Reaction of Dimethylzinc with Tantalum(V) Chloride and Some Co-ordination Compounds of Methyltantalum(V) Chloride, Dimethyltantalum(V) Chloride and Methylniobium(V) Chloride

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It has been shown that the reaction between dimethylzinc and tantalum(V) chloride involves equilibria in which zinc chloride takes part. $MeTaCl_4$ and Me_2TaCl_3 were present in the reaction mixtures and it was possible to prepare and characterise a series of their complexes with a variety of monodentate and bidentate ligands. Some further complexes of $MeNbCl_4$ have been prepared. The stoicheiometry of the complexes fall into the categories $MeNbCl_4$,L, $MeTaCl_4$,L, Me_2TaCl_3,L, $2MeNbCl_4$,L, $2MeTaCl_4$,L, and $2Me_2TaCl_3$,L, apart from $4MeTaCl_4$,3diox. Proposed structures based on i.r. and n.m.r. spectra involve six-co-ordinated metal atoms in most instances, although seven-co-ordination seems probable with complexes formed by some bidentate ligands.

THE only reported σ-bonded alkyls of tantalum are Me_3TaCl_2,[1] $Ta_2(CSiMe_3)_2(CH_2SiMe_3)_4$ [2] which contains a four-membered Ta–C–Ta–C ring, and $(Me_3C{\cdot}CH_2)_3$-$TaCl_2$.[3] Accordingly we have extended our study of the niobium(V) chloride–dimethylzinc [4] reaction to the analogous one with tantalum(V) chloride.

RESULTS AND DISCUSSION

Reaction between $TaCl_5$ *and* Me_2Zn.—As with the related $NbCl_5$ reaction, we have used n.m.r. spectroscopy to establish which species are present in a given equilibrium mixture. Thus the methyl group resonances are quite distinct for the series $MeMCl_4$, Me_2MCl_3, Me_3MCl_2, the resonance shifting to higher field as chlorine atoms are replaced by methyl groups. (See Table 1).

From such spectra it may be seen that when a pentane solution of Me_2Zn is allowed to react with $TaCl_5$ at room temperature in 0·5 : 1·0 molar ratio for periods in excess of 1 h, a mixture of $MeTaCl_4$ (80%) and Me_2TaCl_3 (20%) results, although a rather higher percentage of the dimethyl compound is present after a shorter reaction time. It seems that Me_2Zn reacts initially with the small amount of $TaCl_5$ in solution to give Me_2TaCl_3 but that more $TaCl_5$ then dissolves and that an equilibrium mixture forms with $MeTaCl_4 : Me_2TaCl_3 = 4 : 1$. A similar behaviour was observed in the reaction between Me_2Zn and $NbCl_5$ [4] under the same conditions. When the $Me_2Zn : TaCl_5$ molar ratio is changed to 1·1 : 1, the equilibrium mixture contains Me_2TaCl_3 (60%) and Me_3TaCl_2 (40%); in the $NbCl_5$–Me_2Zn system pure Me_2NbCl_3 is formed under these conditions.[4]

With time, both the $MeTaCl_4$–Me_2TaCl_3 and Me_2TaCl_3–Me_3TaCl_2 equilibrium mixtures undergo disproportionation reactions in the absence of $ZnCl_2$ and $TaCl_5$. Thus in the $MeTaCl_4$–Me_2TaCl_3 solution, the Me_2TaCl_3 resonance increases in intensity with time and a small resonance due to Me_3TaCl_2 also appears. In the Me_2TaCl_3–Me_3TaCl_2 solution the resonance associated with the Me_2TaCl_3 falls with a commensurate increase in the Me_3TaCl_2 resonance and the appearance of a small $MeTaCl_4$ resonance. These results may be rationalised on the basis of the following equilibria:

$$2MeTaCl_4 \rightleftharpoons Me_2TaCl_3 + TaCl_5$$
$$2MeTaCl_3 \rightleftharpoons Me_3TaCl_2 + MeTaCl_4$$

By using a $TaCl_5 : Me_2Zn$ ratio of 1 : 1·58 pure Me_3TaCl_2 may be prepared; its chemistry is being investigated at the moment.

Complexes of $MeNbCl_4$ *and* $MeTaCl_4$.—Although neither monomethyl compound could be isolated in a pure state, complexes could be prepared from the $MeMCl_4$–Me_2MCl_3 mixtures by a suitable choice of reaction conditions. In particular, conditions were chosen such that the Me_2MCl_3 complexes were either soluble or not formed. Complexes were isolated with ligands containing nitrogen, oxygen, or sulphur donor atoms (Table 2). Thus the following were prepared:

$MeNbCl_4$,L where L = tpps; CCl_3CN; diox;[4]
$MeTaCl_4$,L where L = CCl_3CN; thf; diox; thiox; pms; tpps;
$2MeNbCl_4$,L′ where L′ = diox;[4] dithian; pte;[4] sppe;
$2MeTaCl_4$,L′ where L′ = dithian; pte; sppe;
$4MeTaCl_4$,3diox
(tpps = triphenylphosphine sulphide; diox = 1,4-dioxan;
thf = tetrahydrofuran; thiox = 1,4-thioxan; pms = pentamethylene sulphide;
pte = 1,2-bis(phenylthio)ethane; sppe = ethylenebis(diphenylphosphine sulphide)

All the complexes reacted extremely rapidly with oxygen and moisture. They could be stored indefinitely under nitrogen at −80 °C, but slowly decomposed at room temperature; the tantalum complexes were a little more thermally stable than their niobium analogues.

The occurrence of disproportionation reactions in

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

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

[3] W. Mowat and G. Wilkinson, *J. Organometallic Chem.*, 1972, **38**, C35.

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

TABLE 1

N.m.r. spectra (τ) in dichloromethane

	Methyl metal resonances			Integrated intensities *			
Complex	MeM	Me$_2$M	Me$_3$M	MeM :	Me$_2$M :	Me$_3$M	Ligand resonances, assignments in brackets
MeNbCl$_4$	6·65						
Me$_2$NbCl$_3$		7·10					
Me$_3$NbCl$_2$			7·40				
MeTaCl$_4$	7·22						
Me$_2$TaCl$_3$		7·81					
Me$_3$TaCl$_2$			8·23				
2MeNbCl$_4$,dithian	6·74	7·12				*a*	6·77(CH$_2$–S)
MeNbCl$_4$,tpps	6·54	7·09		1	6	0	2·24, 2·43 (aryl protons) [b]
MeNbCl$_4$,CCl$_3$CN	6·63	7·08		1	0·5	0	
4MeTaCl$_4$,3diox	7·31	7·80		1	0·7	0	5·72(CH$_2$–O)
MeTaCl$_4$,diox	7·36	7·80		1	1·5	0	5·95(CH$_2$–O)
MeTaCl$_4$,thf	7·53	7·88	8·22			*a*	5·81(α-protons),[b] 7·92(β-protons) [b]
MeTaCl$_4$,thiox	7·49	7·90		1	0·2	0	5·85(CH$_2$–O),[c] 7·15(CH$_2$–S) [c]
MeTaCl$_4$,pms	7·61	7·94				*a*	7·02(α-protons),[b] 8·12 [b](β- and γ-protons) [b]
2MeTaCl$_4$,dithian	7·36	7·79	8·20	1	1·5	0·1	6·67(CH$_2$–S)
2MeTaCl$_4$,pte	7·38	7·86	8·35	1	1·33	0·1	2·52(Ph–S), 6·59(CH$_2$–S)
MeTaCl$_4$,tpps	7·57	7·79	8·20	1	4	0·8	2·11, 2·36(aryl protons) [b]
MeTaCl$_4$, CCl$_3$CN	7·21	7·80		1	3·6	0	
Me$_2$TaCl$_3$,dme	7·42	7·76	8·21	0·3	1	1·8	6·34(CH$_2$O), 6·54(CH$_3$–O)
Me$_2$TaCl$_3$,tppo	8·21	8·27	8·33	0·9	1	0·8	2·31(aryl protons) [b]
Me$_2$TaCl$_3$,tht	7·52	8·00	8·21				6·67(α-protons),[b] 7·92(β-protons) [b]
2Me$_2$TaCl$_3$,dithian	7·42	7·80	8·20	0·2	1	0·7	6·86(CH$_2$–S)
Me$_2$TaCl$_3$,mte		7·79	8·24	0	1	0·8	6·90(CH$_2$–S), 7·55(CH$_3$–S)
Me$_2$TaCl$_3$,ete		7·76	8·21	0	1	0·8	6·99(CH$_2$–S), 7·20(CH$_3$–CH_2–S),[d] 8·65(CH_3–CH$_2$–S) [c]
Me$_2$TaCl$_3$,tpps	7·56	7·73	8·15	0·3	1	1	2·11, 2·39(aryl protons) [b]
2Me$_2$TaCl$_3$,sppe	7·53	7·80	8·21	0·1	1	0·4	2·16, 2·44(aryl protons),[b] 7·12(CH$_2$–P)
Me$_2$TaCl$_3$,MeCN	7·67	8·11	8·22	0·1	1	0·1	7·48(CH$_3$–CN)
Me$_2$TaCl$_3$,Pr^{n}CN	*e*	8·08	*e*			*a*	7·13(CH$_2$–CN),[c] 8·1(–CH_2–CH$_2$CN),[b] 8·78(CH_3–CH$_2$–) [c]
Me$_2$TaCl$_3$,PhCN	7·58	8·00	8·23	0·1	1	0·2	2·20(aryl protons) [b]
Me$_2$TaCl$_3$,PPh$_3$	7·52	7·83	8·21	0·1	1	0·6	2·55, 2·62(aryl protons) [b]

[a] Integrated intensities could not be determined because of the proximity of ligand and methyl-metal resonances. [b] Complex multiplet. [c] Triplets. [d] Quartet. [e] Not located; hidden by ligand bands.

* The integrated intensities were measured for freshly prepared solutions.

TABLE 2

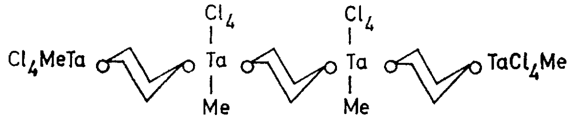
Analytical data for complexes prepared

		Found (%)		Calculated (%)	
Ligand	Complex	Cl	*M*	Cl	*M*
1,4-Dithian	2MeNbCl$_4$,dithian	45·2	29·8	45·8	30·0
	2MeTaCl$_4$,dithian	35·6	45·1	35·6	45·5
	2Me$_2$TaCl$_3$,dithian	27·7	47·2	28·2	47·9
1,2-Bis(phenylthio)ethane	2MeTaCl$_4$,pte	30·4	39·4	30·8	39·3
Triphenylphosphine sulphide	MeTaCl$_4$,tpps	22·1	28·9	22·4	28·6
	MeNbCl$_4$,tpps	26·1	16·9	26·1	17·1
Ethylenebis(diphenylphosphine sulphide)	2MeTaCl$_4$,sppe	25·2	31·9	24·9	31·8
	2MeNbCl$_4$,sppe	29·8	20·0	29·8	19·3
	2Me$_2$TaCl$_3$,sppe	20·2	33·0	19·4	33·0
Trichloroacetonitrile	MeNbCl$_4$,CCl$_3$CN	36·2	23·5	36·0	23·6
	MeTaCl$_4$,CCl$_3$CN	29·6	37·8	29·4	37·5
1,2-Dimethoxyethane	Me$_2$TaCl$_3$,dme	26·0	44·9	26·1	44·4
Triphenylphosphine oxide	Me$_2$TaCl$_3$,tppo	18·0	30·8	17·9	30·4
Tetrahydrothiophen	Me$_2$TaCl$_3$,tht	26·3	44·6	26·2	44·6
1,2-Bis(methylthio)ethane	Me$_2$TaCl$_3$,mte	24·2	41·7	24·2	41·2
1,2-Bis(ethylthio)ethane	Me$_2$TaCl$_3$,ete	22·7	38·5	22·8	38·7
Triphenylphosphine sulphide	Me$_2$TaCl$_3$,tpps [a]	16·9	28·8	17·4	29·6
1,4-Dioxan	4MeTaCl$_4$,3diox	35·1	44·4	35·1	44·8
	MeTaCl$_4$,diox	33·2	43·0	33·3	42·5
Tetrahydrofuran	MeTaCl$_4$,thf	33·4	43·1	33·7	43·1
1,4-Thioxan	MeTaCl$_4$,thiox	32·2	40·8	32·1	40·9
Pentamethylene sulphide	MeTaCl$_4$,pms	32·4	41·3	32·2	41·1
Methyl cyanide	Me$_2$TaCl$_3$,MeCN	29·5	50·6	29·7	50·5
n-Propyl cyanide	Me$_2$TaCl$_3$,Pr^{n}CN	27·4	46·9	27·5	46·8
Benzonitrile	Me$_2$TaCl$_3$,PhCN	25·1	43·4	25·3	43·0
Triphenylphosphine	Me$_2$TaCl$_3$,PPh$_3$	18·0	31·4	18·4	31·3

[a] Contaminated with a small quantity of unco-ordinated ligand; confirmed by i.r. spectrum.

solution (see discussion of n.m.r.) precluded molecular weight measurements so that we have had to rely on spectroscopic studies to provide structural evidence.

Although $MeTaCl_4$ forms a 1 : 1 complex with dioxan as does $MeNbCl_4$, we were unable to prepare a tantalum complex of comparable stoicheiometry to $2MeNbCl_4$,diox,[4] even with an excess of $MeTaCl_4$. Another complex could be obtained, however, with composition $4MeTaCl_4$,3diox. The i.r. spectrum shows clearly that both oxygen atoms of the dioxan molecule are co-ordinated,[5,6] there being modified C–O–C stretches at 1094 and 852 cm^{-1} (free dioxan values 1125 and 876 cm^{-1}).



FIGURE

A possible structure is shown in the Figure where two of the tantalum atoms are seven-co-ordinate as seen in the crystal structure of Me_3TaCl_2bipy.[7] In contrast, the spectrum of $MeTaCl_4$,diox shows both modified and unmodified C–O–C stretching modes, showing the ligand to be monodentate. While dimerisation through chlorine bridging cannot be ruled out, a simple six-co-ordinate structure is more likely.

The metal atoms would also appear to be six-co-ordinate in the majority of the other $MeMCl_4$ complexes in view of their spectra. Thus pms and thf appear to co-ordinate in the usual way and there is no evidence for $M–Cl \longrightarrow M$ bridging. In the $2MeMCl_4$,L complexes formed by dithian, the i.r. spectra show the ligand to be bridging in the centrosymmetric chair form, and in $2MeTaCl_4$,pte the ligand appears to bridge two tantalum atoms and be in the *trans*-form (band at 1204 cm^{-1} attributable to *trans*-form).[8] The reactions of the $\geqslant$P=S ligands tpps and sppe with $MeMCl_4$ were of interest since it was possible either that sulphur might be extracted to yield $NbSCl_3$ derivatives, by analogy with the known reaction of Me_2NbCl_3 with Ph_3PO which gives a $NbOCl_3$ species,[4] or that addition might occur across the double bond. In every case the i.r. spectrum shows a lowering of the frequency of the P=S stretching mode, and it is clear that simple co-ordination has occurred, with the bidentate ligand sppe presumably bridging two metal atoms.

With thioxan, $MeTaCl_4$ gave a complex of 1 : 1 stoicheiometry but only an unidentified oil could be obtained from the analogous $MeNbCl_4$ reaction. There are two possible donor atoms, oxygen and sulphur, and previous workers have used the i.r. spectra of complexes to establish the mode of bonding.[9] The spectrum of $MeTaCl_4$,thioxan clearly establishes co-ordination through oxygen, but provides no evidence either way about sulphur bonding or the presence of free ligand. However, in the n.m.r. spectrum the resonances of both sets of methylene protons have shifted downfield by τ *ca.* 0·35 (compared to the free ligand), as these shifts are less than those of the α protons in $MeTaCl_4$,pms (τ 0·51) and $MeTaCl_4$,thf (τ 0·59) bonding through sulphur and oxygen is indicated. This suggests a rapid ligand exchange taking place in solution; the resonances observed being some average between those for co-ordinated and unco-ordinated thioxan. With CCl_3CN the complexes formed were rather unstable and the ligand was easily lost at the pump. The n.m.r. spectra show that the products contain the $MeMCl_4$ entity, although a second weak resonance at τ 9·15 for the tantalum complex could be interpreted on the basis of some addition across the triple CN bond and the formation of $Cl_4Ta–N=CMeCCl_3$. Analogous additions have been oserved in the reaction between tungsten(VI) chloride and trichloroacetonitrile.[10,11]

In addition to providing information about the mode of co-ordination of ligands, the i.r. spectra of the complexes clearly show M–C and M–Cl stretching modes (see Table 3). The M–C modes which occur in the 450—550 cm^{-1} range are at slightly higher wavenumbers for tantalum than niobium complexes. Metal–chlorine stretching frequencies are observed as a complex group of strong bands in the 300—400 cm^{-1} region. The two possible stereochemical arrangements for $MeMCl_4$,L complexes, *trans* C_{4v} and *cis* C_s, require one and three i.r.-active M–Cl stretching modes respectively, and the complexity of the spectra suggests that the complexes adopt the *cis*-configuration.

The n.m.r. spectra of the complexes (Table 1) show quite clearly that the complexes undergo considerable disproportionation in dichloromethane solution. The niobium complexes decompose too quickly for measurements to be made over a period of time, but with some tantalum complexes ($MeTaCl_4$,tpps and $2MeTaCl_4$,dithian) there is a steady growth of the resonances associated with dimethyl and trimethyltantalum chlorides at the expense of the $MeTaCl_4$ resonance.

Although this n.m.r. data shows the presence, in solution, of mono-, di-, and trimethyltantalum species, it is nevertheless clear that in the solid state the complexes are those of $MeTaCl_4$ and not a mixture. The latter possibility is ruled out by the consistent analytical data, solubility behaviour, thermal stability, and i.r. spectra.

Complexes of Me_2TaCl_3.—The complexes prepared (Table 2) were mainly of stoicheiometry Me_2TaCl_3,L where L = MeCN, Pr^nCN, PhCN, PPh_3, dme, tppo, tht, tpps, mte, and ete (dme = 1,2-dimethoxyethane;

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

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

[7] M. G. B. Drew, G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, unpublished work.

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

[9] R. A. Walton, *Inorg. Chem.*, 1966, **5**, 643.

[10] M. G. B. Drew, G. W. A. Fowles, D. A. Rice, and N. Rolfe, *Chem. Comm.*, 1971, 232.

[11] M. G. B. Drew, K. C. Moss, and N. Rolfe, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1219.

tppo = triphenylphosphine oxide; tht = tetrahydrothiophen; mte = 1,2-bis(methylthio)ethane; ete = 1,2-bis(ethylthio)ethane), although with dithian and sppe the complexes had the stoicheiometry $2Me_2TaCl_3$,L.

All complexes with simple monodentate ligands appeared to be straightforward six co-ordinate adducts, the i.r. spectra showing all the usual peaks (modified) of co-ordinated ligands. I.r. spectra of the $2Me_2TaCl_3$,L complexes indicate that in each case the ligand acts in a bridging bidentate manner.

TABLE 3

I.r. bands associated with $M-CH_3$ and M–Cl groups/cm^{-1}

Complex	δ-(CH_3)	Absorption bands 600—250 cm^{-1} [a]
$2MeNbCl_4$,dithian	1143wm	482sh, *466s*, 402sh, 380sh, 360sh, 348sbr, 333sh, 317sh, 303sh
$MeNbCl_4$,tpps		580s, 563sh, 512ms, *468m*, 451sh, 433sh, 358sh, 335sbr, 309sh, 278sh
$2MeNbCl_4$,sppe		581m, 566sh, 502m, 492m, 480sh, 405sh, 391sh, 383sh, 353sbr, 333sh, 323sh, 308sh
$MeNbCl_4$,CCl_3CN	1138m	513m, *472ms*, 425sh, 415sh, 384s, 369sh, 358sh, 347sh, 328sh, 305sh
$4MeTaCl_4$,3diox		590brsh, *548s*, 430br,sh, 400sh, 380sh, 360sh, 342s, 320sh, 309sh, 280sh, 270sh
$MeTaCl_4$,diox		*542ms*, 377sh, 357sh, 325sbr, 292sh, 282sh
$MeTaCl_4$,thiox		571ms, *537s*, 380sh, 360sh, 348sh, 327s, 307sh, 294sh, 280sh, 270sh
$MeTaCl_4$,pms		533sh, 524w, *479ms*, 463sh, 378sh, 358sh, 341s, 308sh, 293sh, 278sh, 268sh
$2MeTaCl_4$,dithian	1117m	560sh, *537s*, 520sh, 491sh, 481w, 379sh, 375sh, 360sh, 330sbr, 305sh, 295sh, 275sh
$2MeTaCl_4$,pte		570sh, *542ms*, 489m, 480sh, 413w, 390sh, 362sh, 337sh, 325sh, 305sh, 282sh
$MeTaCl_4$,tpps		592s, 570sh, 513s, *488sh*, 468sh, 433sh, 360sh, 341sh, 320sbr, 288sh, 270sh
$2MeTaCl_4$,sppe		592s, 574sh, 561sh, 522m, 506ms, 487m, 479sh, 456w, 375brsh, 343sh, 319sbr, 280sh
$MeTaCl_4$,CCl_3CN	1129ms	*512w*, 383sh, 358sh, 343sh, 333sbr, 318sh, 305sh, 283sh
Me_2TaCl_3,dme		565w,br, *514s*, 500sh, *467ms*, 400sh, 349s, 340sh, 327sh, 318sh, 305sh
Me_2TaCl_3,tppo		538s, 520sh, 495br,sh, 473sh, 450sh, 425sh, 353sh, 313sh, 290s,br
Me_2TaCl_3,tht	1115ms	*482s*, 467sh, 460sh, 390sh, 358sh, 340sh, 322s,br, 307sh, 293sh, 280sh
$2Me_2TaCl_3$,dithian		*530 wm*, 480m, 385sh, 358sh, 325s,br, 285sh
Me_2TaCl_3,mte		*509s*, 490sh, *468s*, 460sh, 364sh, 354sh, 327sh, 310s,br, 285sh, 265sh
Me_2TaCl_3,ete		512sh, *502s*, *469ms*, 435sh, 385sh, 337s,br
Me_2TaCl_3,tpps		590m, 578sh, 515s, 486sh, 466sh, 449sh, 429w, 345sh, 310s,br, 275sh
Me_2TaCl_3,sppe		592s, 577sh, 525sh, 500m, 487m, 457m, 367sh, 347sh, 320s,br, 285m
Me_2TaCl_3,MeCN	1140m	517sh, *501s*, 480sh, 440wm, 410w, 377sh, 360sh, 315s,bvr
Me_2TaCl_3,Pr-CN		*487s*, 477sh, 456sh, 380sh, 367sh, 325s,br, 305sh, 290sh, 275sh
Me_2TaCl_3,PhCN	1120ms	563s, 552sh, 505sh, *487s*, 460sh, 357sh, 345sh, 322sh, 317s,br, 280sh
Me_2TaCl_3,PPh_3		523sh, 517sh, 500s, *487sh*, 450sh, 425sh, 362sh, 354sh, 342sh, 305s,br, 270sh

[a] Bands given in italics are assigned to M–C stretches.

A single Ta–C stretching frequency having a slight shoulder (Table 3) was found for every complex formed with a monodentate or bridging bidentate ligand, which could indicate a *trans*-arrangement of the methyl groups. The slight asymmetry presumably arises from the symmetric Ta–C stretching frequency, which should be weak as the vibration only involves a small change in dipole moment. A similar feature was observed with complexes of Me_2NbCl_3 with monodentate donors and with complexes of the type *trans*-Me_2SnCl_2,B (B = bidentate ligand).[12]

Other potentially bidentate ligands, mte, ete, and dme, also appear to co-ordinate through both donor atoms, but the i.r. spectra show the ligands to be in the *gauche* form, and show two distinct bands of almost equal intensity in the 450—550 cm^{-1} region which may be assigned to symmetric and asymmetric Ta–C stretching frequencies. It would seem that in these complexes the tantalum atom may be seven-co-ordinate; the analogous niobium complexes Me_2NbCl_3,L (L = mte and ete) also appeared [4] to have this structure.

The n.m.r. spectra of all complexes (*cf.* Table 1) show resonances attributable to Me_2TaCl_3 and Me_3TaCl_2 groupings, and in some cases there is a further resonance that appears to arise from $MeTaCl_4$. This again shows that complexes disproportionate in solution, and indeed in some cases, over a period of a few days, the $TaCl_5$ complexes precipitated from CH_2Cl_2 solution. The spectrum of Me_2TaCl_3,PPh_3 was studied in the most detail because the ligand resonances did not interfere and $TaCl_5$,PPh_3 is soluble in dichloromethane. Over a period of 22 days the resonances associated with $MeTaCl_4$ and Me_2TaCl_3 entities gradually disappeared until finally only the Me_3TaCl_2 resonance could be observed.

The rate of disproportionation, as judged by the change in n.m.r. spectra, varied considerably from complex to complex, and while there was a considerable change over a few days for the six-co-ordinate complexes Me_2TaCl_3,tpps, Me_2TaCl_3,PPh_3, and $2Me_2TaCl_3$,dithian, there was only a slight change in resonance after 16 days for the seven-co-ordinate complexes Me_2TaCl_3,mte and Me_2TaCl_3,ete. These observations can be rationalised by postulating that methyl group exchange is facilitated by the formation of a bimolecular species, which is not easily achieved by a seven-co-ordinate complex.

EXPERIMENTAL

Analytical procedures, the preparation ot dimethylzinc, the purification of ligands and solvents, and the manipula-

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

tive techniques have been described previously.[4] N.m.r. spectra were recorded on either a Perkin-Elmer R10 or a Varian T60 spectrometer.

Tantalum(v) chloride was prepared by the direct chlorination of sheet tantalum (Found: Cl, 50·8; Ta, 49·0. $TaCl_5$ requires Cl, 50·5; Ta, 49·5%).

Ethylenebis(diphenylphosphine sulphide) (*sppe*) was prepared by adding, under nitrogen, a slurry of sulphur (1·6 g) in carbon disulphide (100 ml), to a solution of 1,2-bisdiphenylphosphinoethane (10 g) in carbon disulphide (100 ml) over a period of 45 min. The mixture was stirred throughout the addition and its temperature kept just below the b.p. of the solvent. The mixture was then heated under reflux for 1 h and cooled. The white crystalline product (m.p. 223—224 °C) was separated by filtration.

$MeTaCl_4$–Me_2TaCl_3 *Mixture.*—$TaCl_5$ (0·01 mol) was allowed to react with Me_2Zn (0·0045 mol) in pentane (30 ml) for 24 h at room temperature. The precipitated $ZnCl_2$ was filtered off, leaving a pale yellow solution containing $MeTaCl_4$ and Me_2TaCl_3; this was used immediately for reaction with the appropriate ligand, and a high yield of complex was always obtained.

Me_2TaCl_3–Me_3TaCl_2.—The preparation was carried out as for the previous one except that 0·011 mol of Mn_2Zn was used.

Me_3TaCl.—A higher yield than that reported in the literature could be obtained by the following procedure. $TaCl_5$ (0·01 mol) was allowed to react with Me_2Zn (0·0158 mol) in pentane (30 ml) for 4 h at room temperature. $ZnCl_2$ and a small amount of an unidentified dark coloured compound were removed by filtration, and the filtrate evaporated to leave a pale yellow solid.

$MeTaCl_4$,L (*where* L = *thiox, thf, pms, and* CCl_3CN), $4MeTaCl_4$,3*diox and* $MeNbCl_4$,CCl_3CN.—A solution of the ligand (0·01 mol) in pentane (20 ml) was added to the $MeMCl_4$–Me_2MCl_3 mixture and the precipitated solid isolated by filtration, washed with pentane and pumped. Where necessary the solutions were concentrated to bring about precipitation. To avoid loss of ligand the CCl_3CN complexes were pumped for 30 min only.

$MeTaCl_4$,diox.—1,4-Dioxan (10 ml) in pentane solution was added to the $MeTaCl_3$–Me_2TaCl_3 mixture. Solvent and unreacted ligand were removed by pumping and the residual solid extracted with pentane; the removal of solvent from the extract solution yielded $MeTaCl_4$,diox as a bright yellow solid.

$2MeNbCl_4$,*dithian*, $2MeTaCl_4$,*dithian*, $MeNbCl_4$,*tpps*, $MeTaCl_4$,*tpps*, $2MeNbCl_4$,*sppe*, $2MeTaCl_4$,*sppe*, *and* $2MeTaCl_4$,*pte*.—A solution of the ligand (0·0025 mol for bidentate, 0·005 mol for monodentate) in pentane (dithian) or CH_2Cl_2 (sppe, tpps) or iso-octane (pte) was added to the $MeMCl$–Me_2MCl_3 mixture, and the solid which precipitated (solution concentrated when necessary) filtered, washed with pentane, and pumped.

Me_2TaCl_3,L (L = *dme, tht, mte, ete*, MeCN, Pr^nCN, *and* PhCN).—A solution of the appropriate ligand (0·009 mol) in pentane was added to the Me_2TaCl_3–Me_3TaCl_2 mixture, and the precipitated complexes isolated by rapid filtration, washed with pentane and pumped for several hours.

Me_2TaCl_3,*tpps*, Me_2TaCl_3,PPh_3, $2Me_2TaCl_3$,*sppe*, $2Me_2TaCl_3$,*dithian, and* Me_2TaCl_3,*tppo*.—A solution of the ligand (0·0025 mol bridging bidentate, 0·005 mol unidentate) in pentane or CH_2Cl_2 (sppe) was added to the Me_2TaCl_3–Me_3TaCl_2 mixture, the solvent removed at the pump and the solid washed thoroughly with pentane and pumped for several hours.

Attempts to make complexes with the bidentate ligands 2,2′-bipyridyl and 1,2-bisdiphenylphosphinoethane were unsuccessful, since the products were mixtures of Me_2TaCl_3 and Me_3TaCl_2 complexes which could not be separated.

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