Insertion of Isocyanides into Niobium– and Tantalum–Halogen Bonds

By **Mahbobeh Behnam-Dahkordy**, **Bruno Crociani**, and **Raymond L. Richards**,* School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Isocyanides RNC (R = Me or Bu^t) insert into the metal–halogen bond of niobium and tantalum pentahalides or tantalum tribromide oxide to give the complexes $[MX_4\{CX(NR)\}(CNR)]$ (A : M = Nb or Ta; X = Cl or Br; R = Me or Bu^t), $[TaBr_2\{CBr(NMe)\}_3(CNMe)]$, and $[TaBr_2O\{CBr(NMe)\}(CNMe)]$. The complex $[NbCl_4\{CCl(NMe)\}(CNMe)]$ gives the further insertion products $[NbCl_3\{CCl(NMe)\}_2L^1]$ on treatment with L^1 = MeNC or PPh_3, but treatment of $[MX_4\{CX(NBu^t)\}(CNBu^t)]$ with L^2 = PPh_3, PMe_2Ph, or $PMePh_2$ or L^3 = $Ph_2PCH_2CH_2PPh_2$ or *cis*-$Ph_2PCH{=}CHPPh_2$ displaces Bu^tNC to give $[MX_4\{CX(NBu^t)\}L^2]$ (M = Ta, X = Cl or Br) and $[MX_3\{CX(NBu^t)\}L^3]X$ (M = Ta, X = Br; M = Nb, X = Cl). The complex $[TaBr_3\{CBr(NMe)\}(dppe)]Br$ (dppe = $Ph_2PCH_2CH_2PPh_2$) has also been prepared from $[TaBr_5(dppe)]$. Reaction of $[NbCl_3\{CCl(NMe)\}_2(CNMe)]$ with $Li[AlH_4]$ gives dimethylamine but no higher amines. Hydrogen or deuterium chloride reacts with $[NbCl_4\{CCl(NMe)\}(CNMe)]$ to give a product with N–H or N–D bonds which could not be purified. The physical properties of these complexes are reported and their structures and possible mechanism of formation are discussed.

ISOCYANIDE complexes of a wide variety of transition metals have been prepared.[1] The nature of the bonding of isocyanides to metals depends on the oxidation state of the metal and its position in the Periodic Table. Most work has been with the later transition metals where, for example, nucleophilic attack at carbon occurs for certain complexes.[2,3] Examples of isocyanide complexes of early transition metals are much fewer, especially when these metals are in their higher oxidation states. However, the insertion of isocyanides into the metal–carbon bonds of $[TaCl_2Me_3]$ [4] and into the metal–halogen bonds of Group 4 and Group 5 halido-complexes has recently been described.[5,6] Here we describe in detail the reactions of isocyanides with halide complexes of niobium and tantalum which lead to insertion of isocyanide into the metal–halogen bonds.

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RESULTS AND DISCUSSION

Preparations.—When treated with 2 mol equiv. of RNC (R = Me or Bu^t) in dry diethyl ether or dichloromethane at 20 °C, niobium and tantalum pentahalides slowly give the mono-inserted products $[MX_4\{CX(NR)\}(CNR)]$ (A: M = Nb or Ta; X = Cl or Br; R = Me or Bu^t) as shown in equation (1). The physical properties

$$\tfrac{1}{2}M_2X_{10} + 2RNC \longrightarrow [MX_4\{CX(NR)\}(CNR)]\ (A) \quad (1)$$

of complexes (A) are shown in the Table. The reactions are quite slow, taking up to 4 d for completion (see Table). An intermediate product appears to be initially formed. It is probably an isocyanide adduct, such as $[MX_5(CNR)]$, but it could not be isolated.

When R = Bu^t, complexes (A; R = Bu^t) are the only products obtained from reaction (1) even in the presence of an excess of isocyanide, but when R = Me further reaction can occur with the insertion of more isocyanide molecules into the metal–halogen bonds, *e.g.* reaction (2). The product (B) can also be obtained by treatment of $[NbCl_4\{CCl(NMe)\}(CNMe)]$ with 1 mol of methyl isocyanide.

Complexes (A) and (B) show strong bands in the 2 200 [$\nu(C\equiv N)$] and 1 650 cm^{-1} [$\nu(C{=}N)$] regions of their i.r. spectra (Table), the intensity of the C=N band being,

$$\tfrac{1}{2}Nb_2Cl_{10} + 3MeNC \xrightarrow[72h,\ 20\ ^\circ C]{Et_2O} [NbCl_3\{CCl(NMe)\}_2(CNMe)]\ (B) \quad (2)$$

as expected, greater relative to the C≡N band for (B) than for (A).

It was shown that (B) was produced by further insertion of isocyanide into an Nb–Cl, rather than an Nb–C, bond by reducing (B) with $Li[AlH_4]$ (Experimental section). This gave only dimethylamine and none of the higher amines which would be expected if insertion into an Nb–C bond had occurred. A product with three molecules of MeNC inserted into Ta–Br bonds $[TaBr_2\{CBr(NMe)\}_3(CNMe)]$ was obtained from the reaction of Ta_2Br_{10} with 5 mol of MeNC in dichloromethane. From a similar reaction with diethyl ether as solvent, an insoluble oxo-complex, $[TaBr_2O\{CBr(NMe)\}(CNMe)]$, was isolated. The source of the oxide ligand is not certain; it may arise from the ether *via* decomposition of a complex such as $TaBr_5{\cdot}OEt_2$ which is known to decompose (at 74 °C) to give $TaBr_3O$,[6] or from

Niobium and tantalum complexes

Complex	Reaction time (t/h), solvent	Colour	Yield (%)	Analysis (%) [a]			I.r. (cm^{-1}) [b]	N.m.r. (δ/p.p.m.) [c]	Other data (units of Λ: S cm^2 mol^{-1})
				C	H	N			
$[NbCl_4\{CCl(NMe)\}(CNMe)]$	48, OEt_2	Purple-brown	94	13.5 (13.6)	2.0 (1.7)	7.8 (7.9) 50.9 (50.3) [d]	2 280 (sh),[e] 2 271vs, br,[e] 1 680 (sh),[f] 1 628vs, br,[f] 360 (sh),[g] 343vs,[g] 326 (sh) [g]	3.88 (br, s) [h] CN*Me*, 3.52 (m) [h] CCl(N*Me*)	m.p.[i] 210—220 °C; *M* 574,[j] 388 [k] (352); Λ [k] 65
$[NbCl_3\{CCl(NMe)\}_2(CNMe)]$	72, OEt_2	Deep purple	89	18.3 (18.3)	2.8 (2.3)	10.1 (10.6) 45.1 (45.0) [d]	2 260 (sh),[e] 2 225vs,[e] 1 685 (sh),[f] 1 640s, br,[f] 1 596 (sh),[f] 360 (sh),[g] 343vs, br [g]	3.73 (s) [h] CN*Me*, 3 45 (m) [h] CCl(N*Me*)	m.p.[i] 140—150 °C; Λ[h] 100
$[NbCl_3\{CCl(NMe)\}_2(PPh_3)]$	96, CH_2Cl_2	Brick-red	60	43.2 (42.9)	3.8 (3.4)	4.5 (4.5)	1 670 (sh),[f] 1 640vs,[f] 1 600 (sh),[f] 340vs,[g] 325vs,[g] 307 (sh) [g]	insoluble	m.p.[i] 140—150 °C; Λ[h] 74.5
$[NbCl_4\{CCl(NBu^t)\}(CNBu^t)]$	16, OEt_2	Cream	71	28.1 (27.5)	4.5 (4.1)	6.5 (6.4)	2 240vs,[e] 1 690—1 625vs, br,[f] 400—250 [g]	1.5—1.8 (m) CN*Bu*^{t}	
$[NbBr_4\{CCl(NBu^t)\}(CNBu^t)]$	60, OEt_2	Dark red	82	20.0 (20.8)	3.6 (3.1)	4.6 (4.8)	2 240vs,[e] 1 700—1 625vs, br [f]	1.5—2.0 (m) CN*Bu*^{t}	
$[NbCl_3\{CCl(NBu^t)\}(dppe)]Cl$ [l]	12, CH_2Cl_2	Dark cream	35	49.4 (49.5)	4.9 (4.4)	1.9 (1.9)	1 650—1 600s, br [g]	1.0—1.17 (m) CN*Bu*^{t}, 7.0—8.4 *Ph*$_2$P(CH$_2$)$_2$P*Ph*$_2$	Λ [h] 60
$[NbBr_3\{CBr(NBu^t)\}(dppe)]Br$ [l,m]	18, CH_2Cl_2	Dark orange	30	39.3 (39.1)	4.0 (3.7)	1.6 (1.3)	1 625s, br [f]	0.8—1.5 (m) CBr(N*Bu*^{t}), 1.5—1.8 Ph$_2$P(*CH*$_2$)$_2$PPh$_2$, 7.2—8.3 *Ph*$_2$P(CH$_2$)$_2$P*Ph*$_2$	Λ [h] 100
$[TaCl_4\{CCl(NMe)\}(CNMe)]$	48, Et_2O	Cream-brown	68	11.1 (10.9)	2.0 (1.3)	6.3 (6.3) 39.6 (40.2) [d]	2 280 (sh),[e] 2 270s,[e] 1 680 (sh),[f] 1 628s, br,[f] 360 (sh),[g] 343s,[g] 326s [g]	3.72 (sf) [h] CN*Me*, 3.5 (m) [h] CCl(N*Me*)	m.p.[i] 255—265 °C Λ [k] 80.5
$[TaBr_2\{CBr(NMe)\}_3(CNMe)]$	18, CH_2Cl_2	Lemon-yellow	35	12.8 (12.9)	2.0 (1.6)	7.2 (7.5) 53.6 (53.7) [n]	2 227vs,[e] 1 650vs, br [f]	insoluble	m.p.[i] 120 °C

TABLE (*Continued*)

Complex	Reaction time (t/h), solvent	Colour	Yield (%)	Analysis (%) [a]			I.r. (cm^{-1}) [b]	N.m.r. (δ/p.p.m.) [c]	Other data (units of Λ: S cm^{2}mol^{-1})
				C	H	N			
$[TaBr_2O\{CBr(NMe)\}(CNMe)]$	24, OEt_2	Pale yellow	85	9.0 (9.2)	2.0 (1.1)	5.6 (5.4)	2 226vs,[e] 1 650s, br,[f] 1 000—900 [o]	insoluble	m.p.[i] 110 °C
$[TaBr_3\{CBr(NMe)\}(dppe)]Br$ [l]	24, CH_2Cl_2	Yellow	30	32.8 (32.9)	3.0 (2.6)	1.4 (1.3)	1 650 [f]	insoluble	
$[TaCl_4\{CCl(NBu^t)\}(CNBu^t)]$	12, OEt_2	Pink	88	22.9 (22.8)	3.5 (3.4)	4.9 (5.3)	2 260vs,[e] 1 625—1 600s, br,[f] 300—200 [g]	1.4—1.6 (m) $\mathrm{CN}\mathit{Bu}^t$, $\mathrm{CCl(N}\mathit{Bu}^t)$	
$[TaBr_4\{CBr(NBu^t)\}(CNBu^t)]$	20, OEt_2	Yellow	65	16.5 (16.1)	2.6 (2.4)	4.1 (3.8)	2 240vs,[e] 1 690—1 625br,[f] 235—220 [g]	1.5—1.8 (m) $\mathrm{CN}\mathit{Bu}^t$, $\mathrm{CBr(N}\mathit{Bu}^t)$	
$[TaCl_4\{CCl(NBu^t)\}(PPh_3)]$	18, CH_2Cl_2	Dark brown	35	40.0 (39.2)	4.1 (3.4)	2.0 (1.9)	1 690—1 625br [f]	1.0—1.6 (m) $\mathrm{CCl(N}\mathit{Bu}^t)$, 7.3—8.0 (m) $\mathrm{P}\mathit{Ph}_3$	
$[TaCl_4\{CCl(NBu^t)\}(PMe_2Ph)]$	24, CH_2Cl_2	Cream	45	27.3 (26.9)	3.6 (3.4)	2.2 (2.4)	1 680—1 600br [f]	1.2—2.4 (m) $\mathrm{CCl(N}\mathit{Bu}^t)$, $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$, 7.4—7.8 (m) $\mathrm{PMe_2}\mathit{Ph}$	
$[TaCl_4\{CCl(NBu^t)\}(PMePh_2)]$ [m]	20, CH_2Cl_2	Cream	37	35.6 (35.2)	4.0 (3.9)	1.8 (2.0)	1 690—1 625s [f]	1.0—1.8 (m) $\mathrm{CClN}\mathit{Bu}^t$, $\mathrm{P}\mathit{Me}\mathrm{Ph_2}$, 7.0—7.6 $\mathrm{PMe}\mathit{Ph}_2$	
$[TaBr_4\{CBr(NBu^t)\}(PMe_2Ph)]$	18, OEt_2 20, CH_2Cl_2	Orange	30	19.5 (19.4)	2.8 (2.4)	1.8 (1.8)	1 690—1 625s [f]	0.8—2.3 (m) $\mathrm{CBr(N}\mathit{Bu}^t)$, $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$, 7.0—7.7 (m) $\mathrm{PMe_2}\mathit{Ph}$	
$[TaBr_3\{CBr(NBu^t)\}(dppe)]Br$ [l,p]	48, CH_2Cl_2	Yellow	30	33.6 (34.9)	3.1 (3.1)	1.2 (1.3)	1 690—1 625s	1.2—1.5 (m) $\mathrm{CBr(N}\mathit{Bu}^t)$, $\mathrm{Ph_2P(}\mathit{CH}_2)_2\mathrm{PPh_2}$, 7.0—8.5 (m) $\mathit{Ph}_2\mathrm{P(CH_2)_2P}\mathit{Ph}_2$	Λ [q] 113
$[TaBr_3\{CBr(NBu^t)\}(dppen)]$ [l,p]	72, CH_2Cl_2	Dark red	43	33.1 (35.1)	3.1 (2.9)	1.4 (1.3)	1 690—1 625s [f]	0.8—1.8 (m) $\mathrm{CBr(N}\mathit{Bu}^t)$, $\mathrm{Ph_2P(}\mathit{CH})_2\mathrm{PPh_2}$, 7.2—8.2 (m) $\mathit{Ph}_2\mathrm{P(CH)_2P}\mathit{Ph}_2$	
$[TaBr_5(dppe)]$ [l]	48, OEt_2	Orange	90	32.4 (31.8)	2.9 (2.4)			insoluble	insoluble

s = Strong, v = very, sh = shoulder, br = broad (i.r.); s = singlet, m = multiplet, sf = singlet with some fine structure, not well resolved (n.m.r.).

[a] Calculated values are given in parentheses. [b] Nujol mulls. [c] Relative to $SiMe_4$ at 100 MHz, in CD_2Cl_2 solution unless otherwise stated, satisfactory integrations obtained. [d] Cl analysis. [e] $\nu(C\equiv N)$. [f] $\nu(C=N)$. [g] Mixture of metal–halogen and other bands. [h] CD_3CN solution. [i] In sealed tube *in vacuo* with decomposition. [j] *ca.* 10^{-2} mol dm^{-3} MeCN solution (see text). [k] *ca.* 10^{-3} mol dm^{-3} MeCN solution (see text). [l] Tentative formulation (see text). [m] Contains $\frac{1}{2}OEt_2$ of crystallisation, observed in n.m.r. spectrum but omitted from Table. [n] Br analysis. [o] Ta=O vibration. [p] Could not be obtained completely pure (see text). [q] *ca.* 10^{-2} mol dm^{-3} $MeNO_2$ solution.

adventitious entry of atmospheric moisture during the reaction. This compound was also synthesised from $TaBr_3O$ [equation (3)]. Triphenylphosphine reacts with

$$TaBr_3O + 2MeNC \longrightarrow [TaBr_2O\{CBr(NMe)\}(CNMe)] \quad (3)$$

(A; M = Nb, X = Cl, R = Me) to cause a second insertion of isocyanide [equation (4)]. Complex (C), as

$$[NbCl_4\{CCl(NMe)\}(CNMe)] + PPh_3 \xrightarrow{CH_2Cl_2} [NbCl_3\{CCl(NMe)\}_2(PPh_3)] \text{ (C)} \quad (4)$$

expected, shows C=N bands in its i.r. spectrum (Table) but no C≡N bands.

A ditertiary phosphine-substituted complex, $[TaBr_3\{CBr(NMe)\}(dppe)]Br$ (dppe = $Ph_2PCH_2CH_2PPh_2$), was prepared directly by reaction of MeNC with $[TaBr_5(dppe)]$ [equation (5)]. The formulation of the poorly soluble (D) as a salt is tentative (see Experimental section).

$$[TaBr_5(dppe)] + MeNC \xrightarrow{CH_2Cl_2} [TaBr_3\{CBr(NMe)\}(dppe)]Br \text{ (D)} \quad (5)$$

More than one insertion does not occur for R = Bu^t, perhaps because of the steric hindrance of this group. Attempts to induce further insertion in complexes of Bu^tNC by the action of tertiary phosphines, in a similar way to reaction (4), resulted only in displacement of the terminal isocyanide ligand, equation (6) (M = Nb or Ta; X = Cl or Br; L^2 = PPh_3, PMe_2Ph, or $PMePh_2$).

$$[MX_4\{CX(NBu^t)\}(CNBu^t)] + L^2 \xrightarrow{CH_2Cl_2} [MX_4\{CX(NBu^t)\}L^2] \text{ (E)} + Bu^tNC \quad (6)$$

If the ditertiary phosphine ligands [L^3 = dppe or $Ph_2P(CH)_2PPh_2$] are used instead of L^2 in reaction (6), then the products $[MX_3\{CX(NBu^t)\}L^3]X$ (F; M = Ta, X = Br; M = Nb, X = Cl or Br) result. Complexes (F) are formulated as six-co-ordinate salts on the basis of their conductivities (Table), but it is difficult to obtain accurate data for these very moisture-sensitive, poorly soluble, complexes (see below) and the possibility that the cation may be dimeric cannot be excluded.

Solution Properties.—In general, these complexes are all very moisture-sensitive materials which tend to decompose in solvents in which they are appreciably soluble. This behaviour has made determination of their solution properties difficult. Solutions in methyl cyanide or dichloromethane as appropriate have sufficient stability to allow determination of the ^{1}H n.m.r. spectra of some complexes (Table). The n.m.r. spectrum of $[NbCl_4\{CCl(NMe)\}(CNMe)]$ (G) in CD_3CN shows a broad singlet and a complex multiplet of equal intensity. The spectrum of (B) is similar, except that the multiplet is twice the intensity of the singlet, therefore this multiplet and that of (G) are assigned to the iminomethyl group coupled to niobium. The singlet resonance, due to ligating MeNC, is probably not coupled to niobium because of exchange with the solvent CD_3CN. The spectrum of $[TaCl_4\{CCl(NMe)\}(CNMe)]$ in CD_3CN is similar to that of (G) but the singlet has some fine structure, possibly because MeNC is less labile when co-ordinated to tantalum than to niobium. The analogous complexes with R = Bu^t are somewhat more soluble than (B) and (G) and their n.m.r. spectra were obtained in CD_2Cl_2 solution. In general, the resonances due to CN*Bu*^{t} and CCl(N*Bu*^{t}) occurred together as a complex multiplet and could not be separately assigned. Some of the complexes (E) were sufficiently soluble for determination of their n.m.r. spectra in CD_2Cl_2 solution and gave satisfactory relative integration values for the multiplets observed for N*Bu*^{t}, P*Ph*, and P*CH*$_n$ (n = 1—3) groups. The occurrence of multiplets for all these resonances is probably due to the presence of coupling to the metal centre and of various isomers in solution, and a detailed assignment of the spectra is not possible at this stage.

The determination of the molecular weight of these complexes was very difficult because of their insolubility, sensitivity to moisture, *etc.* as noted above. Complex (B) has been studied in the most detail, in anhydrous methyl cyanide. The molecular-weight values obtained (by osmometry) vary with concentration and, moreover, the solution conducts (Table). Thus dissociation of halide from the metal in acetonitrile solution probably occurs and the observed molecular-weight values are expected to be low. They are in fact higher than the calculated monomer values (Table), indicating that complex (B) is probably dimeric. This complex probably contains an Nb–N(Me)=C(Cl)–Nb bridging unit, which is similar to the imino-nitrogen-bridged structure proposed for some analogous gold complexes.[7] It also seems likely that such a bridging unit will aid the stability of the CCl(NR) ligand by preventing its reversion to the parent isocyanide and halide ligands; probably most if not all of the complexes of this series contain such bridges.

Reaction with Hydrogen Halides.—The basic properties of CX=NR ligands (X = alkyl, aryl, alkylamino, or alkoxy) are well known [2] and reversible protonation of the nitrogen atom to give carbene-type ligands has been reported.[2] Complex (A; M = Nb, R = Me, X = Cl) clearly protonated at the imino-nitrogen atom when it was treated with anhydrous HCl in dichloromethane or diethyl ether. The i.r. spectrum of the impure solid obtained after acid treatment showed an N–H band at 3 250 cm^{-1} which shifted to a broad absorption at 2 380—2 450 cm^{-1} in the deuterio-analogue. A similar reaction was observed when complexes (A) were treated with $[HOEt_2][BF_4]$ in anhydrous diethyl ether but only oily uncharacterisable products could be obtained on work-up.

Mechanism of the Reaction.—The insertion of isocyanides into metal–carbon and –nitrogen bonds is well documented. Their insertion into metal–halogen bonds is so far confined to the examples described here and to Group 4 halides and vanadium halides.[6] The insertion reaction (4) clearly involves prior ligation of isocyanide to the metal. An intermediate has also been observed in reaction (1) which is probably an isocyanide complex. The products of reactions (1) and (2) result from an insertion step and an addition of a terminal ligand to the metal. It is therefore reasonable to suppose that, in all the insertion reactions, halide transfer to the carbon atom of ligating isocyanide is induced by an incoming nucleophilic isocyanide or tertiary phosphine ligand, perhaps by an intramolecular mechanism related to that proposed for the insertion of isocyanide into the Pt–C bond,[8] but a binuclear mechanism cannot be excluded.

EXPERIMENTAL

Air-sensitive materials were manipulated in an atmosphere of dry dinitrogen using conventional Schlenk-tube and glove-bag techniques. Solvents were distilled under dinitrogen from appropriate drying agents. t-Butyl isocyanide, methyl isocyanide, and tertiary phosphine ligands were prepared by published methods.[9] Niobium and tantalum pentachlorides were purchased from Koch–Light Ltd., and the pentabromides were prepared from the metal by published methods and sublimed before use.[10] Tantalum tribromide oxide was prepared by the published method from $TaBr_5\cdot OEt_2$.[11]

Infrared spectra were determined with Perkin-Elmer 457 or Grubb–Parsons D.M.4 instruments and n.m.r. spectra with JEOL P.S. 100 or Varian E.M. 360 instruments. Conductivities were measured with a Portland Electronics conductivity bridge, molecular weights with a Hitachi–Perkin-Elmer 115 osmometer, and melting points with a Kofler hot stage. Microanalyses were by Mr. and Mrs. A. G. Olney of these laboratories or by A. Bernhardt Microanalytical Laboratories, West Germany. Analytical details, *etc.* of all the new complexes are shown in the Table.

Reaction of M_2X_{10} (M = Nb *or* Ta, X = Cl *or* Br) *with* RNC (R = Me *or* Bu^t).—Since the technique is a general one, one specific example is given, reaction times and solvents for all the preparations being shown in the Table.

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Tetrachloro[chloro(methylimino)methyl](methyl isocyanide)niobium(V), $[\mathrm{NbCl_4\{CCl(NMe)\}(CNMe)}]$. The compound $\mathrm{Nb_2Cl_{10}}$ (3.25 g) was almost completely dissolved in diethyl ether (50 $\mathrm{cm^3}$) to give a yellow solution to which was added, dropwise, with stirring under dinitrogen during 15 min, MeNC (1.28 $\mathrm{cm^3}$, 2 mol). A yellow solid began to precipitate on the first addition of MeNC and became progressively brown as more MeNC was added. After stirring the mixture for 20 h a purple-brown *precipitate* was obtained which was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C) (4.0 g).* Attempts to isolate the initial yellow intermediate product of this reaction using identical conditions but only 1 mol of MeNC gave only impure mixtures of products.

Trichlorobis[chloro(methylimino)methyl](methyl isocyanide)niobium(V), $[\mathrm{NbCl_3\{CCl(NMe)\}_2(CNMe)}]$. (*a*) *From* $\mathrm{Nb_2Cl_{10}}$. Methyl isocyanide (1.03 $\mathrm{cm^3}$, 3.9 mol) was added dropwise over 15 min to a stirred suspension of $\mathrm{Nb_2Cl_{10}}$ (1.74 g) in $\mathrm{CH_2Cl_2}$ (50 $\mathrm{cm^3}$). The initial yellow suspension slowly became violet, then gradually turned purple. After 72 h the solvent was reduced to small volume *in vacuo*, then addition of diethyl ether precipitated a deep purple *solid* which was filtered off, washed with diethyl ether and hexane, and dried (10^{-3} mmHg, 20 °C) (1.7 g).

(*b*) *From* $[\mathrm{NbCl_4\{CCl(NMe)\}(CNMe)}]$ (G). Methyl isocyanide (0.1 $\mathrm{cm^3}$, 1.3 mol) was added to a suspension of (G) (0.5 g) in $\mathrm{CH_2Cl_2}$ (25 $\mathrm{cm^3}$) and the mixture was stirred for 16 h during which time the purple-brown colour of (G) changed to give a deep purple *solid* which was filtered off, washed with diethyl ether and hexane, and dried (10^{-3} mmHg, 20 °C) (0.48 g). It was shown to be identical to the product from (*a*) by its i.r. spectrum and by analysis.

Dibromo[bromo(methylimino)methyl](methyl isocyanide)oxotantalum(V), $[\mathrm{TaBr_2O\{CBr(NMe)\}(CNMe)}]$. (*a*) *From* $\mathrm{Ta_2Br_{10}}$. Methyl isocyanide (0.07 $\mathrm{cm^3}$) was added to a stirred solution of $\mathrm{Ta_2Br_{10}}$ (0.48 g) in diethyl ether (20 $\mathrm{cm^3}$) at 20 °C. A dark yellow precipitate formed which slowly lightened over 24 h. Filtration then gave a pale yellow *solid* which was washed with diethyl ether and dried (10^{-3} mmHg, 20 °C).

(*b*) *From* $\mathrm{TaBr_3O}$. A mixture of MeNC (0.12 $\mathrm{cm^3}$), $\mathrm{TaBr_3O}$ (0.95 g), and diethyl ether (30 $\mathrm{cm^3}$) was stirred for 16 h. The original dark yellow colour of the starting material became lighter and the resulting pale yellow *solid* was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). It was shown to be identical to the product from (*a*) by its i.r. spectrum and analysis.

The other complexes which contained only ligating isocyanides or their insertion products were prepared by similar methods.

Preparation of Complexes containing Tertiary Phosphine Ligands.—Again, the methods are general and only one specific example of each is given, the complexes prepared being shown in the Table.

Tetrabromo[bromo(t-butylimino)methyl](dimethylphenylphosphine)tantalum(V), $[\mathrm{TaBr_4\{CBr(NBu^t)\}(PMe_2Ph)}]$. (*a*) *In diethyl ether*. A mixture of $[\mathrm{TaBr_4\{CBr(NBu^t)\}(CNBu^t)}]$ (0.58 g) and $\mathrm{PMe_2Ph}$ (0.12 $\mathrm{cm^3}$) in diethyl ether (30 $\mathrm{cm^3}$) was stirred at 20 °C. The yellow colour of the mixture gradually changed to orange over 18 h and the precipitated orange *solid* was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C).

(*b*) *In dichloromethane*. Dimethylphenylphosphine (0.14 $\mathrm{cm^3}$) was added to $[\mathrm{TaBr_4\{CBr(NBu^t)\}(CNBu^t)}]$ (0.57 g) in $\mathrm{CH_2Cl_2}$ (40 $\mathrm{cm^3}$) with stirring at 20 °C. The solution changed from yellow to dark orange over 24 h, then the solvent was removed *in vacuo* to small volume, and diethyl ether was added to precipitate an orange *solid* which was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C).

[1,2-Bis(diphenylphosphino)ethane]trichloro[chloro(t-butylimino)methyl]niobium(V) *chloride*, $[\mathrm{NbCl_3\{CCl(NBu^t)\}(dppe)]Cl}$. The compound dppe (0.42 g) was added to $[\mathrm{NbCl_4\{CCl(NBu^t)\}(CNBu^t)}]$ (0.46 g) in dichloromethane with stirring at 20 °C. The solution slowly changed colour from cream to dark red over 12 h. The solvent was then removed *in vacuo* to small volume and addition of diethyl ether precipitated a dark orange *solid* which was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C).

The other phosphine-containing products were prepared by similar methods with the exception of the adduct below.

[1,2-Bis(diphenylphosphino)ethane]tribromo[bromo(methylimino)methyl]tantalum(V) *bromide*. Methyl isocyanide (0.02 $\mathrm{cm^3}$) was added to $[\mathrm{TaBr_5(dppe)}]$ (0.37 g) in $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$) and the mixture was stirred for 24 h at 20 °C. The resulting yellow solution was filtered to remove a small amount of solid impurity, then the solvent was removed *in vacuo* to small volume. Addition of diethyl ether then precipitated a yellow *solid* which was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C). This complex is tentatively formulated as a six-co-ordinate salt by analogy with complexes (F) (see text), which conduct in solution (Table). It is too insoluble for conductivity measurements, however, and the possibility that it is non-ionic or dimeric cannot be excluded.

Reactions with Hydrogen Chloride and Deuterium Chloride.—One example is given to illustrate the general technique.

$[\mathrm{NbCl_4\{CCl(NMe)\}(CNMe)}]$ *with* HCl. Hydrogen chloride (1.1 mol) was condensed at −196 °C on to $[\mathrm{NbCl_4\{CCl(NMe)\}(CNMe)}]$ (0.55 g) in diethyl ether (35 $\mathrm{cm^3}$) and the mixture was warmed to 20 °C. The purple-brown colour of the starting suspension changed to red-brown, and after stirring the resulting suspension for 6 h the diethyl ether was removed to about one-third volume *in vacuo*. The dark red-brown *product* was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 0 °C). It showed ν(N–H) at 3 250 $\mathrm{cm^{-1}}$ in its i.r. spectrum, but it could not be purified. In a similar reaction, but using DCl, the solid product had ν(N–D) at 2 380—2 450 $\mathrm{cm^{-1}}$ (broad absorption). Treatment of (A: M = Nb or Ta, X = Cl, R = Me; M = Ta, X = Cl or Br, R = $\mathrm{Bu^t}$) with HCl or with $[\mathrm{HOEt_2}][\mathrm{BF_4}]$ in diethyl ether gave impure oily products with (N–H) bands in the 3 200—3 350 $\mathrm{cm^{-1}}$ region.

Preparation of [1,2-Bis(diphenylphosphino)ethane]pentabromotantalum(V).—To a suspension of $\mathrm{Ta_2Br_{10}}$ (1.14 g) in diethyl ether (45 $\mathrm{cm^3}$) was added dppe (0.78 g). The colour of the solution instantly changed from yellow to orange and the reaction mixture was stirred at room temperature for 48 h. The orange solid *precipitate* was filtered off, washed with diethyl ether, and dried (10^{-3} mmHg, 20 °C) (1.74 g, 90%). The poor solubility of this complex does not allow conductivity measurements and so it is tentatively formulated as a seven-co-ordinate adduct {like $[\mathrm{TaCl_5(dppe)}]$ [12]} but it could be a six-co-ordinate bromide salt or similar complex.

Reduction of (B) *with Lithium Tetrahydridoaluminate*(III).

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* Throughout this paper: 1 mmHg $\approx$ 13.6 × 9.8 Pa.

[12] J. D. Wilkins, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2095.

—To (B) (0.1 g) in OEt_2 (30 cm^3) was added $Li[AlH_4]$ (0.1 g) and the mixture was stirred for 18 h then carefully hydrolysed at 0 °C with an excess of aqueous hydrochloric acid. The mixture was filtered and the solvent removed to small volume *in vacuo*. The resulting solution was neutralised with sodium hydroxide solution, filtered, then extracted with deuteriochloroform. The n.m.r. spectrum of the $CDCl_3$ extract showed only the resonance of dimethylamine (identical to an authentic sample) which was further identified by an i.r. spectrum of the solution. No higher amines were detected.

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