Electrophilic Behaviour of the Co-ordinated Nitrosyl Cation: Reactions of Pentahalogenonitrosyliridate(1–)

By **Frank Bottomley,*** **Steven G. Clarkson**, and (in part), **Shiu-Bor Tong**, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

The complexes $[Ir(X)_5NO]^-$ (X = Cl or Br) are attacked at the nitrosyl nitrogen atom by nucleophiles according to the equations: (i) $[Ir(X)_5NO]^- + 2OH^- \rightleftharpoons [Ir(X)_5NO_2]^{3-} + H_2O$; (ii) $[Ir(X)_5NO]^- + NH_2OH \longrightarrow [Ir(X)_5H_2O]^{2-} + N_2O + H^+$; (iii) $[Ir(X)_5NO]^- + N_3^- + H_2O \longrightarrow [Ir(X)_5H_2O]^{2-} + N_2O + N_2$; and (iv) $[Ir(X)_5NO]^- + 2NH_3 \longrightarrow [Ir(X)_5NH_3]^{2-} + N_2 + H_3O^+$. Hydrazine hydrate and $[Ir(Br)_5NO]^-$ form $[IrBr_3(N_2H_4)_3],0{\cdot}5H_2O$ by an unknown route. Equilibrium constants for the reversible reaction with OH^- are compared with the analogous reactions of NO^+ and $[Fe(CN)_5NO]^{2-}$.

IN the last few years there has been an increasing interest in the reactivity of co-ordinated NO^+,[1-13] and the long known, but apparently anomalous, behaviour of the ion $[Fe(CN)_5NO]^{2-}$ towards OH^- (ref. 1) has been shown to be one example of a rather general class of reactions. However, other examples have been rather scattered and in addition several unsuccessful attempts at nucleophilic attack at co-ordinated NO^+ have been reported.[12,14-16] We recently proposed that complexes containing NO^+ having $\bar{\nu}(NO)$ greater than *ca.* 1 886 cm^{-1} [or f(N–O) greater than 13·8 mdyn $Å^{-1}$] † would be susceptible to nucleophilic attack at the nitrosyl nitrogen atom.[17] The complexes $[Ir(X)_5NO]^-$ [18,19] [X = Cl, $\bar{\nu}(NO)$ = 2 008 cm^{-1}; X = Br, $\bar{\nu}(NO)$ = 1 953 cm^{-1}] clearly provide an excellent test of this idea, $[Ir(Cl)_5NO]^-$ having the highest $\nu(NO)$ value yet reported for a nitrosyl complex. The high $\nu(NO)$ frequencies also provide assurance that the complexes formally contain NO^+ rather than NO^-.[20] We have therefore investigated reactions of the ions $[Ir(X)_5NO]^-$ with the nucleophiles NH_3, N_3^-, N_2H_4, NH_2OH, and H_2O and report the results in detail here.

RESULTS AND DISCUSSION

The deep-red ions $[Ir(X)_5NO]^-$ were largely present only in very acidic ($[H^+] > 0{\cdot}5$M) solutions.‡ In neutral or alkaline solutions they converted to $[Ir(X)_5NO_2]^{3-}$, which could be precipitated out with ethanol. Equilibrium constants for the reactions (1) are compared with

$$[Ir(X)_5NO]^- + 2OH^- \rightleftharpoons [Ir(X)_5NO_2]^{3-} + H_2O \quad (1)$$

similar reactions of NO^+ and $[Fe(CN)_5NO]^{2-}$ in the Table. The constants were determined spectrophotometrically at 25 °C and I = 1·0M, and were quite reproducible. The value for $[Ir(Cl)_5NO]^-$ is an estimate because it was impossible to obtain a solution of sufficient acidity (without decomposing the complex) to convert all the complex to the nitrosyl form. This demonstrates the ease of nucleophilic attack at $[Ir(Cl)_5NO]^-$. The electronic spectrum of the ion $[Ir(Cl)_5NO_2]^{3-}$ was not suitable for accurate determination of its concentration. Even for $[Ir(Br)_5NO]^-$ the high acidity required to obtain the nitrosyl form limited the range of concentration over which the equilibrium constants could be measured. This is known to produce errors.[21]

Equilibrium constants for reaction (1)

Ion	$K/l^2\ mol^{-2}$	$\bar{\nu}(NO)/cm^{-1}$
NO^+	$2{\cdot}3 \times 10^{31}$ (ref. 1)	2 220
$[Ir(Cl)_5NO]^-$	$>6 \times 10^{29}$	2 008
$[Ir(Br)_5NO]^-$	$6{\cdot}8 \times 10^{27}$	1 953
$[Fe(CN)_5NO]^{2-}$	$1{\cdot}5 \times 10^{6}$ (ref. 1)	1 938

Even allowing for these limitations the contrast between the K values for $[Fe(CN)_5NO]^{2-}$ and $[Ir(X)_5NO]^-$ shown in the Table is striking, and indicates the electron density at the nitrosyl nitrogen atom in the ion $[Ir(X)_5NO]^-$ is much closer to that in NO^+ than to that in $[Fe(CN)_5NO]^{2-}$, despite the formal similarity of the complexes. However, in the i.r. spectra, $\bar{\nu}(NO)$ of NO^+ is over 200 cm^{-1} greater than for any of the complexes, for which there is a spread of only 50 cm^{-1}. It has been pointed out that for CO and N_2 the decrease in $\nu(CO)$ or $\nu(N_2)$ on co-ordination is a function not only of the energy of the ligand π-acceptor orbitals but also of the energy of the ligand orbital involved in σ-bonding to the metal atom.[22] For CO this latter orbital is slightly antibonding, whereas for N_2 it is bonding,[22] and calculations here indicate it is bonding for NO^+ also.§ Donation of electrons from NO^+ to the metal decreases the electron density at the nitrogen atom and decreases $\nu(NO)$; back donation of metal electrons to NO^+ antibonding orbitals

---

† 1 dyn = 10^{-5}N.

‡ 1M = 1 mol dm^{-3}.

§ A minimal-basis *ab initio* s.c.f. calculation by Dr. F. Grein of this department.

[1] J. H. Swinehart, *Co-ordination Chem. Rev.*, 1967, **2**, 385.

[2] E. J. Baran and A. Müller, *Chem. Ber.*, 1969, **102**, 3915.

[3] E. J. Baran and A. Müller, *Z. anorg. Chem.*, 1969, **370**, 283.

[4] T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Comm.*, 1970, 872.

[5] F. Bottomley and J. R. Crawford, *Chem. Comm.*, 1971, 200.

[6] J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, 1971, **10**, 2150.

[7] F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, 1971, **93**, 1294.

[8] P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, 1971, **93**, 84.

[9] P. G. Douglas and R. D. Feltham, *J. Amer. Chem. Soc.*, 1972, **94**, 5254.

[10] F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.

[11] F. Bottomley and J. R. Crawford, *J. Amer. Chem. Soc.*, 1972, **94**, 9092.

[12] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1972, 1243.

[13] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5084.

[14] H. Brunner, *Z. anorg. Chem.*, 1969, **368**, 120.

[15] F. Bottomley and S. B. Tong, *J.C.S. Dalton*, 1973, 217.

[16] G. Dolcetti, L. Busetto, and A. Palazzi, *Inorg. Chem.*, 1974, **13**, 222.

[17] F. Bottomley, W. V. F. Brooks, S. G. Clarkson, and S. B. Tong, *J.C.S. Chem. Comm.*, 1973, 919.

[18] M. Angoletta and L. Malatesta, *Angew. Chem.*, 1963, **75**, 209.

[19] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372.

[20] N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, 47.

[21] R. M. Guidry and R. S. Drago, *J. Amer. Chem. Soc.*, 1973, **95**, 6645.

[22] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841.

increases the electron density and decreases ν(NO). Hence the electron density in a NO^+ complex can be similar to that of NO^+, despite the 200 cm^{-1} difference in $\bar{\nu}$(NO). Comparing the ions $[Ir(X)_5NO]^-$ and $[Fe(CN)_5NO]^{2-}$, the difference in electron density is much more closely related to the π-acceptor function of the ligand, and hence to ν(NO). It is clear from the large difference in K values but small difference in $\bar{\nu}$(NO) that the i.r. spectra are a very coarse measure of electron density. This is further illustrated when $[Fe(CN)_5NO]^{2-}$ is compared with $[RuCl(bipy)_2NO]^{2+}$, for which $\bar{\nu}$(NO) is 1927 cm^{-1} but K is $1{\cdot}6 \times 10^9$.[6]

On setting aside in neutral solution, the ion $[Ir(X)_5NO_2]^{3-}$ underwent ligand substitution and $[IrBr_4(NO_2)H_2O]^{2-}$ was isolated from such a solution. This behaviour is not found for $[Ir(X)_5NO]^-$, and must be due to the *trans*-labilising influence of NO_2^-;[23,24] NO^+ exerts an opposite influence in related complexes.[25]

Reactions of the ion $[Ir(Br)_5NO]^-$ with aqueous NH_2OH, N_3^-, or NH_3 were instantaneous. All gaseous as well as iridium-containing products were investigated, and the reactions are represented by equations (2)—(4). Less-detailed investigation of reactions of the ion $[Ir(Cl)_5NO]^-$ indicates analogous behaviour.

$$[Ir(Br)_5NO]^- + NH_2OH \longrightarrow [Ir(Br)_5H_2O]^{2-} + N_2O + H^+ \quad (2)$$

$$[Ir(Br)_5NO]^- + N_3^- + H_2O \longrightarrow [Ir(Br)_5H_2O]^{2-} + N_2 + N_2O \quad (3)$$

$$[Ir(Br)_5NO]^- + 2NH_3 \longrightarrow [Ir(Br)_5NH_3]^{2-} + N_2 + H_3O^+ \quad (4)$$

Despite the alkaline nature of the reaction solutions, $[Ir(Br)_5H_2O]^{2-}$ (ref. 26) and $[Ir(Br)_5NH_3]^{2-}$ (ref. 27) were obtained cleanly, with no evidence for $[Ir(Br)_5OH]^{3-}$ or other hydroxoiridium complexes. Reaction (2) is presumed to occur in the same way as that between $[Ru(NH_3)_5NO]^{3+}$ and NH_2OH, *i.e.* by initial attack of NH_2OH at the nitrosyl N atom.[5,11] The resultant ion $[Ir(Br)_5N_2O]^{2-}$ must decompose rapidly, as does $[Ru(NH_3)_5N_2O]^{2+}$.[11] Reaction (3) has previous analogues in the reactions of $[RuCl(L)_2NO]^{2+}$ [L = *o*-phenylenebis(dimethylarsine), 2,2′-bipyridine (bipy), or 1,10-phenanthroline] with N_3^-.[7,9] As here, N_2 and N_2O are evolved, and a reasonable mechanism for the reaction, involving initial attack of N_3^- at the nitrosyl, has been proposed.[9] Reaction (4) has no direct analogue, though co-ordinated amide attacks $[Ru(NH_3)_5NO]^{3+}$, forming $[Ru(NH_3)_5(N_2)]^{2+}$,[28] and RNH_2 (R = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$) attacks $[RuCl(bipy)_2NO]^{2+}$ forming $[RuCl(bipy)_2(N_2R)]^{2+}$.[13] Nucleophilic attack of NH_3 at $[Ir(Br)_5NO]^-$ would give the ion $[Ir(Br)_5(N_2)]^{2-}$. The rapid decomposition of the N_2 complex in contrast to the stability of the NO^+ and CO[29] complexes illustrates the delicate balance of σ- and π-bonding required to stabilize N_2 complexes.[22]

Hydrazine hydrate also reacted with the ion $[Ir(Br)_5NO]^-$, rapidly giving $[Ir(Br)_3(N_2H_4)_3]{,}0{\cdot}5H_2O$ (56%) and 0·23 mol N_2 per mol $[Ir(Br)_5NO]^-$. Hydrazine has been shown to give co-ordinated N_3^-,[8,11] N_2O,[11] or N_2[5,11] when it reacts with nitrosyl complexes. It is possible that co-ordinated N_3^- or N_2 is formed in the present reaction, since the product often showed a sharp absorption at 2 057 cm^{-1}, in the region expected for these ligands. However, the course of the reaction is not certain. The complex $[Ir(Br)_3(N_2H_4)_3]{,}0{\cdot}5H_2O$ may be monomeric with unidentate hydrazine or polymeric with bridging hydrazine. It has been suggested these types may be distinguished by their i.r. spectra, $\bar{\nu}$(N–N) being 931—936 cm^{-1} in the former case and 948—980 cm^{-1} in the latter.[30] The band closest to this region in $[Ir(Br)_3(N_2H_4)_3]{,}0{\cdot}5H_2O$ was at 940 cm^{-1}, which does not allow an assignment of the structure.

All attempts to prepare the ion $[Ir(I)_5NO]^-$ were unsuccessful. Addition of NO_2^- to a solution of $[IrI_6]^{3-}$ followed by acidification produced colour changes as for the chloro- and bromo-complexes, but no nitrosyl-containing material could be isolated.

EXPERIMENTAL

Iridium trichloride was obtained from Johnson, Matthey, and Mallory, Montreal, and used as received. The salts $K[Ir(X)_5NO]$ (X = Cl or Br) were prepared by a considerably modified version of the literature methods.[18,19]

Potassium Pentahalogenonitrosyliridate, $K[Ir(X)_5NO]$ (X = Cl *or* Br).—To a solution of the salt $K_3[IrCl_6]$ (0·40 g) in the minimum volume of water (10 cm^3) was added $NaNO_2$ (0·10 g), and the resulting solution heated with an accompanying change in colour from green to yellow. When the volume had been reduced to *ca.* one half, concentrated HCl (15 cm^3) was added. Continued heating produced gas evolution, a darkening of the solution to a deep red colour, and, finally, appearance of a deep red precipitate. The mixture was cooled to 5 °C, the product collected by filtration, and air dried. It was washed with methanol (2×3 cm^3) and diethyl ether (2×3 cm^3) and dried *in vacuo*; the air-dried solid frequently contained water of crystallization, yield 0·20 g (60%) (Found: Cl, 40·5. Calc. for Cl_5IrKNO: Cl, 40·4%). ν(NO) (anhydrous material, Nujol mull) at 2 008 cm^{-1}. $\lambda_{max.}$ 268 nm ($\varepsilon > 1 \times 10^4$ dm^3 mol^{-1} cm^{-1}). The bromo-complex was similarly prepared in 60% yield (Found: Br, 60·2. Calc. for Br_5IrKNO: Br, 60·45%). ν(NO) (Nujol mull) at 1 958 cm^{-1}; aqueous solution, 0·025 mm CaF_2 cell, 1 953 cm^{-1}. $\lambda_{max.}$ 322 (ε $1{\cdot}07 \times 10^4$) and 289 nm (ε $1{\cdot}0 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

Reaction of Pentahalogenonitrosyliridate(1—) *with Hydroxide Ion: Tripotassium Pentahalogenonitroiridate*, $K_3[Ir(X)_5NO_2]$ (X = Cl *or* Br).—To an ice-cold slurry of the salt $K[Ir(Br)_5NO]$ (0·30 g) in water (1 cm^3) was added one pellet

---

[23] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 1962, **4**, 381.

[24] F. Bottomley, *J.C.S. Dalton*, 1972, 2148.

[25] J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 1420.

[26] W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals,' Interscience, London, 1969, p. 289.

[27] J. C. Chang and C. S. Garner, *Inorg. Chem.*, 1965, **4**, 209.

[28] It has been shown that $[Ru(NH_3)_5NO]^{3+}$ is attacked by $[RuNH_2(NH_3)_4NO]^{2+}$, not, as previously suggested,[5,10] by NH_3 (F. Bottomley, S. G. Clarkson, and E. M. R. Kiremire, unpublished work).

[29] L. Maltesta, L. Maldini, and F. Cariati, *J. Chem. Soc.*, 1964, 961.

[30] A. Braibanti, F. Dallavalle, M. A. Pellinghelli, and E. Laporati, *Inorg. Chem.*, 1968, **7**, 1430.

(0·2 g) of KOH; the KOH and red $K[Ir(Br)_5NO]$ dissolved to give a green solution of $[Ir(Br)_5NO_2]^{3-}$. Addition of 95% ethanol gave a green precipitate which was collected by filtration, washed with 95% ethanol and diethyl ether, and dried *in vacuo*, yield 0·12 g (62%) (Found: Br, 52·65; N, 1·75. Calc. for $Br_5IrK_3NO_2$: Br, 52·9; N, 1·85%). The chloro-complex was obtained in a similar manner from $K[Ir(Cl)_5NO]$, except that it often precipitated as a hydrate of unknown stoicheiometry. The water of crystallization was removed *in vacuo*, yield 78% (Found: Cl, 33·25; N, 2·45. Calc. for $Cl_5IrK_3NO_2$: Cl, 33·25; N, 2·65%). The i.r. spectrum of the chloro-complex was in good agreement with the published spectrum,[31] and that of the bromo-complex was similar. The electronic spectrum of $[Ir(Cl)_5NO_2]^{3-}$ showed two bands at 350 (ε $6{\cdot}5 \times 10^2$) and at 280 nm (ε $1{\cdot}3 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and $[Ir(Br)_5NO_2]^{3-}$ a shoulder at 272 nm (ε 8×10^4 dm^3 mol^{-1} cm^{-1}) on a high-energy tail.

Aquation of Pentabromonitroiridate(3–): *Dipotassium Aquatetrabromonitroiridate*, $K_2[IrBr_4(NO_2)H_2O]$.—A solution of the salt $K_3[Ir(Br)_5NO_2]$ (0·30 g) in water (2 cm^3) was set aside at 5 °C for 16 h. Addition of 95% ethanol gave a yellow-brown precipitate which was collected by filtration, washed with ethanol and diethyl ether, and dried *in vacuo*, yield 0·20 g (80%) (Found: Br, 49·05; N, 2·05. Calc. for $H_2Br_4IrK_2NO_3$: Br, 48·85; N, 2·15%). The complex was a 1 : 2 electrolyte in aqueous solution. The i.r. spectrum showed bands at 1 350s, 1 355(sh), 1 271s, and 857w cm^{-1} assignable to co-ordinated NO_2^-, and 3 460 and 1 610 cm^{-1} assignable to co-ordinated H_2O.

Reaction of Pentahalogenonitrosyliridate(1–) *with Ammonia: Dipotassium Amminepentahalogenoiridate*, $K_2[Ir(X)_5NH_3]$ (X = Cl or Br).—The salt $K[Ir(Br)_5NO]$ (0·30 g) was added to aqueous ammonia (*d* 0·880 g cm^{-3}; 3 cm^3). A rapid exothermic reaction, accompanied by vigorous gas evolution, gave a green solution which on cooling deposited a green precipitate of $K[NH_4][Ir(Br)_5NH_3]$. This was collected by filtration, washed with methanol and diethyl ether, and air dried (yield 0·18 g, 58%). The chloro-complex was obtained similarly in 48% yield. The bromo-complex was converted to $K_2[Ir(Br)_5NH_3]$ by air evaporation of an aqueous ethanol solution in the presence of KBr (Found: Br, 57·8; N, 2·15. Calc. for $H_3Br_5IrK_2N$: Br, 58·15; N, 2·05%). The product was a 1 : 2 electrolyte in aqueous solution and showed i.r. absorption bands appropriate to an ammine complex.

Reaction of Pentabromonitrosyliridate(1–) *with Hydroxylamine: Dipotassium Aquapentabromoiridate*, $K_2[Ir(Br)_5H_2O]$.—One pellet (0·2 g) of KOH was added to a solution of NH_2OH,HCl (0·47 g) in water (2 cm^3) and then $K[Ir(Br)_5NO]$ (0·30 g) added in small portions. When all the $K[Ir(Br)_5NO]$ was in solution, and the accompanying gas evolution had ceased, the green product was precipitated by addition of 95% ethanol (20 cm^3). The product was collected by filtration, washed with 95% ethanol and diethyl ether, and dried *in vacuo*, yield 0·24 g (77%) (Found: Br, 58·15. Calc. for $H_2Br_5IrK_2O$: Br, 58·1%). The complex was a 1 : 2 electrolyte in aqueous solution, and had properties similar to those described in the literature.[26] The i.r. spectrum showed bands attributable to co-ordinated H_2O, unaltered by prolonged drying *in vacuo*.

Reaction of Pentahalogenonitrosyliridate(1–) *with Azide Ion*.—To a solution of KN_3 (0·02 g) in water (1 cm^3) was slowly added the salt $K[Ir(Br)_5NO]$ (0·09 g). When the resultant vigorous gas evolution ceased, 95% ethanol was added giving a green precipitate. This was collected by filtration, washed with 95% ethanol and diethyl ether, and air dried (yield 0·08 g, 80%). The chloro-complex was prepared similarly. The chemical and physical properties of the bromo-complex were similar to those of that produced by the hydroxylamine reaction above.

Reaction of Pentabromonitrosyliridate(1–) *with Hydrazine Hydrate: Tribromotrihydrazineiridium Hydrate* (2/1), $[IrBr_3(N_2H_4)_3],0{\cdot}5\,H_2O$.—Hydrazine hydrate (85%, 1 cm^3) was slowly added to a stirred slurry of the salt $K[Ir(Br)_5NO]$ (1·0 g) in cold water (5 cm^3). There was an immediate exothermic reaction with gas evolution. The yellow precipitate which formed was collected by filtration, washed with water, ethanol, and diethyl ether, and dried *in vacuo*, yield 0·45 g (56%) (Found: Br, 41·5; H, 2·40; N, 15·85. Calc. for $H_{26}Br_6Ir_2N_{12}O$: Br, 44·6; H, 2·45; N, 15·65%). The complex was insoluble in all common solvents, diamagnetic, and showed i.r. absorption bands assignable to hydrazine and water.

I.r. spectra were measured on a Perkin-Elmer 457 instrument; electronic spectra on a Bausch and Lomb Spectronic 505; magnetic moments by the Gouy method; conductivities on a Beckman conductivity bridge; and hydrogen-ion concentrations on a Beckman Research pH meter. Gas-evolution experiments were carried out by adding the salts $K[Ir(X)_5NO]$ to the appropriate frozen, degassed, reagent solution and, after evacuation, allowing the mixture to warm up on the vacuum line. Gas volumes were determined by a Toepler pump–manometer system, and analysed on a Hitachi–Perkin-Elmer RMU-60 mass spectrometer. Microanalyses were by A. Bernhardt, West Germany.

We thank the National Research Council of Canada and the University of New Brunswick Research Fund for support, Johnson, Matthey, and Mallory, Montreal, for a generous loan of iridium trichloride, and Dr. F. Grein of this Department for the molecular-orbital calculation on NO^+.

[4/663 *Received*, 1st *April*, 1974]

---

[31] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1967, 1144.