Insertion of Methyl Isonitrile into Niobium- and Tantalum-Chlorine Bonds

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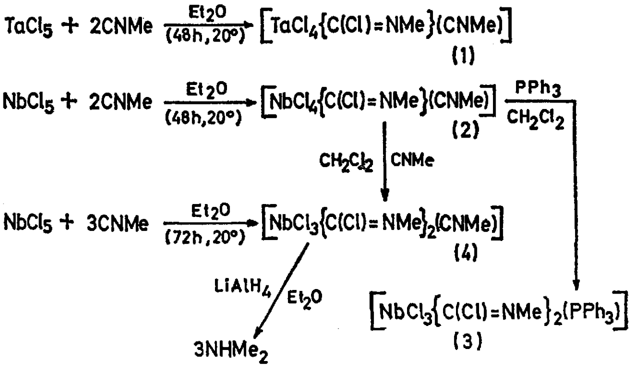
Summary Methyl isonitrile inserts into the metal–chlorine bond of niobium and tantalum pentachlorides to give $[MCl_4\{C(Cl){=}NMe\}(MeNC)]$ (M = Nb or Ta) and $[NbCl_3\{C(Cl){=}NMe\}_2(CNMe)]$; the complex $[NbCl_3\{C(Cl){=}NMe\}_2PPh_3]$ has also been prepared.

IN recent investigations of the chemistry of isonitrile complexes, particularly those of the Group VIII metals, a prominent feature is the ready insertion of isonitrile into metal–carbon and metal–nitrogen bonds.[1] We have extended our studies of metal–isonitrile complexes[2] to include the hitherto little investigated Group V metals and find there a ready insertion of methyl isonitrile into niobium– or tantalum–chlorine bonds. The Scheme summarises the reactions we have studied and the assignment of structures therein follows from the observations below.

Niobium or tantalum pentachlorides, when treated with methyl isonitrile (2 mol equiv.) in ether slowly form the purple-brown products (**1**) and (**2**) (Scheme) which have strong i.r. bands in the ranges 2286—2271 cm^{-1} [ν(N$\equiv$C) of ligating MeNC] and 1680—1628 cm^{-1}. With a further mole of MeNC in CH_2Cl_2, (**2**) gives (**4**), whose i.r. spectrum has similar bands to that of (**2**) [2260—2225 cm^{-1} and 1685—1596 cm^{-1}] but the latter ones are of increased relative intensity. Compound (**4**) is also obtained from $NbCl_5$ and three moles of MeNC. With PPh_3, (**2**) gives the adduct (**3**) which has no (N$\equiv$C) i.r. band and thus no ligating MeNC but strong bands at 1670, 1640, and 1600 cm^{-1}



SCHEME. *Reactions of methyl isonitrile with* $NbCl_5$ *and* $TaCl_5$. *Formulae are empirical, see text.*

The bands in the 1700—1600 cm^{-1} region of the above compounds are assigned to ν (C=N) of $\cdot C(Cl){=}NMe$ ligands, obtained by insertion of MeNC into metal–chlorine bonds. In accord with this structure[3] (**2**) gives with HCl a compound having a protonated nitrogen atom and ν(N–H) at 3250 cm^{-1} [ν(N–D) at 2450—2380 cm^{-1} in the deuterio-analogue]. This protonation reaction gives a novel chloro-substituted carbene ligand which is under investigation.

The reaction probably proceeds *via* initial co-ordination of MeNC, which then inserts into the metal–chlorine bond under the influence of a second ligand or a basic solvent. The second insertion *i.e.* (**2**) $\rightarrow$ [(**3**) or (**4**)] is not into the first-formed niobium–carbon bond, because reduction of (**4**) with lithium aluminium hydride gives only dimethylamine and none of the higher amines.

The ^{1}H n.m.r. spectrum of (**2**) shows a broad singlet (τ 6·22) and a complex multiplet (τ 6·48) of equal intensity. That of (**4**) is similar except that the multiplet (τ 6·55) has twice the intensity of the singlet (τ 6·27), therefore this multiplet and that of (**2**) are assigned to the imino-methyl group, coupled to niobium. The singlet peak, due to ligating MeNC, is probably not coupled to niobium because of exchange with the solvent, acetonitrile. The n.m.r. spectrum of (**1**) is similar to that of (**2**) (m τ 6·56; s τ 6·28] but the singlet has some fine structure, possibly MeNC is less labile when co-ordinated to tantalum than to niobium.

The above compounds were prepared analytically pure but react with solvents in which they are soluble. Their lifetime in acetonitrile is sufficient for n.m.r., conductivity, and m.wt. measurements which indicate that (**1**) and (**2**) are dimeric. Probably they are bridged by the imino-nitrogen as has been suggested for some related gold complexes.[4]

Further i.r. studies in THF show that four and probably five molecules of MeNC undergo insertion, with a progressively slower rate for each step. We are investigating the products of these reactions.

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