Isonitrile Complexes of Osmium and their Reactions to give Hydride, Amine, and Carbene Complexes

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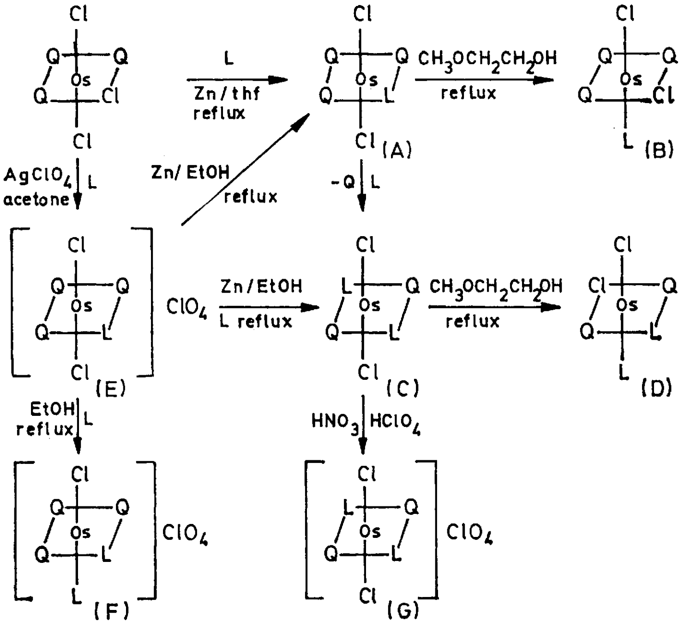
Uncharged and cationic isonitrile complexes of osmium of the types $[OsCl_2(RNC)_2(PR^1_3)_2]$, $[OsCl_2(RNC)(PMe_2Ph)_3]$, $[OsBr_2(MeNC)_4]$, $[OsCl_2(RNC)(PR^1_3)_3]ClO_4$, $[OsCl_2(RNC)_2(PR^1_3)_2]ClO_4$, $[OsCl(RNC)_2(PR^1_3)_3]ClO_4$, and $[Os(MeNC)_6](ClO_4)_2$ (R = Me, Ph, p-$MeOC_6H_4$, or p-$NO_2C_6H_4$; PR^1_3 = PMe_2Ph, PEt_2Ph, $PBu^n{}_2Ph$, or PEt_3) and the carbonyl–isonitrile complexes $[OsCl_2(CO)(PhNC)(PEt_3)_2]$, $[OsCl(CO)(RNC)(PR^1_3)_3]ClO_4$ (R = Me or Ph; PR^1_3 = PMe_2Ph or PEt_3) and $[OsCl_2(CO)(PhNC)(PEt_3)_2]ClO_4$ have been prepared. Some of the above compounds react with sodium borohydride or appropriate primary amines to give the compounds $[OsHCl(PhNC)(PMe_2Ph)_3]$ and $[OsCl_2(R^2NH_2)(PhNC)(PEt_3)_2]$ (R^2 = Me or Et), the bis-carbene complex $[Os(MeNC)_4\{C(NHMe)_2\}_2](ClO_4)_2$ and the tris-carbene complex $[Os(MeNC)_3\{C(NHMe)_2\}_3](ClO_4)_2$. A few ruthenium complexes of the type $[RuCl_2(RNC)_2(PR^1_3)_2]$ (PR^1_3 = PMe_2Ph, $PPr^n{}_2Ph$, or PBu^nPh) were also prepared and did not react with amines or alcohols. ^1H N.m.r. and i.r. data are used to assign the configuration of the above compounds.

The reactivity towards nucleophiles of ligating isonitrile correlates with the magnitude of the increase of its N≡C stretching frequency on co-ordination.

WHEN co-ordinated in certain metal complexes, isonitriles are susceptible to attack by nucleophilic reagents such as alcohols and amines, to give carbene complexes.[1,2] Kinetic studies have shown that nucleophilic attack is at the relatively electron-deficient isonitrile atom.[3,4] Prominent amongst the metals promoting this reaction are platinum(II),[1] palladium(II),[3] iron(II),[5] and rhodium(I),[6] and the frequency of the N≡C stretching mode of ligating isonitrile [ν(N≡C)] in their reactive complexes is considerably higher than for the free isonitriles. Other isonitrile complexes, where ν(N≡C) does not rise appreciably, *e.g.* those of molybdenum(0)[7] do not show this reactivity.

To gain further information on the necessary requirements for activation of ligating isonitriles, particularly that of the nature of the metal, we have prepared a series of octahedral complexes of osmium in which the metal oxidation state, the charge on the complex, and the nature of the co-ligands can all be varied and we have examined their reactivity towards nucleophilic



SCHEME Preparation of osmium isonitrile complexes
(Q = PMe_2Ph, PEt_2Ph, PBu^nPh, or PEt_3; L = MeNC, PhNC, p-$MeOC_6H_4NC$, p-$NO_2C_6H_4NC$, or CO)

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[1] 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.

[2] L. Busetto, A. Palazzi, B. Crociani, U. Belluco, E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J.C.S. Dalton*, 1972, 1800.

[3] B. Crociani, T. Boschi, M. Nicolini, and U. Belluco, *Inorg. Chem.*, 1972, **11**, 1292.

[4] J. Chatt, R. L. Richards, and G. H. D. Royston, *Inorg. Chim. Acta*, 1972, **6**, 669.

[5] R. J. Angelici and R. M. Charley, *J. Organometallic Chem.*, 1970, **24**, 205.

[6] P. R. Branson and M. Green, *J.C.S. Dalton*, 1972, 1303.

[7] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J.C.S. Dalton*, 1972, 1246.

reagents such as primary amines, sodium borohydride, and alkoxide ion.

Preparation of Compounds.—General methods of preparation and configurations assigned are shown in the Scheme. Preparations not included in the Scheme are described below as appropriate. Analytical data, *etc.* for all compounds prepared are given in Table 1.

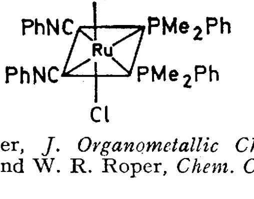
TABLE 1

Analytical data *etc.*, for osmium and ruthenium isonitrile complexes

Compound [a]	Colour	M.p.	Yield %	Analyses [b] C	H	N	ν(N≡C) [c]/cm^{-1} Nujol	CHCl$_3$	ν(Os–Cl)/cm^{-1}	Molecular weight or molar conductivity (Λ^{-1} cm^2 mol^{-1})[d]
$[OsCl_2(PhNC)_2(PEt_3)_2]$(C)	Yellow	192—194	85	44·7(44·4)	5·8(5·7)	4·0(4·0)	2065	2070		697(704)
$[OsCl_2(PhNC)_2(PEt_3)_2]$(D)	White	134—135	60	44·7(44·4)	5·8(5·7)	4·0(4·0)	2115, 2060, 2010	2110, 2055, 2010		
$[OsCl_2(PhNC)_2(PEt_2Ph)_2]$(C)	Yellow	230—233	60	50·9(51·1)	4·8(5·0)	3·7(3·5)	2065	2070		
$[OsCl_2(PhNC)_2(PEt_2Ph)_2]$(D)	White	197—199	70	51·5(51·1)	5·0(5·0)	3·8(3·5)	2110, 2050, 2010	2115, 2050, 2010		
$[OsCl_2(MeNC)_2(PEt_2Ph)_2]$(C)	Yellow	208—210	65	42·6(42·7)	5·2(5·4)	4·3(4·2)	2130	2120		
$[OsCl_2(MeNC)_2(PEt_2Ph)_2]$(D)	White	184—188	40	42·3(42·7)	5·4(5·4)	4·2(4·2)	2160, 2110			
$[OsCl_2(p\text{-}NO_2C_6H_4NC)_2(PBu^n_2Ph)_2]$(C)	Brown	204—207	95	50·4(50·4)	5·4(5·4)	5·7(5·6)	2040	2040		
$[OsCl_2(p\text{-}NO_2C_6H_4NC)(PMe_2Ph)_3]$(B)	Brown	165—167	75	45·0(45·2)	4·7(4·5)	3·5(3·4)	1870			
$[OsCl_2(p\text{-}MeOC_6H_4NC)_2(PBu^n_2Ph)_2]$(C)	Yellow	173—175	75	55·0(54·4)	6·3(6·2)	3·1(2·9)	2075	2075		942(972)
trans-$[OsBr_2(MeNC)_4]$	Orange	>300	15	18·9(18·9)	2·4(2·4)	10·7(10·9)	2160			
$[OsCl_2(CO)(PhNC)(PEt_3)_2]$(C)	Yellow	120—122	70	38·3(38·2)	5·6(5·6)	2·2(2·2)	2160, 1940,[e] 1950 [e]		305	632(628)
$[RuCl_2(PhNC)_2(PPr^n_2Ph)_2]$(C)	Yellow	185—187	60	60·3(59·5)	6·6(6·3)	3·8(3·7)	2100	2095		
$[RuCl_2(PhNC)_2(PBu^n_2Ph)_2]$(C)	Yellow	175—178	65	61·4(61·3)	6·7(6·9)	3·9(3·4)	2100	2140		
$[RuCl_2(PhNC)_2(PMe_2Ph)_2]$(H)	Orange	206—210	85	55·2(55·1)	4·9(4·9)	4·3(4·3)	2135, 2095	2145, 2100		
$[RuCl_2(PhNC)_2(PMe_2Ph)_2]$(C)	Yellow	207—209	5	55·1(55·1)	4·9(4·9)	4·4(4·3)	2090	2140w, 2090		
$[RuCl_2(PhNC)_2(PMe_2Ph)_2]$(D)	White	205—210	80	55·1(55·1)	5·1(4·9)	4·4(4·3)	2135, 2080	2135, 2080		654(654)
$[RuCl_2(p\text{-}NO_2C_6H_4NC)_2(PBu^n_2Ph)_2]$(C)	Red	237—238	90	56·4(55·3)	6·1(6·0)	6·4(6·1)	2070	2065		923(913)
$[RuCl_2(p\text{-}MeOC_6H_4NC)_2(PBu^n_2Ph)_2]$(C)	Yellow	170—171	40	61·0(59·9)	6·9(6·9)	3·3(3·2)	2100	2100		
$[OsCl_2(PhNC)(PEt_3)_3]^+$(E)	Purple	121—124	85	36·7(36·7)	6·2(6·2)	2·0(1·7)	2135	2140	323	165
$[OsCl_2(PhNC)(PMe_2Ph)_3]^+$(E)	Brown	135—136	90	42·7(42·4)	4·5(4·4)	1·5(1·6)	2150	2160	314	
$[OsCl_2(PhNC)(PBu^n_2Ph)_3]^+$(E)	Green	105—115	40	52·2(52·0)	6·7(6·6)	1·4(1·2)	2140		313	155
$[OsCl_2(MeNC)(PEt_3)_3]^+$(E)	Mauve	111—113	75	31·8(31·8)	6·3(6·4)	2·0(1·9)	2200	2205	309	
$[OsCl_2(MeNC)(PMe_2Ph)_3]^+$(E)	Blue	155—156	70	38·3(38·3)	4·5(4·5)	1·9(1·7)	2225	2220		
$[OsCl_2(p\text{-}NO_2C_6H_4NC)(PMe_2Ph)_3]^+$(E)	Green	129—131	65	40·4(40·3)	4·0(4·0)	3·1(3·0)	2160			
$[OsCl(MeNC)_2(PMe_2Ph)_3]^+$(F)	White	164—165	70	40·9(40·9)	5·1(4·8)	3·4(3·4)	2205, 2115			
$[OsCl(PhNC)_2(PBu^n_2Ph)_3]^+$(F)	White	163—165	40	56·1(56·4)	6·6(6·6)	2·5(2·3)	2130, 2080			
$[OsCl(PhNC)_2(PEt_3)_3]^+$(F)	White	165—166	30	43·4(43·4)	6·5(6·3)	3·1(3·2)	2135, 2080	2145, 2075		156
$[OsCl(MeNC)_2(PEt_3)_3]^+$(F)	White	159—160	55	34·9(34·7)	6·8(6·9)	3·7(3·7)	2200, 2155			
$[OsCl(CO)(PhNC)(PEt_3)_3]^+$(F)	White	158—160	90	38·9(38·5)	6·4(6·2)	1·8(1·7)	2125, 1980 [e]		318	
$[OsCl(CO)(MeNC)(PMe_2Ph)_3]^+$(F)	White	215—216	60	40·1(40·1)	4·6(4·5)	1·8(1·7)	2190, 2005 [e]			
$[OsCl_2(PhNC)_2(PEt_3)_2]^+$(G)	Green	185—188	90	38·9(38·9)	5·2(5·0)	3·5(3·5)	2155		317	130
$[OsCl_2(PhNC)(CO)(PEt_3)_2]^+$(G)	Green	137—140	40	32·5(33·0)	4·9(4·9)	2·1(1·9)	2195, 2040 [e]			
$[Os(CNMe)_6]^{2+}$	White	>350	60	22·9(22·7)	2·8(2·8)	13·1(13·2)	2235			
$[OsHCl(PhNC)(PMe_2Ph)_3]$	White	125—129	20	51·5(50·1)	5·6(6·3)	2·0(1·9)	1900, 1830, 1930 [f]			
$[OsCl_2(EtNH_2)(PhNC)(PEt_3)_2]$ [g]	Yellow	121—124 [h]	90	39·4(39·1)	6·6(6·6)	4·4(4·3)	1870, 3320w [i], 3260m [i], 2470w [j], 2410m [j]		292	
$[OsCl_2(MeNH_2)(PhNC)(PEt_3)_2]$	Yellow	126—128 [h]	65	38·5(38·1)	6·5(6·4)	4·5(4·4)	1850 3340w [i] 3250m [i]			
cis-$[Os(MeNC)_4\{C(NHMe_2\}_2]^{2+}$	White	*ca.* 230 [k]	50	24·4(24·1)	4·2(4·0)	16·0(16·1)	2250m, 2185, 3425m,[i] 3355m,[i] 2545m,[j] 2485m [j]			164
mer-$[Os(MeNC)_3\{C(NHMe)_2\}_3]^{2+}$	White	*ca.* 230 [k]	10	24·9(24·7)	4·6(4·6)	17·0(17·3)	2220m, 2160, 3450m,[i] 3370m [i]			177

[a] Configurations in parentheses; anion ClO_4^- in all cases. [b] Required values in parentheses. [c] Principal bands, strong unless otherwise stated. [d] Values are molecular weights in $C_2H_4Cl_2$ solution (for neutral compounds) when calculated values appear in parentheses, or molar conductivities in *ca.* 2 × 10^{-3}M-Me_2CO solution (for cationic compounds). [e] ν(C≡O). [f] ν(Os–H). [g] Chlorine analysis 11·8(11·0). [h] In a sealed, evacuated tube. [i] ν(N–H). [j] ν(N–D). [k] With decomposition and resolidification

Uncharged Osmium(II) *and Ruthenium*(II) *Complexes.*—The series of compounds $[OsCl_2(RNC)_2(PR^1_3)_2]$ and $[OsCl_2(RNC)(PMe_2Ph)_3]$ (for preparation see Scheme and ref. 8) has been extended to include complexes of p-$MeOC_6H_4NC$ and p-$NO_2C_6H_4NC$, since these isonitriles have, respectively, decreased and increased susceptibility to nucleophilic attack when co-ordinated to palladium(II) or to platinum(II).[3,4] The isomers shown in the Scheme and Table 1 were isolated and their configurations assigned from their i.r. and ^{1}H n.m.r. spectra (Tables 1 and 2) as in ref. 8. Some ruthenium analogues (Tables 1 and 2) were prepared similarly; some others have been prepared by different routes.[9] For the complex $[RuCl_2(PhNC)_2(PMe_2Ph)_2]$ an isomer of configuration (H) was obtained as well as the typical (C) and (D) configurations (Scheme).



(H)

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[8] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 1169, and references therein.

[9] B. E. Prater, *J. Organometallic Chem.*, 1972, **34**, 379; D. F. Christian and W. R. Roper, *Chem. Comm.*, 1971, **20**, 1271.

TABLE 2

^1H N.m.r. data [a]

Compound [b]	Resonance (τ ±0·01)	Integration [c]	*J* Value (Hz ±0·2)	Assignment
$[OsCl_2(PhNC)_2(PEt_3)_2]$(C)	8·80q	18(18)	7·3 [e]	*trans*-P*Me*
	7·85n	11(12)	3·7 [e]	*trans*-PCH_2
	2·8—5·3m			aromatic
$[OsCl_2(PhNC)_2(PEt_3)_2]$(D)	8·93q	18(18)	7·4 [e]	*trans*-P*Me*
	7·91n	12(12)	3·6 [e]	*trans*-PCH_2
	2·9—3·3m			aromatic
trans-$[OsBr_2(MeNC)_4]$	6·29s			*trans*-*Me*NC
$[OsCl(PhNC)_2(PEt_3)_3]^+$(F)	8·77m	27(27)		P*Me*
	7·84m	18·5(18)		PCH_2
	2·4—2·9m	10(10)		aromatic
$[OsCl(MeNC)_2(PEt_3)_3]^+$(F)	8·81m	27(27)		P*Me*
	7·98m	18·5(18)		PCH_2
	6·42s	3(3)		*Me*NC
	6·29s	3(3)		*Me*NC
$[OsCl(MeNC)_2(PMe_2Ph)_3]^+$(F)	8·42d	6(6)	8·0 [f]	*cis*-PMe_2Ph
	8·28t	12(12)	7·0 [g]	*trans*-PMe_2Ph
	8·17t		7·0 [g]	*trans*-PMe_2Ph
	6·83s	3(3)		*Me*NC
	6·48s	3(3)		*Me*NC
	2·4—2·8m	16(15)		aromatic
$[OsCl(CO)(MeNC)(PMe_2Ph)_3]^+$(F)	8·48d	6(6)	7·7 [f]	*cis*-PMe_2Ph
	8·03t	12(12)	7·0 [g]	*trans*-PMe_2Ph
	8·19t		6·8 [g]	*trans*-PMe_2Ph
	6·38s	3(3)		*MeNC*
	2·5—2·8m	15(15)		aromatic
$[Os(MeNC)_6]^{2+}$ [h]	6·35s			*Me*NC
$[OsHCl(PhNC)(PMe_2Ph)_3]$ [i]	15·91dt	*ca.* 1(1)	24 [e] 83 [e]	Os*H*
	8·63d	6(6)	7·5 [f]	*cis*-PMe_2Ph
	8·14dt	12(12)	7·5 [g]	*trans*-PMe_2Ph
	2·4—3·2			aromatic
$[RuCl_2(PhNC)_2(PMe_2Ph)_2]$(C)	8·05t	12(12)	7·0 [g]	*trans*-PMe_2Ph
	2·3—3·2m			aromatic
$[RuCl_2(PhNC)_2(PMe_2Ph)_2]$(D)	8·00t	12(12)	7·5 [g]	*trans*-PMe_2Ph
	2·3—3·4m			aromatic
$[RuCl_2(PhNC)_2(PMe_2Ph)_2]$(H)	8·36dd	12(12)	8·5 [f]	*cis*-PMe_2Ph
	2·3—2·8			aromatic
$[OsCl_2(PhNC)(EtNH_2)(PEt_3)_2]$	9·23t	3·5(3)	6·5 [j]	*Me*CH_2NH_2
	8·90q	18(18)	7·0 [e]	*trans*-P*Me*
	8·04m	12(12)		*trans*-PCH_2
	7·06qar	2(2)	7·0 [j]	MeCH_2NH_2 [k]
	7·06br [l]	2(2)		Me$CH_2\mathit{NH}_2$
	2·5—3·2m	5(5)		aromatic
$[OsCl_2(PhNC)(MeNH_2)(PEt_3)_2]$ [i]	8·92q	18(18)	7·0 [e]	*trans*-PMe
	8·10m	12(12)		*trans*-PCH_2
	7·70t	3(3)	6·0 [j]	*Me*NH [k]
	7·28br [l]	2(2)		MeNH_2
	2·6—3·3m	5(5)		aromatic
cis-$[Os(MeNC)_4\{C(NHMe)_2\}_2]^{2+}$ [h]	7·25d	6(6)	4·8 [j]	*Me*NH [k]
	7·02d	6(6)		*Me*NH [k]
	6·46s	12(12)	5·0 [j]	*Me*NC
	6·43s			*Me*NC
	3·50br [l]	4(4)		Me*NH*
mer-$[Os(MeNC)_3\{C(NHMe)_2\}_3]^{2+}$ [h]	7·30d	9(9)		*Me*NH [k]
	7·25d			*Me*NH [k]
	7·12d	3·5(3)	4·5 [j]	*Me*NH [k]
	7·03d	6(6)	4·5 [j]	*Me*NH [k]
	6·48s	9(9)		*Me*NC
	6·46s			*Me*NC
	3·5—3·9br [l]	6(6)		Me*NH*

[a] Unless otherwise stated, in $CDCl_3$ relative to tetramethylsilane internal reference. [b] Configurations in parentheses, anion ClO_4^-. [c] Calculated values in parentheses. [e] Separation of adjacent peaks, see ref. 8. [f] ^2J(PH). [g] ^2J(PH) + ^4J(PH). [h] In CD_3CN. [i] In C_6D_6. [j] ^3J(HH). [k] Assigned after addition of D_2O to remove N–H coupling. [l] Disappears on addition of D_2O.

br = Broad; qar = quartet; q = quintet; t = triplet; d = doublet; m = multiplet; n = nonatet; s = singlet; dt = doublet of triplets; dd = doublet of doublets.

The compound *trans*-[$OsBr_2(MeNC)_4$] was obtained, in low yield, by treatment of $(NH_4)_2OsBr_6$ with an excess of methyl isonitrile in ethanol at reflux. The *trans*-configuration is assigned since only one N≡C stretching band occurs in its i.r. spectrum and the methyl resonance in its n.m.r. spectrum is a singlet. Phenyl isonitrile did not give tractable products under the above conditions.

A carbonyl-isonitrile complex was obtained by reaction (1).

$$[OsCl_2(CO)_2(PEt_3)_2](C) + PhNC(excess) \xrightarrow[\text{reflux}]{\text{thf}} [OsCl_2(CO)(PhNC)(PEt_3)_2](C) + CO \quad (1)$$

The *trans*-configuration (C) is assigned from the *trans*-coupled PEt_3 n.m.r. pattern [8] (Table 2) and the single Os–Cl stretching band in the i.r. spectrum (Table 1).

Cationic Osmium(III) *Complexes*.—The intensely coloured air-stable complexes [$OsCl_2(RNC)(PR^1_3)_3$]ClO_4 were prepared as equation (2).

$$mer\text{-}[OsCl_3(PR^1_3)_3] + RNC + AgClO_4 \xrightarrow[20°]{\text{acetone}} [OsCl_2(RNC)(PR^1_3)_3]ClO_4(E) + AgCl \quad (2)$$

Although their configuration is not definitely established it is most probably (E) (see Scheme), since they have a single Os–Cl stretching band in their i.r. spectra (Table 1) and the *mer*-configuration of phosphine ligands proposed for them is established for the osmium(II) compounds obtained from them by reduction (see below).

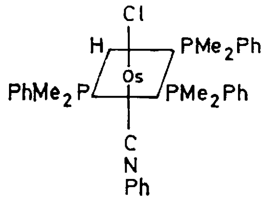
The osmium(III) cationic complexes [$OsCl_2(PhNC)_2(PEt_3)_2$]ClO_4 and [$OsCl_2(CO)(PhNC)(PEt_3)_2$]$ClO_4$ [configuration (G)] were prepared by oxidation of their osmium(II) analogues with a mixture of nitric and perchloric acids. They are assigned configuration (G) since they have single N≡C and Os–Cl stretching bands in their i.r. spectra (Table 1).

Cationic Osmium(II) *Complexes*.—When complexes of the type [$OsCl_2(RNC)(PR^1_3)_3$]ClO_4 were treated with an excess of isonitrile in ethanol at reflux, they were reduced to the air-stable, colourless osmium(II) complexes [$OsCl(RNC)_2(PR^1_3)_3$]ClO_4 (R = Me or Ph, PR^1_3 = PMe_2Ph, $PBu^n{}_2Ph$, or PEt_3) whose configuration [(F) see Scheme] follows from the n.m.r. spectrum of the PMe_2Ph analogue [8] (Table 2). The complexes [$OsCl(CO)(RNC)(PR^1_3)_3$]ClO_4 (R = Me or Ph, $PR^1_3 = PMe_2Ph$ or PEt_3) were similarly obtained by reduction of [$OsCl_2(RNC)(PR^1_3)_3$]ClO_4 by ethanol in the presence of carbon monoxide.

The colourless complex [$Os(MeNC)_6$]$(ClO_4)_2$ was prepared by reaction of $K_4[Os(CN)_6]$ with dimethyl sulphate or, better, with methyl fluorosulphonate. The single N≡C stretching band and singlet methyl n.m.r. absorption are expected since the compound has essentially O_h symmetry.

Reactions with Nucleophiles.—Representative examples of each of the above types of compound were treated with primary alcohols, primary amines, and in some cases, sodium borohydride or ethoxide ion.

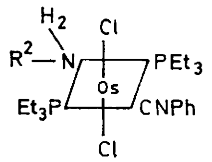
The uncharged ruthenium(II) and osmium(II) complexes were inert to all reagents except sodium borohydride, with which [$OsCl_2(PhNC)(PMe_2Ph)_3$] [(A) or (B) isomer] gave [$OsHCl(PhNC)(PMe_2Ph)_3$]. The configuration of this hydrido-complex (I) follows from its ^1H n.m.r. spectrum [8] (Table 2).



(I)

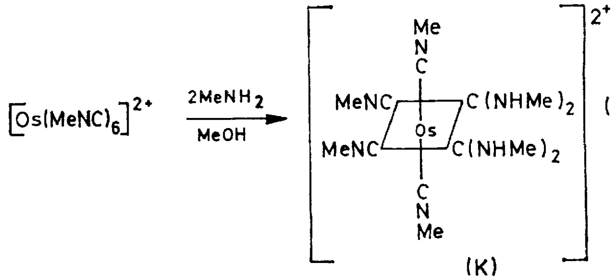
The osmium(II) cationic complexes [$OsCl(RNC)_2(PR^1_3)_3$]ClO_4 were inert to amines and even to alkoxide ion.

When treated with primary aliphatic amines, the cationic osmium(III) complexes [$OsCl_2(RNC)_2(PR^1_3)_2$]ClO_4 and [$OsCl_2(RNC)(PMe_2Ph)_3$]ClO_4 were rapidly reduced to the corresponding neutral osmium(II) complexes and no further reaction occurred. However, the compound [$OsCl_2(PhNC)(PEt_3)_3$]ClO_4 undergoes both reduction and displacement of a PEt_3 ligand to give the yellow, air-sensitive amine complexes [$OsCl_2(PhNC)(R^2NH_2)(PEt_3)_2$] ($R^2$ = Me or Et). The quintet n.m.r. P*Me* absorption [8] and single Os–Cl stretching i.r. band (Tables 1 and 2) show the configuration of these complexes to be (J). It is notable also that ν(N≡C) for these compounds is particularly low (1870—1850 cm^{-1}) as might be expected since the presence of the amine ligands with no *d*-acceptor orbitals allows a greater donation of osmium non-bonding *d*-electron density into the π*-isonitrile orbitals. In contrast, the carbonyl-isonitrile complexes described above all show an increase of ν(N≡C) relative to their isonitrile analogues, since CO competes (probably more effectively) for π-electrons with isonitrile.



(J)

The di-cationic complex [$Os(MeNC)_6$]$(FSO_3)_2$ reacts with methylamine in methanol at reflux to give a colourless, bis-carbene complex as the major product [equation (3)]. In its i.r. spectrum, this complex has two N–H

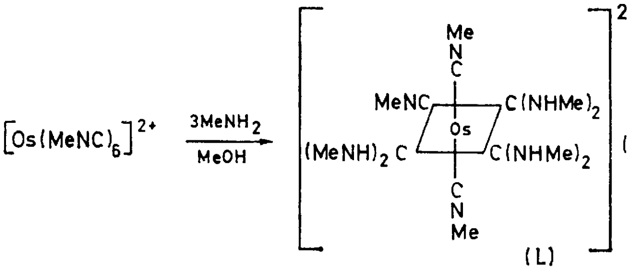


(3)

(K)

and two N≡C stretching bands (Table 1). Its ^{1}H n.m.r. spectrum shows two singlet resonances (two sets of unreacted MeNC groups), two doublets which simplify to two singlets on D_2O addition (carbene methyl groups) and a broad absorption which disappears on addition of D_2O (carbene N–H). Hence its structure is (K).

A minor product from the above reaction is the triscarbene complex (L) [equation (4)]. This complex exhibits two N–H and two N≡C stretching bands in its i.r. spectrum (Table 1). Its ^{1}H n.m.r. spectrum shows two singlet resonances of relative intensity 2 : 1 (three unreacted MeNC groups, two being equivalent), two sets of two doublets of relative integrations 2 : 1 (two equivalent and one unique carbene groups) and a broad absorption which disappears on addition of D_2O (carbene N–H). Thus its structure is (L). The doublets assigned to the two equivalent carbene groups collapse to singlets on D_2O addition, whereas those assigned to the unique carbene only partially collapse during the same period. It is not yet clear why the exchange rate of the unique carbene ligand is slow, possibly steric crowding is responsible, or the differing *trans*-effect of carbene and MeNC ligands. The most likely configuration of the carbene ligands, from the above evidence and on steric grounds, is the *amphi*-one.[10] This contrasts with square planar complexes of platinum(II) having this ligand, where a mixture of isomers was observed.[2] A further contrast is with the product obtained, in a similar reaction, from $[Fe(CNMe)_6]^{2+}$, which contains a chelate carbene-type ligand.[10] It is not clear what factors determine the different products in these cases, but steric effects are presumably important.



(4)

(L)

DISCUSSION

Electron-withdrawing substituents on ligating isonitrile, by decreasing electron density at isonitrile carbon, enhance its reactivity towards nucleophilic attack.[3,4] It would be expected that increase of the oxidation state of the metal or of its positive charge would similarly decrease electron density at the ligating isonitrile carbon and enhance its reactivity. The results of this investigation suggest that the effect of the metal is the dominant one, since uncharged osmium(II) compounds are inert regardless of the isonitrile substituents, whereas the dicationic compound is the one containing reactive isonitrile. Probably the ready reduction of the unipositive osmium(III) complexes to the inert osmium(II) state prevents reaction of their isonitrile ligands.

A significant feature of the series of complexes we have prepared is the wide variation of ν(N≡C). Table 3 lists a representative series of isonitrile complexes to show the change of ν(N≡C) on passing from unbound isonitrile to isonitrile co-ordinated in different environments. The ν(N≡C) value increases with rise of oxidation state of the central metal or with increase of the positive charge of the complex. It is notable that in this series of osmium compounds the complex with reactive ligating methyl isonitrile has the largest increase of ν(N≡C) (Δν) and this value (65 cm^{-1}) is similar to those observed for reactive methyl isonitrile complexes of platinum(II) and iron(II). Thus the criterion of reactivity of ligating methyl isonitrile towards amines appears to be that $\Delta\nu \geqslant 65$ cm^{-1}. Values for phenyl isonitrile are similar but other metals and isonitriles have different values, *e.g.* for rhodium(I) and Bu^{t}NC, Δν need only be 40 cm^{-1} (Table 3). This correlation between a large value of Δν and susceptibility of ligating isonitrile to nucleophilic attack parallels that suggested between the reactivity of ligating carbon monoxide and the force constant of its stretching mode.[11]

Removal of electron density from the 'lone pair' orbital primarily on isocyanide carbon causes an increase of the N≡C force constant[12] (*via* strengthening of the

TABLE 3

Values of Δν/cm^{-1} for some isonitrile complexes [a]

Complex [b]	Δν	Ref.
$[OsCl_2(MeNC)(PMe_2Ph)_3]$(B)	−100	8
$[OsCl_2(MeNC)(PMe_2Ph)_3]$(A)	−20	8
$[OsCl_2(MeNC)_2(PEt_3)_2]$(C)	−60	8
$[OsCl_2(MeNC)_2(PEt_2Ph)_2]$(D)	−35	8
trans-$[OsBr_2(MeNC)_4]$	−10	*c*
$[OsCl(MeNC)_2(PMe_2Ph)_3]ClO_4$(F)	−10	*c*
$[OsCl(MeNC)_2(PEt_3)_3]ClO_4$(F)	+10	*c*
$[OsCl_2(MeNC)(PEt_3)_3]ClO_4$(E)	+30	*c*
$[OsCl_2(MeNC)(PMe_2Ph)_3]ClO_4$(E)	+55	*c*
$[Os(MeNC)_6](ClO_4)_2$	+65 [d]	*c*
cis-$[PtCl_2(MeNC)(PEt_3)]$	+75 [d]	1
trans-$[PtCl(MeNC)(PEt_3)_2]ClO_4$	+90 [d]	2
trans-$[PtMe(MeNC)(PMe_2Ph)]SbF_6$	+70 [d]	*e*
$[Fe(MeNC)_6](HSO_4)_2$	+75 [d]	10
$[OsCl_2(PhNC)_2(PEt_3)_2]$(C)	−65	*c*
$[OsCl_2(PhNC)_2(PEt_3)_2]$(D)	−70	*c*
$[OsCl_2(PhNC)(PMe_2Ph)_3]$(B)	−110	8
$[OsCl(PhNC)_2(PEt_3)_3]ClO_4$(F)	−20	*c*
$[OsCl_2(PhNC)(PMe_2Ph)_3]ClO_4$(E)	+20	*c*
$[OsCl_2(PhNC)(PEt_3)_3]ClO_4$(E)	+5	*c*
cis-$[PtCl_2(PhNC)(PEt_3)]$	+70 [d]	1
cis-$[PdCl_2(PhNC)(PPh_3)]$	+80 [d]	1
$[Rh(Bu^tNC)_4]BF_4$	+40 [d]	6
$[Fe(\pi\text{-}C_5H_5)(p\text{-}MeOC_6H_4NC)_3]ClO_4$	+40 [d]	5

[a] $\Delta\nu = [\nu(N{\equiv}C)_{free} - \nu(N{\equiv}C)_{co\text{-}ordinated}]$; where more than one band occurs, the mean has been used. Mull spectra. [b] Configurations in parentheses. [c] This work. [e] Corresponding compound reacts with nucleophiles to give carbene complex. [e] H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 503.

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C–N σ-system [13]) and hence ν(N≡C) of the isonitrile molecule. Thus when the metal–isonitrile carbon bond has mainly σ-character, there will be a relatively large increase in ν(N≡C) and a decrease in electron density at isonitrile carbon, causing its susceptibility to nucleophilic attack. If the metal–carbon bond has an appreciable π-component, Δν is small or negative and the isonitrile carbon, which does not then have a lowered electron density, is inert to nucleophiles, as is observed above.

EXPERIMENTAL

All manipulations involving air-sensitive materials were carried out using standard Schlenk or high vacuum techniques. Tetrahydrofuran (thf) was distilled from sodium diphenylketyl before use. The compounds *mer*-[$MCl_3(PR^1_3)_3$] [14] (M = Os or Ru), methyl isonitrile,[15] and other isonitriles [16] were prepared by established methods.

The i.r. spectra were determined with Perkin-Elmer 457 and Grubb–Parsons DM 4 instruments and a Varian H.A. 100 instrument was used to measure ^1H n.m.r. spectra. Molecular weights were determined with a Hitachi–Perkin-Elmer 115 osmometer, conductivities were obtained using a Portland Electronics conductivity bridge, and m.p.s were measured with a Kofler hot stage. Microanalyses were by Mr. and Mrs. A. G. Olney of these laboratories and analytical data for all new compounds prepared are in Table 1.

Uncharged Osmium(II) *and Ruthenium*(II) *Complexes.*—(a) Complexes of the type [$MCl_2(RNC)_2(PR^1_3)_2$] (M = Os or Ru) and [$OsCl_2(RNC)(PMe_2Ph)_3$] were prepared by published methods [8] where the configurations are (A), (B), and (C) (see Scheme and Table 1). Those compounds of configuration (D) were obtained by thermal isomerisation of complexes of configuration (C) or (H), *e.g. dichlorobis*(*phenyl isonitrile*)*bis*(*diethylphenylphosphine*)*osmium*(II), [$OsCl_2(PhNC)_2(PEt_2Ph)_2$] [*configuration* (D)] was obtained when [$OsCl_2(PhNC)_2(PEt_2Ph)_2$] [configuration (C)] (0·14 g) was heated in 2-methoxyethanol (30 ml) at reflux for 48 h, the solution concentrated, the product precipitated with ether and recrystallised from ethanol as white *hexagons* (0·10 g, 70%).

(b) *Dichlorobis*(*phenyl isonitrile*)*bis*(*dimethylphenylphosphine*)*ruthenium*(II), [$RuCl_2(PhNC)_2(PMe_2Ph)_2$] [configuration (H)] was obtained when *mer*-[$RuCl_3(PMe_2Ph)_3$] (0·39 g), phenyl isonitrile (0·3 ml), and amalgamated zinc (2 g) were heated together under reflux in thf (50 ml) for 1 h, the solution filtered, taken to dryness, and the more soluble fraction of the residue recrystallised from ethanol–chloroform to give orange *hexagons* (0·30 g, 85%). The less soluble residue fraction was separated by fractional crystallisation to give the isomer of configuration (C) as yellow *rhombs* (0·02 g, 5%).

(c) *Dichlorocarbonyl*(*phenyl isonitrile*)*bis*(*triethylphosphine*)*osmium*(II), [$OsCl_2(CO)(PhNC)(PEt_3)_2$] [*configuration* (C)]. [$OsCl_2(CO)_2(PEt_3)_2$] [Configuration (C)] (0·65 g) in thf (50 ml) was refluxed for 2·5 h with an excess of phenyl isonitrile (0·3 g). The solution was evaporated to dryness *in vacuo* and the residue was recrystallised from ethanol as yellow *crystals* (0·59 g, 70%).

(d) trans-*Dibromotetrakis*(*methyl isonitrile*)*osmium*(II), *trans*-[$OsBr_2(MeNC)_4$]. Ammonium hexabromo-osmate (0·50 g) was stirred with an excess of methyl isonitrile (0·25 g) in ethanol (30 ml) at reflux for 12 h. The resulting solution was filtered and concentrated to give an orange solid which gave orange *prisms* on recrystallisation from ethanol (0·05 g, 15%).

Osmium(III) *Cationic Complexes.*—Methods are general and typical examples are given here, analytical data, *etc.* are in Table 1.

(a) *Dichloro*(*phenyl isonitrile*)*tris*(*triethylphosphine*)*osmium*(III) *Perchlorate*, [$OsCl_2(PhNC)(PEt_3)_3]ClO_4$ [*configuration* (E)]. *mer*-[$OsCl_3(PEt_3)_3$] (1·30 g) was dissolved in acetone (25 ml) and an excess of phenyl isonitrile (0·3 g) was first added, followed by a solution of silver perchlorate (0·44 g) in acetone (20 ml). A white precipitate immediately formed and the solution turned deep blue. After stirring for 0·5 h, the solution was filtered and concentrated to give a blue-black solid which was washed with ether (removing a green impurity) and recrystallised from ethanol as shining, deep purple *crystals* (1·35 g, 85%). *N.B.* On one occasion a sample of this compound deflagrated, apparently spontaneously, while being transferred from a sinter to a sample tube.

(b) *Dichlorobis*(*phenyl isonitrile*)*bis*(*triethylphosphine*)*osmium*(III) *Perchlorate*, [$OsCl_2(PhNC)_2(PEt_3)_2]ClO_4$ [*configuration* (G)]. [$OsCl_2(PhNC)_2(PEt_3)_2$] [Configuration (C)] (0·64 g) was dissolved in ethanol and concentrated nitric acid (1 ml) followed by perchloric acid (5 ml, 60% w/w solution) was added. The solution immediately turned bright green, ether was added, and the green solid obtained by cooling was filtered and recrystallised from ethanol–ether as intensely green shining platelets (0·68 g, 90%).

Osmium(II) *Cationic Complexes.*—For those of the type [$OsCl(RNC)_2(PR_3)_3]ClO_4$ the method is general, a typical example is given and analytical data, *etc.* for all compounds prepared are in Table 1.

Chlorobis(*methyl isonitrile*)*tris*(*dimethylphenylphosphine*)*osmium*(II) *Perchlorate*, [$OsCl(MeNC)_2(PMe_2Ph)_3]ClO_4$ [*Configuration* (F)].—[$OsCl_2(MeNC)(PMe_2Ph)_3]ClO_4$ [Configuration (E)] (0·30 g) was heated with an excess of methyl isonitrile (0·30 g) in ethanol at reflux until the solution was almost colourless (6 h). The solution was concentrated and recrystallisation of the pale green product from ethanol gave white *needles* (0·20 g, 70%).

Hexakis(*methyl isonitrile*)*osmium*(II) *Perchlorate*, [$Os(MeNC)_6](ClO_4)_2$.—Thoroughly dried and finely powdered potassium hexacyano-osmate $K_4Os(CN)_6$ (2·7 g) was suspended in methyl fluorosulphonate (20 ml) and stirred for 4 h at 80 °C, under dry dinitrogen. The solution was filtered and the white residue washed with water. This aqueous extract was then concentrated under vacuum and cooled to yield crude [$Os(MeNC)_6](FSO_3)_2$ (1·80 g). A further crop (0·20 g) was obtained from the filtrate by ether precipitation. The product was dissolved in aqueous methanol and a methanolic solution of sodium perchlorate (2·0 g) added, the perchlorate salt was immediately precipitated (2·0 g, 60%) and a sample completely purified by two recrystallisations from a large volume of methanol to give long white *needles*.

Reactions of Isonitrile Complexes with Nucleophiles.—(a) *Preparation of hydridochloro*(*phenyl isonitrile*)*tris*(*dimethylphenylphosphine*)*osmium*(II), [$OsHCl(PhNC)(PMe_2Ph)_3$] [*configuration* (I)]. [$OsCl_2(PhNC)(PMe_2Ph)_3$] [Configuration

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(A)] (0·47 g) and fresh sodium borohydride (0·5 g) in ethanol (100 ml) were stirred until the yellow solution was colourless (4 h). The solvent was removed under vacuum and the residue extracted with dry, degassed benzene which was then removed *in vacuo*. The oily residue, after several recrystallisations from dry, degassed methanol, gave the product as colourless *needles* (0·10 g, 20%).

(b) *Preparation of dichloro(methylamine)(phenyl isonitrile)bis(triethylphosphine)osmium*(II), $[OsCl_2(MeNH_2)(PhNC)(PEt_3)_2]$ [*configuration* (J)]. $[OsCl_2(PhNC)(PEt_3)_3]ClO_4$ (0·50 g) was dissolved in dry, degassed ethanol (30 ml) and methylamine was bubbled into the solution for 1 min. The solution turned yellow and smelled of PEt_3. After stirring the solution under dinitrogen for 0·25 h and then removing some solvent under vacuum, cooling gave a yellow precipitate which was recrystallised from dry, degassed ethanol as air-sensitive, yellow *crystals* (0·24 g, 65%). The ethylamine analogue was similarly prepared.

(c) *Preparation of* cis-*tetrakis(methyl isonitrile)bis[di(methylamino)carbene]osmium*(II) *perchlorate, cis*-$[Os(MeNC)_4\{C(NHMe)_2\}_2](ClO_4)_2$ and mer-*tris(methyl isonitrile)tris[di(methylamino)carbene]osmium*(II) *perchlorate, mer*-$[Os(MeNC)_3\{C(NHMe)_2\}_3](ClO_4)_2$. $[Os(MeNC)_6](FSO_3)_2$ (0·73 g) in dry methanol (50 ml) was refluxed with exclusion of moisture for 12 h with methylamine continuously passing into the solution. After filtration of some insoluble material, a solution of sodium perchlorate (1·0 g) in methanol (20 ml) was added, the solution again filtered, then concentrated under vacuum to give chunky white *crystals* of the bis-carbene complex (I). From the filtrate a further small crop of white *needles* of the tris-carbene compound (L) was obtained. Both these were purified by the same procedure: the compounds were first dissolved in methyl cyanide, the solutions filtered (to remove a white, feathery impurity) and evaporated to dryness under vacuum, the residues being recrystallised from ethanol [(K) 0·36 g, 50%; (L) 0·08 g, 10%].

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