Preparation of Monomethyl-niobium(v) and -tantalum(v) Halides and of some of their Complexes

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Monoalkylated compounds $MeNbCl_4$, $MeTaCl_4$, and $MeNbBr_4$ have been synthesized by treating the corresponding metal(v) halides with either $HgMe_2$ or $SnMe_4$. With the chlorides the reactions were rapid and simple: only the *mono*alkyl derivatives were formed and isolated in quantitative yields, along with either $HgCl_2$ or $ClSnMe_3$. No further substitution was observed in the presence of an excess of either of the alkylating agents. The reaction of $HgMe_2$ with $NbBr_5$ was much slower and MeHgBr was formed. The reaction of $SnMe_4$ with $NbBr_5$ does not go to completion. The new compounds have been characterized by elemental analysis, cryoscopic molecular-weight determinations, n.m.r. and i.r. spectroscopy, mass spectrometry, and by the identification of a range of adducts, several of which were isolated, *i.e.* $[MeNbCl_4],L$ (L = PPh_3, $Ph_2PCH_2CH_2PPh_2$, or γ-picoline) and $[MeNbBr_4],L$ (L = $Ph_2PCH_2CH_2PPh_2$ or 2,2′-bipyridine).

THE only previously isolated σ-bonded alkyl compounds of niobium(v) are dichlorotrimethylniobium [1] and bridged $[Nb_2(CSiMe_3)_2(CH_2SiMe_3)_4]$.[2] Fowles *et al.*[3] recently reported the preparation of Me_2NbCl_3 from $NbCl_5$ and dimethylzinc, but they could not isolate the *mono*methylniobium derivative, $MeNbCl_4$, which is also formed in this reaction. Accordingly we now describe the successful preparation and isolation, in a pure state, of the *mono*methyl derivatives $MeNbCl_4$, $MeTaCl_4$, and MeNbBr, which we obtained in quantitative yields by treating the metal pentahalides with dimethylmercury or tetramethyltin. The new compounds were also characterized by the preparation of some of their adducts.

RESULTS

Reaction of Niobium(v) *Chloride and Tantalum*(v) *Chloride with Dimethylmercury.*—The reaction between dimethylmercury and niobium pentachloride was performed at −35 °C in dichloromethane. Formation of methylniobium(v) chloride, as followed by n.m.r. spectroscopy at this temperature, is immediate in these conditions. The only signal to be seen during the addition at −35 °C was a peak at 2·98 p.p.m. which we attribute to $MeNbCl_4$ (δ 2·78 p.p.m. for $MeTiCl_3$ [4]). The signal of $HgMe_2$ (δ 0·27 p.p.m.) [5] appeared only when the $HgMe_2 : NbCl_5$ ratio became greater than 0·5 : 1. The mixed chloromethylmercury compound (δ 0·93 p.p.m.) [5] was not detected, neither was formation of the *di*- or *tri*-methylniobium halogeno-compounds even in the presence of an excess of dimethylmercury. The stoicheiometric amount of insoluble $HgCl_2$ was recovered.

The same reaction was observed to occur in toluene (−30 °C), but not in pentane (−40 to +10 °C). In acetonitrile, a two-fold excess of dimethylmercury was necessary to complete the reaction, which then gave the complex $[MeNbCl_4]$, MeCN, and chloromethylmercury. This complex was characterised by the appearance of a signal for co-ordinated

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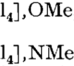
acetonitrile (Table 1) with a 1 : 1 MeNb : MeCN peak-area ratio. Peaks for co-ordinated and unco-ordinated MeCN coalesce above −25 °C.

TABLE 1

N.m.r. spectra (p.p.m. from Me_4Si) at −35 °C measured from CH_2Cl_2 as internal reference

Compound	δ_{Nb-Me}	Co-ordinated-ligand resonances (assignments)
$[MeNbCl_4]$	2·98 [a]	
$[MeNbBr_4]$	2·73	
$[MeTaCl_4]$	2·9	
$[MeNbCl_4]$,MeCN	2·6	2·5 (CH_3–CN)
$[MeNbCl_4]$,OMe_2	2·9 (3·0) [b]	4·17 (CH_3–O) (4·23) [b]
$[MeNbCl_4]$,NMe_3	2·9 [c]	2·6 (CH_3–N)
$[MeNbCl_4]$,γ-picoline	2·8	2·5 (CH_3–C)
$[MeNbCl_4]$,SMe_2	*d*	2·8 (CH_3–S)
$[MeNbCl_4]$,	2·8	4·02 (CH_2–O), 3·0 (CH_2–S)
$[MeNbCl_4]$,$P(NMe_2)_3$	2·93	2·86 (CH_3–N) doublet J_{P-H} 12 Hz
$[MeNbCl_4]$,PPh_3	2·8	7·63 (H_0), 7·73 (H_m, H_p)
$[MeNbCl_4]$,$AsPh_3$	2·87	8·75 (aryl protons of ligand)
$[MeNbCl_4]$,$OP(NMe_2)_3$	*d*	2·85 (CH_3–N) doublet J_{P-H} 10·5 Hz
$[MeNbCl_4]$,$OP(OMe)_3$	2·92 (2·94) [b]	4·1 (CH_3–O) (4·0) [b] doublet J_{P-H} 12 Hz
$[MeNbCl_4]$,$OPPh_3$	2·85	7·95 (H_0), 7·75 (H_m, H_p)
$[MeNbCl_4]$,$OPMe_3$	2·82 [e]	2·07 [e] (CH_3–P), J_{P-H} 13·5 Hz
$[MeNbCl_4]$,$(Ph_2PCH_2CH_2PPh_2)$	2·92	3·4 (CH_2–P), multiplet J_{P-H} 13 Hz 7·62 (H_0), 7·72 (H_m, H_p)
$[MeNbBr_4]$,$(Ph_2PCH_2CH_2PPh_2)$	*f*	
$[MeNbBr_4]$,bipy [g]	2·7	$\Delta\delta(H_\alpha)$ + 0·5 p.p.m.

[a] Previously reported[3] 3·36 p.p.m. [b] When the molar ratio L : Nb > 1 : 1 formation of a 2 : 1 complex is observed (δ in parentheses). [c] The n.m.r. spectrum has been measured at −50 °C [d] Obscured by ligand signal. [e] When the L : Nb molar ratio becomes greater than 1 : 1 the ligand signal becomes more complex. [f] Resonances could not be definitely located because of the low solubility of the complex. [g] In MeCN.

Tetrachloromethylniobium was obtained in quantitative yields, as orange-brown crystals, after separation of $HgCl_2$ and evaporation of the solvent and excess of $HgMe_2$ in the cold. Purification was achieved by low-temperature recrystallization from a mixture of methylene chloride and pentane. The compound is very soluble in the usual non-complexing solvents and slightly soluble in light petroleum; it decomposes in carbon tetrachloride. It must be freed from $HgCl_2$ in the cold since a slow exchange reaction takes place between $MeNbCl_4$ and $HgCl_2$ which gives MeHgCl and a brown insoluble solid when the reaction mixture is set aside at room temperature. Once pure, $MeNbCl_4$ is stable at room temperature: no changes in appearance or in m.p. were noticed after 8 weeks. The compound was characterized by elemental analysis, a molecular-weight determination in solution, n.m.r. and i.r. spectroscopy, mass spectrometry, and by the preparation and characterization of some of its adducts.

The cryoscopic molecular weight in benzene showed the compound to be dimeric [Found (Calc.) 440 (500)], while mass-spectral analysis showed it to be monomeric in the vapour phase. The mass spectra consisted mainly of a series of isotopic patterns centred at 254, 238, 202, 166, and 129 mass units, characteristic of the presence of the chlorone atoms in the fragments $CH_3NbCl_4^+$ (mass peaks), $NbCl^+$, $NbCl_3^+$, $NbCl_2^+$, and $NbCl^+$. Peaks at 52 and 50 mass units ($MeCl^+$) may be due to some decomposition during the measurement. The n.m.r. spectrum consisted of a single peak (Table 1) and showed no change with temperature between −80 and +30 °C in either dichloromethane or toluene. Absorption bands at 530 and 510 cm^{-1} in the i.r. spectrum (Table 2) are attributed to ν(Nb–C) stretching frequencies.[6,7] The presence of the methyl group is further established by symmetric and antisymmetric ν(C–H) stretching vibrations at 3 040, 2 980, and 2 540 cm^{-1},[8] the antisymmetric deformation vibration of the group at 1 390 cm^{-1}, and rocking vibrations at 890 and 820 cm^{-1} which are characteristic of methyl groups bonded to a metal atom.[6] Bands at 405, 375, and 370 cm^{-1}, which are also present in the i.r. spectrum of $NbCl_5$,[9] are attributed to Nb–Cl bonds.

TABLE 2

I.r. spectra/cm^{-1}

Compound	ν(Nb–C)	ρ(CH_3)	Other bands (< 500 cm^{-1})
$[MeNbCl_4]$	530m, 510m	890s, 820s	400s, 395s, 375s ν(Nb–Cl)
$[MeNbBr_4]$	500m	850s, 800s	470w,450w, 425w
$[MeTaCl_4]$	545m, 520m	820s	400s ν(Ta–Cl)
$[MeNbCl_4]$,PPh_3	525m, 500m	870s, 850s	440m ν(Nb–P) [a]
$[MeNbCl_4]$,$(Ph_2PCH_2CH_2PPh_2)$	500s	855s, 820s	450m, 430m ν(Nb–P) [a]
$[MeNbBr_4]$,$(Ph_2PCH_2CH_2PPh_2)$	490m	785s	450m ν(Nb–P) [a]
$[MeNbBr_4]$,bipy	470m	*b*	360s ν(Nb–Br)

[a] Ref. 28. [b] Obscured by ligand bands: m = medium; s = strong; and w = weak.

Dimethylmercury reacts in a very similar way with tantalum pentachloride affording, after sublimation of the product, pure tetrachloromethyltantalum in nearly quantitative yields. The physical and spectral characteristics of the product are very close to those of the niobium analogue (Tables 1 and 2 and Experimental section). It is however less stable and decomposes near 50 °C.

Reaction of Niobium(V) *and Tantalum*(V) *Chlorides with Tetramethyltin.*—Very similar results were obtained when tetramethyltin was employed as an alkylating agent instead of dimethylmercury. The reaction is rapid and conversion of the pentahalides was quantitative at −35 °C. Only one chlorine atom was substituted by a methyl group, even in the presence of an excess of tetramethyltin, while only chlorotrimethyltin (δ 0·63 p.p.m.)[10] was formed as a by-product, which could be separated from $MeNbCl_4$ or $MeTaCl_4$ by solubility differences.

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Adducts of $MeNbCl_4$.—The reaction of $MeNbCl_4$ with a range of common monodentate and with a few bidentate ligands was investigated by low-temperature n.m.r. spectroscopy (Table 1). Several adducts were isolated and further characterized by elemental analysis and i.r. spectroscopy. The compound $MeNbCl_4$ gave only 1 : 1 adducts, even in the presence of an excess of most of the ligands which were tested [MeCN, NMe_3, SMe_2, , $P(NMe_2)_3$, PPh_3, and $AsPh_3$], as evidenced by a single peak in the n.m.r. spectra for CH_3–Nb (δ 2·6—3·05 p.p.m.) at −35 °C, and two sets of signals for the co-ordinated (Table 1) and unco-ordinated ligand with the expected MeNb : co-ordinated ligand signal-area ratios. A similar range of chemical shifts was observed for comparable $MeTiCl_3$ complexes (δ 2·19—3·0 p.p.m.).[11-13] An ebulliometric molecular-weight determination on the isolated adduct $[MeNbCl_4],PPh_3$ shows it to be monomeric, which implies that the niobium atom is six-co-ordinated. Two CH_3–Nb signals were however observed for L = OMe_2 and $OP(OMe)_3$ together with a new set of co-ordinated-ligand signals (Table 1), the relative area of which depend on the L : Nb ratio. In these cases the peak which appeared for higher L : Nb ratios is attributed to formation of a 2 : 1 adduct on the basis of peak-area ratios.

More complex reactions, involving the abstraction of oxygen from the ligand, occurred for L = $OPMe_3$, $OPPh_3$, and $OP(NMe_2)_3$ and resulted in the formation of oxo-species [ν(Nb=O) 935 cm^{-1}].[14] Addition of amines to the compound $MeNbCl_4$ generally resulted in immediate decomposition at room temperature. However a 1 : 1 adduct with NMe_3 could be identified at low temperature. It rapidly decomposed when the temperature was allowed to rise above −50 °C. We nevertheless succeeded in preparing and isolating the $MeNbCl_4$,γ-picoline adduct, provided ligand addition and purification were performed at −50 °C. The adduct decomposes readily above 0 °C. For 1,4-thioxan both n.m.r. and i.r. spectra are consistent with co-ordination through the sulphur atom, *i.e.* the 'softest' of the two potential donor atoms, as is the case for $NbCl_5$ [15] and for Me_2NbCl_3.[3] The bidentate ligand 1,2-bis(diphenylphosphino)ethane gave a 1 : 1 adduct. The symmetric behaviour of the two donor atoms was established by the proton n.m.r. spectroscopy which gave only one set of doublets (δ 3·4 p.p.m. J_{H-P} 13 Hz) for the methylene groups down to −65 °C. This implies that the niobium atom is seven-coordinate in this complex.

Reaction of Niobium(V) *Pentabromide with Dimethylmercury and with Tetramethyltin.—Preparation of tetrabromomethylniobium and some of its adducts.* The reaction of dimethylmercury with $NbBr_5$ differs appreciably from its reaction with $NbCl_5$. (i) It takes a two-fold excess of the alkylating agent to complete the reaction and the $HgMe_2$ is converted into MeHgBr instead of $HgBr_2$, which makes the isolation of the compound $MeNbBr_4$ more difficult. (ii) The reaction is much slower, taking 3 days at −20 °C (or 10 h at 0 °C) to be completed, whatever solvent was employed (toluene, dichloromethane, or dibromomethane). When acetonitrile was used as a solvent, the adduct $[MeNbBr_4],MeCN$ (δ_{MeNb} 2·65, δ_{MeCN} 2·55 p.p.m.) was formed but not isolated. An excess of the alkylating agent did not result in further substitution.

The compound $MeNbBr_4$ could be separated from MeHgBr by solubility differences as orange-brown crystals which are very sensitive to air and moisture, and which are thermally less stable than their chlorinated analogues. Physical and spectral characteristics of the product are given in Tables 1 and 2 and the Experimental section. The presence of bromomethylmercury in the reaction mixture is inconvenient: it often prevents the preparation of complexes of the alkylniobium derivative *in situ* since it reacts with many donors according to reaction (1),[16] and makes it thus difficult to isolate the adducts of $MeNbBr_4$ in a pure state.

$$MeHgBr + L \rightleftharpoons HgMe_2 + HgBr_2,L \qquad (1)$$

The reaction of $NbBr_5$ with an equivalent amount of tetramethyltin is initially faster, with *ca.* 50% of the metal halide converted into the compound $MeNbBr_4$ at 0 °C in 1 h compared to *ca.* 10% only with $HgMe_2$ under the same conditions. The reaction later slows down and stops after *ca.* 2 h at 0 °C with only 70% of the expected $MeNbBr_4$ being formed. In spite of the lower overall conversion obtained by this method, we found it sometimes convenient for the preparation of complexes with bidentate ligands since it allows direct *in situ* addition of the ligand to the reaction mixture with no need of separating the alkylniobium bromide first: Me_3SnBr remains generally unreacted and uncomplexed with bidentate ligands.[17,18]

Adducts of $MeNbBr_4$. Adducts of $MeNbBr_4$ with 2,2′-bipyridine (bipy) and 1,2-bis(diphenylphosphino)ethane were prepared *in situ* by treating the ligands with solutions of the niobium derivative prepared with $SnMe_4$ as an alkylating agent. The compound $BrSnMe_3$ present in the reaction mixture did not interfere. Analytical and spectral data are reported in Tables 1 and 2 and in the Experimental section. All the protons α to the nitrogen atoms are shifted *ca.* 0·5 p.p.m. towards lower fields in the bipy adduct, which is indicative of bidentate coordination.[19] The 1,2-bis(diphenylphosphino)ethane complex was too insoluble to allow n.m.r. measurements.

Miscellaneous Experiments.—No alkylation was observed when either $HgMe_2$ or $SnMe_4$ were added to NbF_5, $Nb(OMe)_5$, $[NbCl(OMe)_4]$, $[NbCl_2(OMe)_3]$, $[Nb(O)Cl_3]$, and $NbCl_4$ under a range of experimental conditions: solvents (toluene, dichloromethane, light petroleum, trichlorofluoromethane, and acetonitrile); temperatures (−78 to +30 °C and up to +60 °C for the alkoxy-group-containing derivatives); and reaction times (up to 1 week).

DISCUSSION

The rapid, simple reactions of either dimethylmercury or tetramethyltin with niobium pentachloride and tantalum pentachloride appear to be in sharp contrast

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with the slow, complex reaction of dimethylzinc with niobium pentachloride: with $HgMe_2$ and $SnMe_4$ the reaction product is solely the *mono*methylniobium or tantalum derivative, which is formed quantitatively, with no further substitution observed even in the presence of an excess of the alkylating agent, whereas with dimethylzinc both *mono*-, *di*-, and *tri*-methylniobium derivatives were formed in proportions which depended on the relative amounts of the reactants and on the reaction time. In the latter case only the trichlorodimethyl derivative could be isolated.[3]

The compounds $MeNbCl_4$ and $MeTaCl_4$ are found to be stable, although highly reactive, and can be indefinitely stored at room temperature. This further supports the idea that there is no intrinsic thermodynamic instability for this type of metal–carbon bond, but rather a very high lability.[20,21] The compound $MeNbBr_4$ is one of the first alkylmetal bromides to be reported, the only previous example being, to our knowledge, $MeTiBr_3$.[22] Its preparation is easiest with $HgMe_2$ unless *in situ* complexing is considered, in which case $SnMe_4$ may sometimes be more expedicious. Its stability is lower than that of the compound $MeNbCl_4$ and does not allow storage at room temperature in the pure, uncomplexed form.

The acceptor power of $MeNbCl_4$ appears to be intermediate between those of $NbCl_5$ and Me_2NbCl_3 as illustrated for example by the shifts in ν(P=O) frequencies in the substitution series {Δν from free $OP(NMe_2)_3$: $NbCl_5$,L, −230; [$MeNbCl_4$],L, −195;* and [Me_2NbCl_3],L, −150 cm^{-1}} or by the intermediate chemical shifts observed in the n.m.r. spectra for the methylene group α to the sulphur atom in the thioxan adduct of $MeNbCl_4$ {Δδ from the free ligand for $-CH_2-S-$: $NbCl_5$,L, −0·7; [$MeNbCl_4$],L, −0·5; [Me_2NbCl_3],L −0·3 p.p.m.}.

EXPERIMENTAL

All the reactions and manipulations were carried out in an atmosphere of oxygen-free dry nitrogen, using Schlenk-tube techniques.[23]

Niobium(V) chloride and bromide were prepared by direct chlorination [24] or bromination [25] of the metal. Niobium(V) fluoride and tantalum(V) chloride were commercial products (Fluka). Dimethylmercury [26] and tetramethyltin [27] were prepared according to the literature by treating iodomethylmagnesium with $HgCl_2$ and $SnCl_4$. The purification and drying of the solvents and commercial ligands were carried out through the usual procedures. Tris(dimethylamino)-phosphine oxide was a gift from Pierrefitte Co.

N.m.r. spectra were recorded on a Jeol C-60 HL spectrometer; i.r. spectra were measured on a Perkin-Elmer model 257 instrument. Mass spectra were obtained at 70 eV on a CEC 21-130 spectrometer. Molecular weights were determined by cryoscopy in benzene. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS.

Tetrachloromethylniobium from Niobium Pentachloride and Dimethylmercury.—$HgMe_2$ (1·29 g, 5·5mM) was added dropwise, at −35 °C, to a suspension of $NbCl_5$ (2·7 g, 10mM) in dichloromethane (50 cm^3) under agitation. Precipitation of $HgCl_2$ took place immediately. The precipitate was collected in the cold and washed with a little dichloromethane. The solvent and excess of $HgMe_2$ were evaporated at −30 °C and the orange crystalline *residue* was recrystallized from dichloromethane–pentane (1 : 1), cooled down to liquid-nitrogen–methanol slurry temperature. Yield 2·35 g (95%), m.p. 65 °C (decomp.) (Found: C, 5·0; H, 1·2; Cl, 56·7. Calc. for CH_3NbCl_4: C, 4·8; H, 1·2; Cl, 56·7%). The complex is soluble in CH_2Cl_2, toluene, and acetonitrile, slightly soluble in CCl_4 and pentane. I.r. spectrum: 890s, 820s ρ(CH_3); 530m, 510m ν(Nb–C); and 400s, 395s, 375s cm^{-1} ν(Nb–Cl).

Tetrachloromethyltantalum from Tantalum Pentachloride and Dimethylmercury.—The same procedure, using $TaCl_5$ (0·72 g, 2mM) gave the *compound* $MeTaCl_4$ (0·55 g, 81%) as yellow crystals. It was recrystallized at −40 °C from pentane; further purification could be achieved through sublimation (−20 °C, 0·1 mmHg), decomp. 50 °C (Found: C, 3·3; H, 0·7; Cl, 41·5. Calc. for CH_3TaCl_4: C, 3·6; H, 0·9; Cl, 42·0%). I.r. spectrum: 820s ρ(CH_3); 542m, 520m ν(Ta–C); and 400s cm^{-1} ν(Ta–Cl).

Tetrachloromethylniobium by treating Niobium Pentachloride with Tetramethyltin.—A solution of $SnMe_4$ (0·9 g, 5mM) in dichloromethane (50 cm^3) was added dropwise, at −35 °C, to a suspension of $NbCl_5$ (1·37 g, 5mM). Chlorotrimethyltin was precipitated by the addition of light petroleum (b.p. 45—60 °C, 5 cm^3) and filtered off at room temperature. The compound $MeNbCl_4$ was precipitated by cooling the filtrate to −78 °C. It was recrystallized as above. Yield 90%.

Tetrachloromethylniobium–Triphenylphosphine.—A solution of the ligand (0·52 g, 2mM) in dichloromethane (20 cm^3) was added to a solution of $MeNbCl_4$ (0·48 g, 2mM) in the same solvent (50 cm^3) at −30 °C. The purple solution was concentrated to 30 cm^3. The complex was precipitated quantitatively by the addition of light petroleum at −40 °C. It was filtered off, washed with light petroleum, and dried under reduced pressure for 48 h at room temperature, yielding 1 g of a purple *powder* which decomposed at 85 °C (Found: C, 40·0; H, 3·2; Cl, 27·0; P, 5·6. Calc. for $C_{19}H_{18}Cl_4PNb$: C, 42·0; H, 3·3; Cl, 27·7; P, 6·0%). The complex is soluble in dichloromethane and acetonitrile. I.r. spectrum: 870s, 850s ρ(CH_3); 740s ν_{asym}(P–Ph); 685s ν_{sym}(P–Ph); 525m, 500m ν(Nb–C); and 450m, 430m, 355s, 330s cm^{-1} ν(Nb–Cl).

Tetrachloromethylniobium–1,2-Bis(diphenylphosphino)-ethane.—The same procedure as above gave 1·27 g of the complex [$MeNbCl_4$],($Ph_2PCH_2CH_2PPh_2$) as red *crystals*, soluble in dichloromethane and acetonitrile, m.p. 105 °C (Found: C, 49·5; H, 3·9; Cl, 21·2. Calc. for $C_{27}H_{27}Cl_4NbP_2$: C, 50·0; H, 4·15; Cl, 22·0%). I.r. spectrum: 855s, 820s

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* Measured as crude complex after evaporation of solvent and low-temperature n.m.r. check of the purity.

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$\rho(CH_3)$; 500 ν(Nb–C); 450m, 430m ν(Nb–P);[28] and 345s, 335s, 310s cm^{-1} ν(Nb–Cl).

Tetrachloromethylniobium–γ-picolin.—The same procedure, but at −50 °C, gave red *crystals* which decompose above 0 °C.

Low-temperature N.M.R. Measurements on the other Complexes.—Reactions of $MeNbCl_4$ with the other ligands given in Table 1 were performed in n.m.r. tubes by the addition of increasing amounts of the ligands to the niobium derivative at −30 °C in CH_2Cl_2.

Tetrabromomethylniobium by Treating Dimethylmercury with Niobium Pentabromide.—$HgMe_2$ (0·46 g; 2·0mM) was added to a suspension of $NbBr_5$ (1 g, 2mM) in methylene chloride (50 cm^3) at 0 °C. The reaction mixture was stirred for 10 h at that temperature. Bromomethylmercury which formed was then precipitated, at −40 °C, by the addition of pentane (5 cm^3) and filtration. The solvents were evaporated and the residue was recrystallized from dichloromethane–pentane (1 : 1) by cooling at −40 °C, yielding 0·75 g (87%) $MeNbBr_4$ as brown *crystals*, m.p. 48 °C, soluble in pentane, toluene, dichloromethane, and acetonitrile. The compound slowly loses bromine at room temperature, thus preventing satisfactory analyses. I.r. spectrum: 850s, 800s $\rho(CH_3)$; 500m ν(Nb–C); and 470w, 450w, 425w cm^{-1}.

Tetrabromomethylniobium by Treating Tetramethyltin with Niobium Pentabromide.—$SnMe_4$ (0·38 g, 2·2mM) was syringed through a serpm cap into a suspension of $NbBr_5$ (1 g, 2mM) in CH_2Cl_2 (50 cm^3). Stirring was maintained for 2 h at 0 °C. Bromotrimethyltin was precipitated by the addition of light petroleum (5 cm^3) and filtered off at room temperature together with some unreacted niobium pentabromide. The *compound* $MeNbBr_4$ was precipitated by cooling the filtrate at −78 °C and filtered off. It was recrystallized as above. Yield 70%.

*Tetrabromomethylniobium–*1,2-*Bis*(*diphenylphosphino*)-*ethane.*—The complex was prepared by adding, at 0 °C, a solution of 1,2-bis(diphenylphosphino)ethane (0·38 g, 1mM) in dichloromethane (10 cm^3) to a solution of the compound $MeNbBr_4$, prepared from $NbBr_5$ (0·65 g, 1·3mM) and $SnMe_4$ (0·24 g, 1·3mM) in dichloromethane (10 cm^3). The complex precipitated at −40 °C. It was filtered and washed with small portions of cold CH_2Cl_2, then with pentane, and dried. Yield 0·82 g. Brown *crystals* were obtained which decomposed at 95 °C and were slightly soluble in CH_2Cl_2 (Found: C, 38·6; H, 3·0; Br, 37·6. Calc. for $C_{27}H_{27}Br_4NbP_2$: C, 39·2; H, 3·3; Br, 38·7%). I.r. spectrum: 785s, 750s $\rho(CH_3)$; 735s ν_{asym}(P–Ph); 685s ν_{sym}(P–Ph); 490m ν(Nb–C); and 400m cm^{-1}.

*Tetrabromomethylniobium–*2,2′-*Bipyridine.*—The same procedure as above, but with acetonitrile as a solvent, gave, by precipitation at −20 °C with a large amount of pentane, 0·4 g (70%) of the *complex*. Decomp. 110 °C. Soluble in dichloromethane and acetonitrile (Found: C, 20·7; H, 1·6; Br, 52·9; N, 4·3. Calc. for $C_{11}H_{11}Br_4N_2Nb$: C, 22·5; H, 1·9; Br, 54·8; N, 4·8%). I.r. spectrum: 1 600s ν(C=C); 760s, 725s $\rho(CH_3)$; 470m ν(Nb–C); and 415s, 360s cm^{-1}.

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