

THE REACTIONS OF ISOCYANATES AND ISONITRILES WITH METHYLNIOBIUM(V) CHLORIDES AND METHYLTANTALUM(V) CHLORIDES

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Summary

The reactions of $\text{Me}_x\text{MCl}_{5-x}$ ($x = 1, 2, 3$, $\text{M} = \text{Nb}, \text{Ta}$) with RNCO ($\text{R} = \text{Me}, \text{Ph}$) have been studied and products of the types $\text{MCl}_3[\text{NR}-\text{C}(=\text{O})-\text{Me}]_2$, $\text{MeMCl}_2[\text{NPh}-\text{C}(=\text{O})\text{Me}]_2$, $\text{MeTaCl}_2[\text{NMe}-\text{C}(=\text{O})\text{Me}]_2$ and $\text{TaCl}_2[\text{NMe}-\text{C}(=\text{O})\text{Me}]_3$ containing acetamide groups arising from insertion of the isocyanate into the metal-carbon bonds have been characterised. The complexes $\text{MeTaCl}_2[\text{C}(\text{Me})=\text{NR}]_2$ ($\text{R} = \text{cyclohexyl}, p\text{-tolyl}$) have been isolated from the reactions of Me_3TaCl_2 with RNC .

Introduction

As part of a continuing study of the reactions of methyltantalum(V) chlorides and methylniobium(V) chlorides their reactions with isocyanates and isonitriles have been investigated. Analogous reactions with isothiocyanates have been reported previously [1].

Insertions of isocyanates into main group metal-carbon bonds have been studied in some detail [2] but this is the first report of their reactivity towards early transition metal-carbon bonds. Isonitriles have been shown to be capable of insertion into metal-carbon bonds [3] and recently insertion of isonitriles into the metal-chlorine bonds of NbCl_5 and TaCl_5 have been reported [4]. However, products arising from insertion into early transition metal-carbon bonds have only been reported for the insertion reagents RNCS , NO , SO_2 and O_2 [1, 5-9].

Results and discussion

Reactions with isocyanates

The alkyls $\text{Me}_x\text{MCl}_{5-x}$ ($x = 1, 2, 3$, $\text{M} = \text{Nb}, \text{Ta}$) were all found to react rap-

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TABLE 1
COMPLEXES PREPARED AND ANALYTICAL DATA

Complex	Colour	Found (calcd) (%)			
		Cl		M	
NbCl ₃ [NMe—C(=O)Me] ₂	orange-brown	31.2	(31.0)	27.1	(27.1)
TaCl ₃ [NMe—C(=O)Me] ₂	pale yellow	24.8	(24.7)	41.8	(41.9)
NbCl ₃ [NPh—C(=O)Me] ₂	red	22.6	(22.7)	19.8	(19.9)
TaCl ₃ [NPh—C(=O)Me] ₂	yellow	20.0	(19.1)	33.4	(32.6)
MeTaCl ₂ [NMe—C(=O)Me] ₂	yellow	17.4	(17.3)	43.5	(44.0)
TaCl ₂ [NMe—C(=O)Me] ₃	yellow	15.3	(15.2)	39.4	(38.7)
MeNbCl ₂ [NPh—C(=O)Me] ₂	orange	20.8	(20.8)	15.7	(15.9)
MeTaCl ₂ [NPh—C(=O)Me] ₂	pale yellow	13.7	(13.3)	33.5	(33.8)
MeTaCl ₂ [C(Me)=NC ₆ H ₁₁] ₂	off-white	13.7	(13.8)	34.7	(35.2)
MeTaCl ₂ [C(Me)=Np-toly] ₂	off-white	13.4	(13.4)	33.8	(34.1)

idly with MeNCO and PhNCO at room temperature in pentane solution yielding products containing the *N*-methylacetamide and *N*-phenylacetamide groups respectively; the reactions and mode of insertion are similar to those already established for MeNCS and PhNCS [1]. The complexes prepared together with the appropriate analytical data are listed in Table 1.

(a) *Reactions of MeNCO and PhNCO with Me₂NbCl₃ and Me₂TaCl₃* Products MCl₃[NR—C(=O)Me]₂ (M = Nb, Ta, R = Me, Ph) were obtained by direct reaction using pentane as solvent: insertion into both metal—carbon bonds clearly occurred. Using less than the stoichiometric quantity of PhNCO Me₂Nb₂Cl₃ gave only the complex NbCl₃[NPh—C(=O)Me]₂

This behaviour is similar to that observed in the reaction between MeNCS and MeNbCl₃ where only NbCl₃[NMe—C(=S)Me]₂ could be isolated; it suggests that the Me—Nb bond in the probable primary product MeNbCl₃[NPh—C(=O)Me] is more reactive towards further reaction with PhNCO than the Me—Nb bonds in the parent Me₂NbCl₃. However the reaction of PhNCO with an excess of Me₂TaCl₃ gave a product which appeared to be a mixture of MeTaCl₃[NPh—C(=O)Me] and TaCl₃[NPh—C(=O)Me]₂; if a larger quantity of PhNCO was used only the latter complex was obtained.

In general the reactions with the MeNCO appeared to take place more rapidly than those with PhNCO but there was some evidence for the formation of MeNbCl₃[NMe—C(=O)Me] in the reaction between Me₂NbCl₃ and MeNCO (in contrast to the reaction with PhNCO discussed above). Thus when a solution of MeNCO (0.0025 mol) in pentane was slowly added to a solution of Me₂NbCl₃ (0.01 mol) in pentane at -20° the solid product was a mixture containing approximately equal quantities of MeNbCl₃[NMe—C(=O)Me] and NbCl₃[NMe—C(=O)Me]₂.

The IR spectra of the products did not show a band at ca. 2300 cm⁻¹ attributable to ν_{as}(—N=C=O), but a strong band present at ca. 1600 cm⁻¹ (see Table 2) was attributed to a C=O stretch of the acetamide groups. *N*-substituted acetamides usually show a C=C stretch at ca. 1650 cm⁻¹ [10] but the shift to lower frequency is consistent with the acetamide moiety acting as a bidentate ligand. This suggests that the complexes MCl₃[NR—C(=O)Me]₂ have structures analogous to that of NbCl₃[NMe—C(=S)Me]₂ where the presence of bidentate

TABLE 2
IR AND PROTON NMR SPECTRA^a

Complex	$\nu(\text{C}=\text{O})(\text{cm}^{-1})$	$\nu(\text{M}-\text{C})(\text{cm}^{-1})$	MeN(τ)	MeC(τ)	MeM(τ)
NbCl ₃ [NMe-C(=O)Me] ₂	1565s(br), 1615s(br)		6.39	7.66	
TaCl ₃ [NMe-C(=O)Me] ₂	1590s, 1633s		6.41	7.74	
NbCl ₃ [NPh-C(=O)Me] ₂	1555s(br)			7.71	
TaCl ₃ [NPh-C(=O)Me] ₂	1565s(br)			7.87	
MeTaCl ₂ [NMe-C(=O)Me] ₂	1580s(br), 1615(br,sh)	500w(br)	6.36	7.67	8.20
TaCl ₂ [NMe-C(=O)Me] ₃	1690m-s, 1583s(br)		<i>b</i>		
MeNbCl ₂ [NPh-C(=O)Me] ₂	1547s(br)	483w		7.84	8.24
MeTaCl ₂ [NPh-C(=O)Me] ₂	1556s(br)	500w(br)		7.78	8.90

^a The latter measured in dichloromethane solution using the solvent as internal reference (τ 4.67). ^b A satisfactory spectrum could not be obtained because of rapid decomposition of the complex in solution.

thioacetamide groups produces a seven-coordinate structure as established by an X-ray study [11]. The proton NMR spectra of the complexes (Table 2) are consistent with these proposed structures showing in each case single resonances attributable to the protons of the MeN and MeC groups. The position of the resonance of the proton of the MeC group (ca. τ 7.7, cf. NbCl₃-[NMe-C(=S)Me]₂ τ 7.36 (MeC) [1]) confirms the mode of addition; if the methyl group had been transferred to the more electronegative oxygen or nitrogen atoms the resonances would be expected at a much lower field. The NMR spectra of the complexes were measured as soon as possible after the solutions were prepared, since after a few minutes standing at room temperature the solutions decomposed yielding solid products of indefinite composition whose IR spectra showed strong broad bands at ca. 800 cm⁻¹ attributable to M-O-M groups. Niobium and tantalum halides are known to readily abstract oxygen from oxygen-containing ligands yielding products containing M-O-M or M=O groups [12]. In the solid state the complexes appear to be stable indefinitely at room temperature.

(b) *Reactions of Me₃MCl₂ with MeNCO.* Although the reactions of both Me₃NbCl₂ and Me₃TaCl₂ with MeNCO have been investigated only the reactions of Me₃TaCl₂ have been studied in detail as the products obtained from the reactions of Me₃NbCl₂ with MeNCO tended to decompose spontaneously at temperatures close to room temperature. The greater ease of decomposition of the niobium complexes presumably arises from the poorer thermal stability of the metal-carbon bond and the greater affinity of niobium for oxygen-containing molecules as compared to tantalum [12].

The reaction of Me₃TaCl₂ with MeNCO in a 4/3 mole ratio at 0° in pentane yielded the complex MeTaCl₂[NMe-C(=O)Me]₂; there was no evidence for the formation of any significant quantities of Me₂TaCl₂[NMe-C(=O)Me]. The IR and NMR spectra (Table 2) are similar to those discussed above for the products of the reactions with Me₂MCl₃.

If the reaction was carried out using 1/3 or 1/5 (Me₃TaCl₂/MeNCO) mole ratios the product was TaCl₂[NMe-C(=O)Me]₃. The IR spectrum of the latter complex in the C=O stretching region (Table 2) showed a very strong band at 1580 cm⁻¹ attributable to a coordinated C=O group and additionally a further band at higher wave-number attributable to an uncoordinated C=O group. It

thus seems likely that the complex is seven coordinate containing two bidentate and one unidentate acetamide groups. Reactions using even larger quantities of MeNCO ($\text{Me}_3\text{TaCl}_2/\text{MeNCO}$, 1/10) gave a product whose analysis suggested that five moles of MeNCO had reacted. The IR spectrum showed bands attributable to coordinated and uncoordinated C=O groups while the proton NMR spectrum showed a complex group of resonances attributable to MeN and MeC groups. It seems likely that insertion into the Ta—N bonds of the initially formed acetamide group has taken place. Insertion of isocyanates into Ti—N and Zr—N bonds have been reported [13]. The possibility of insertion into Ta—Cl bonds (cf. reaction of RNC with MCl_5 [4]) cannot be excluded but the presence of a fairly strong broad band at 300 cm^{-1} , characteristic of a Ta—Cl stretching vibration suggests that at least some of the TaCl bonds remain intact.

(c) *Reactions of Me_3NbCl_2 and Me_3TaCl_2 with PhNCO.* The complexes $\text{MeMCl}_2[\text{NPh—C(=O)Me}]_2$ were obtained if the reactions were carried out in a ca. 1/2 mole ratio in pentane but if smaller quantities of PhNCO were used the products were contaminated with $\text{Me}_2\text{MCl}_2[\text{NPh—C(=O)Me}]$ (contrast the reaction with MeNCO) though the latter complex could not be isolated in a pure state. If the reactions were carried out using larger quantities of PhNCO the products were contaminated with some $\text{MCl}_2[\text{NMe—C(=O)Me}]_3$ but the latter complex could not be obtained in a pure state even if a large excess of PhNCO was used. The IR and proton NMR spectra of $\text{MeMCl}_2[\text{NPh—C(=O)Me}]_2$ were similar to those of the other complexes except for the presence of metal—carbon stretches at ca. 500 cm^{-1} (Table 2). The tantalum complex was stable indefinitely at room temperature in the absence of air but the niobium complex showed signs of decomposition after storage for several weeks at room temperature.

(d) *Reactions of MeMCl_4 with MeNCO and PhNCO.* Although MeMCl_4 (M = Nb, Ta) cannot be prepared in a pure state in pentane solution but only as a mixture of 80% MeMCl_4 and 20% Me_2MCl_3 the reactions of these solutions with MeNCO and PhNCO in pentane have been studied to establish the mode of insertion [15]. Products of the type $\text{MCl}_4[\text{NR—C(=O)Me}]$ (contaminated with ca. 20% of $\text{MCl}_3[\text{NR—C(=O)Me}]_2$) were obtained whose IR and proton NMR spectra showed that the mode of insertion was the same as that discussed above for the products derived from Me_2MCl_3 and Me_3MCl_2 .

Qualitatively, the rates of the insertion reactions followed the sequences $\text{MeMCl}_4 > \text{Me}_2\text{MCl}_3 > \text{Me}_3\text{MCl}_2$ and $\text{MeNCO} > \text{PhNCO}$, which are the same as those previously established for the corresponding reactions with RNCS [1]. However, isocyanates are much more reactive than the isothiocyanates; hence, while only a trace amount of product was obtained from the reaction of Me_3TaCl_2 with PhNCS the corresponding reaction with PhNCO took place giving the insertion product in high yield. As the insertion reaction probably proceeds via the formation of an intermediate donor-acceptor complex the greater reactivity of RNCO as compared to RNCS presumably arises from a greater affinity of the alkyls for the oxygen donor, RNCO, compared to the sulphur donor, RNCS.

Reactions with isonitriles

The methyl-metal chlorides $\text{Me}_x\text{MCl}_{5-x}$ ($x = 1, 2, 3$) all react rapidly with RNC ($\text{R} = p\text{-tolyl, benzyl, cyclohexyl}$) at ca. -30° in pentane. Isolation and characterisation of the products was hampered by the poor thermal stability of the products and no characterised products could be isolated from reactions with the niobium alkyls. The reactions of Me_3TaCl_2 with cyclohexyl isonitrile and $p\text{-tolylisonitrile}$ at -30° yields the products $\text{MeTaCl}_2[\text{C}(\text{Me})=\text{NR}]_2$ even though in each case an excess of Me_3TaCl_2 was used. Reactions using more than the stoichiometric quantity of the isonitrile yielded only oily products. The IR spectra of the products clearly indicated that a 1, 1 insertion of the isonitrile had taken place; there was no band at ca. 2150 cm^{-1} attributable to a $\text{C}\equiv\text{N}$ stretch but a complex group of bands in the $1600\text{-}1700\text{ cm}^{-1}$ region attributable to $\text{C}=\text{N}$ stretches. Unfortunately, satisfactory NMR spectra of the complexes could not be obtained as the complexes decomposed in solvents suitable for NMR measurements.

The solid complexes $\text{MeTaCl}_2[\text{C}(\text{Me})=\text{NR}]_2$ decomposed at temperatures close to room temperature presumably because of the presence of a β -carbon-hydrogen bond which provides a facile decomposition route.

The reactions of a pentane solution of MeTaCl_4 (contaminated with ca. 20% Me_2TaCl_3 , see ref. 15) with cyclohexyl isonitrile ($\text{C}_6\text{H}_{11}\text{NC}$) and benzyl isonitrile (BzNC) have also been studied. The products were contaminated with ca. 20% of the product derived from Me_2TaCl_3 but the mode of insertion and stoichiometry of the product has been ascertained. The reaction of an excess of MeTaCl_4 with BzNC in pentane at -30° yields the complex $\text{TaCl}_4[\text{C}(\text{Me})=\text{NBz}]$, BzNC [$\nu(\text{C}\equiv\text{N}) = 2243\text{ cm}^{-1}$] while under similar conditions $\text{C}_6\text{H}_{11}\text{NC}$ yields $\text{TaCl}_4[\text{C}(\text{Me})=\text{NC}_6\text{H}_{11}]$ but $\text{TaCl}_4[\text{C}(\text{Me})=\text{NC}_6\text{H}_{11}]$, $\text{C}_6\text{H}_{11}\text{NC}$ [$\nu(\text{C}\equiv\text{N}) = 2224\text{ cm}^{-1}$] is obtained if an excess of the isonitrile is employed.

Experimental

Analyses were carried out as described previously [14]. Proton NMR spectra were recorded with Varian A-60 and Perkin-Elmer R12B instruments; IR spectra ($4,000\text{-}250\text{ cm}^{-1}$) were recorded as nujol or hexachlorobutadiene mulls using Perkin-Elmer 257, 457, 577 spectrometers.

All manipulations were carried out in vacuo or in an atmosphere of dry oxygen-free nitrogen. The ligands MeNCO (Eastman-Kodak) and PhNCO (Koch-Light) were dried with phosphorus(V) oxide before use. The isonitriles were prepared by published methods [16, 17] and dried with molecular sieves (4A). Solvents were dried by standard procedures.

Solutions of the alkyls $\text{Me}_x\text{MCl}_{5-x}$ ($\text{M} = \text{Nb, Ta, } x = 1, 2, 3$) in pentane were prepared immediately prior to use by methods previously described [14, 15]. Quantities used in the reactions described below are based on the quantity of MCl_5 used to prepare the alkyl.

Preparation of $\text{NbCl}_3[\text{NMe}-\text{C}(=\text{O})\text{Me}]$

A solution of MeNCO (0.02 mol) in pentane (20 ml) was added to a solution of Me_2NbCl_3 (0.01 mol) in pentane (20 ml) at 0° . The mixture was stirred

for 1 h at 0° and the solid product isolated by filtration, washed with pentane and pumped dry.

The compound $\text{TaCl}_3[\text{NMe}-\text{C}(=\text{O})\text{Me}]_2$ was prepared similarly but using 0.01 mol of MeNCO.

Preparation of $\text{NbCl}_3[\text{NPh}-\text{C}(=\text{O})\text{Me}]_2$

A solution of PhNCO (0.015 mol) in pentane (20 ml) was added to a solution of Me_2NbCl_3 (0.01 mol) in pentane (20 ml) at 0°. The mixture was stirred at 0° for 15 min and the solid product isolated as above.

Preparation of $\text{TaCl}_3[\text{NPh}-\text{C}(=\text{O})\text{Me}]_2$

A solution of PhNCO (0.02 mol) in pentane (20 ml) was rapidly added to a solution of Me_2TaCl_3 (0.01 mol) in pentane (20 ml) at 0°. The mixture was stirred at 0° for 15 min and the solid product isolated as above.

Preparation of $\text{MeTaCl}_2[\text{NMe}-\text{C}(=\text{O})\text{Me}]_2$

A solution of MeNCO (0.0075 mol) in pentane (20 ml) was slowly added (ca. 15 min) to a solution of Me_3TaCl_2 (0.1 mol) in pentane (20 ml) at 0°. The mixture was stirred at 0° for 30 min and isolated as above.

Preparation of $\text{TaCl}_2[\text{NMe}-\text{C}(=\text{O})\text{Me}]_3$

A solution of MeNCO (0.03 mol) in pentane (20 ml) was allowed to react with a solution of Me_3TaCl_2 (0.01 mol) in pentane (20 ml) at 20° for 15 min. The solid product was isolated as above.

Preparation of $\text{MeNbCl}_2[\text{NPh}-\text{C}(=\text{O})\text{Me}]_2$

A solution of PhNCO (0.015 mol) was added to a solution of Me_3NbCl_2 (0.01 mol) at 0° and stirred for 40 min at 0°. The solid was separated by filtration and discarded. The filtrate was left to stand for 2 h at room temperature followed by 24 h at -30°. The solid product was isolated as above.

Preparation of $\text{MeTaCl}_2[\text{NPh}-\text{C}(=\text{O})\text{Me}]_2$

A solution of PhNCO (0.01 mol) in pentane (20 ml) was added to a solution of Me_3TaCl_2 (0.01 mol) in pentane at 0°. The mixture was stirred for 5 h at 0° and the solid product isolated as above.

Preparation of $\text{MeTaCl}_2[\text{C}(\text{Me})=\text{NR}]_2$ ($R = \text{C}_6\text{H}_{11}, \text{Bz}$)

A solution of RNC (0.008 mol) in pentane (30 ml) was slowly added to a solution of Me_3TaCl_2 (0.01 mol) in pentane (20 ml) at -30°. The solid product was isolated by filtration at -30°, washed with pentane and pumped dry at -30°.

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References

- 1 J.D. Wilkins, *J. Organometal. Chem.*, **65** (1974) 383.
- 2 M.F. Lappert and B. Prokai, *Advan. Organometal. Chem.*, **5** (1967) 225.
- 3 P.M. Treichel, *Advan. Organometal. Chem.*, **11** (1973) 21.
- 4 B. Crociani and R.L. Richards, *Chem. Commun.*, (1973) 127.
- 5 A.J. Shortland and G. Wilkinson, *J. Chem. Soc. Dalton*, (1973) 872.
- 6 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organometal. Chem.*, **33** (1971) 181.
- 7 C. Beerman and H. Bestian, *Angew. Chem.*, **71** (1959) 613.
- 8 R.J.H. Clark and M.A. Coles, *J. Chem. Soc. Dalton*, (1972) 2454.
- 9 R.J.H. Clark and A.J. McAlees, *J. Chem. Soc. A*, (1970) 2026.
- 10 L.J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Methuen, London, 1966.
- 11 M.G.B. Drew and J.D. Wilkins, *J. Chem. Soc. Dalton*, in press.
- 12 F. Fairbrother, *The Chemistry of Niobium and Tantalum*, Elsevier, Amsterdam, 1967.
- 13 G. Chandra, A.D. Jenkins, M.F. Lappert and R.C. Srivastava, *J. Chem. Soc. A*, (1970) 2550.
- 14 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, *J. Chem. Soc. Dalton*, (1972) 2313.
- 15 G.W.A. Fowles, D.A. Rice and J.D. Wilkins, *J. Chem. Soc. Dalton*, (1973) 961.
- 16 I. Ugi, R. Meyr, M. Lipinski, F. Bodesheim and F. Rosendahl, *Org. Synth.*, **41** (1961) 12.
- 17 I. Ugi and R. Meyr, *Org. Synth.*, **41** (1961) 101.