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THE REACTIONS OF ISOTHIOCYANATES AND THIOCYANATES WITH METHYLNIOBIUM(V) CHLORIDES AND METHYLTANTALUM(V) CHLORIDES

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Summary

The reactions of Me_xMCl_{5-x}, $x = 1,2,3$, $M = Nb, Ta$ with RNCS, R = Me, Ph have been studied, and products of the types $MCl_4[NR—C(S)Me]$, $MeTaCl_3[NR—C(S)Me]$ and $NbCl_3[NMe—C(S)Me]_2$ containing thioacetamide groups, arising from insertion into the metal—carbon bonds have been characterised.

Reactions with MeSCN yield the complexes $MeMCl_4 \cdot MeSCN$ and $Me_2MCl_3 \cdot MeSCN$, the presence of S- and N-bonded isomers is indicated by the infrared spectra.

Introduction

In reactions of methylmetal chlorides, Me_xMCl_{5-x}, M = Nb, Ta, $x = 1,2,3$ with simple donor ligands, donor-acceptor complexes in which the methyl—metal groups were retained have in general been obtained [1 - 3] $NbCl_5$ and $TaCl_5$ are reported to form 1/1 donor-acceptor complexes with MeNCS and MeSCN [4,5] while $TaCl_5$ and PhNCS yield the complex $TaSCl_3 \cdot PhNCCl_2$ [5]

Insertion of isothiocyanates into main group metal—carbon bonds is well established [6] and examples of insertion into titanium—nitrogen and zirconium—nitrogen bonds have been reported [7] but the reactions described in this paper are the first examples of isothiocyanate insertion into early transition metal—carbon bonds. Products arising from insertion into early transition metal—methyl bonds have only previously been reported with NO, SO_2 and O_2 [8 - 15].

Other insertion reactions of methylniobium(V) chlorides and methyltantalum(V) chlorides are being studied and will be reported later.

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Results and discussion

The complexes prepared together with appropriate analytical data are shown in Table 1, structural formulae for some of the complexes are shown in Fig 1.

Reactions with methyl isothiocyanate

Insertion into the metal—carbon bonds takes place readily at room temperature in pentane solution yielding *N*-methylthioacetamide complexes in each case, thus $MeNbCl_4$, $MeTaCl_4$ and Me_2TaCl_3 yield complexes arising from insertion into one metal—carbon bond [(Ia), (Ib), (IIa)] while Me_2NbCl_3 gives a product (III) resulting from insertion into two methyl—niobium groups A single crystal X-ray study of (III) has confirmed that the complex contains two bidentate *N*-methylthioacetamide groups [16]. The coordination sphere of (III) is a pentagonal bipyramid with chlorine atoms in the axial positions; full details of this structure will be published later

The IR and proton NMR spectra (Table 2) are consistent with the presence of the *N*-methylthioacetamide group in the products, thus, there is no band at ca. 2150 cm^{-1} attributable to the asymmetric —N=C=S stretch while the other bands are similar to those observed for *N*-methylthioacetamide [17] showing strong characteristic bands at ca 1550, 1200 and 720 cm^{-1} The proton NMR spectra are distinctly different from the spectra expected for a donor-acceptor complex e g (Ia) shows a MeC resonance at τ 7 64 ppm while $MeNbCl_4$ shows a resonance at τ 6.64 ppm [1]. The resonance assigned to the protons of the methyl—metal group for (IIa) is typical of $MeTaCl_4$ complexes rather than Me_2TaCl_3 complexes [2], this is consistent with replacement of a methyl group by a more electronegative amido nitrogen atom.

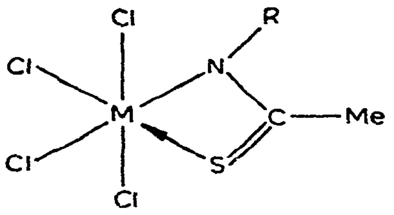
Attempts to produce the tantalum analogue of (III) by the reaction of (IIa) with MeNCS in CH_2Cl_2 have yielded only oily products, but the proton NMR spectrum of the reaction mixture showed that insertion into the remaining MeTa group had taken place. Surprisingly the complex $MeNbCl_3$-[NMe—C(S)Me] (IV) could not be isolated from the Me_2NbCl_3/MeNCS reaction even using excess Me_2NbCl_3, and moreover there was no evidence for this complex in solution when the reaction was followed by NMR spectroscopy.

TABLE 1

COMPLEXES PREPARED AND ANALYTICAL DATA

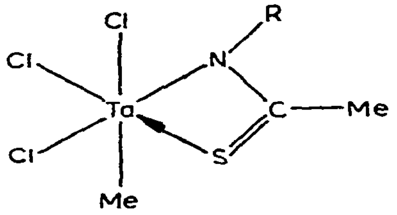
Complex	Colour	Found (%)		Calcd (%)	
		Cl	M	Cl	M
$MeNbCl_4$ MeSCN	Red	44 2	28 9	43 9	28 8
Me_2NbCl_3 MeSCN	Purple-red	35 3	30 4	35 2	30 7
$MeTaCl_4$ MeSCN	Yellow	34 2	44 0	34 5	44 0
Me_2TaCl_3 MeSCN	Yellow	26 8	46 2	27 3	46 3
$NbCl_4$[NMe—C(S)Me]	Dull purple-red	43 5	28 5	43 9	28 8
$NbCl_3$[NMe—C(S)Me]$_2$	Dark red	28 6	25 0	28 3	24 7
$TaCl_4$[NMe—C(S)Me]	Bright orange	34 5	44 2	34 5	44 0
$MeTaCl_3$[NMe—C(S)Me]	Orange	27 1	45 9	27 3	46 3
$TaCl_4$[NPh—C(S)Me]	Yellow	29 0	38.2	30 0	38 3
$MeTaCl_3$[NPh—C(S)Me]	Orange	22 6	39 9	23 5	40 0

(I)



(Ia), M = Nb, R = Me
(Ib), M = Ta, R = Me
(Ic), M = Ta, R = Ph

(II)



(IIa), R = Me
(IIb), R = Ph

(III)

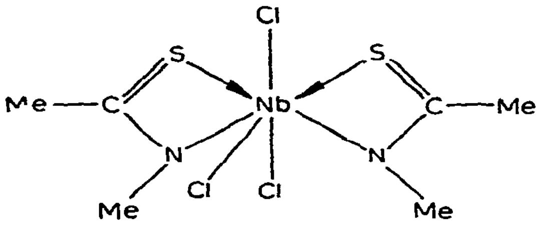


Fig 1 Structural formulae for insertion products Although (II) is drawn as the *fac* configuration we could not distinguish between the possible *mer* and *fac* isomers

This suggests that (IV) disproportionates rapidly if formed or that insertion into the remaining methyl—niobium group takes place more readily than the first insertion.

In studies of the reactions of Me_3NbCl_2 and Me_3TaCl_2 with MeNCS analytically pure products have not been obtained but the IR and NMR spectra

TABLE 2

PROTON NMR SPECTRA (τ PPM) IN DICHLOROMETHANE SOLUTION[a] AND ν(M—C) (cm^{-1})[b]

Complex	Me_xM[c]	MeN	MeC	MeS	ν(M—C)
$MeNbCl_4$ MeSCN	6 82			7 15	[d]
Me_2NbCl_3 MeSCN	7 38			7 16	[d]
$MeTaCl_4$ MeSCN	7 68			7 16	[d]
Me_2TaCl_3·MeSCN	8 14			7 16	[d]
$NbCl_4$[NMe—C(S)Me]		5 99	7 35		
$NbCl_3$[NMe—C(S)Me]$_2$		6 12	7 36		
$TaCl_4$[NMe—C(S)Me]		6 03	7 39		
$MeTaCl_3$[NMe—C(S)Me]	7.76	6 04	7 35		517
$TaCl_4$[NPh—C(S)Me]			7 52		
$MeTaCl_3$[NPh—C(S)Me]	7 31		7.50		491

[a] Dichloromethane used as internal standard τ = 4 67 ppm. The integrated intensities were consistent with the formulations [b] All the complexes showed a strong broad band in the 300 - 400 cm^{-1} region attributable to ν(M—Cl) [c] *x* and M as appropriate [d] See Table 3.

of these products suggests that insertion into two methyl—metal groups takes place.

Reactions with phenyl isothiocyanate

Both the $MeTaCl_4$ and Me_2TaCl_3 [(Ic), (IIb)] yield solid complexes in which 1 mol of PhNCS has inserted into a methyl—tantalum bond under similar conditions to those employed for the MeNCS reactions The IR and proton NMR spectra are consistent with the presence of the *N*-phenylthioacetamide group. The complex (IIb) was obtained even if a 1/3 mol ratio of reactants was used but in a ca. 20% solution of (IIb) in a 75/25 v/v mixture of CH_2Cl_2 and PhNCS at 35° the resonance in the proton NMR spectrum attributable to the MeTa group fell in intensity over a period of ca 7 days accompanied by an increase in the complexity and intensity of the MeC resonance at τ 7.50 ppm. The reactions of $MeNbCl_4$ and Me_2NbCl_3 under a variety of conditions have yielded only small quantities of non-stoichiometric solid products or dark purple-red oils which could not be solidified. The IR and proton NMR spectra of the product obtained from Me_2NbCl_3 suggested that insertion of PhNCS into both the MeNb groups had taken place, thus the proton NMR spectrum of a reaction mixture in CH_2Cl_2 showed a resonance at τ 7 56 ppm (cf. Table 2) together with some other weaker resonances. The absence of a strong resonance in the τ 6.5—7.0 ppm region suggests that $MeNbCl_3$[NPh—C(S)Me] was not present in solution.

The trimethyl compounds, Me_3NbCl_2 and Me_3TaCl_2 reacted only slowly with PhNCS at room temperature, thus after several weeks at room temperature a reaction between Me_3TaCl_2 and PhNCS in pentane yielded only a trace of product.

The observed rates of the insertion reactions under comparable conditions were found qualitatively to follow the sequences, $MeMCl_4 > Me_2MCl_3 > Me_3MCl_2$ and MeNCS > PhNCS which follows the established order of acceptor properties of the methyl—metal chlorides [1 - 3] and the anticipated order of donor properties of the thiocyanates suggesting that an important step in the insertion mechanism is formation of a donor-acceptor complex prior to insertion.

Reactions with methyl thiocyanate (MeSCN)

$MeMCl_4$ and Me_2MCl_3 (M = Nb, Ta) form 1/1 complexes with MeSCN at room temperature, but complexes derived from Me_3MCl_2 could not be isolated (cf. analogous reactions with MeCN [1 - 3]). The proton NMR spectra (Table 2) are typical of complexes of $MeMCl_4$ and Me_2MCl_3 showing the expected methyl—metal resonances. The complexes $MeNbCl_4$, MeSCN and $MeTaCl_4$, MeSCN slowly disproportionate in solution; resonances attributable to Me_2MCl_3 species appear on standing. The complex Me_2TaCl_3,MeSCN also disporportionates in solution showing resonances attributable to $MeTaCl_4$, Me_2TaCl_3 and Me_3TaCl_2 species Similar disproportionation reactions have previously been observed for complexes of these alkyls [1,2].

Methyl thiocyanate is capable of bonding to a metal via sulphur or nitrogen atoms, the mode of bonding depending on the class a or class b character of the metal [18]. The IR spectra and low temperature NMR spectra of the complexes were examined in an attempt to ascertain the mode of bonding of the ligand.

The IR spectra of the complexes in the C≡N, C—S and M—C stretching regions are shown in Table 3; no significant changes were observed in the other bands on co-ordination. The presence of two C≡N stretches for the complexes $MeMCl_4$, MeSCN and Me_2MCl_3, MeSCN suggests that MeSCN is co-ordinated in two ways, via the —C≡N group and via the S atom. The shift of one of the —C≡N stretches to higher frequency by 30—40 cm^{-1} is similar to the shift of $\nu(C{\equiv}N)$ for complexes of the type $MCl_5 \cdot RCN$ [19] and comparable with the shift in $\nu(C{\equiv}N)$ for N-bonded alkyl thiocyanate complexes, while complexes containing S-bonded alkyl thiocyanates show a smaller shift of 15—20 cm^{-1} to higher frequency [20 - 22] The presence of two bands in the C—S stretching region (600—700 cm^{-1}) [23] and the presence of two bands attributable to metal—carbon stretches for each complex is also indicative of the presence of a mixture of isomers containing S and N bonded MeSCN. The two M—C stretches observed for the complexes $Me_2MCl_3 \cdot MeSCN$ are unlikely to arise from a *cis* arrangement of methyl groups as other complexes of Me_2MCl_3 with a wide range of unidentate ligands show only a single M—C stretch [1,2].

The proton NMR spectra of the complexes $MeTaCl_4 \cdot MeSCN$ and $Me_2TaCl_3 \cdot MeSCN$ in dichloromethane solution were measured down to −85° and −100° respectively but only single sharp methyl—metal and ligand resonances were observed suggesting that there is either some degree of non-rigidity at these low temperatures or only a single isomer is present in solution at low temperature

Thus while the NMR evidence is inconclusive at least in the solid state a mixture of S and N bonded isomers seems to be present suggesting that the metal lies on the borderline between class a and class b character. A similar effect has been observed with the ligand 1,4-thioxane (Thiox), thus $TaCl_5 \cdot$ Thiox exists in solution [24] and the solid state [25] as a mixture of O and S bonded complexes while $MeTaCl_4 \cdot$Thiox in the solid state contains O bonded thioxane [2].

Experimental

Analyses were carried out as described previously [1] Proton NMR spec-

TABLE 3

IR SPECTRA (cm^{-1})[a]

Complex	$\nu(C{\equiv}N)$	600 — 700 cm^{-1} region	$\nu(M{-}C)$
$NbCl_5$ MeSNC	2186s	664w	
$MeNbCl_4$ MeSCN	2168s 2185(sh)	665w, 639m	459s
Me_2NbCl_3 MeSCN	2170s 2195s	670w, 663m	478s 465br(sh)
$TaCl_5$ MeSCN	2187s	665w	
$MeTaCl_4$ MeSCN	2196(sh), 2176s	667w 634w	493m, 472s
Me_2TaCl_3 MeSCN	2174s, 2202s	668w, 633m	498s, 474s
MeSCN	2162s	696m, 670m, 640w	

[a] s strong m medium, w weak, br broad, sh shoulder

tra were measured with Varian A-60 or Perkin—Elmer R12B instruments, IR spectra (4000—250 cm^{-1}) were recorded with Perkin—Elmer 257, 457 or 577 instruments as nujol or hexachlorobutadiene mulls.

All manipulations were carried out in vacuo or dry oxygen free nitrogen. The ligands [MeNCS, MeSCN (Aldrich); PhNCS (Koch—Light)] were dried with phosphorus(V) oxide before use. Solvents were dried by standard procedures.

Solutions of the alkyls Me_xMCl_{5-x}, $x = 1,2,3$, M = Nb, Ta in pentane were prepared immediately prior to use as reported previously [1,2] Quantities used in the reactions described below are based on the quantity of MCl_5 used to prepare the alkyl. Although the solutions of $MeNbCl_4$, $MeTaCl_4$ and Me_2TaCl_3 prepared by these methods were contaminated with small quantities of other alkyls (see ref. [1] and [2]) pure final products, as judged by their analysis and NMR spectra, were obtained. Solutions containing only $MeNbCl_4$ and $MeTaCl_4$ were prepared by reactions in carbon tetrachloride solution

Preparation of MCl_4[NMe—C(S)Me] M = Nb, Ta.

A solution of MeNCS (0.005 mol) in pentane (20 ml) was added to a solution of $MeMCl_4$ (0.01 mol) in pentane (20 ml) at 0° and the mixture stirred at this temperature for 4 h. The solid product was isolated by filtration, washed with pentane and pumped dry.

Preparation of $NbCl_3$[NMe—C(S)Me]$_2$

MeNCS (0.015 mol) in pentane (20 ml) was allowed to react with Me_2NbCl_3 (0.01 mol) in pentane (20 ml) for 2 h at 0° yielding a dark purple-red solution and a trace of solid. The reaction mixture was stored for 12 h at −30° and the product isolated as above.

Preparation of $MeTaCl_3$[NMe—C(S)Me]

MeNCS (0.005 mol) was allowed to react with Me_2TaCl_3 (0 01 mol) for 1 h at room temperature in pentane (40 ml). The yellow-orange solution was maintained at −30° for 2 h and the solid complex isolated as above.

Preparation of $TaCl_4$[NPh—C(S)Me]

$MeTaCl_4$ (0 01 mol) was reacted with PhNCS (0.005 mol) in pentane (25 ml) for 4 h at room temperature. The solid product which crystallised after cooling to 0° was isolated as above.

Preparation of $MeTaCl_3$[NPh—C(S)Me]

Me_2TaCl_3 (0.01 mol) was reacted with PhNCS (0.005 mol) in pentane (25 ml) for 24 h. The yellow solution was cooled to −30° to precipitate the product which was isolated as above.

Preparation of $MeMCl_4 \cdot MeSCN$, M = Nb, Ta

A solution of MeSCN (0.0075 mol) in CCl_4 (15 ml) was added to a solution of $MeMCl_4$ (0 01 mol) in CCl_4 (20 ml) at 0°. The solvent was rapidly removed by pumping and the residual solid washed thoroughly with pentane and pumped dry.

Preparation of $Me_2MCl_3 \cdot MeSCN$, $M = Nb, Ta$

A solution of MeSCN (0.0075 mol) in pentane (20 ml) was added to a solution of Me_2MCl_3 (0.01 mol) in pentane (20 ml) yielding a solid complex which was isolated as above.

The complexes $MCl_5 \cdot MeSCN$ were prepared by the literature method but using CCl_4 as solvent [4].

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