Isonitrile Complexes of Chromium(0) and Molybdenum(0): Characterisation and Reactivity

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The preparation of a series of isonitrile complexes, $[(CO)_{6-x}M(CNR)_x]$ (x = 1—3; M = Cr, Mo; R = Me, Et, Pr^i, C_6H_{11}, Bu^t, *p*-tolyl, Ph, *p*-ClC_6H_4) is reported. The results of spectroscopic (i.r., u.v., mass, and n.m.r.—particularly aromatic solvent induced shifts) and electrochemical measurements are employed to assess the nature of the bonding in these systems. It is shown that the contribution of ($d \rightarrow \pi^*$) π-bonding is negligible and that variations in the donor strength of the isonitrile ligand are principally responsible for the changes observed. The compounds $(RNC)Cr(CO)_5$ do not react with weak nucleophiles (amines, alcohols). Ketimine formation does not result from the reaction between $(RNC)Cr(CO)_5$ and a silane in the presence of pyridine. The reaction between $(RNC)_2Cr(CO)_4$ and $(Me_2PCH_2)_2$(dmpe) affords *cis*-$(RNC)_2$(dmpe)$Cr(CO)_2$ as the principal product, together with $(dmpe)_2Cr(CO)_3$.

THERE has been a resurgence of interest in the chemistry of isonitriles[1] and the transition-metal complexes[2] which they form. This has received added impetus from the recent discovery that, in some cases, complexes of isonitriles undergo nucleophilic attack to give co-ordinated carbenes. Such nucleophilic attack has

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[1] 'Isonitrile Chemistry,' ed. I. Ugi, Academic Press, London, 1971.

[2] L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley, London, 1969.

been observed in certain complexes in which the *d*-electron configuration of the metal atom is either d^7 (Fe^I)[3] or d^8 (Pd^{II}, Pt^{II}) [4] (but see ref. 5).

Isonitrile complexes of formally d^6, zerovalent Group VI metals have been described on a number of occasions in the past,[2] but no detailed examination of their physical properties has been undertaken until now. We have therefore prepared three series of compounds of the type $LM(CO)_5$, $L_2M(CO)_4$, and $L_3M(CO)_3$ (L = isonitrile) and attempted to carry out nucleophilic substitution reactions on some of them.

RESULTS AND DISCUSSION

Preparations.—The compounds [$(RNC)Cr(CO)_5$] and [$(RNC)_2Cr(CO)_4$] were prepared by treating the salt, $Et_4N[ICr(CO)_5]$, with an excess of RNC in CH_2Cl_2 solution in an atmosphere of carbon monoxide at room temperature.[6] While the yield of monosubstituted product is always greater than that of the disubstituted product, the ratio of the yields is consistently greater for the aryl (*ca.* 5·5) than for the alkyl isonitriles (*ca.* 2·2). This finding reflects the stronger basic properties of the latter ligands which enables them to displace both carbonyl and iodide ligands more readily. The $(RNC)_2Mo(CO)_4$ compounds were prepared from [(norbornadiene)$Mo(CO)_4$],[7] whilst the [$(RNC)_3M(CO)_3$] (M = Cr, Mo) compounds were prepared from the corresponding [(cycloheptatriene)$M(CO)_3$] complex; [8] the yields of these reactions were generally good.

I.r. Spectra.—The spectra of the new complexes in the region 2250—1850 cm^{-1} are listed in Tables 1 and 2. All the spectra were recorded in hexane solution and can be compared with those of the compounds $(CO)_xMo(CNR)_{6-x}$ (x = 3, 4; R = Me, Et) prepared earlier, which were obtained in cetane ($C_{16}H_{34}$).[9] The solubility of the $(RNC)_3Cr(CO)_3$ compounds in hexane contrasts with previous reports.[8]

TABLE 1

Isonitrile stretching frequencies, ν(−N≡C) [a]

			$(RNC)M(CO)_5$	*cis*-$(RNC)_2M(CO)_4$		*fac*-$(RNC)_3M(CO)_3$		
R	M	RNC [b] (free)	A_1	A_1	B_1	A_1	E	
Me	Cr	2158	2180	2175	2139			
	Mo			2176	2140 [c]	2174	2133	*c*
Et	Cr	2148	2167	2162	2128			
	Mo			2165	2131 [c]	2160	2122	*c*
Pr^i	Cr	2140	2158	2153	2110	2144	2081	2043
	Mo			2154	2134	2145	2085	2040
Bu^t	Cr	2143	2153	2146	2107	2136	2096	2057
	Mo			2146	2109	2136	2093	2061
p-$MeC_6H_4^-$	Cr	2132	2140	2136	2081	2131	2061	2037
	Mo			2135	2082	2130	2062	2034
p-$ClC_6H_4^-$	Cr	2132	2134	2134	2070	2130	2051	2009
	Mo			2030	2070	2129	2052	

[a] In n-hexane solution. [b] Ref. 2, pp. 12—15. [c] Ref. 9.

TABLE 2

Carbonyl stretching frequencies, ν(C≡O) [a]

		$(RNC)Cr(CO)_5$		*cis*-$(RNC)_2M(CO)_4$				*fac*-$(RNC)_3M(CO)_3$	
R	M	A_1''	A_1',E	A_1	A_1'	B_1	B_2	A_1	E
Me	Cr	2071	1964	2022	1949	1934	1927		
	Mo			2022	1943	1931	1923 [b]	1957	1896 [b]
Et	Cr	2067	1961	2018	1945	1933	1926		
	Mo			2018	1941	1930	1921 [b]	1952	1895 [b]
Pr^i	Cr	2065	1960	2015	1943	1931	1925	1948	1898
	Mo			2018	1943	1933	1924	1949	1896
Bu^t	Cr	2063	1961	2012	1942	1931	1924	1944	1898
	Mo			2015	1942	1932	1923	1947	1896
p-$MeC_6H_4^-$	Cr	2058	1966	2011	1955	1944		1954	1923
	Mo			2013	1955	1944		1945	1920
p-$ClC_6H_4^-$	Cr	2053	1968	2018	1960	1949		1957	1933
	Mo			2018	1960	1949		1959	1932

[a] In n-hexane solution. [b] Ref. 9.

The isonitrile, ν(N≡C), stretching frequencies of the complexed ligands (Table 1) may be compared with those of the free ligand. For the $(RNC)Cr(CO)_5$ complexes it is found that ν(N≡C) (complex) is greater than ν(N≡C) (free) with Δν (complex-free) in the range +2 to +20 cm^{-1}. This difference is small compared to that

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[3] P. M. Treichel, J. J. Benedict, R. W. Hess, and R. P. Stenson, *Chem. Comm.*, 1970, 1627.

[4] E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 21; B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, 1970, **9**, 2021.

[5] J. W. Dart, M. K. Lloyd, J. A. McCleverty, and R. Mason, *Chem. Comm.*, 1971, 1197.

[6] H. D. Murdoch and R. Henzi, *J. Organometallic Chem.*, 1966, **5**, 166.

[7] R. B. King, 'Organometallic Syntheses,' Academic Press, London, 1965.

[8] F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, 1961, **83**, 351.

[9] M. Bigorgne and A. Bouquet, *J. Organometallic Chem.*, 1963, **1**, 101.

found in isonitrile adducts of the main group elements [*e.g.* in MeNC,BMe$_3$, $\Delta\nu = +89$ cm^{-1} (ref. 10)] in which compounds only σ-donation can be present. Such increases of ν(N≡C) on formation of a complex suggest an increase in the N–C bond order. With transition metals ($d \rightarrow \pi^*$) back bonding from the metal would tend to reduce the N–C bond order: that this is not observed in the (RNC)Cr(CO)$_5$ complexes suggests that the isonitrile ligands function largely, if not exclusively, as σ-donor ligands in this instance, albeit to a lesser degree than in the main-group element adducts. Similar conclusions have been drawn for the isonitrile complexes of iron(0).[11] The alternative explanation, that isomerisation to the nitrile has occurred, can be discounted as there is no absorption in the region 2300—2200 cm^{-1} (*cf.* [(MeCN)Cr(CO)$_5$] shows ν(C≡N) 2283 cm^{-1} [ref. 12]). The complexes *cis*-(RNC)$_2$M(CO)$_4$ (M = Cr, Mo) show two sharp bands of medium intensity in the region 2180—2070 cm^{-1}. These bands have been assigned to the A_1 (higher frequency) and B_1 (lower frequency) isonitrile stretching vibration modes.[9] The complexes *fac*-(RNC)$_3$M(CO)$_3$ (M = Cr, Mo) show two similar bands in the region 2175—2030 cm^{-1} which are assigned as A_1 and E modes in like manner. As the bulk of the substituent group, R, increases the E mode splits into two components whose relative intensities are variable.

TABLE 3

Ultraviolet and visible spectra in the region $\lambda_{\text{max.}} > 260$ nm

		(RNC)M(CO)$_5$				*cis*-(RNC)$_2$M(CO)$_4$						*fac*-(RNC)$_3$M(CO)$_3$					
R	M	$\lambda_{\text{max.}}$	log ε	$\lambda_{\text{max.}}$	log ε	$\lambda_{\text{max.}}$	log ε	$\lambda_{\text{max.}}$	log ε	$\lambda_{\text{max.}}$	log ε	log ε	max.	λ_{max}	log ε	$\lambda_{\text{max.}}$	log ε
Me	Cr			325	3·30					334	3·58						
Et	Cr			323	3·81					335	3·76						
Pr^i	Cr			333	3·34					341	3·81			293	4·30	346	3·74
	Mo							286	4·11	348	3·49			308	4·26	349	3·65
Bu^t	Cr			322	3·62					334	3·67			288	4·30	346	3·73
	Mo							284	4·08	348	3·42			308	4·36	349	3·78
p-MeC$_6$H$_4$–	Cr	289	4·54	337	4·26	274	4·85	303	4·77	353	4·61	298	4·10	361	4·20	377	4·28
	Mo					275	4·72	310	4·58	360	4·88	293	4·43	346	4·11	382	4·15
p-ClC$_6$H$_4$–	Cr	296	4·55	348	4·38	273	4·60	306	4·51	364	4·42	299	4·59	*		388	4·43
	Mo					273	4·56	313	4·38	367	4·15	298	4·94	366	4·69	391	4·79

* Masked by band having $\lambda_{\text{max.}}$ 388 nm.

Considering only the frequency of the A_1 ν(N≡C) mode in the complexes (RNC)$_x$M(CO)$_{6-x}$, it is observed that $\Delta\nu$(complex-free), decreases as x increases, becoming nearly zero for $x = 3$. This suggests that the electron density of the N≡C bond changes as the number of isonitrile ligands increases, becoming more like the free ligand itself.

The decrease in $\Delta\nu$ (complex-free) between complexes of alkyl isonitriles and those of aryl isonitriles for the same value of x, reflects the ability of the aromatic ring in the latter systems to conjugate with the $^-$N≡C bond. A simultaneous increase in the stretching frequency of the carbonyl groups *trans* to RNC ($x = 1$, 2) is also observed.

For analogous complexes of chromium and molybdenum it appears that the metal has no significant effect on either ν(N≡C) or ν(C≡O) for any pair of complexes. The geometries of the complexes ($x = 2, 3$) are confirmed by the pattern of carbonyl stretching frequencies (Table 2).

U.v. Spectra.—The alkyl isonitrile complexes (RNC)$_x$M(CO)$_{6-x}$ ($x = 1$, M = Cr; $x = 2, 3$, M = Cr, Mo) show two bands in the region 200—700 nm. The higher-energy band ($\lambda_{\text{max.}}$ *ca.* 245 nm) is the more intense (log ε *ca.* 4·4) and occurs at approximately the same energy in all the complexes; it is assigned to a ($L \rightarrow M$) charge transfer transition and shows a lot of fine structure. The lower-energy transition (log ε *ca.* 3·7) is assigned to a ($M \rightarrow L$) charge-transfer transition and varies slightly in energy with the nature of the group, R, and with the number of isonitrile ligands, x.[13] The results (Table 3) reflect the very weak π-acceptor properties of the alkyl isonitrile ligands and suggest that the σ-bonding strength decreases as x increases. The observed decrease in the energy of the ($M \rightarrow L$) charge-transfer transition on going from alkyl to aryl isonitrile complexes is consistent with the greater acceptor properties of the latter ligands.

Bands appear in the spectra of aryl isonitrile complexes at energies intermediate between the ($M \rightarrow L$) and ($L \rightarrow M$) charge-transfer transitions. These bands arise from transitions of the aromatic system and are similar to certain features in the spectra of heterocyclic carbene complexes.[13] The energy of the bands decrease as a result of complexing and also as the number of aryl isonitrile ligands per metal atom increases. This provides further evidence of conjugation between the aromatic system and both the –N≡C group and the metal atom in the complexes. Similar features in the spectra of alkyl isonitrile complexes, (RNC)$_2$Mo(CO)$_4$ and (RNC)$_3$M(CO)$_3$ (M = Cr, Mo), arise from the RNC ligands which show u.v. absorptions below 200 nm in the free state.[1,2]

The metal appears to have very little influence upon the position of the lower energy ($M \rightarrow L$) charge-transfer band in either of the two sets of complexes (RNC)$_x$M(CO)$_{6-x}$ ($x = 2, 3$; M = Cr, Mo). This is consistent with the conclusions drawn from i.r. spectroscopy.

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[10] J. Casanova and R. E. Schuster, *Tetrahedron Letters*, 1964, 405.

[11] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1960, 1440.

[12] B. L. Ross, J. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, 1963, **2**, 1023.

[13] J. A. Connor and E. M. Jones, *J. Chem. Soc.* (*A*), 1971, 1974, 3368; and unpublished work.

N.m.r. Spectra.—The formation of an isonitrile complex results in the disappearance [2] of the $^2J(^{14}N-^1H)$ coupling which is consistent with evidence already presented to show that charge separation is increased by the formation of a complex.

Comparison of the spectra of alkyl isonitriles and their complexes, $LCr(CO)_5$, in deuteriochloroform solution shows that all hydrogens experience a deshielding effect on formation of a complex. This effect is more pronounced for hydrogens which are α- to nitrogen than for β-hydrogens. Deshielding of the α-protons in the increasing order $Pr^i < Et < Me$ demonstrates the shielding caused by β-methyl substituents. In benzene solution the protons of the R group in the complex are more shielded than in the pure isonitrile, RNC, in contradistinction to the observations in chloroform solution. It is possible that the deshielding of the alkyl protons in the complexes might be due to extra long-range shielding effects from the $M(CO)_n$ group.

TABLE 4

N.m.r. chemical and ASI shifts for the complexes (Hz) at 60 MHz

			RNC		$(RNC)M(CO)_5$		*cis*-$(RNC)_2M(CO)_4$		*fac*-$(RNC)_3M(CO)$	
R		M	δ	Δ	δ	Δ	δ	Δ	δ	Δ
Me	CH_3	Cr	−187	51	−206	106				
Et	CH_3	Cr	−79	26	−86	61	−83	50		
	CH_2		−205	32	−218	80	−215	64		
Pr^i	CH_3	Cr	−82	25	−85	51	−84	40	−82	34
	CH		−227	30	−237	66	−236	52	−233	46
Bu^t	CH_3	Cr	−86	24	−88	41	−87	32	−86	23
		Mo					−87	34	−87	26
p-MeC_6H_4−	CH_3	Cr	−142	29	−143	33	−141	33	−140	30
		Mo					−142	34	−141	32
	C_6H_4	Cr	−433	27	−433	42	−432	36	−431	29
		Mo					−434	39	−438	34
p-ClC_6H_4−	C_6H_4	Cr	−440	49	−440	55				

δ Refers to $CDCl_3$ solution. Δ Refers to $[\delta(C_6D_6) - \delta(CDCl_3)]$

TABLE 5

Relative abundances of ions in fragmentation of $[(RNC)Cr(CO)_5]$

Ion	R:	Me	Et	Pr^i	Bu^t	p-MeC_6H_4	p-ClC_6H_4 [a]	X [b]
$(CO)_5Cr(CNR)^+$		14	16(—) [c]	13 (1)	16 (1)	14	19	37
$(CO)_4Cr(CNR)^+$		1	1 (1)	1 (5)	1 (10)	1	1	2
$(CO)_3Cr(CNR)^+$		1	1 (—)	2 (2)	4 (3)	8	9	2
$(CO)_2Cr(CNR)^+$		2	2 (—)	2 (2)	3 (4)	8	10	2
$(CO)Cr(CNR)^+$		25	19 (—)	18 (2)	18 (3)	15	25	30
$Cr(CNR)$		100	100 (2)	100 (2)	100 (4)	100	100	100
$Cr(CNH)^+$		4	11	8	100	1	2	1
$Cr(CN)^+$		20	25	47	20	5	7	9
Cr^+		100	73	22	27	60	69	80
L^+		112	6	28	1	40	16	900
R_I		2·3	2·6	2·7	2·4	2·2	1·6	1·4

[a] Abundance measured on ^{35}Cl isotope peaks only. [b] $X = [(MeCN)Cr(CO)_5]$. [c] Values in brackets refer to abundance of $(ion-15)^+$ (β-fission).

Investigations of aromatic solvent induced shifts (ASIS) in organic compounds [14] and in certain organometallic complexes [13] have suggested that the benzene solvent molecule interacts with centres of positive charge in the solute. The results (Table 4) show that the value of the ASIS parameter, Δ, for each type of hydrogen in an alkyl isonitrile is much greater in the complex $(RNC)Cr(CO)_5$ than in the free ligand. This suggests that there may be a greater positive charge on the nitrogen atom in the complex. The value of Δ for α-hydrogens is greater than for β-hydrogens which is consistent with the former being closer to the centre of interaction. In both the complexed and free alkyl isonitriles the value of Δ for both α- and β-protons decreases in the order $Me > Et > Pr^i > Bu^t$. This order is consistent with the stereo-electronic effect of additional methyl groups which tend to shield the α-protons and to weaken the solute–solvent interaction. Similar but smaller ASIS effects are observed for aryl isonitriles and their complexes. There is a satisfactory correlation between the conclusions drawn from ASIS measurements and the results of dipole-moment measurements on $C_6H_{11}NC$ ($\mu = 3{\cdot}5$ D) [15] and its complex $[(C_6H_{11}NC)Cr(CO)_5]$ ($\mu = 5{\cdot}62$ D).[16]

As the number of isonitrile ligands per metal atom increases the value of $\delta(CDCl_3)$ decreases, becoming closer to its value in the free ligand, but this change is much less spectacular than the concomitant change in Δ. The value of Δ in the complexes $(RNC)_3M(CO)_3$ (M = Cr, Mo) is close to that in the free ligand. Changing the metal atom has no significant effect upon either δ or Δ. These results establish that the positive charge on the ligand decreases with increasing substitution.

Mass Spectra.—(a) $[(RNC)Cr(CO)_5]$ *Compounds.* The primary fragmentation of these molecules (Table 5) is

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[14] P. Laszlo, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 231.

[15] R. G. A. New and L. E. Sutton, *J. Chem. Soc.*, 1932, 1415.

[16] W. Strohmeier and H. Hellmann, *Ber. Bunsengesellschaft Phys. Chem.*, 1964, **68**, 481.

similar to that of other $LCr(CO)_5$ molecules.[17] The parameter R_I, defined in the usual manner,[18] reflects the σ-donor : π-acceptor ratio of a ligand, L. In agreement with this, the values of R_I for complexes of aryl isonitriles are less than for those of alkyl isonitriles. The strong donor property of methyl isonitrile is stressed when the values of R_I for $[(MeNC)Cr(CO)_5]$ and $[(MeCN)Cr(CO)_5]$ are compared.

(b) $[(RNC)_2M(CO)_4]$ *Compounds*. Fragmentation involves the sequential loss of four carbonyl groups to give ML_2^+ which then loses one L to give ML^+ (assigned a relative abundance of 100) (Table 6). Carbon monoxide is lost in preference to the ligand L which indicates that the $L_2M(CO)_x^+$ ion formed after fragmentation is more stabilised than if the $LM(CO)^+_{x+1}$ ion were to be formed. This would appear to be the result of delocalisation of the positive charge through the –N≡C bond.

TABLE 6

Relative abundances of ions in fragmentation of *cis*-$(RNC)_2M(CO)_4$

R:	Me	Et	Pr^i		Bu^t		*p*-MeC_6H_4–		*p*-ClC_6H_4 [a]	
Ion M:	Cr	Cr	Cr	Mo	Cr	Mo	Cr	Mo	Cr	Mo
$(CO)_4M(CNR)_2^+$	33	43 (—) [b]	27 (—)	63 (—)	100 (4)	158 (—)	19	2	14	1
$(CO)_3M(CNR)_2^+$	2	0·3 (0·3)	0·5 (6)	15 (15)	1 (50)	27 (69)		2		1
$(CO)_2M(CNR)_2^+$	3	1 (0·2)	2 (—)	80 (24)	6 (2)	142 (100)	1	3	1	4
$(CO)M(CNR)_2^+$	3	1 (2)	3 (7)	60 (15)	9 (23)	116 (26)	6	3	6	4
$M(CNR)_2^+$	100	60 (—)	191 (6)	330 (18)	356 (56)	427 (11)	160	9	119	32
$(NC)M(CNR)^+$	9	12	14	54		206			2	
$(CO)_3M(CNR)^+$								27		36
$(CO)_2M(CNR)^+$								70		71
$(CO)M(CNR)^+$								63		67
$M(CNR)^+$	100	100 (—)	100 (—)	100 (57)	100 (26)	100 (—)	100	100	100	100
$M\ CN^+$	26	30	18	54	69	111	6	13	10	26
M^+	47	40	18	21	100	37	68	50	62	79
L^+	88	5	19	36	9	4	23	77	21	83

[a] Refers to ^{35}Cl isotope peaks only. [b] Values in brackets refer to abundance of (ion-15)$^+$ (β-fission).

The absence (M = Cr) or very low relative abundance (M = Mo) of the $L_2M(CO)_3^+$ ion from the spectra of the aryl isonitrile complexes is similar to certain features of the mass spectra of the carbene complexes, $[(CO)_5Cr\ C(2\text{-furyl})(XPh)]$ (X = O, S), which show no $[(CO)_3Cr$ carbene$]^+$ ion.[19] In these latter instances this is thought to be due to stabilisation of the $[(CO)_2Cr$ carbene$]^+$ ion by the formation of a π-bonded arene ring, Figure 1(a). This hypothesis has received strong support from a study of the structure of the thermal decomposition product of $[(dam)Cr(CO)_5]$ which is $[(dam)Cr(CO)_2]$ in which one phenyl ring is π-bonded to the metal atom.[20] In the present instance stabilisation of the $[L_2M(CO)_2]^+$ ion may be visualised in terms of a structure such as Figure 1(b). π-Arene complexes of aryl isonitriles have not been described. The spectra of the molybdenum complexes are complicated by the presence of ions arising from $[(RNC)Mo(CO)_5]$ and $[(RNC)_3Mo(CO)_3]$ complexes which are formed from $(RNC)_2Mo(CO)_4$ at temperatures in the range 130—150°. Such a relatively high source temperature was necessary to achieve vaporisation of these complexes.

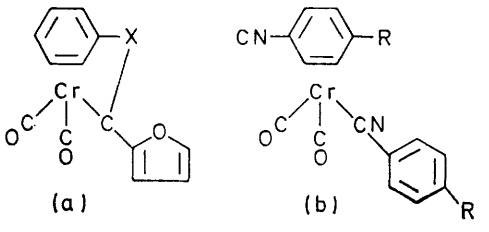

FIGURE 1

(c) $[(RNC)_3M(CO)_3]$ *Compounds*. Once again, carbonyl ligands are lost in preference to isonitrile ligands (Table 7). The elevated source temperatures required for the production of the spectra result in extensive thermal decomposition, especially of the molybdenum compounds. This problem is more severe for aryl than for alkyl isonitrile complexes.

(d) *Fragmentation of the Co-ordinated Isonitrile*.—The mass spectra of alkyl isonitriles show that both α- and β-fragmentation are important.[21] Similar behaviour is found in the complexes considered here (Tables 5—7). α-Cleavage is particularly dominant in complexes of Bu^tNC and this reflects the stability of the Me_3C^+ ion. β-Cleavage is observed not only in the ions ML^+ and ML_2^+ but also in the carbonyl-containing ions $(CO)_{5-x}CrL^+$ (x = 0—5), $(CO)_{4-x}ML_2^+$ (x = 0—4) and $(CO)_{3-x}ML_3^+$ (x = 0—3). The extent of β-cleavage decreases in the order $Bu^t > Pr^i >$ Et, as stabilisation of the resulting ions, either by the inductive effect of the methyl group or by conjugation with the metal, is reduced. The observation of α-cleavage to give $ML(CN)^+$ and $ML_2(CN)^+$ ions is similar to that reported in the mass spectrum of $(\pi\text{-}C_5H_5)(CO)_2Mn(CNC_6H_{11})$ [18] where β-cleavage is not possible.

Voltammetry.—All the compounds described here

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[17] J. Müller and J. A. Connor, *Chem. Ber.*, 1969, **102**, 1148.

[18] J. Müller and M. Herberhold, *J. Organometallic Chem.*, 1968, **13**, 399.

[19] J. A. Connor and E. M. Jones, *J. Organometallic Chem.*, 1971, **31**, 389.

[20] G. B. Robertson, P. O. Whimp, R. Colton, and C. J. Rix, *Chem. Comm.*, 1971, 573.

[21] R. G. Gillis and J. Occolowitz, *J. Org. Chem.*, 1963, **28**, 2924.

TABLE 7

Relative abundances of ions in fragmentation of *fac*-(RNC()$_3$MCO)$_3$

Ion	R:	Pr^i		Bu^t		p-MeC$_6$H$_4$		p-ClC$_6$H$_4$ [a]	
	M:	Cr	Mo	Cr	Mo	Cr	Mo	Cr	Mo
$(CO)_3M(CNR)_3^+$		10 (—) [b]	13 (1)	15 (—)	30 (—)	0·3	0·2	0·2	
$(CO)_2M(CNR)_3^+$		0·3 (—)	3 (—)	0·1 (—)	9 (6)	0·2	0·2	0·1	
$(CO)M(CNR)_3^+$		0·5 (—)	28 (—)	0·2 (—)	93 (15)		1		0·5
$M(CNR)_3^+$		5 (3)	23 (—)	11 (5)	41 (4)	1	1	0·1	1
$(CO)_4M(CNR)_2^+$			8 (—)			12	16	11	22
$(CO)_3M(CNR)_2^+$						1	12	1	15
$(CO)_2M(CNR)_2^+$			10 (3)			3	42	3	46
$(CO)M(CNR)_2^+$			9 (—)		13 (—)	3	27	4	36
$M(CNR)_2^+$		100 (4)	100 (—)	100 (—)	100 (—)	100	100	100	100
$(NC)M(CNR)_2^+$		6	12	6	26				
$(NC)M(CNR)^+$		6	13	3	50	3		4	
$M(CNR)^+$		45	25	6	13	93	100	182	91
$M(CN)^+$		5	13	3	11	8	7	32	18
M^+		5	5	3	4	67	58	187	318

[a] Refers to ^{35}Cl isotope peak only. [b] Values in brackets refer to abundance of (ion-15)$^+$ (β-fission).

undergo a one-electron oxidation, in dichloromethane, at a rotating platinum electrode. In most of the cases studied, this oxidation is accompanied by a coupled chemical reaction; the nature and products of these coupled chemical reactions will be discussed at a later date. A number of oxidations, particularly those of molybdenum complexes, were accompanied by electrode coating, thereby making the extraction of useful data difficult.

The half-wave potential (Table 8) for the general reaction

$$[(RNC)_nM(CO)_{6-n}]^\circ \rightleftharpoons [(RNC)_nM(CO)_{6-n}]^+ + e^-$$

was found to depend upon R, M, and n. Thus, there is an increase in $E_{\frac{1}{2}}$ in going from a complex containing an alkyl isonitrile to one containing an aryl isonitrile ligand which is consistent with the superior π-acceptor capacity of the latter. Within the aryl isonitrile series of complexes, the marked difference in $E_{\frac{1}{2}}$-values between those species containing R = p-ClC$_6$H$_4$ and those with R = p-MeC$_6$H$_4$ can readily be understood in terms of the inductive and/or mesomeric effects of the *para*-substituents on the benzene rings. However, within a given series of isonitrile complexes varying only in their alkyl substituents (R = Me, Et, Pr^i, Bu^t), there is no significant difference in $E_{\frac{1}{2}}$-values, suggesting that, as far as these complexes are concerned, alkyl isonitrile ligands are 'electronically' alike and that there is no steric effect operating on $E_{\frac{1}{2}}$.

There is a significant difference (*ca.* 200 mV) between the $E_{\frac{1}{2}}$-values obtained from the series of chromium complexes and their molybdenum analogues, indicating that there is a substantial metal effect on $E_{\frac{1}{2}}$. This implies that the redox orbital consists not only of considerable ligand (CNR) character but also of a substantial metal contribution. A comparison of the data obtained from [(Bu^{t}NC)$_2$M(CO)$_4$] and [(Bu^{t}NC)$_3$M(CO)$_3$] (M = Cr, Mo, W *) reveals that the ease of oxidation of these compounds decreases in the order M = Cr > W > Mo.

As n, in [(RNC)$_n$M(CO)$_{6-n}$], increases, $E_{\frac{1}{2}}$-values decrease reflecting the stepwise replacement of a good π-acceptor (CO; high $E_{\frac{1}{2}}$) by a less effective one (CNR). This is consistent with the decrease in the A_1 (ν_{CO}) stretching frequency as n increases in these compounds.

TABLE 8

Voltammetric data obtained from metal carbonyl isonitrile complexes [M(CNR)$_n$(CO)$_{6-n}$]

			Voltammetry			Cyclic voltammetry		
M	n	R	$E_{\frac{1}{2}}$ [a]	R [b]	D [c]	E_{p_1} [d]	E_{p_2} [d]	Comments [e]
Cr	1	Me	1·10	58	9 [f]			R.
		Et	1·09	50	34	1·20	0·94	R.
		Pr^i	1·09	80	32	1·17	0·95	R.
		Bu^t	1·09	85	35	1·20	1·00	C.C.R. (R)
		p-MeC$_6$H$_4$	1·14	60	32	1·23	1·03	C.C.R. (R)
		p-ClC$_6$H$_4$	1·16	58	32	1·25	1·06	C.C.R. (R)
	2	Me	0·59	89	32	0·67	0·49	R.
		Et	0·57	75	34	0·67	0·43	R.
		Pr^i	0·58	74	33	0·65	0·45	R.
		Bu^t	0·57	62	34	0·65	0·49	C.C.R. (R)
		p-MeC$_6$H$_4$	0·67	67	32	0·76	0·60	C.C.R. (R)
		p-ClC$_6$H$_4$	0·76	65	36	0·82	0·67	C.C.R. (R)
	3	Pr^i	0·20	74	37	0·24	0·08	C.C.R. (R)
		Bu^t	0·19	74	35	0·24	0·09	C.C.R. (R)
		C$_6$H$_{11}$	0·20	76	36	0·25	0·09	C.C.R. (R)
		p-MeC$_6$H$_4$	0·40	75	36	0·45	0·29	C.C.R. (R)
		p-ClC$_6$H$_4$	0·51	70	35	0·60	0·41	R.
Mo	2	Pr^i	0·80	101	39	Yes [g]	No	E.C.
		Bu^t	0·80	87	36	Yes	No	E.C.
		C$_6$H$_{11}$	0·78	79	35	Yes	No	E.C.
		p-MeC$_6$H$_4$	0·89	93	38	Yes	No	E.C.
		p-ClC$_6$H$_4$	0·98	60	35	1·05		E.C.
	3	Pr^i	0·40	87	35	0·42		E.C.
		Bu^t	0·40	109	42	0·42		I.
		C$_6$H$_{11}$	0·40	72	38	0·43	0·18	C.C.R. (R)
		p-MeC$_6$H$_4$	0·56	75	39	0·59	0·37	C.C.R. (R)
		p-ClC$_6$H$_4$	0·68	100	37	0·69	0·48	C.C.R. (R)

[a] In V, at rotating Pt electrode; in dichloromethane; all solutions 10^{-3}M in complex and 0·05M in [Et$_4$N][ClO$_4$]; data quoted *vs.* SCE 1M in aqueous LiCl; estimated error ±10 mV and, where necessary, results corrected for iR drop; data recorded at 20 ± 2°. [b] Reversibility criterion, $R = E_{\frac{3}{4}} - E_{\frac{1}{4}}$, in mV; for a reversible, one-electron process, R = 59 mV. [c] $D = i_d/C$ in μA/mM (calculated for n = 1); for the one-electron process $[Ni\{S_2C_2(CN)_2\}_2]^- + e^- \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{2-}$, D = 30·5 at the electrode used in this work. [d] Peak positions for anodic and cathodic scans in cyclic voltammograms; sweep rate = 0·05 V/s; data obtained in dichloromethane using stationary Pt wire. [e] Data reversible (R), or quasi-reversible with a coupled chemical reaction (C.C.R.), irreversible (I) or obscured by electrode coating (E.C.). [f] Data from *J. Organometallic Chem.*, 1971, **30**, C75. [g] Anodic peak detected but, because of coating at electrode, cathodic peak absent.

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* Only the Bu^t complexes of tungsten were prepared, and the bis- and the tris-substituted compounds were not separated.

Not unexpectedly, the $E_{\frac{1}{2}}$-values for the aryl isonitrile complexes decrease by less, as n increases, than those in the corresponding alkyl isonitrile compounds. The substituent effect, defined by $|E_{\frac{1}{2}}(\text{average aryl}) - E_{\frac{1}{2}}(\text{average alkyl})|$, in $[(RNC)M(CO)_5]$ is much smaller (60 mV) than that in $[(RNC)_2M(CO)_4]$ (140 mV) or in $[(RNC)_3M(CO)_3]$ (260 mV), which suggests that, in the monosubstituted complexes, the isonitrile ligand plays a minimal role as a π-acceptor whereas in the bis- and particularly in the tris-substituted species, the increase in charge donated to the metal can only be released effectively by $(d \rightarrow \pi^*)\pi$ donation from the metal to both the CO and the CNR ligands.

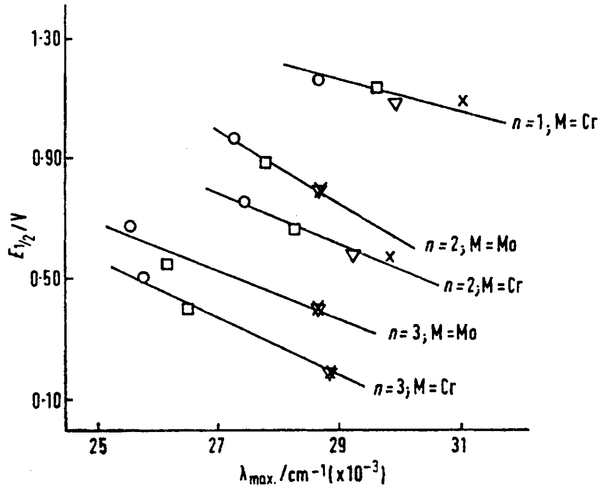

FIGURE 2 Plot of $E_{\frac{1}{2}}$ *vs.* S.C.E. against $\lambda_{max.}$/cm^{-1} ($\times 10^{-3}$) [M → CNR] charge-transfer band for the complexes $[(RNC)_nM(CO)_{6-n}]$ ▽, R = Pr^i; ×, R = Bu^t; □, R = p-MeC$_6$H$_4$; ○, R = p-ClC$_6$H$_4$

The half-wave potentials in certain iron complexes have been correlated with the metal-to-ligand charge-transfer bands in their electronic spectra.[22] A plot of $E_{\frac{1}{2}}$ *vs.* the energy of the (M → CNR) charge-transfer band in the $[(RNC)_nM(CO)_{6-n}]$ complexes is shown in Figure 2. In the absence of unusual variations in the free energies of solvation, the oxidation potentials of the complexes should provide a measure of the energy of the highest filled molecular orbital in the molecules (redox orbital), whence a linear relationship between $E_{\frac{1}{2}}$ and the (M → CNR) charge transfer energy was to be expected.

Reactions with Bases.—The addition of amines (RNH_2, R_2NH) or alcohols to solutions of $[(MeNC)Cr(CO)_5]$ in hexane does not result in nucleophilic substitution of the type described by Badley *et al.*,[4] the components were re-isolated unchanged. When a stronger base, butyllithium, was used a vigorous reaction took place. Methylation (with trimethyloxonium tetrafluoroborate) of the product, which may be expected to contain either or both of the anions $[(CO)_5CrC(Bu)NMe]^-$ and $[(CO)_4(MeNC)CrC(O)Bu]^-$, gave a complex mixture of products which we are still studying.

Treatment of the complex *cis*-$[(Bu^tNC)_2Cr(CO)_4]$ with the diphosphine, $(Me_2PCH_2)_2$(dmpe), in ether or in ethanol at reflux did not result in displacement of either isonitrile or carbonyl ligands after several hours. Subsequently the complex was heated in an excess of the pure dmpe at 100°. Reaction proceeded slowly and after 80 h the products, in addition to unchanged starting material, consisted of *cis*-$[(Bu^tNC)_2(CO)_2Cr(dmpe)]$ and $[(dmpe)_2Cr(CO)_3]$ which may have the *fac*-configuration.

The addition of an organosilicon hydride, R_3SiH, to an isonitrile to give a *C*-silyl ketimine, $R_3SiCH{:}NR$, is known to be catalysed by transition-metal compounds.[23] Treatment of $[(EtNC)Cr(CO)_5]$ with Et_3SiH in the presence of pyridine at reflux for 14 days did not lead to the formation of any $Et_3SiCH{:}NEt$. Instead $[(EtNC)Cr(CO)_5]$ (40%) was recovered together with *cis*-$[(EtNC)_2Cr(CO)_4]$ and *cis*-$[(py)_2Cr(CO)_4]$. The yield of bis-isonitrile complex based on the amount of starting material consumed according to the equation,

$$2C_5H_5N + 2[(EtNC)Cr(CO)_5] \longrightarrow [(EtNC)_2Cr(CO)_4] + [(C_5H_5N)_2Cr(CO)_4] + 2CO$$

is almost quantitative. These reactions establish that the isonitrile complexes $[(RNC)_xCr(CO)_{6-x}]$ ($x = 1, 2$) are remarkably insensitive to ligand displacement reactions and also to nucleophilic attack by weak bases.

General Conclusions.—From the preceding discussion it is clear that there is no firm evidence of a net π-acid character in the isonitrile ligands in this series of compounds. This is in contrast to the well established behaviour of carbon monoxide which is a strong π-acceptor and weak σ-donor ligand.[24] All the present results can be explained either by a gradual variation in the σ-donor strength of the isonitrile or by a similar variation in the σ-acceptor strength of the metal. The evidence in favour of the variable behaviour of the isonitrile ligand is strong and ASIS measurements have been especially helpful in this context.

EXPERIMENTAL

Materials and Methods.—Methyl, ethyl, isopropyl, t-butyl, *p*-tolyl, and *p*-chlorophenyl isonitrile were prepared by standard methods.[25] Norbornadiene(tetracarbonyl)-molybdenum,[7] cycloheptatrienetricarbonyl-chromium and -molybdenum,[8] and tetraethylammonium iodopentacarbonylchromate [6] were prepared and purified, and then dried and purged with dioxygen-free dinitrogen before use.

I.r. spectra were recorded in hexane solution (0·5-mm cells) on a Perkin-Elmer 521 grating spectrometer. U.v./-visible spectra were recorded in hexane solution on a Unicam SP 800 instrument. N.m.r. spectra were measured on a Perkin-Elmer R12A 60 MHz instrument using $CDCl_3$ and C_6D_6 as solvents and tetramethylsilane as an internal standard. Mass spectra were recorded on an AEI MS 12

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instrument with a nominal beam energy of 70 eV. Voltammetric data was obtained using a Beckman Electroscan 30 polarograph, using carefully purified dichloromethane as solvent and a Pt electrode rotating at 620 rev. min^{-1}.

Further information concerning the yields, appearance, melting point, and analyses of the compounds $[(RNC)_nCr(CO)_{6-n}]$ (n = 1, 2) which were prepared by the method of Murdoch,[6] is collected in Table 9, together with similar information for the other new compounds.

TABLE 9

Analysis, melting point, and appearance of the $(RNC)_nM(CO)_{6-n}$ complexes.

R	n	Formula	Analyses % found (% required) C	H	N	Cr	M.p. (°C)	Yield	Appearance
Chromium complexes									
Me	1	$C_7H_3CrNO_5$	36·2 (36·0)	1·1 (1·3)	6·3 (6·0)	22·3 (22·3)	68—69	50	White needles
	2	$C_8H_6CrN_2O_4$	39·4 (39·0)	2·2 (2·4)	11·7 (11·4)	21·0 (21·1)	137—138	21	White needles
Et	1	$C_8H_5CrNO_5$	38·4 (38·9)	1·9 (2·0)	6·1 (5·7)	20·6 (21·0)	31—32	48	Colourless needles
	2	$C_{10}H_{10}CrN_2O_4$	46·4 (43·8)	4·1 (3·7)	10·1 (10·2)	18·7 (19·0)	80—81	24	Colourless needles[a]
Pr^i	1	$C_9H_7CrNO_5$	41·4 (41·5)	2·5 (2·7)	5·6 (5·4)	20·1 (19·9)	47—48	64	Yellow needles
	2	$C_{12}H_{14}CrN_2O_4$	46·6 (47·6)	4·4 (4·6)	9·3 (9·3)	17·2 (17·2)	96—97	27	Colourless needles
	3	$C_{15}H_{21}CrN_3O_3$	52·5 (52·5)	6·7 (6·1)	12·0 (12·2)		97—98	72	Colourless plates
Bu^t	1	$C_{10}H_9CrNO_5$	43·0 (43·7)	3·2 (3·3)	5·4 (5·1)	18·8 (18·9)	99—100	34	Colourless needles
	2	$C_{14}H_{18}CrN_2O_4$	51·0 (51·0)	5·6 (5·5)	8·5 (8·5)	15·6 (15·8)	124—125	25	Colourless needles
	3	$C_{18}H_{27}CrN_3O_3$	56·5 (56·1)	7·5 (7·0)	10·9 (10·9)		166—167	78	Colourless plates
p-MeC_6H_4-	1	$C_{13}H_7CrNO_5$	50·6 (50·4)	2·1 (2·3)	4·5 (4·5)	16·8 (16·8)	116—117	45	Colourless needles
	2	$C_{20}H_{14}CrN_2O_4$	60·3 (60·2)	3·4 (3·5)	7·0 (7·0)	13·6 (13·1)	147—149	11	Yellow needles
p-ClC_6H_4	1	$C_{12}H_4ClCrNO_5$	50·1 (43·8)	3·0 (1·2)	6·7 (4·3)	7·8 (15·8)	94—95	73	Colourless needles[a]
	2	$C_{18}H_8Cl_2CrN_2O_4$	48·9 (49·2)	1·7 (1·8)	6·4 (6·4)	11·7 (11·8)	171—172	10	Yellow-green needles
	3	$C_{24}H_{12}Cl_3CrN_3O_3$	52·5 (52·8)	2·2 (2·1)	7·7 (7·5)		125—127		Yellow needles
Molybdenum complexes									
Bu^t	2	$C_{14}H_{18}MoN_2O_4$	45·0 (44·9)	4·5 (4·8)	7·9 (7·5)		127—128	*ca.* 65	Yellow needles
	3	$C_{18}H_{27}MoN_3O_3$	49·9 (50·3)	6·5 (6·3)	9·8 (9·8)		178—180	*ca.* 65	Yellow needles
p-MeC_6H_4-	2	$C_{20}H_{14}MoN_2O_4$	54·6 (54·3)	3·1 (3·2)	6·1 (6·3)		137—139	*ca.* 65	Yellow needles
p-ClC_6H_4-	2	$C_{18}H_8Cl_2MoN_2O_4$	44·7 (44·6)	1·7 (1·7)	5·8 (5·9)		164—165	*ca.* 65	Yellow needles
	3	$C_{24}H_{12}Cl_3MoN_3O_3$	48·5 (48·6)	2·6 (2·0)	6·9 (7·1)		129—130	*ca.* 65	Yellow needles

[a] Analytical figures poor: compound photosensitive producing free isonitrile.

Preparation of $[(p\text{-}Cl\text{-}C_6H_4NC)_2Mo(CO)_4]$.—Norbornadiene(tetracarbonyl)molybdenum (0·6 g, 2 mmol) was dissolved in light petroleum and stirred under nitrogen. p-Chlorophenyl isonitrile (0·54 g, 6 mmol) dissolved in ether (10 ml) was added dropwise to the stirred solution. A yellow precipitate of the *complex* was formed immediately. The solution was stirred for a further 10 min to complete precipitation; the mixture was then filtered. The solid was recrystallised from chloroform–hexane and obtained as a yellow crystalline complex (0·64 g, 66%).

Reaction of cis-$[(Bu^tNC)_2Cr(CO)_4]$ *with* dmpe.—Tetramethyldiphosphinoethane[26] (0·6 ml, 3·1 mmol) was added to *cis*-$[(Bu^tNC)_2Cr(CO)_4]$ (0·1 g, 0·3 mmol) and the mixture was heated at 100° (oil-bath) for 80 h. The excess of dmpe was removed by distillation and the residue was sublimed. Fractional sublimation of the volatile material succeeded in partially separating two products. The more volatile was shown by mass spectrometry to be, most probably, $[(dmpe)_2Cr(CO)_3]$ (m/e, I: 436, 21; 408, 4; 352, 100, also metastable at 303·6 corresponding to $408 \longrightarrow 352 + 2 \times 28$). The less-volatile material which was present in greater amounts and was obtained in a pure state, was shown to be *cis*-$[(Bu^tNC)_2(CO)_2Cr(dmpe)]$ [i.r. (hexane) 2089, 2043 (νNC), 1934, 1870 (νCO) cm^{-1}; mass spectrum (m/e, I) 424, 0·1; 396, 0·1; 368, 17; 285, 67; 228, 100, also metastable at 319·3 corresponding to $424 \longrightarrow 368 + 2 \times 28$; n.m.r. ($CDCl_3$) δ 1·35 p.p.m. (s, CMe_3), 1·0—2·0 p.p.m. (complex multiplet)].

Attempted Preparation of $Et_3SiCH{:}NEt$.—Triethylsilane (0·27 g, 2·2 mmol) and pyridine (0·9 ml, 8 mmol) were added to a solution of $[(EtNC)Cr(CO)_5]$ (0·5 g, 2·0 mmol) in hexane. The reaction mixture was heated at reflux for 14 days, after which the hexane soluble fraction was extracted and all solvents were removed under reduced pressure. The benzene soluble extracts of this fraction were separated by chromatography (silica) to give $[(EtNC)Cr(CO)_5]$ (0·2 g, 0·8 mmol) and *cis*-$[(EtNC)_2Cr(CO)_4]$ (0·11 g, 0·4 mmol). The hexane-insoluble residue was shown to be $[(pyridine)_2Cr(CO)_4]$ (0·11 g, 0·35 mmol) by i.r. spectroscopy and elemental analysis.

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