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REACTIONS OF METHYLNIOBIUM(V) AND METHYLTANTALUM(V) CHLORIDES WITH KETONES

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Summary

The reactions of Me_xMCl_{5-x} (M = Nb, Ta, x = 1, 2) with a variety of ketones have been investigated. Bulky ketones give complexes of the type $Me_xMCl_{5-x} \cdot RR'CO$ for R = R' = cyclohexyl; R = Me, R' = t-Bu; R = Me, R' = neopentyl. Addition of the methylmetal group to the carbonyl group takes place with less bulky ketones and benzaldehyde. Reactions with oxygen and γ-picoline-*N*-oxide have also been investigated.

Introduction

As part of a study of the reactions of methylniobium(V) and methyltantalum(V) chlorides their reactions with the unsaturated reagents RNC, RNCO, RNCS, RNCNR and NO have been investigated [1–4], products resulting from insertion of the unsaturated reagent into the metal—carbon bonds being obtained. We have extended our studies to reactions with oxygen and oxygen containing molecules. The reactions of the alkyls Me_xMCl_{5-x} with the oxygen donor ligands, tetrahydrofuran, 1,2-dimethoxyethane, 1,4-dioxan and triphenylphosphine oxide have been previously reported [5, 6]. The reactions yield in each case donor—acceptor complexes in which the methylmetal groups are retained. The reactions of Me_xMCl_{5-x} with ketones were of particular interest to see if either a donor—acceptor complex was obtained or if addition of the methylmetal groups to the C=O group took place. Reactions have been carried out with a variety of ketones with a view to establishing the factors governing the reactions. The reactions of Me_2NbCl_3 have been studied in most detail but in some cases analogous reactions of $MeNbCl_4$, $MeTaCl_4$ and Me_2TaCl_3 have been studied.

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Results and discussion

(i). Reactions with bulky ketones

The reactions of some rather bulky ketones RR'CO, R = R' = cyclohexyl (DCK), R = Me, R' = t-Bu (MBK) and R = Me, R' = neopentyl (MNK) with Me_xMCl_{5-x} (M = Nb, Ta, x = 1, 2) have been studied: donor—acceptor complexes of the type $Me_xMCl_{5-x}\cdot RR'CO$ have been isolated (see Table 1). As would be expected in the light of the bulky nature of the ligands the complexes were rather weak; thus $Me_2MCl_3\cdot MBK$ (M = Nb, Ta) sublimed in vacuo at room temperature while complexes of Me_2MCl_3 with NMK could not be isolated. Care was taken always to use less than the stoichiometric quantity of ketone for the preparation of the complexes; larger quantities of the ketones made isolation of a pure complex difficult.

The IR spectra show bands typical of the coordinated ligands, the C=O stretch shows the typical shift to lower frequency observed for coordinated ketones (Table 2) [7, 8]. The $MeMCl_4$ complexes show somewhat larger shifts to lower frequency than the Me_2MCl_3 compared to $MeMCl_4$. The complexes of the type Me_2MCl_3, RR'CO show only single bands attributable to ν(M—C) suggesting that the methyl groups are *trans*, an arrangement which has been previously observed for complexes of this type [5, 6].

Although complexes of MCl_5 with a variety of ketones have been isolated [10], it is perhaps surprising that complexes of Me_xMCl_{5-x} with compounds containing ketonic groups can be isolated but the nature of the ketone is critical for the isolation of a simple donor—acceptor complex. Thus reactions with less bulky ketones such as acetone (see later), diethyl ketone, diisopropyl ketone, di-n-butyl ketone and methyl isobutyl ketone give products in which addition of

TABLE 1

COMPLEXES PREPARED AND ANALYTICAL DATA

Complex	Colour	Analysis found (calcd.) (%)	
		Cl	M
$MeNbCl_4\cdot DCK$	Red	31.5 (32.0)	20.7 (21.0)
$MeTaCl_4\cdot DCK$	Yellow	27.0 (26.7)	34.3 (34.0)
$Me_2NbCl_3\cdot DCK$	Purple-red	24.8 (25.1)	22.0 (21.9)
$Me_2TaCl_3\cdot DCK$	Yellow	21.3 (20.8)	34.9 (35.4)
$MeNbCl_4\cdot MBK$	Red	40.4 (40.5)	26.7 (26.6)
$MeTaCl_4\cdot MBK$	Yellow	33.0 (32.4)	41.4 (41.3)
$Me_2NbCl_3\cdot MBK$	Red	31.3 (32.3)	27.8 (28.2)
$Me_2TaCl_3\cdot MBK$	Orange-yellow	25.6 (25.5)	43.9 (43.3)
$MeTaCl_4\cdot MNK$ [a]	Pale yellow-orange	31.1 (31.4)	40.4 (40.0)
$Me_2NbCl_3\cdot C_6H_7NO$	Red	30.4 (31.4)	27.7 (27.5)

[a] An analytically pure complex $MeNbCl_4\cdot MNK$ could not be obtained.

TABLE 2

IR (cm^{-1}) AND NMR (τ, ppm) SPECTRA

Complex	$\nu(C=O)$ [a]	$\nu(M-C)$	τ(MeM)	τ(Me)	τ(t-Bu)
$MeNbCl_4 \cdot DCK$ [d]	1640 s	465 s	7.17		
$MeTaCl_4 \cdot DCK$ [d]	1638 s	487 ms	7.81		
$Me_2NbCl_3 \cdot DCK$ [d]	1645 s	482 s	7.49		
$Me_2TaCl_3 \cdot DCK$ [d]	1645 s	480 s	8.21		
$MeNbCl_4 \cdot MBK$	1641 s	*b*	6.94, 7.12 [c]	7.21, 7.24 [c]	8.66, 8.70 [c]
$MeTaCl_4 \cdot MBK$	1632 s	*b*	7.74, 7.93	7.15, 7.35	8.61, 8.69
$Me_2NbCl_3 \cdot MBK$	1660 s	485 s	*e*	*e*	*e*
$Me_2TaCl_3 \cdot MBK$	1655 s	509 s	8.20	7.46	8.74

[a] Pure DCK shows $\nu(C=O)$ at 1704 cm^{-1} and pure MBK shows $\nu(C=O)$ at 1711 cm^{-1}; s = strong, m = medium [b] $\nu(M-C)$ obscured by ligand bands. [c] Spectrum at −20° [d] Show additional resonances typical of cyclohexyl groups. [e] The complex decomposed too rapidly to obtain a reliable spectrum.

the methylmetal groups to the ketone group takes place. This strongly suggests that addition is preceded by formation of a donor—acceptor complex followed by formation of a four centred transition state prior to transfer of the methyl group. Formation of the tansition state is thus hindered by the bulky ligands.

Proton NMR spectra

The NMR spectra of the dicyclohexyl ketone complexes showed the expected methylmetal and ligand resonances (Table 2); satisfactory proton NMR spectra of the complexes $MeMCl_4 \cdot MNK$ (M = Nb, Ta) could not be obtained because of rapid decomposition of the complexes in solution. The spectra of the complexes $MeMCl_4 \cdot MBK$ were rather more complex and have been studied in more detail. At room temperature the complex $MeTaCl_4 \cdot$t-BuCOMe shows 6 resonances (Table 2) which can be split into 3 pairs of resonances, each pair being attributable to MeTa, MeCO and t-BuCO groups. This has been interpreted in terms of the presence of *cis* and *trans* isomers of the complex in solution. The relative intensities of the individual resonances of each pair changed on standing at room temperature and after 5 min about 50% of each isomer was present. If further MBK was added to the solution of $MeTaCl_4 \cdot MBK$ resonances attributable to the two isomers of the complex were still discernible suggesting that the exchange process between free and complexed ligand at +35° is slow on the NMR time scale. (N.B. The presence of the split resonances cannot be attributed to an equilibrium of the type $MeMCl_4 \cdot MBK \rightleftharpoons MeMCl_4 + MBK$, as the resonances of the tert-butyl groups of the complexes are significantly different from that of free MBK.)

The spectrum of the complex $MeNbCl_4 \cdot MBK$ showed at room temperature only rather broad resonances but on cooling to 0° distinct resonances attributable to *cis* and *trans* isomers were observed. A similar isomerism has recently been reported for the complexes $MeSbCl_4 \cdot L$ (L = pyridine-*N*-oxide) on the basis of NMR evidence [11].

The spectrum of the complex $Me_2TaCl_3 \cdot MBK$ shows only single ligand and methylmetal group resonances as would be expected and moreover when the spectrum was recorded at ca. −40° no splitting of the resonances could be detected. This is consistent with the complexes $Me_2MCl_3 \cdot MBK$ having a *trans* arrangement of methyl groups (see above and ref. 6) and hence no isomerism of the type discussed above for $MeMCl_4 \cdot MBK$ is possible.

(ii). Reaction of Me_2NbCl_3 with PhCHO

Me_2NbCl_3 reacts readily with PhCHO in pentane at 0° yielding a non-stoichiometric orange solid [ν(Nb—O—Nb) = 750 cm^{-1}] and a solution from which 1-phenyl-1-chloroethane was isolated. It thus appears that the reaction proceeds by way of addition of a methyl-metal group to the carbonyl group prior to elimination of the alkylchloride as shown below:

$$2PhCHO + Me_2NbCl_3 \rightarrow (PhCHMeO)_2NbCl_3$$
$$(PhCHMeO)_2NbCl_3 \rightarrow \text{“}(PhCHO)NbOCl_2\text{”} + PhCHMeCl$$

Thermal decomposition of a variety of early transition metal alkoxides have been shown to involve elimination of alkylchlorides [12—15].

(iii). Reactions of Me_2NbCl_3 with acetone

When a solution of acetone in pentane was mixed with a solution of Me_2NbCl_3 in pentane a purple-red solution formed which faded after a few minutes and a white solid precipitated from the solution. The composition of the solid product approached $2[(t\text{-}BuO)NbOCl_2]\cdot Me_2CO$. The IR and proton NMR spectra (see experimental) showed that the product was not a simple donor—acceptor complex of Me_2NbCl_3, thus the IR spectrum showed a strong, very broad band at 850 cm^{-1} [ν(Nb—O—Nb)], bands typical of coordinated acetone [9], and additionally bands typical of metal-tert-butoxide groups were present at 1245 and 1159 cm^{-1} [16]. The proton NMR spectrum showed the resonances expected for coordinated acetone (τ 7.27) and the butoxide group (τ 8.30 ppm). The transient purple-red colour observed in the initial stages of the reaction (see above) is typical of donor—acceptor complexes of Me_2NbCl_3 [5] which is presumably formed prior to transfer of the methyl group giving a tert-butoxide which then eliminates a molecule of alkyl chloride as discussed above for the reaction with PhCHO.

(iv). Reactions with oxygen

It has been previously reported that Me_2NbCl_3 reacts explosively with pure oxygen [5]. However, if pentane solutions of the alkyls Me_2NbCl_3 and Me_3MCl_2 (M = Nb, Ta) are treated with a 50/50 mixture of N_2 and O_2 at —80° a smooth reaction takes place giving solid products whose IR spectra show that insertion of oxygen into the metal—carbon bonds has taken place. Thus bands attributable to C—O and M—OMe stretches are present at ca. 1100, 950 and 500—600 cm^{-1} respectively. Insertion of oxygen into metal—carbon bonds in this way has been reported for $MeTiCl_3$ [17, 18] and a wide range of other compounds containing metal—carbon bonds [19]. Unfortunately, although the analytical data for the complexes approached $(MeO)_2NbCl_3$ and $(MeO)_3MCl_2$ the M/Cl ratio was always low, and the IR spectra showed bands of moderate intensity at ca. 800 cm^{-1} attributable to the presence of M—O—M species.

(v) Reactions with pyridine-N-oxides

As amine-*N*-oxides have been found to convert trialkylboranes to trialkoxyboranes in almost quantitative yield [20], it was of interest to see if the reaction between Me_2NbCl_3 and γ-picoline-*N*-oxide yielded $(MeO)_2NbCl_3$ or a donor—acceptor complex of Me_2NbCl_3.

If an excess of Me_2NbCl_3 was allowed to react with γ-picoline-*N*-oxide at 0° a solid complex $Me_2NbCl_3 \cdot C_6H_7NO$ was obtained which tended to decompose explosively at temperatures above 0°. A satisfactory IR spectrum could not be obtained but an NMR spectrum showed a resonance at τ 6.73 ppm (CH_2Cl_2 solution) attributable to the methyl-metal groups. Prolonged reaction of γ-picoline-*N*-oxide or pyridine-*N*-oxide with Me_2NbCl_3 under a variety of conditions yielded products showing bands attributable to niobium oxy complexes presumably arising from decomposition of the initially formed methoxides.

Experimental

Analyses were carried out as described previously [5]. Proton NMR spectra were recorded using Perkin—Elmer R12B, Varian A-60 or T-60 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 in an atmosphere of dry oxygen-free nitrogen. Solutions of the alkyls Me_xMCl_{5-x} (M = Nb, Ta, x = 1, 2) in pentane were prepared immediately prior to use as reported previously [5, 6]. Quantities used in the reactions described below are based on the quantity of MCl_5 used to prepare the alkyl. Although the solutions of $MeMCl_4$ and Me_2TaCl_3 prepared by these methods were contaminated with small quantities of other alkyls (see refs. 5 and 6) pure final products as judged by their analysis and proton NMR spectra were obtained.

Solvents were dried by standard procedures. The ketones (B.D.H., Koch—Light, Aldrich or Columbia) were dried with molecular sieves (4Å). γ-Picoline-*N*-oxide (Aldrich) was dried by prolonged pumping in vacuo. Gases were dried with molecular sieves.

Preparation of complexes

$MeMCl_4 \cdot DCK$ and $Me_2MCl_3 \cdot DCK$, M = Nb, Ta. A solution of DCK (0.005 mol) in pentane (20 ml) was added to a solution of the alkyl (0.01 mol) in pentane (20 ml) at 0°. The solution was concentrated to induce precipitation if necessary; the solid product was isolated by filtration, washed with pentane and pumped dry at 0°.

$MeMCl_4 \cdot MBK$, $Me_2MCl_3 \cdot MBK$ and $MeTaCl_4 \cdot MNK$. The complexes were prepared as above except that the complexes were isolated at ca. −25°. Because of the high solubility of the complexes $Me_2MCl_3 \cdot MBK$ they were only washed with a small quantity of pentane.

Reaction of Me_2NbCl_3 with PhCHO

A solution of PhCHO (0.02 mol) in pentane (30 ml) was added to a solution of Me_2NbCl_3 (0.01 mol) in pentane (30 ml) at 0° over a period of 15 min and then stirred at room temperature for 15 min. The orange solid was removed by filtration and the solvent removed from the filtrates leaving 1-phenyl-1-chloroethane as a pale yellow liquid which was identified by comparison (IR, NMR spectra) with an authentic sample prepared from *D,L*-1-phenylethanol and thionyl chloride.

Reactions of Me_2NbCl_3 with acetone

Acetone (0.02 mol) in pentane (20 ml) was added to a solution of Me_2NbCl_3 (0.01 mol) in pentane (30 ml) over a period of 5 min. A transient purple-red colour formed initially which was followed by precipitation of a white solid which after the mixture had been stirred for 30 min was isolated by filtration, washed with pentane and pumped dry. (Found: Cl, 23.7; Nb, 30.9. $2[NbOCl_2(O\text{-}t\text{-}Bu)]\cdot Me_2CO$ calcd.: Cl, 22.8; Nb, 29.9%.)

Preparation of $Me_2NbCl_3\cdot C_6H_7NO$ (C_6H_7NO = γ-picoline-N-oxide)

A solution of C_6H_7NO (0.005 mole) in CH_2Cl_2 (20 ml) was added to a solution of Me_2NbCl_3 (0.01 mol) in pentane (40 ml) at 0°. The solid product was isolated by filtration, washed with pentane and pumped dry at 0°.

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