Reaction of Niobium(v) Chloride with Dimethylzinc and Some Co-ordination Compounds of Mono- and Di-methylniobium(v) Chloride

By **G. W. A. Fowles,* D. A. Rice,** and **J. D. Wilkins,** Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD

The reaction between niobium(V) chloride and dimethylzinc has been shown to involve equilibria with zinc chloride and both the mono- and di-methylniobium(V) chlorides. $MeNbCl_4$ has not been isolated but its complexes with 1,2-diphenylthioethane and 1,4-dioxan have been prepared. Me_2NbCl_3 has been isolated and a series of complexes formed with a range of monodentate and bidentate ligands containing nitrogen, phosphorus, oxygen, and sulphur donor atoms; these complexes have been characterised through measurements of i.r. and n.m.r. spectra. Monodentate donors (L) yield six-co-ordinate complexes (Me_2NbCl_3,L) in which the methyl groups are *trans*. Bidentate ligands (B) give complexes in which the niobium may be seven-co-ordinate (Me_2NbCl_3,B) or six-co-ordinate ($2Me_2NbCl_3$,B) with the ligand linking two niobium atoms.

THE σ-bonded alkyls of niobium have received little attention. The preparation of Me_3NbCl_2 has been reported by Juvinall.[1] Wilkinson *et al.*[2] have prepared $Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4$ in which the bridging $CSiMe_3$ groups form part of a four-membered quasi-aromatic $\overline{\text{M–C–M–C}}$ ring.

We now report a study of the reaction between dimethylzinc and niobium(V) chloride from which Me_2NbCl_3 has been isolated in a pure state. Attempts to isolate $MeNbCl_4$ gave a mixture of the mono- and di-methyl products, although it was possible to isolate three adducts of $MeNbCl_4$. Work is in progress on the chemistry of other alkyls of both niobium and tantalum and will be reported later.

RESULTS AND DISCUSSION

The reaction between dimethylzinc and niobium(V) chloride at room temperature in n-pentane is complex. With a mole ratio $Me_2Zn : NbCl_5$ of 1·1 : 1, Me_2NbCl_3 is formed provided at least 12 h is allowed for reaction; shorter reaction periods result in contamination with $MeNbCl_4$. In an attempt to make $MeNbCl_4$, dimethylzinc and niobium(V) chloride were reacted in a 1 : 2 molar ratio. Reaction for a period of between 45 min and 22 days gives a mixture of $MeNbCl_4$ (80%) and Me_2NbCl_3 (20%). Increasing the amount of niobium(V) chloride does not significantly change the reaction mixture. A short reaction time (<15 min) results in a mixture of Me_2NbCl_3 and Me_3NbCl_2; the n.m.r. spectrum of the mixture shows that there is no $MeNbCl_4$ present. Zinc chloride and niobium(V) chloride are only slightly soluble in n-pentane and if they are removed from the solution containing a 1 : 4 mixture of Me_2NbCl_3 and $MeNbCl_4$ the orange-red solution slowly deposits niobium(V) chloride until after six days (at 33·5 °C) the n.m.r. spectrum of the solution shows an increase in Me_2NbCl_3 concentration and no $MeNbCl_4$.

These changes can be understood on the basis of the solubility of the various species in n-pentane. Thus both $MeNbCl_4$ and Me_2NbCl_3 are very soluble in pentane whereas niobium(V) chloride is only slightly soluble; hence the small amount of niobium(V) chloride in solution will be alkylated at first to give Me_2NbCl_3 and Me_3NbCl_2, which will subsequently react with niobium(V) chloride, as it dissolves, to give a mixture of $MeNbCl_4$ and Me_2NbCl_3.

---

[1] G. L. Juvinall, *J. Amer. Chem. Soc.* 1964, **86**, 4202.

[2] F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1971, 1477.

The n.m.r. spectra of $MeNbCl_4$, Me_2NbCl_3, and Me_3NbCl_2 at 33·5 °C in CH_2Cl_2 solution are given in Table 1. Previously the only spectrum reported was that for Me_3MbCl_2 at —10 °C which was said to show a resonance at τ 10·5.[1] Our value is τ 7·4 and it seems unlikely that the difference represents a temperature shift, especially since our value follows the trend towards higher field with an increasing degree of methylation previously observed for Me_xSnCl_{4-x}.[3]

Table 1

N.m.r. spectra [a] in CH_2Cl_2 at 33·5 °C

Compound	Nb–Me	Ligand resonances (assignments in parentheses)
$MeNbCl_4$	6·64	
Me_2NbCl_3	7·10	
Me_3NbCl_2	7·40	
Me_2NbCl_3,thf	7·25	7·99 (β protons) [b] 5·96 (α protons) [b]
Me_2NbCl_3,moe	7·06	6·51 (CH_3–O) 6·34 (CH_2–O)
$2Me_2NbCl_3$,diox	7·09	6·15 (CH_2–O)
Me_2NbCl_3,Ph_3PO	7·39	2·30 (aryl protons) [b]
Me_2NbCl_3,SMe_2	7·29	7·47 (CH_3–S)
Me_2NbCl_3,mte	7·18	7·49 (CH_3–S) 6·80 (CH_2–S)
Me_2NbCl_3,ete	7·15	8·61 (CH_3–CH_2) [c] 7·07 (CH_2–CH_3) [d] 6·83 (CH_2–S)
$2Me_2NbCl_3$,pte	7·11	6·79 (CH_2–S) 2·65 (aryl protons)
Me_2NbCl_3,thiox	7·34	7·12 (CH_2–S) [c] 5·92 (CH_2–O) [c]
Me_2NbCl_3,tht	7·36	7·97 (β protons) [b] 6·75 (α protons) [b]
Me_2NbCl_3,pms	7·29	8·32 (γ protons) [b] 7·85 (β protons) [b] 7·02 (α protons) [b]
$2Me_2NbCl_3$,dithian	7·19	6·78 (CH_2–S)
Me_2NbCl_3,MeCN	7·34	7·34 (CH_3–CN)
Me_2NbCl_3,PhCN	7·31	2·27, 2·16, 2·03, 1·89 (aryl protons)
Me_2NbCl_3,py	7·46	2·36 (γ protons) [b] 1·92 (β protons) [b] 0·84 (α protons) [b]
Me_2NbCl_3,bipy	7·38	*e*
Me_2NbCl_3,tren	7·52	7·37 (CH_3–N) 7·15 (CH_2–N)
Me_2NbCl_3,PPh_3	7·17	2·49 (aryl protons)
Me_2NbCl_3,ppe,C_6H_6	7·38	6·93 (CH_2–P) [f] 2·60 (C_6H_6) 2·50 [b] (aryl protons of ligand)
Me_2NbCl_3,ppe,C_7H_8	7·41	7·62 (CH_3-aryl) 6·94 (CH_2–P) [f] 2·78 (aryl protons of C_7H_8 2·50 (aryl protons of ligand)
$[Et_4N][Me_2NbCl_4]$	7·26	8·63 (CH_3) [g] 6·72 (CH_2) [d]
$2MeNbCl_4$,diox	6·70, 7·11	5·72 (CH_2O)
$2MeNbCl_1$,pte	6·78, 7·10	6·48 (CH_2S) 2·55 (aryl protons)

[a] CH_2Cl_2 used as internal standard (J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon, Oxford, 1965, vol. 2) (τ = 4·67). [b] Complex peaks. [c] Triplet. [d] Quintet. [e] Resonances could not be definitely located because of low solubility of complex. [f] Doublet, J(H–P) = 14 Hz. [g] Triplet of triplets arising from coupling to ^{14}N.

Complexes of Me_2NbCl_3.—Me_2NbCl_3 reacts explosively with oxygen and the solid gradually darkens even when stored away from the light at room temperature. The various co-ordination compounds formed by this alkyl are somewhat less sensitive to both air and moisture than the pure alkyl. Analytical data are given in Table 2.

(i) *Complexes with monodentate ligands.* Me_2NbCl_3 reacts with a range of monodentate ligands (L = MeCN, PhCN, pyridine, PPh_3, tetrahydrofuran, Ph_3PO, Me_2S, pms, and tht), to give 1 : 1 adducts in which niobium appears to be six-co-ordinate. The i.r. spectra of the complexes show the expected co-ordinated ligand bands; with the MeCN and PhCN complexes, for instance, there is the usual increase in ν(CN), and no indication of addition across the CN bond such as occurs with many organometallic compounds.[4] The spectrum of the Ph_3PO complex shows the ν(P=O) band 150 cm^{-1} lower than for the free ligand; this shift is less than that observed [5,6] (200 cm^{-1}) for $NbCl_5$,Ph_3PO, and reflects the poorer acceptor power of Me_2NbCl_3. When the Me_2NbCl_3,Ph_3PO complex is prepared, an excess of ligand has to be avoided since it leads to oxygen abstraction and the formation of an oxoniobium species [ν(Nb–O) 950 cm^{-1}].

Attempts to prepare 1 : 1 complexes with NMe_3 and $PhCH_2NMe_2$ by reaction in pentane were unsuccessful because immediate reduction occurs in each case with the formation of an unidentified brown solid; $MeTiCl_3$ reacts in a similar way.[7]

1,4-Thioxan is a potentially bidentate donor but differs from the rest of the bidentate donors considered in that it contains two types of donor atoms, sulphur and oxygen. The i.r. spectrum of the complex shows that oxygen is not co-ordinated since the C–O–C stretching frequencies [8] (1105 and 834 cm^{-1}) are the same as in the free ligand. The n.m.r. spectrum of the co-ordinated ligand (Table 1) shows shifts that are consistent with the thioxan molecule being sulphur bonded as seen in $NbCl_5$,thioxan.[9]

(ii) *Complexes with bidentate ligands* (*B*). Me_2NbCl_3 forms two series of complexes, of stoicheiometry Me_2NbCl_3,B and $2Me_2NbCl_3$,B. The first category is given with the ligands 1,2-dimethoxythane (moe), 1,2-dimethylthioethane (mte), 1,2-diethylthioethane (ete), 1,2-bisdiphenylphosphinoethane (ppe), 2,2′-bipyridyl (bipy), and *NNN′N′*-tetramethyl-1,2-diaminoethane (tren), and the second category with 1,2-diphenylthioethane (pte), 1,4-dioxan (diox), and 1,4-dithian.

All the 1 : 1 adducts (except Me_2NbCl_3,bipy) are sufficiently soluble for conductance and molecular weight measurements to be made on CH_2Cl_2 and C_6H_6 solutions respectively (Table 2). These determinations show the complexes to be monomeric non-electrolytes, so that the niobium atom is seven-co-ordinate in each complex provided both donor atoms of the ligand are bonded to niobium, a point established by the i.r. spectra of the complexes.

Thus the i.r. spectra of the complexes formed with $RSCH_2CH_2SR$ (R = Me or Et) indicated the ligands were in the *gauche* and presumably chelating form (no band at 1200—1210 cm^{-1} indicative of the *trans*-isomer [10]).

---

[3] H. C. Beachell and S. A. Butter, *Inorg. Chem.*, 1965, **4**, 1133.

[4] G. E. Coates and K. Wade, 'Organometallic Compounds,' Methuen, 1967, vol. 1.

[5] D. Brown, J. F. Easey, and J. G. H. Du Preez, *J. Chem. Soc.* (*A*), 1966, 258.

[6] D. B. Copley and F. Fairbrother, *J. Less-Common Metals*, 1965, **8**, 256.

[7] G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J. Chem. Soc.* (*A*), 1971, 1920.

[8] O. H. Ellestad, P. Klaboe, and G. Hagen, *Spectrochim. Acta*, 1972, **28A**, 137.

[9] K. Feenan and G. W. A. Fowles, *J. Chem. Soc.*, 1965, 2449.

[10] M. Hayashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Japan*, 1966, **39**, 118.

The spectra of Me_2NbCl_3,B (B = bipy or tren) are typical of the co-ordinated ligand.[11]

Further evidence for seven-co-ordination comes from the n.m.r. spectrum of Me_2NbCl_3,ppe (Table 1) where the methylene resonances appear as a doublet which is typical of chelating 1,2-bisdiphenylphosphinoethane.[12,13]

Me_2NbCl_3,ppe invariably contains approximately a mole of solvent (benzene or toluene), which cannot be removed by pumping. These solvent molecules are trapped in the lattice rather than bonded since the n.m.r. spectra show the resonances to be the same as for the pure solvent. Similar 'trapped' solvent molecules are reported[7,14] for the analogous complex $MeTiCl_3$,ppe.

TABLE 2

Ligand	Complex	Colour	Found (%) Cl	Found (%) Nb	Calc. (%) Cl	Calc. (%) Nb	*M* Found	*M* Calc.	Molar conductance *	Solvent used for addition of ligand [a]
Tetrahydrofuran	Me_2NbCl_3,thf	Dark red	35·3	30·8	35·3	30·8				
1,2-Dimethoxyethane	Me_2NbCl_3,moe [b]	Orange	30·9	28·7	33·3	29·1			0·81(1·75)	
1,4-Dioxan	$2Me_2NbCl_3$,diox [b]	Dark red	36·1	33·9	38·9	34·0				
Triphenylphosphine oxide	Me_2NbCl_3,Ph_3PO	Violet	21·0	18·3	21·0	18·3				Dichloromethane
Dimethyl sulphide	Me_2NbCl_3,SMe_2	Scarlet	36·5	32·1	36·5	31·9				
1,2-Dimethylthioethane	Me_2NbCl_3,mte	Orange	29·6	26·6	30·2	26·4	310	351	1·29(0·99)	
1,2-Diethylthioethane	Me_2NbCl_3,ete	Orange-red	27·6	24·2	28·0	24·5	364	380	1·5(1·1)	Iso-octane
1,2-Diphenylthioethane	$2Me_2MbCl_3$,pte	Purple-red	28·3	24·8	28·0	24·9			1·22(0·97)	
1,4-Thioxan	Me_2NbCl_3,thiox	Scarlet	31·8	27·6	31·9	27·9				
Tetrahydrothiophen	Me_2NbCl_3,tht	Orange	33·4	29·0	33·5	29·3				
Pentamethylene sulphide	Me_2NbCl_3,pms	Dark red	31·0	28·2	32·1	28·0				
1,4-Dithian	$2Me_2NbCl_3$,dithian	Purple-red	36·7	31·3	36·7	32·1			0·62(0·81)	
Acetonitrile	Me_2NbCl_3,MeCN	Purple-red	39·6	34·1	39·3	34·4	243	270	3·36(0·73)	
Benzonitrile	Me_2NbCl_3-PhCN [c]	Deep purple red	31·1	27·2	32·0	28·0				
Pyridine	Me_2NbCl_3,py [c]	Red	32·8	28·8	34·5	30·1				
2,2′-Bipyridyl	Me_2NbCl_3,bipy	Yellow-orange	27·3	24·1	27·6	24·1				Benzene
N,*N*,*N′*,*N′*-tetramethyl-1,2-diaminoethane	Me_2NbCl_3,tren	Orange-yellow	30·2	26·7	30·8	26·9	368	346	0·59(0·40)	
Triphenylphosphine	Me_2NbCl_3,PPh_3	Red	21·9	19·1	21·7	18·9				Cyclohexane
1,2-Bisdiphenylphosphinoethane	Me_2NbCl_3,ppe,-C_6H_6 [d]	Orange-red	14·5	12·3					2·27(0·86)	Benzene
	Me_2NbCl_3,ppe,C_7H_8 [d]	Orange-red	15·6	13·5						Toluene
	$[Et_4N][Me_2NbCl_4]$	Violet	35·6	23·2	35·8	23·5			31·25(0·43)	
1,4-Dioxan	$2MeNbCl_4$,diox	Yellow-orange	48·2	31·7	48·3	31·6			0·35(0·77)	
	$MeNbCl_4$,diox	Grey-brown	42·0	27·5	42·0	27·5				
1,2-Diphenylthioethane	$2MeNbCl_4$,pte	Bright red	38·3	24·8	38·0	24·9				Iso-octane

* Ω^{-1} cm^2 mol^{-1}, concentration in mmol l^{-1} in parentheses.

[a] n-Pentane was used unless otherwise stated. [b] Analytical figures indicate that some oxygen abstraction has taken place. [c] Analytical figures indicate the presence of a slight excess of ligand which could not be removed by prolonged pumping. [d] Contaminated with about 1·4 mol benzene or 0·7 mol of toluene.

The 2 : 1 complexes $2Me_2NbCl_3$,B (B = dithian, dioxan, 1,2-diphenylthioethane) behave as non-electrolytes in CH_2Cl_2 solution and their i.r. spectra show that the bidentate ligands bridge two Me_2NbCl_3 groups. Thus the spectra of the dioxan and dithian complexes show the ligands to be in the chair centrosymmetric form, while the pte complex has a band attributed to a CH_2 wag of the *trans*-isomer at 1204 cm^{-1}.[15] Experiments revealed that irrespective of the molar ratios of reactants 1,2-dimethyl- and 1,2-diethyl-thioethane always gave 1 : 1 adducts while pte gave a 2 : 1 complex.

Complexes of $MeNbCl_4$.—Some complexes of $MeNbCl_4$ can be obtained from the 4 : 1 mixture of $MeNbCl_4$ and Me_2NbCl_3 by preparing complexes of both species and separating the complexes by virtue of their differing solubilities in n-pentane. Thus the soluble complexes $2Me_2NbCl_3$,pte and $2Me_2NbCl_3$,diox can be washed out of the reaction product leaving the complexes $2MeNbCl_4$,pte and $2MeNbCl_4$,diox; the latter complex reacts with excess of dioxan to give $MeNbCl_4$,diox. In the 2 : 1 complexes the i.r. spectra show the ligands to be bidentate while in the 1 : 1 complex, $MeNbCl_4$,diox,

---

[11] D. A. Baldwin and G. J. Leigh, *J. Chem. Soc.* (*A*), 1968, 1431.

[12] N. Marisch, A. Camus, and E. Cebulec, *J. Inorg. Nuclear Chem.*, 1972, **34**, 933.

[13] M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1968, **21**, 1143.

[14] R. J. H. Clark and A. J. McAlees, *J. Chem. Soc.* (*A*), 1970, 2026.

[15] R. J. H. Clark and W. Errington, *Inorg. Chem.*, 1966, **5**, 650.

there is a strong band at 1125 cm^{-1} indicating the ligand is monodentate.[16,17]

The n.m.r. spectra of the $MeNbCl_4$ complexes give further information regarding the equilibria that exist between $MeNbCl_4$ and Me_2NbCl_3. By comparing integrated intensities it can be seen that in solution the $MeNbCl_4$ complexes equilibrate to give 1 : 1 mixtures of Me_2NbCl_3 and $MeNbCl_4$ the other product being niobium(v) chloride. The formation of a 1 : 1 mixture is in contrast to the 4 : 1 mixture formed during the reaction of dimethylzinc with an excess of niobium(v) chloride when some zinc chloride is present. The possibility of the $MeNbCl_4$ complexes being mixtures in the solid state can be eliminated as the Me–Nb stretch (Table 3) occurs at a different position in the $MeNbCl_4$ complexes to that in the Me_2NbCl_3 adducts and the metal to chlorine ratio is 1 : 4.

TABLE 3

I.r. spectra (cm^{-1})

Compound	Nb–C	$\delta_s(CH_3)$	Other bands 250—400 cm^{-1}
Me_2NbCl_3,thf	519s	*	382sh, 267sh, 352s,br, 337sh, 307sh, 282w
Me_2NbCl_3,moe	495s, 459s	1120w	381sh, 360sh, 340s,br, 320sh, 305sh, 282w
$2Me_2NbCl_3$,diox	515s	*	380sh, 360s,br, 340sh, 325sh, 320sh, 305sh
Me_2NbCl_3,Ph_3PO	476m	*	359sh, 340sh, 310s,br, 280sh
Me_2NbCl_3,SMe_2	479s	1129w	380sh, 362s, 342sh, 337sh, 320sh, 305sh, 280w
Me_2NbCl_3,mte	492s, 454s	1123w	360sh, 325s,vbr, 290sh, 265sh
Me_2NbCl_3,ete	485s, 465s	*	377sh, 365sh, 332s,br, 282w
$2Me_2NbCl_3$,pte	486s	1154w	386sh, 376s, 364sh, 351sh, 340sh, 320sh, 305w
Me_2NbCl_3,thiox	491s	1139w	400sh, 388sh, 355sh, 336s, 318sh, 304sh, 295sh
Me_2NbCl_3,tht	483s	1140w	359sh, 337s,br, 307sh, 292sh, 280sh
Me_2NbCl_3,pms	485s	*	400sh, 387sh, 380sh, 360s,br, 347sh, 332sh, 305w, 277w
$2Me_2NbCl_3$,dithian	485s	1130m	362sh, 347s,br, 308sh, 280m, 267sh
Me_2NbCl_3,MeCN	491s	1141m	376sh, 364sh, 341s,br, 315sh, 306sh, 282sh
Me_2NbCl_3,PhCN	486s	1123w	394sh, 380sh, 365s, 344sh, 320sh, 285w
Me_2NbCl_3,py	492s	1120m	362sh, 330s,br, 307sh, 285w
Me_2NbCl_3,bipy	*	*	380sh, 360sh, 339s, 313m, 300m, 280sh
Me_2NbCl_3,tren	493s, 450s	*	345sh, 340sh, 330sh, 310s,br, 280sh
Me_2NbCl_3,PPh_3	*	*	383sh, 358sh, 330s,br, 308sh, 283w
Me_2NbCl_3,ppe,C_6H_6	*	*	358sh, 330s,br, 312sh, 277w
Me_2NbCl_3,ppe,C_7H_8	*	*	
$[Et_4N][Me_2NbCl_4]$	465s	1120w	393sh, 357sh, 347sh, 330s,br, 310sh, 297sh
$2MeNbCl_4$,diox	528s	1146m	381sh, 355s, 340sh, 329sh, 319sh, 307w, 281w
$MeNbCl_4$,diox	491m	*	363sh, 340s, 310sh, 295sh, 282sh
$2MeNbCl_4$,pte	465s	1142w	400sh, 390sh, 360s,vbr, 330sh, 310sh, 290sh

* Obscured by ligand bands.

Stereochemistry of Complexes; Infrared Spectral Considerations.—For Me_2NbCl_3,L, $2Me_2NbCl_3$,B, $MeNbCl_4$,L, and $2MeNbCl_4$,B complexes, there is good evidence for niobium being six-co-ordinate, while the metal would appear to be seven-co-ordinate in complexes of stoicheiometry Me_2NbCl_3,B. In an attempt to establish a more detailed stereochemistry we have measured the i.r. spectra over the range (250—600 cm^{-1}) in which Nb–C and Nb–Cl stretching frequencies should be observed.

For the six-co-ordinate complexes, the possible structures are one involving *trans*-dimethyl (C_{2v}) and two having *cis*-dimethyl (C_s). From group theory it can be shown that both arrangements should have two metal–carbon stretching frequencies but for the *trans*-arrangement the frequency involving a symmetric stretch involves such a small change in dipole moment we suggest it is unlikely to be observed or if at all as a weak absorption. A similar argument has been put forward to explain the absence of a second M–C stretch in the *trans*-complexes Me_2SnCl_2,B (B = bidentate).[18] All the complexes show a strong band in the 470—520 cm^{-1} region, but it is asymmetric on the low frequency side and it seems likely this series arises from a second weaker Me–Nb absorption. In the well established systems formed by Me_2SnCl_2,2L a single band is observed for *trans*-dimethyl complexes.[19,20] In some instances, however, the single strong band in the *trans*-species is associated with a second, much weaker, band. We accordingly apply the same argument to the niobium complexes and propose a *trans*-configuration.

The Nb–Cl stretching frequencies, which fall in the 250—400 cm^{-1} region, are poorly resolved. There are two possible structures for the anion of the complex $[Et_4N][Me_2NbCl_4]$, *trans* (D_{4h}) and *cis* (C_{2v}), and their spectra should differ with the *trans*-structure giving one Nb–C and one Nb–Cl stretching frequency and the *cis*-structure giving two Nb–C and four Nb–Cl frequencies. An unambiguous *trans*-configuration has

---

[16] G. W. A. Fowles, R. A. Hoodles, and R. A. Walton, *J. Chem. Soc.*, 1963, 5873.

[17] G. W. A. Fowles, D. F. Lewis, and R. A. Walton, *J. Chem. Soc.* (*A*), 1968, 1468.

[18] R. J. H. Clark, A. G. Davies, and R. J. Puddephat, *J. Chem. Soc.* (*A*), 1968, 1828.

[19] H. C. Clark and R. G. Geol, *J. Organometallic Chem.*, 1967, **7**, 263.

[20] N. W. Isaacs, C. H. L. Kennard, and W. Kitching, *Chem. Comm.*, 1968, 820.

been assigned to the analogous anion $[Me_2SnCl_4]$,[21,22] but our spectrum is not as easy to interpret because, while there is a single strong Nb–C stretching frequency, the region in which Nb–Cl frequencies are expected (250—400 cm^{-1}) is quite complex and contains a number of bands.

In the spectra of the seven-co-ordinate Me_2NbCl_3,B complexes two strong Nb–C stretching frequencies are observed. These frequencies are at slightly lower wavenumbers than those observed for the six-co-ordinate complexes as would be expected. In some of the complexes where there are no ligand bands in the region 1120—1150 cm^{-1} we were able to assign bands to the symmetric CH_3 deformation mode (Table 3). These assignments are supported by evidence from methyltitanium species [23–25] and by empirical predictions.[26]

The spectra of the $MeNbCl_4$ complexes all show the expected single Nb–C stretching frequency and a complex series of bands attributable to Nb–Cl in the region 250—400 cm^{-1}.

N.m.r. Spectra of Complexes.—For all complexes formed by Me_2NbCl_3 (except those with ethers) there is a shift of methyl resonances to slightly higher field, all being in the range τ 7·05—7·50. The methyl resonances for $MeTiCl_3$ [27,28] and its adducts [7,14] fall into a similar range. As expected the ligand resonances shift to slightly lower field on co-ordination. The integrated intensities are consistent with the analytical data.

The n.m.r. spectra of Me_2NbCl_3,SMe_2 and Me_2NbCl_3,mte have been measured over a temperature range. At room temperature two resonances at τ 7·29 and 7·47 are found for Me_2NbCl_3,SMe_2. The latter resonance, which is assigned to the sulphur–methyl groups, is broader than the niobium–methyl resonance, and it sharpens and shifts to lower field as the temperature is lowered. The presence of a single methyl resonance at low temperature showed that the methyl groups are in the same environment and the i.r. spectrum indicated that the methyl groups are *trans*.

The spectrum of the mte complex becomes more complex as the temperature is lowered. The Nb–Me resonance splits into two peaks separated by τ 0·43, showing that the two methyl groups are in different environments and the i.r. spectrum suggests a non-linear Me–Nb–Me group. The S–Me resonance also becomes a doublet on lowering the temperature and on reaching −57 °C each peak of the doublet acquires a shoulder on the high field side. A similar splitting of the S–Me resonance was observed for $MeTiCl_3$,mte.[14] The appearance of a shoulder at the lowest temperature was attributed to the presence of two conformational isomers of the five-membered ring involving the ligand. In one isomer both methyl groups are on the same side of the ring while in the other there is one methyl group on either side of the ring.

EXPERIMENTAL

Niobium was determined by ignition of a weighed sample to the oxide, either directly, or after precipitation as the hydrated oxide. Chloride was determined gravimetrically as silver chloride after removal of hydrated niobium oxide; phosphorus ligands and 1,2-diphenylthioethane interfered with both chloride and niobium analyses and had to be removed by solvent extraction.

Niobium(v) chloride was prepared by direct chlorination of sheet niobium (Found: Cl, 65·6; Nb, 34·5. $NbCl_5$ requires: Cl, 65·6; Nb, 34·4%). The preparation of dimethylzinc, purification of ligands, drying of solvents, measurements of spectra, and manipulative procedures were carried out as described earlier.[7] The variable temperature n.m.r. spectra were measured with a Joel 100 MHz spectrometer.

Trimethylniobium(v) *Chloride*.—This was prepared by the previously reported method.[1]

Dimethylniobium(v) *Chloride*.—$NbCl_5$ (0·01 mol) was allowed to react with $ZnMe_2$ (0·011 mol) in n-pentane (30 ml) for 12 h at room temperature, and the mixture filtered to remove $ZnCl_2$ and a trace of a dark coloured, reduced, niobium species. Solvent was removed by pumping the orange-red solution and Me_2NbCl_3 was isolated as a yellow-orange solid; complexes were prepared by appropriate *in situ* reactions of the solution.

Reaction of Me_2NbCl_3 *with Ligands*.—(a) *With* thf, diox, moe, Me_2S, mte, ete, thiox, tht, pms, MeCN, PhCN, *and* tren. A solution of the ligand (0·011 mol if monodentate, 0·006 mol if bidentate) in pentane was added to the solution of Me_2NbCl_3 (0·01 mol). Precipitation usually took place immediately, and then the complex was filtered off, washed with pentane, and pumped for several hours. The thf and Me_2S adducts were quite volatile and were therefore pumped for only 15 min. The thf, diox, and pms adducts which were soluble in pentane were isolated by removing the solvent at the pump.

(b) *With* Ph_3PO, pte, dithian, Ph_3P, *and* ppe. The technique used was the same as in (a) except that rather less ligand was used (0·009 mol if monodentate, 0·004 mol if bidentate). The complexes were often fairly soluble so the solutions were concentrated to effect precipitation. The pte complex was subjected to only a short period (10 min) of pumping since it otherwise lost Me_2NbCl_3.

(c) *With* py *and* bipy. To avoid reduction of niobium these reactions were carried out at −30 °C and the products pumped at 0 °C.

Preparation of $[Et_4N][Me_2NbCl_4]$.—Et_4NCl (0·0045 mol) was allowed to react with Me_2NbCl_3,MeCN (0·005 mol) in 20 ml of MeCN for 30 min. The solvent was removed at the pump and the residual mixture of red and violet solids was washed with benzene until the washings were colourless, and then with pentane. The solid remaining was pumped for 2 h.

Preparation of a $MeNbCl_4$–Me_2NbCl_3 *Mixture*.—$NbCl_5$

---

[21] J. P. Clark and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1966, 871.

[22] I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1963, 1519.

[23] H. Burger and H. J. Neese, *J. Organometallic Chem.*, 1969, **20**, 129.

[24] A. P. Gray, *Canad. J. Chem.*, 1963, **41**, 1511.

[25] H. H. Eysel, H. Siebert, G. Groh, and H. J. Berthold, *Spectrochim. Acta*, 1970, **26A**, 1595.

[26] N. Sheppard, *Trans. Faraday Soc.*, 1955, **51**, 1465.

[27] J. F. Hanlan and J. D. McCowan, *Canad. J. Chem.*, 1972, **50**, 747.

[28] F. S. D'Yachkovskii, N. E. Khrushch, and A. E. Shilov, *Kinetika i Kataliz*, 1968, **9**, 1006.

(0·01 mol) was allowed to react with $ZnMe_2$ (0·0045 mol) in pentane (30 ml) at room temperature for 5 h. The precipitated $ZnCl_2$ was filtered off to leave an orange solution containing a 4 : 1 mixture of $MeNbCl_4$ and Me_2NbCl_3.

Preparation of $2MeNbCl_4$,diox *and* $2MeNbCl_4$,pte.—A solution of the ligand (0·006 mol of dioxan in 30 ml of n-pentane or 0·0025 mol of 1,2-diphenylthioethane in 40 ml of iso-octane) was added to a mixture of $MeNbCl_4$ and Me_2NbCl_3 prepared as above. The precipitated solid was filtered off, washed with pentane, and pumped for several hours to remove traces of Me_2NbCl_3. The solution was concentrated to precipitate the pte complex.

Preparation of $MeNbCl_4$,dioxan.—$2MeNbCl_4$,dioxan (0·0015 mol) was shaken with dioxan (0·012 mol) in n-pentane (30 ml) for several hours. The solid adduct was isolated by filtration.

We thank the University of Reading for the award of a Monck Studentship (to J. D. W.) and Dr. K. Orrell for assistance with the n.m.r. spectra.

[2/1079 *Received*, 12*th May*, 1972]