0, 61.5, 62.0, and 64.5 pm, respectively[13]). Previous workers have made similar mechanistic assignments for Fe(III), Al(III), and Ga(III).[8,14,15] Thus, our generalization[1,12] that cationic octahedral complexes of trivalent *transition* metals other than Co(III) undergo simple substitution in solution by an I_a mechanism can probably be extended to octahedral cationic complexes of *all* trivalent metals having ionic radii greater than about 60 pm.[16]

If the charge-to-radius ratio alone determined ΔH^* for reaction 1 in a given solvent system, ΔH^* would be about the same for Cr(III) and Ga(III). The excess of ~36 kJ mol^{-1} for $Cr(DMF)_6^{3+}$ over $Ga(DMF)_6^{3+}$ can be attributed to ligand field effects[1,17,18] and amounts to ~1.8 times the ligand field splitting parameter Dq (Table IV). Hush[18] has calculated ligand field contributions to ΔH^* for I_a exchange reactions of octahedral complexes proceeding via a transition state of C_{2v} ("octahedral wedge") geometry, which we favor for substitution at Cr(III) centers on stereochemical and kinetic grounds.[1] According to Hush, a ligand field contribution of $1.8Dq$ to ΔH^* would be expected for a transition state in which the bonds to the incoming and outgoing ligands are at 109.5° to each other and are elongated by 25%, which seems reasonable. However, ionic radii are themselves subject to ligand field effects;[19] the "field-free" ionic radius of Cr^{3+}, interpolated between Sc^{3+}, Fe^{3+} (high spin), and Ga^{3+}, is 68–69 pm,[13] so that a ligand field contribution of 50–60 kJ mol^{-1} (~$3Dq$) to ΔH^* might be anticipated for the $Cr(DMF)_6^{3+}$–DMF exchange on the basis of Table IV. This can still be accommodated by Hush's calculations on the basis of a bond angle nearer to 90° between the incoming and outgoing ligands, which again seems reasonable on steric grounds, but clearly no definitive quantitative interpretation of ligand field effects on ΔH^* is yet possible for mechanisms of the associative type.

On a purely empirical level, we note that ΔH^* is close to $5.0Dq$ for all four $Cr(solvent)_6^{3+}$–solvent exchange reactions listed in Table IV. The correlation is probably fortuitous in the case of the $Cr(NH_3)_6^{3+}$–NH_3 exchange, which evidently proceeds via conjugate base and ion aggregate formation,[20] but it may be that ΔH^* values appear to be directly proportional to Dq because the latter parameter can influence not only the energies of the d electrons of the metal ion but also the centripetal force field and steric factors (through the ionic radius). This may account for the apparent success of ligand field theories in correlating ΔH^* data for several substitution reactions of the I_d type.[1]

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Registry No. $[Cr(DMF)_6](ClO_4)_3$, 33594-59-1; $[Cr(DMF)_6(BPh_4)_3$, 55156-33-7; DMF, 68-12-2; ClO_4^-, 14797-73-0.

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Iron Complexes with Macrocyclic Ligands Containing the α-Diimine Functional Unit and Its Position-Specific Formation under the Influence of the Iron Atom

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The low-spin iron(II) complex $[Fe([14]aneN_4)(CH_3CN)_2](BF_4)_2$, where $[14]aneN_4$ is the tetradentate macrocyclic ligand *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, is found to undergo oxidative dehydrogenation in acetonitrile solution. The product initially isolated is a cyclic triimine having an α-diimine functional unit. In basic acetone the coordinated triimine can be converted rapidly to a tetraimine ligand containing two α-diimine units. The isolated iron(II) complexes all have the general formula $[Fe(MAC)(X)_2]^{n+}$, where MAC is the macrocycle and X is CH_3CN, imidazole, SCN^-, NO_2^-, CN^-, CNH, $CNCH_3$, and Cl^- and $n = 0$ or 2. The complexes containing the triimine ligand are air sensitive and are further dehydrogenated by molecular oxygen to the corresponding complexes of the tetraimine macrocycle. The bound cyanide ligands of the dicyano complex with the tetraimine macrocycle are sensitive to electrophilic reagents and can be protonated in a stepwise manner or alkylated. All of the complexes isolated, with the exception of the two *trans*-dichloroiron(III) derivatives, display charge-transfer bands in the visible region of their electronic spectra. The positions of these bands have been discussed in terms of the π-bonding abilities of the axial ligands.

Introduction

We have recently reported a series of iron complexes incorporating the 14-membered cyclic structure *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($[14]aneN_4$),[2] Figure 1(a), and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($[14]4,11\text{-}dieneN_4$),[3] Figure 1(b). The six-coordinate low-spin divalent iron(II) complexes with both ligands are air sensitive, and in the presence of molecular oxygen they are oxidatively dehydrogenated to yield complexes of cyclic ligands that contain higher degrees of unsaturation.[4] In the case of $[Fe[14]4,11\text{-}dieneN_4)(CH_3CN)_2]^{2+}$, dehydrogenation produced complexes structurally identical with those obtained using Ni(II) as the central ion.[5] However, the Fe(II) complex containing 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazatetracyclotetradeca-1,4,8,11-tetraene ($[14]1,4,8,11\text{-}tetraeneN_4$), Figure 1(c), was found to undergo a tautomerization[6] to give a coordinated macrocycle with two imines in the same five-membered chelate ring, i.e., an α-diimine group. Thus it was apparent early that the presence of iron as the central atom favored α-diimine formation in the ligands. To determine to what extent this tendency toward α-diimine formation affects the course of oxidative dehydrogenation reactions, $[Fe^{II}([14]aneN_4)(CH_3CN)_2]^{2+}$ was chosen as a reactant. Unlike $[14]4,11\text{-}dieneN_4$ no unsaturated linkages are present in the starting material so that dehydrogenation could occur at any of a number of positions in the macrocyclic ligand. Thus the formation of α-diimine groupings in this case demonstrates the strong directive influence of the iron atom in the oxidative dehydrogenation process. The products formed are among the most stable complexes of iron with synthetic macrocyclic ligands. A variety of interesting materials have been synthesized with these new ligands.

Experimental Section

Materials. All materials were reagent grade and used without further purification unless otherwise noted. Some of the syntheses were carried out in a Vacuum Atmospheres Corp. controlled-atmosphere drybox and the remainder on the "bench top" under a blanket of nitrogen gas.

Physical Measurements. Visible and near-infrared absorption spectra were obtained on a Cary Model 14-R recording spectrophotometer. All signals were recorded from 5 kK to the high-energy cutoff point resulting from the solvent absorption. For the air-sensitive complexes, spectra were recorded, using Teflon-stoppered cells, immediately after preparation under nitrogen and then again 30 min later. In order to determine extinction coefficients, weighings were carried out in contact with the atmosphere and the samples were quickly transferred to the drybox where solutions were prepared. The