

Some Co-ordination Compounds of Trimethylniobium(v) Dichloride and Trimethyltantalum(v) Dichloride

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The reactions of Me_3NbCl_2 and Me_3TaCl_2 with a range of unidentate (L) and bidentate (B) ligands yield complexes with the following stoichiometries: $\text{Me}_3\text{MCl}_2\cdot\text{L}$; $\text{Me}_3\text{MCl}_2\cdot 2\text{L}$; $\text{Me}_3\text{MCl}_2\cdot\text{B}$. The complexes have been isolated and characterised by analysis and measurements of their spectra.

Temperature-dependent n.m.r. studies are interpreted as showing $\text{Me}_3\text{MCl}_2\cdot\text{B}$ complexes to be seven-co-ordinate.

THE compounds Me_3NbCl_2 and Me_3TaCl_2 have been prepared,¹ but there has been no report of the formation of any co-ordination compounds. Some co-ordination compounds of MeMCl_4 and Me_2MCl_3 ($\text{M} = \text{Ta}$ or Nb) have been reported.^{2,3} Here we report studies we have made of the reactions of these alkyls with a range of unidentate and bidentate ligands.

RESULTS AND DISCUSSION

The trimethyl compounds Me_3MCl_2 ($\text{M} = \text{Nb}$ and Ta) can be prepared by the reaction of dimethylzinc with the appropriate pentachloride in n-pentane solution. The ratio metal halide : dimethylzinc must be carefully controlled (1 : 1.65 for niobium and 1 : 1.58 for tantalum) in order to obtain a *ca.* 75% yield of the trimethyl derivatives. Smaller amounts of dimethylzinc result in serious contamination by other alkyls,^{2,3} and larger amounts give lower yields.

Since these trimethyl derivatives are very sensitive to both air and moisture, they were not normally isolated

but prepared filtered free from any insoluble material and reacted *in situ* with the various ligands. The isolated complexes (see Table 1) are also air- and moisture-sensitive, but rather less so than the parent alkyls; they can be stored indefinitely at -78°C but decompose slowly at room temperature. The niobium complexes, which are more reactive than the tantalum analogues, are sensitive to light, the complexes formed by nitrogen ligands being especially sensitive.

The acceptor properties of Me_3MCl_2 ($\text{M} = \text{Nb}$ or Ta) are considerably less than those of Me_2MCl_3 , and MeMCl_4 .^{2,3} A large number of unidentate ligands were allowed to react with the alkyls but only pyridine (py), 3-methylpyridine (3-mpy), the chloride ion, and triphenylphosphine oxide (tppo) yielded products that could be isolated (Table 1). 3-mpy and tppo gave 1 : 1 complexes while the other two ligands gave 1 : 2 species (in contrast to the 1 : 1 complexes formed by these ligands with Me_2NbCl_3).² The infrared spectra ($4000\text{--}600\text{ cm}^{-1}$) of the complexes formed by the unidentate ligands show the spectra associated with the co-ordinated

¹ G. L. Juvinal, *J. Amer. Chem. Soc.*, 1964, **86**, 4202.

² G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1972, 2313.

³ G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1973, 961.

ligands [for example $\nu(\text{P}=\text{O})$ shifts by *ca.* 137 cm^{-1} on co-ordination], and there is no evidence for the existence of protonated pyridine or 3-methylpyridine. In addition $\text{Me}_3\text{TaCl}_2, 2(3\text{-mpy})$ is non-conducting in dichloromethane solution, which suggests that the species $\text{Me}_3\text{MCl}_2, 2\text{L}$ are seven-co-ordinate.

Complexes of the type $\text{Me}_3\text{MCl}_2, \text{B}$ (B = bidentate donor) have been prepared with 1,2-dimethoxyethane (dme), $\text{Me}_3\text{N}[\text{CH}_2]_2\text{NMe}_2$ (tren), 2,2'-bipyridyl (2,2'-bipy), 4,4'-bipyridyl (4,4'-bipy), $\text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2$ (ppe), $\text{MeS}[\text{CH}_2]_2\text{SMe}$ (mte), $\text{EtS}[\text{CH}_2]_2\text{EtS}$ (ete), and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (ppm). The following evidence indicates that in all the complexes the ligands chelate to give seven-co-ordinate complexes.

co-ordinate ⁶ both species are assumed to have the same structure.

The infrared spectrum of *trans*- $\text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2$ (ppe) has been recently assigned.⁷ Both complexes of the type $\text{Me}_3\text{MCl}_2, \text{ppe}, \text{C}_7\text{H}_8$ show two bands at 830 and 860 cm^{-1} which are absent in the free solid ligand and thus it would seem likely these are associated with the *cis*-chelating conformer. In addition the n.m.r. spectra show the characteristic resonance (CH_2CH_2) associated with the chelating conformer.⁸ Similarly, although the infrared spectra of the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (ppm) complexes provide no evidence regarding the ligand conformation,⁹ the n.m.r. spectra shows a triplet (τ 6.72) that is said to be indicative of the ligand acting as a bidentate donor.¹⁰

TABLE I

Analytical and selected infrared data

Complex	Analyses (%)				Infrared spectra		
	Found		Calculated		$\nu\delta\text{s}(\text{CH}_3)/\text{cm}^{-1}$	$\nu(\text{M}-\text{C})/\text{cm}^{-1}$	$\nu(\text{M}-\text{Cl})/\text{cm}^{-1}$ ^f
	Cl	M	Cl	M			
$\text{Me}_3\text{NbCl}_2, \text{dme}$	23.7	31.4	23.7	31.4		504s, 479sh	
$\text{Me}_3\text{TaCl}_2, \text{dme}$	18.5	47.1	18.3	46.8		520s, 499s	345s, br
$\text{Me}_3\text{NbCl}_2, \text{tppo}^b$	15.2	19.7	14.6	19.1		e	
$\text{Me}_3\text{TaCl}_2, \text{tppo}$	12.4	31.4	12.4	31.4		e	300s, br
$\text{Me}_3\text{NbCl}_2, \text{mte}^a$	20.8	27.6	21.4	28.1		487s, 466sh	
$\text{Me}_3\text{TaCl}_2, \text{mte}$	17.4	42.8	16.9	43.2	1180m	511s, 487sh	314s, br
$\text{Me}_3\text{NbCl}_2, \text{ete}^a$	18.8	25.2	19.8	25.9		490s, br, 477sh	
$\text{Me}_3\text{TaCl}_2, \text{ete}$	15.9	40.5	15.6	40.4	1185w	508s, 498s	320vs, br
$\text{Me}_3\text{NbCl}_2, 2\text{py}$	19.2	25.6	19.3	25.6		489sbr, 464sh	
$\text{Me}_3\text{TaCl}_2, 2\text{py}$	15.7	39.5	15.6	39.7	1195w	520m-s, 480m-s	300s, br
$\text{Me}_3\text{NbCl}_2, 2(3\text{-mpy})$	18.2	24.0	18.0	23.5		494sbr, 480sh	
$\text{Me}_3\text{TaCl}_2, 2(3\text{-mpy})$	14.9	38.1	14.7	37.5	1194w	505s, 492s	275s, br
$\text{Me}_3\text{NbCl}_2, 2, 2'\text{-bipy}$	18.7	25.3	19.4	25.4		465m, br	
$\text{Me}_3\text{TaCl}_2, 2, 2'\text{-bipy}$	15.6	39.4	15.7	39.9	1193w	516ms, 482ms	310s, br
$\text{Me}_3\text{NbCl}_2, 4, 4'\text{-bipy}$	19.3	25.4	19.4	28.4		488sbr	
$\text{Me}_3\text{TaCl}_2, 4, 4'\text{-bipy}^a$	15.0	39.0	15.7	39.9	1198w	511m-s, 488m-s	286s, br
$\text{Me}_3\text{NbCl}_2, \text{tren}$	22.0	28.3	21.8	28.6		480s, 464sh	
$\text{Me}_3\text{TaCl}_2, \text{tren}$	17.4	43.6	17.2	43.8	1198w-m	500sbr, 465sh	275s, br
$\text{Me}_3\text{NbCl}_2, \text{ppm}, \text{C}_7\text{H}_8^c$	9.3	11.2				e	
$\text{Me}_3\text{TaCl}_2, \text{ppm}, \text{C}_7\text{H}_8^c$	8.4	21.3				e	285s, br
$\text{Me}_3\text{NbCl}_2, \text{ppe}, \text{C}_7\text{H}_8^c$	9.6	11.8				e	
$\text{Me}_3\text{TaCl}_2, \text{ppe}, \text{C}_7\text{H}_8^d$	8.7	22.7				e	290s, br
$[\text{Et}_4\text{N}][\text{Me}_3\text{NbCl}_3]$	27.8	24.4	28.4	24.8	1130m	486s, br, 270sh	
$[\text{Et}_4\text{N}][\text{Me}_3\text{TaCl}_3]$	22.7	39.8	23.0	39.1		495br, 468s	300s, br

^a Lost Me_3NbCl_2 on pumping. ^b Contaminated with a small quantity of Me_3NbCl_2 . ^c Contaminated with *ca.* 2.0 mol of toluene. ^d Contaminated with *ca.* 1.5 mol of toluene. ^e Obscured by ligand bands. ^f Thermal decomposition of the niobium complexes took place while attempts were made to obtain spectra below 400 cm^{-1} .

The infrared spectra of all these complexes suggest that both donor atoms are co-ordinated. $\text{Me}_3\text{MCl}_2, 4, 4'\text{-bipy}$ is thus envisaged to have a polymeric structure, which is consistent with the low solubility of the complex in dichloromethane. The complexes of mte, dme, etc, show spectra characteristic of the chelating ligands, and the bands associated with *trans*- $\text{MeS}[\text{CH}_2]_2\text{SMe}$,⁴ and $\text{MeO}[\text{CH}_2]_2\text{OMe}$ ⁵ ligands are not observed.

The 2,2'-bipyridyl complexes $\text{Me}_3\text{MCl}_2, 2, 2'\text{-bipy}$ (M = Nb or Ta) have identical infrared spectra above 600 cm^{-1} and since the tantalum analogue is known to be seven-

Infrared Spectra (600–200 cm^{-1}).—In Table I are recorded the $\nu(\text{M}-\text{C})$ bands, assignable for those species where there are no ligand bands in the region 530–450 cm^{-1} . In general, these absorptions occur at a higher wavenumber for the tantalum species than the analogous niobium compound, a feature that has been previously noted.³

For the anions $\text{Me}_3\text{MCl}_3^-$ (M = Nb or Ta) two distinct bands were observed, but as the highest wavenumber band is broad for both species we are unable to say if the ions are *mer*, C_{2v} (3 bands) or *fac*, C_{3v} (2 bands). The

⁴ M. Hagashi, Y. Shiro, T. Oshima, and H. Murata, *Bull. Chem. Soc. Japan*, 1966, **39**, 118.

⁵ R. Iwamoto, *Spectrochim. Acta*, 1971, **27A**, 2385.

⁶ M. G. B. Drew, and J. D. Wilkins, *J.C.S. Dalton*, 1973, 1830.

⁷ M. Bacci, *Spectrochim. Acta*, 1972, **28A**, 2286.

⁸ N. Marisch, A. Camus, and E. Cebulec, *J. Inorg. Nuclear Chem.*, 1972, **34**, 933.

⁹ W. W. Fogleman and H. B. Jonassen, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1536.

¹⁰ M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1968, **21**, 1143.

complex nature of the $\nu(\text{M}-\text{C})$ for the remaining complexes is in agreement with the known seven-co-ordinate structure of $\text{Me}_3\text{TaCl}_2, 2, 2'$ -bipy⁶ and the likely seven-co-ordinate nature of the remainder.

N.m.r. Spectra

The n.m.r. spectra of the complexes are listed in Table 2. All the complexes are appreciably less stable in dichloromethane solution than in the solid state, and some of the niobium species are so unstable that spectra could only be obtained at a low temperature.

nificant shift of the resonance from τ 7.40 and no splitting.

To provide further structural information the n.m.r. spectra of a number of the complexes was studied over a temperature range. The results are discussed under the headings six-co-ordinate and seven-co-ordinate complexes.

Six-co-ordinate Complexes.—The spectra of $\text{Me}_3\text{-TaCl}_2, \text{tppo}$ and $\text{Me}_3\text{TaCl}_3^-$ both show a single methyl resonance over all the temperatures at which they were measured (30 °C to *ca.* -80 °C). All three isomers

TABLE 2
N.m.r. spectra in dichloromethane

Complex	Temp. (<i>t</i> /°C) ^a	Me_3M resonance (τ)	Methyl resonance coalescence temperature (<i>t</i> /°C)	Ligand resonances/ τ , assignment in parentheses
$\text{Me}_3\text{NbCl}_2, \text{dme}$	5	7.47	—	6.39 ($\text{CH}_2\text{-O}$), 6.59 ($\text{CH}_3\text{-O}$)
	-50	7.40, 7.75 (Ratio 1 : 2)	-30	6.14 ($\text{CH}_2\text{-O}$), 6.37 ($\text{CH}_2\text{-O}$)
$\text{Me}_3\text{NbCl}_2, \text{tppo}$	-28	7.70	—	2.37 (aryl protons) ^j
$\text{Me}_3\text{NbCl}_2, \text{mte}$	-30	7.37, 7.87 ^b	—	6.95 ($\text{CH}_2\text{-S}$), 7.72 ($\text{CH}_3\text{-S}$)
$\text{Me}_3\text{NbCl}_2, 2\text{py}$	28	7.62	—	1.12, 2.12, 2.46 (aryl protons) ^j
	-60	7.27, 7.85 (Ratio 1 : 2)	—	1.20, 2.83 (aryl protons) ^d 7.58 ($\text{CH}_3\text{-C}_4\text{H}_4\text{N}$)
$\text{Me}_3\text{NbCl}_2, 2(3\text{-mpy})$	25	7.60	—	1.02, 1.71, 2.46 (aryl protons) ^j
	-80	7.80, 7.87 (Ratio 1 : 2)	-50	7.41 ($\text{CH}_2\text{-N}$), 7.45 ($\text{CH}_3\text{-N}$)
$\text{Me}_3\text{NbCl}_2, 2, 2'$ -bipy	16	8.21	-60	6.83 ($\text{CH}_2\text{-N}$), 8.75 ($\text{CH}_3\text{-CH}_2$)
	-80	7.94, 8.76 (Ratio 2 : 1)	—	6.49 ($\text{CH}_2\text{-O}$), 6.67 ($\text{CH}_3\text{-O}$)
$\text{Me}_3\text{NbCl}_2, \text{tren}$	-30	<i>ca.</i> 7.4, 7.86 ^c	—	6.29 ($\text{CH}_3\text{-O}$), 5.97 ($\text{CH}_2\text{-O}$)
	-26	7.82	-35	2.44 (aryl protons) ^j
$\text{Me}_3\text{TaCl}_2, \text{dme}$	—	8.22	—	6.96 ($\text{CH}_2\text{-S}$), 7.69 ($\text{CH}_3\text{-S}$)
$\text{Me}_3\text{TaCl}_2, \text{tppo}$	—	8.44	—	6.80, 7.12 ($\text{CH}_2\text{-S}$), 7.64, 7.87 ($\text{CH}_3\text{-S}$)
	-40	8.11, 8.57	-20	7.21 ($\text{CH}_2\text{-S}$), 7.38 ($\text{S-CH}_2\text{-CH}_3$), ^g 8.71 ($\text{CH}_3\text{-CH}_2$) ^e
$\text{Me}_3\text{TaCl}_2, \text{ete}$	—	8.23	—	1.20, 2.20, 2.60 (aryl protons) ^j
$\text{Me}_3\text{TaCl}_2, 2\text{py}$	—	8.40	—	1.19, 2.80 (aryl protons) ^d 7.60 ($\text{CH}_3\text{-C}_4\text{H}_4\text{N}$)
$\text{Me}_3\text{TaCl}_2, 2(3\text{-mpy})$	—	8.40	—	0.73, 1.68, 2.38 (aryl protons) ^j
	-60	8.49	-30	1.20, 2.39 (aryl protons) ^j
$\text{Me}_3\text{TaCl}_2, 2, 2'$ -bipy	—	8.15, 9.24 (Ratio 2 : 1)	—	7.30 ($\text{CH}_2\text{-N}$), 7.39 ($\text{CH}_3\text{-N}$)
	-60	8.29	25	—
$\text{Me}_3\text{TaCl}_2, 4, 4'$ -bipy	—	8.50	—	—
$\text{Me}_3\text{TaCl}_2, \text{tren}$	-60	8.17, 8.64 (Ratio 1 : 2)	—	2.34, 2.52 (aryl protons of ligand) ^j
	—	8.26	—	2.80 ($\text{CH}_3\text{-C}_6\text{H}_5$), 6.72 ($\text{CH}_2\text{-P}$), ⁱ 7.65 ($\text{CH}_3\text{-C}_6\text{H}_5$)
$\text{Me}_3\text{TaCl}_2, \text{ppm}, \text{C}_7\text{H}_8$	—	8.41	—	2.34, 2.52 (aryl protons of ligand) ^j
$\text{Me}_3\text{TaCl}_2, \text{ppe}, \text{C}_7\text{H}_8$	—	8.41	—	2.77 ($\text{CH}_3\text{-C}_6\text{H}_5$), 7.06 ($\text{CH}_2\text{-P}$), ^h 7.61 ($\text{CH}_3\text{-C}_6\text{H}_5$)
$[\text{Et}_3\text{N}][\text{Me}_3\text{TaCl}_3]$	—	8.30	—	6.77 ($\text{CH}_2\text{-N}$), ^g 8.71 ($\text{CH}_3\text{-CH}_2$) ^f

^a Temperature 35 °C unless specified. ^b Spectrum only obtained below coalescence temperature. ^c Spectrum only obtained below coalescence temperature; one of methyl niobium resonances is hidden by ligand resonances. ^d Doublet. ^e Triplet. ^f Triplet of triplets. ^g Quartet. ^h Doublet $J_{(\text{P}-\text{H})} = 13$ Hz. ⁱ Doublet $J_{(\text{P}-\text{H})} = 3$ Hz. ^j Complex multiplet.

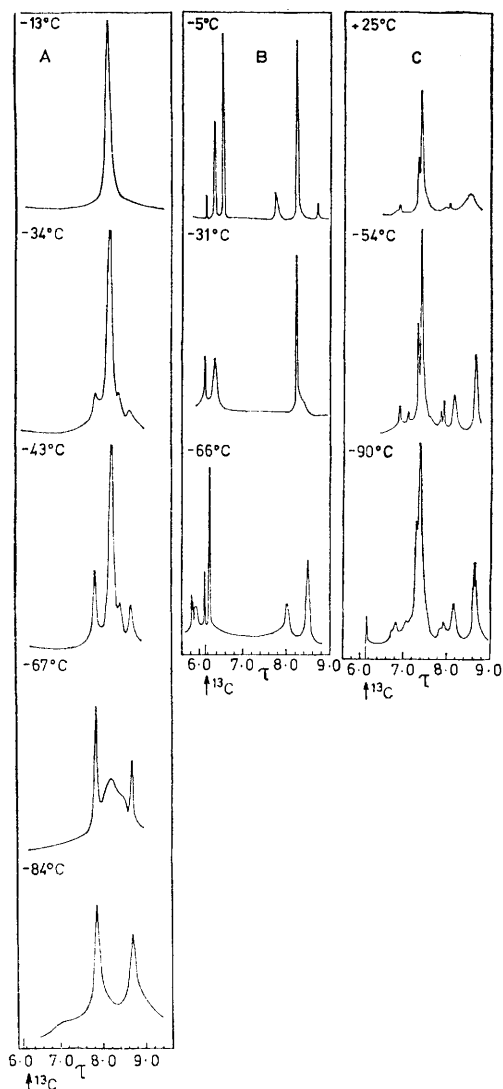
At room temperature and at temperatures close to room temperature all the complexes (except $\text{Me}_3\text{TaCl}_2, \text{tren}$) show a single resonance attributable to the trimethyl group, the resonance being at a slightly higher field than that seen for the corresponding free alkyl. We have previously reported² that Me_3NbCl_2 shows a single resonance at τ 7.40 in contrast to an earlier report of a resonance at τ 10.5 at -10 °C.¹ We have measured the n.m.r. spectrum of Me_3NbCl_2 in dichloromethane solution down to -70 °C and have observed no sig-

based on an octahedron that can be formulated for $\text{Me}_3\text{TaCl}_2, \text{tppo}$ should show a 2 : 1 splitting of the methyl resonance at low temperature, thus the observation of a single Me-M resonance for $\text{Me}_3\text{TaCl}_3^-$ cannot be interpreted with any confidence as evidence for a *fac* rather than a *mer* form.

Seven-co-ordinate Complexes.—(i) *The metal-methyl resonances.* Unlike the six-co-ordinate complexes all the complexes for which a seven-co-ordinate structure is suggested show splitting of the methyl resonances at

low temperature and one $\text{Me}_3\text{TaCl}_2\text{tren}$, shows some splitting at room temperature.

Although the X-ray structure of $\text{Me}_3\text{TaCl}_2\text{,2,2'-bipy}$ shows all three methyl groups to be in different crystallographic environments,⁶ an inspection of a molecular



Variable-temperature n.m.r. A = $\text{Me}_3\text{NbCl}_2\text{,2,2'-bipy}$;
B = $\text{Me}_3\text{TaCl}_2\text{,dme}$; C = $\text{Me}_3\text{TaCl}_2\text{,tren}$

model shows two of the methyl groups to have a similar disposition to the ligand. At low temperature the n.m.r. spectrum of $\text{Me}_3\text{TaCl}_2\text{,2,2'-bipy}$ shows two M-Me resonances in the ratio 1 : 2. The more intense ratio is at lower field and is quite broad. $\text{Me}_3\text{NbCl}_2\text{,2,2'-bipy}$ behaves similarly.

In contrast $\text{Me}_3\text{NbCl}_2\text{,2py}$ and $\text{Me}_3\text{NbCl}_2\text{,2(3-mpy)}$ while showing two Me-M resonances in the ratio 1 : 2 at low temperature have the more intense resonance at high field (Table 2). Similarly the complexes $\text{Me}_3\text{MCl}_2\text{,B}$ (B = mte, dme, tren, M = Nb or Ta) show 1 : 2 Me-M resonance splits with the more intense band at high

field. For all those complexes showing the more intense peak at high field the split is similar and much less than that found for $\text{Me}_3\text{MCl}_2\text{,2,2'-bipy}$ (Table 2). Thus we would suggest that there are two types of seven-co-ordinate structure shown by the species $\text{Me}_3\text{MCl}_2\text{,B}$.

(ii) *Ligand resonances.* Pyridine bases. The resonances of the co-ordinated pyridine bases pyridine, 3-methylpyridine, and 2,2'-bipyridyl show no great change over the temperature for which they were studied.

$\text{MeO}[\text{CH}_2]_2\text{OMe}$. As the temperature is lowered the ligand resonances shift to lower field, broaden, and then sharpen again, showing only single MeO and CH_2 resonances at -80°C (Figure), thus suggesting that the ligand is present in a symmetrical form. The initial broadening followed by the final sharp resolution suggests the slowing down of an exchange process on lowering the temperature.

$\text{Me}_2\text{N}[\text{CH}_2]_2\text{NMe}_2$. The ligand resonances show no broadening or shift as the temperature is lowered. This may be caused by the larger bulk of the ligand compared to $\text{MeO}[\text{CH}_2]_2\text{OMe}$ or alternatively the exchange process involving the ligand is slowed down at a much higher temperature for $\text{Me}_2\text{N}[\text{CH}_2]_2\text{NMe}_2$ than for $\text{MeO}[\text{CH}_2]_2\text{OMe}$. This later suggestion is supported by the 60°C difference in metal-methyl coalescence temperature between $\text{Me}_3\text{TaCl}_2\text{,dme}$ and $\text{Me}_3\text{TaCl}_2\text{,tren}$ (Table 2 and Figure).

$\text{MeS}[\text{CH}_2]_2\text{SMe}$. The spectrum of $\text{Me}_3\text{TaCl}_2\text{,mte}$ shows single MeS and CH_2 resonances at 25°C . As the temperature is lowered the resonances broaden and finally both split into two components in ca. 4 : 1 ratio the weaker resonances being at higher field. Thus it would appear two isomers of $\text{Me}_3\text{TaCl}_2\text{,mte}$ exist in solution at low temperature. We were unable to decide if $\text{Me}_3\text{NbCl}_2\text{,mte}$ exhibits similar behaviour because the Me-Nb and ligand resonances overlapped.

EXPERIMENTAL

The preparative methods, analytical procedures, and manipulative techniques used have been described previously.² N.m.r. spectra were recorded by means of Perkin-Elmer R10 (room temperature) or Varian T60 (variable temperature) instruments.

The compound Me_3NbCl_2 was prepared in higher yield than previously by means of the following procedure. NbCl_5 (0.01 mol) was allowed to react with Me_2Zn (0.0165 mol) in pentane (25 cm^3) for 4 h. Filtration gave a yellow-orange solution of Me_3NbCl_2 .

Preparation of the Complexes.—Solutions of Me_3NbCl_2 and Me_3TaCl_2 ³ in pentane prepared from the appropriate halide (0.01 mol) were allowed to react with ligands as follows.

(i) $\text{Me}_3\text{MCl}_2\text{,tppo}$. Triphenylphosphine oxide (0.005 mol) in dichloromethane (20 cm^3) was added to a solution of the alkyl at 0°C . Solvent was removed at the pump and the residual solid was washed with pentane and pumped for 2 h.

(ii) $\text{Me}_3\text{MCl}_2\text{,L}$ [L = dme, mte, etc, 2py, 2(3-mpy), 2,2'-bipy, 4,4'-bipy, or tren] and $\text{Me}_3\text{MCl}_2\text{,C}_7\text{H}_8\text{,L}$ (L = ppm or ppe). A solution of the ligand (0.005 mol bidentate, 0.01

mol unidentate) in an appropriate solvent (toluene for ppm and ppe, dichloromethane for 2,2'-bipy and 4,4'-bipy, pentane for dme, mte, etc, py, 3-mpy, and tren) at 0 °C was added to Me_3MCl_2 (0.01 mol) in pentane at 0 °C. The majority of complexes precipitated from solution after it had been stirred for a few minutes, but when necessary precipitation was induced by concentration of the solution. The solids were filtered, washed with pentane, and pumped for 1 h.

Preparation of $(\text{Et}_4\text{N})[\text{Me}_3\text{TaCl}_3]$ (M = Nb, Ta).—A

solution of Et_4NCl (0.005 mol) in dichloromethane (20 cm^3) was added to a solution of Me_3MCl_2 (0.01 mol) in pentane at 0 °C. Solvent was removed from the filtrate, and the residue was thoroughly washed with pentane and pumped for 2 h.

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