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THE REACTIONS OF SOME EARLY-TRANSITION-METAL CHLORIDES AND METHYLMETAL CHLORIDES WITH NITRILES

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Summary

The complexes $TiCl_4,C_6F_5CN$, $TiCl_4,2C_6F_5CN$, $VCl_4,2C_6F_5CN$, MCl_5,C_6F_5CN, $MeMCl_4,C_6F_5CN$, (M = Nb, Ta) and $WOCl_4,C_6F_5CN$ have been prepared and characterised. The reaction between WCl_6 and C_6F_5CN has also been studied. The complexes Me_2NbCl_3,ICH_2CN, $Me_2NbCl_3,ClCH_2CN$, $MeTaCl_4$,an and Me_2NbCl_3,an (an = acrylonitrile) and $NbCl_5$,bmd (bmd = benzylidinemalononitrile) have been prepared; no addition to the unsaturated system takes place but with tetracyanoethylene the alkyls Me_xMCl_{5-x} (x = 1-3; M = Nb, Ta) appear to add 1,4 to the unsaturated system.

Introduction

The reactions of some early-transition-metal chlorides and methylmetal chlorides with a range of nitriles containing electron-withdrawing groups or in which the nitrile group is conjugated with a C=C group have been studied. The reactions of many metal halides with many nitriles such as MeCN and PhCN lead to reduction of the metal [1-3]. It has been found that this can be blocked by using nitriles such as CCl_3CN where the reduction mode is blocked [4,5]. In some cases insertion of the nitrile into the M—Cl bond takes place [5]. We were interested to see if we could effect insertion of a nitrile group into an early-transition-metal—carbon bond. The reactions of Me_xMCl_{5-x} (x = 1-3; M = Nb, Ta) with heterocummulenes has shown that insertion into the metal—carbon bond can take place [6-8]. The reactions of Me_xMCl_{5-x} with MeCN, PhCN and CCl_3CN yield, in each case, only simple adducts [9,10] except for the formation of a small quantity of insertion product in the reaction between $MeTaCl_4$ and CCl_3CN [10].

Results and discussion

The complexes prepared together with the relevant analytical data are listed in Table 1.

(i) Reactions with pentafluorobenzonitrile

Pentafluorobenzonitrile would be expected to show some properties similar to CCl_3CN, by virtue of the absence of C—H bonds and the presence of a strong electron-withdrawing group. The reaction of $TiCl_4$ with C_6F_5CN yields 1/1 and 1/2 complexes while only a 1/2 complex has been isolated with VCl_4. The latter complex was found to be very air sensitive and sublimed readily in vacuo at room temperature. The 1/2 complexes are presumably six-coordinate monomers while the complex $TiCl_4,C_6F_5CN$ is presumably six-coordinate having a chloride bridged structure analogous to $TiCl_4,CCl_3CN$ [4].

A solid complex could not be isolated from the reaction between $VOCl_3$ and C_6F_5CN contrasting with the reaction of $VOCl_3$ with PhCN which yields a 1/2 complex [11]. The strongly electron-withdrawing C_6F_5 group presumably results in a decrease of the donor properties of the ligand; a similar phenomenon has been observed with CCl_3CN [4].

TABLE 1

ANALYTICAL DATA AND SELECTED IR AND NMR SPECTRAL DATA

Complex	Colour	Found (calcd.) (%)		ν(C≡N)	ν(M—C)	τ(MeM)[a]
		Cl	M			
$TiCl_4,C_6F_5CN$	pale yellow	36.9 (36.9)	12.5 (12.5)	2294s 2299(sh)		
$TiCl_4,2C_6F_5CN$	pale yellow	24.7 (24.6)	8.5 (8.3)			
$VCl_4,2C_6F_5CN$	brown	24.2 (24.5)	8.3 (8.9)			
$NbCl_5,C_6F_5CN$	yellow	37.8 (38.3)	20.1 (20.1)	2285s 2292s		
$TaCl_5,C_6F_5CN$	white	31.5 (32.2)	32.9 (32.8)	2293s 2305s		
$MeNbCl_4,C_6F_5CN$	red	30.7 (32.0)	20.0 (21.0)	2296s 2301s	463m	6.72, 7.18[b]
$MeTaCl_4,C_6F_5CN$	yellow	26.5 (26.7)	34.0 (34.0)	2290s 2306s	482m	7.50, 7.86[b]
$WOCl_4,C_6F_5CN$	orange	26.2 (26.5)	35.1 (34.4)	2296s 2300s		
$Me_2NbCl_3,ClCH_2CN$	purple-red	35.3 (34.9)	30.9 (30.5)		482m	7.38
Me_2NbCl_3,ICH_2CN	purple red	27.5 (26.8)	23.4 (23.4)			7.35
$MeTaCl_4$,an	yellow-orange	36.7 (36.3)	46.8 (46.3)	2278s 2308w	487m	7.62, 7.94[b]
Me_2NbCl_3,an	purple-red	37.3 (37.7)	32.9 (32.9)	2260s		7.20
$NbCl_5$,bmd	pale yellow	40.7 (41.8)	22.0 (21.9)	2240m 2276s		

[a] CH_2Cl_2 solution, solvent used as internal standard (τ = 4.67). [b] Shows two MeM resonances because of disproportionation in solution, see text.

The halides MCl$_5$ and MeMCl$_4$ (M = Nb, Ta) both from 1/1 complexes with C$_6$F$_5$CN. The IR spectra (Table 1) of the complexes show the presence of a C≡N stretch which is shifted to higher frequency than that of the pure nitrile [ν(C≡N) 2253 cm^{-1}]. In most of the complexes the C≡N stretch is split very slightly, suggesting that there is a slight inequivalence of the C≡N groups in the solid complexes. The proton NMR spectra (Table 1) show the expected resonances attributable to the presence of methylmetal groups. The complexes MeMCl$_4$,C$_6$F$_5$CN disproportionate in solution in the same way as for other MeMCl$_4$ complexes [10].

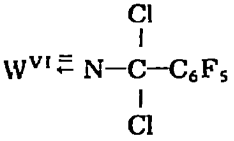
$$2\ \mathrm{MeMCl_4,L} \rightarrow \mathrm{Me_2MCl_3,L} + \mathrm{MCl_5,L}$$

The reaction between Me$_2$NbCl$_3$ and C$_6$F$_5$CN yielded a very air sensitive complex whose proton NMR spectrum suggested that it was the complex Me$_2$NbCl$_3$,C$_6$F$_5$CN [τ(MeNb) 7.27].

Thus we have found that there is no evidence for the addition of the methylmetal group to the C≡N group in any of the above MeMCl$_4$ or Me$_2$NbCl$_3$ complexes. Samples of the solutions of the complexes in CH$_2$Cl$_2$ were left to stand at room temperature for several days, but no resonances appeared in the proton NMR spectrum consistent with an addition reaction having taken place.

The reaction between WOCl$_4$and C$_6$F$_5$CN yields a 1/1 complex presumably containing six-coordinate tungsten. A band in the IR spectrum could not be definitely assigned to ν(W=O) because of the presence of strong ligand bands in the 950-1050 cm^{-1} region, but there were no bands at lower wavenumbers which could be assigned to ν(W—O—W) modes.

We have studied the reaction between WCl$_6$ and C$_6$F$_5$CN in an attempt to isolate a complex containing a tungsten—nitrogen multiple bond, analogous to the product from the reaction between WCl$_6$ and CCl$_3$CN [5]. We have carried out the reaction between WCl$_6$ and C$_6$F$_5$CN in CCl$_4$ under reflux conditions and for prolonged periods at room temperature but have not been able to isolate a pure product. A pale yellow solid was formed (which had a moderate solubility in CCl$_4$) which could not be separated from unreacted WCl$_6$. On attempting to sublime the complex in vacuo considerable decomposition took place. The IR spectrum of the complex showed a band at 2300 cm^{-1} [ν(C≡N)] and a band at 1185 cm^{-1} attributable to ν(W≡N) (c.f. previous assignments [5]) suggesting that some addition across the C≡N group had taken place giving a grouping of the type shown below:



$$\mathrm{W^{VI}} \overset{=}{\leftarrow} \mathrm{N{-}\overset{\displaystyle Cl}{\overset{|}{\underset{\underset{\displaystyle Cl}{|}}{C}}}{-}C_6F_5}$$

(ii). Reactions of ICH$_2$CN and ClCH$_2$CN with Me$_2$NbCl$_3$

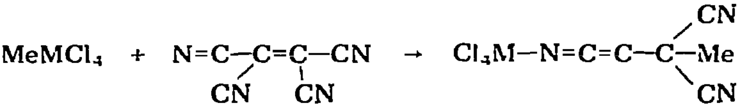
The reactions of iodoacetonitrile and chloroacetonitrile with Me$_2$NbCl$_3$ yield 1/1 complexes. The proton NMR spectra show that in each case the methylmetal groups are retained in the complexes. There is no evidence for addition to the C≡N group or cleavage of the CH$_2$I group.

(iii) Reactions with unsaturated nitriles

The reactions of unsaturated nitriles containing the C=C—C≡N group with the methylmetal chlorides Me_xMCl_{5-x} (M = Nb, Ta, x = 1-3) are of interest to see if a 1,4-addition takes place. Both $MeTaCl_4$ and Me_2NbCl_3 yielded 1/1 complexes with acrylonitrile (an) in which the proton NMR and IR spectra clearly show that the complexes are just simple donor—acceptor complexes. The reactions of fumaronitrile and benzylidinemalononitrile (bmd) with Me_2NbCl_3 at room temperature yielded products having stoichiometries between $Me_2NbCl_3 \cdot L$ and $2Me_2NbCl_3 \cdot L$. The ^1H NMR spectra showed resonances attributable to the Me_2Nb group at ca. τ7.25 and the IR spectra showed the expected C≡N stretches, indicating that no addition to the organic moiety had taken place. There was no reaction between Me_3TaCl_2 and bmd; Me_3TaCl_2 is apparently too weak an acceptor to form a complex with bmd.

$NbCl_5$ yielded a 1/1 complex with bmd but the IR spectrum showed two well-separated C≡N stretches which are attributable to the presence of coordinated and un-coordinated C≡N groups suggesting that the ligand is acting as a unidentate rather than a bidentate ligand.

Tetracyanoethylene has been found to undergo a variety of reactions with transition-metal organometallic compounds. We have studied the reactions of Me_xMCl_{5-x} with tetracyanoethylene (tcne) and found that it is very reactive towards these alkyls. Unfortunately we have not been able to isolate analytically pure products from these reactions but the IR spectra of the products give some indication of the mode of the reaction. The products show a band at 2230 cm^{-1} attributable to a C≡N stretch (tcne shows bands at 2220 wm and 2258 s cm^{-1}) and a further much stronger and broader band at ca. 2110 cm^{-1} which appears to be typical of a C=C=N group [12,13] suggesting that a 1,4-addition of the methylmetal group to the unsaturated system has taken place, e.g.:



$$MeMCl_4 + N{=}C{-}\underset{CN}{C}{=}\underset{CN}{C}{-}CN \rightarrow Cl_4M{-}N{=}C{=}C{-}\overset{CN}{\underset{CN}{C}}{-}Me$$

Unfortunately the complexes were too insoluble to obtain satisfactory proton NMR spectra. This type of 1,4-addition has been previously observed in other reactions of tcne [12,13].

Experimental

The complexes were prepared and handled in vacuo or in an atmosphere of dry oxygen-free nitrogen.

Analyses. Metals were determined by direct ignition of a weighed sample of the complex to the oxide (TiO_2, V_2O_5, Nb_2O_5, Ta_2O_5, WO_3) at 650° (550° for V_2O_5). Chloride was determined gravimetrically as AgCl after hydrolysis of the complex. The complexes were hydrolysed with acid (Ti and V complexes) or dilute ammonia followed by acidification and removal of the hydrated oxide by filtration (Nb, Ta complexes). The tungsten complex was hydrolysed in 2*M* NaOH solution, boiled with hydrogen peroxide and then acidified with dilute HNO_3.

Spectral measurements. IR spectra were recorded using Perkin—Elmer 457 or 577 instruments. NMR spectra were recorded with Perkin—Elmer R12 or R12B instruments.

Preparation and purification of starting materials. $TiCl_4$ was purchased from B.D.H. and distilled before use. VCl_4, $NbCl_5$, $TaCl_5$ and WCl_6 were prepared by chlorination of the appropriate metal. $VOCl_3$ [14] and $WOCl_4$ [15] (prepared from WO_3 and WCl_6) were prepared by the literature methods. The methylmetal chlorides Me_xMCl_{5-x} (M = Nb, Ta; x = 1-3) were prepared by published methods [9,10], molar quantities given below refer to the quantity of MCl_5 used in the preparation. The nitriles were all commercial products which were dried with molecular sieves (4A) before use. Solvents were dried by standard methods.

Preparation of complexes

$TiCl_4,C_6F_5CN$. A solution of C_6F_5CN (0.005 mol) in pentane (20 ml) was added to a solution of $TiCl_4$ (0.01 mol) in pentane (20 ml) and the mixture stirred for 24 h. The pale-yellow solid was isolated by filtration, washed with pentane and pumped dry.

$TiCl_4,2C_6F_5CN$. $TiCl_4$ (0.0025 mol) was allowed to react with C_6F_5CN (0.01 mol) in pentane (20 ml) for 2 days. The pale yellow solid was filtered off, washed with pentane and pumped dry.

$VCl_4,2C_6F_5CN$. A solution of C_6F_5CN (0.02 mol) in pentane (20 ml) was added to a solution of VCl_4 (0.01 mol) in pentane (20 ml) at 0°. The mixture was stirred for 1 h at 0°, the solid product filtered off and pumped for a few minutes only.

MCl_5,C_6F_5CN (M = Nb, Ta). The halide (0.01 mol) was allowed to react with C_6F_5CN (0.011 mol) in pentane (40 ml) at room temperature for 3 days. The solid was filtered off washed with pentane and pumped dry.

$MeMCl_4,C_6F_5CN$, $MeTaCl_4$,an. A solution of "$MeMCl_4$" (0.01 mol) in pentane (30 ml) was treated with C_6F_5CN (0.005 mol) or 0.005 mol in pentane (30 ml) at 0°. The mixture was stirred for 10 min and the solid isolated by filtration, washed with pentane and pumped dry.

Me_2MCl_3,C_6F_5CN. A solution of C_6F_5CN (0.0075 mol) in pentane (20 ml) was added to a solution of Me_2MCl_3 (0.01 mol) in pentane (20 ml). The solution was concentrated until the product precipitated from the solution, the complex was filtered off and pumped for a few minutes only.

$WOCl_4,C_6F_5CN$. $WOCl_4$ (0.01 mol) was allowed to react with C_6F_5CN (0.012 mol) in CCl_4 (50 ml). After 3 days an orange solution had formed; traces of insoluble material were filtered off and the solvent removed in vacuo to give a solid product.

Me_2NbCl_3,ICH_2CN, $Me_2NbCl_3,ClCH_2CN$ and Me_2NbCl_3,an. The nitrile (0.0075 mol) was added to a solution of Me_2NbCl_3 (0.01 mol) in pentane (30 ml) and the mixture was stirred for a few minutes. The complex was filtered off, washed with pentane and pumped for ca. 2 h.

$NbCl_5$,bmd. $NbCl_5$ (0.01 mol) was allowed to react with benzylidinemalononitrile (0.011 mol) in CH_2Cl_2 (40 ml) for 24 h. The pale yellow solid was washed with pentane and pumped dry.

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