

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

By Catherine Santini-Scampucci and Jean G. Riess,* Laboratoire de Chimie Minérale, Institut de Mathématiques et Sciences Physiques, Parc Valrose, 06034 Nice, France

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 *monoalkyl* 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.* $[\text{MeNbCl}_4]\cdot\text{L}$ ($\text{L} = \text{PPh}_3$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, or γ -picoline) and $[\text{MeNbBr}_4]\cdot\text{L}$ ($\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ or 2,2'-bipyridine).

THE only previously isolated σ -bonded alkyl compounds of niobium(v) are dichlorotrimethylniobium¹ and bridged $[\text{Nb}_2(\text{CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4]$.² Fowles *et al.*³ recently reported the preparation of Me_2NbCl_3 from NbCl_5 and dimethylzinc, but they could not isolate the *monomethyl*-niobium 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 *monomethyl* derivatives MeNbCl_4 , MeTaCl_4 , and MeNbBr_4 , 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 dimethyl-

mercury 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 $\text{HgMe}_2:\text{NbCl}_5$ 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 stoichiometric amount of insoluble HgCl_2 was recovered.

The same reaction was observed to occur in toluene (-30°C), but not in pentane (-40 to $+10^\circ\text{C}$). In acetonitrile, a two-fold excess of dimethylmercury was necessary to complete the reaction, which then gave the complex $[\text{MeNbCl}_4]$, MeCN , and chloromethylmercury. This complex was characterised by the appearance of a signal for co-ordinated

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.

³ G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1972, 2313.

⁴ J. F. Hanlan and J. D. McCowan, *Canad. J. Chem.*, 1972, **50**, 747.

⁵ M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, 1964, **3**, 761.

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	$\delta_{\text{Nb-Me}}$	Co-ordinated-ligand resonances (assignments)
$[\text{MeNbCl}_4]$	2.98 ^a	
$[\text{MeNbBr}_4]$	2.73	
$[\text{MeTaCl}_4]$	2.9	
$[\text{MeNbCl}_4], \text{MeCN}$	2.6	2.5 ($\text{CH}_3\text{-CN}$)
$[\text{MeNbCl}_4], \text{OMe}_2$	2.9	4.17 ($\text{CH}_3\text{-O}$) (4.23) ^b
	(3.0) ^b	
$[\text{MeNbCl}_4], \text{NMe}_3$	2.9 ^c	2.6 ($\text{CH}_3\text{-N}$)
$[\text{MeNbCl}_4], \gamma\text{-picoline}$	2.8	2.5 ($\text{CH}_3\text{-C}$)
$[\text{MeNbCl}_4], \text{SMe}_2$	<i>d</i>	2.8 ($\text{CH}_3\text{-S}$)
$[\text{MeNbCl}_4], \text{S} \begin{array}{c} \text{O} \\ \parallel \end{array}$	2.8	4.02 ($\text{CH}_2\text{-O}$), 3.0 ($\text{CH}_2\text{-S}$)
$[\text{MeNbCl}_4], \text{P}(\text{NMe}_2)_3$	2.93	2.86 ($\text{CH}_3\text{-N}$) doublet $J_{\text{P-H}}$ 12 Hz
$[\text{MeNbCl}_4], \text{PPh}_3$	2.8	7.63 (H_0), 7.73 (H_m, H_p)
$[\text{MeNbCl}_4], \text{AsPh}_3$	2.87	8.75 (aryl protons of ligand)
$[\text{MeNbCl}_4], \text{OP}(\text{NMe}_2)_3$	<i>d</i>	2.85 ($\text{CH}_3\text{-N}$) doublet $J_{\text{P-H}}$ 10.5 Hz
$[\text{MeNbCl}_4], \text{OP}(\text{OMe})_3$	2.92	4.1 ($\text{CH}_3\text{-O}$) (4.0) ^b
	(2.94) ^b	doublet $J_{\text{P-H}}$ 12 Hz
$[\text{MeNbCl}_4], \text{OPPh}_3$	2.85	7.95 (H_0), 7.75 (H_m, H_p)
$[\text{MeNbCl}_4], \text{OPMe}_3$	2.82 ^e	2.07 ^e ($\text{CH}_3\text{-P}$), $J_{\text{P-H}}$ 13.5 Hz
$[\text{MeNbCl}_4], (\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$	2.92	3.4 ($\text{CH}_2\text{-P}$), multiplet $J_{\text{P-H}}$ 13 Hz
		7.62 (H_0), 7.72 (H_m, H_p)
$[\text{MeNbBr}_4], (\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$	<i>f</i>	
$[\text{MeNbBr}_4], \text{bipy}$ ^g	2.7	$\Delta\delta(\text{H}_\alpha) + 0.5 \text{ p.p.m.}$

^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 chlorine atoms in the fragments $\text{CH}_3\text{NbCl}_4^+$ (mass peaks), NbCl_4^+ , 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 $+30^{\circ}\text{C}$ in either dichloromethane or toluene. Absorption bands at 530 and 510 cm^{-1} in the i.r. spectrum (Table 2) are attributed to $\nu(\text{Nb-C})$ stretching

TABLE 2
I.r. spectra/ cm^{-1}

Compound	$\nu(\text{Nb-C})$	$\rho(\text{CH}_3)$	Other bands ($< 500 \text{ cm}^{-1}$)
$[\text{MeNbCl}_4]$	530m, 510m	890s, 820s	400s, 395s, 375s $\nu(\text{Nb-Cl})$
$[\text{MeNbBr}_4]$	500m	850s, 800s	470w, 450w, 425w
$[\text{MeTaCl}_4]$	545m, 520m	820s	400s $\nu(\text{Ta-Cl})$
$[\text{MeNbCl}_4], \text{PPh}_3$	525m, 500m	870s, 850s	440m $\nu(\text{Nb-P})$ ^a
$[\text{MeNbCl}_4], (\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$	500s	855s, 820s	450m, 430m $\nu(\text{Nb-P})$ ^a
$[\text{MeNbBr}_4], (\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$	490m	785s	450m $\nu(\text{Nb-P})$ ^a
$[\text{MeNbBr}_4], \text{bipy}$	470m	<i>b</i>	360s $\nu(\text{Nb-Br})$

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

frequencies.^{6,7} The presence of the methyl group is further established by symmetric and antisymmetric $\nu(\text{C-H})$ stretching vibrations at 3040 , 2980 , and 2540 cm^{-1} ,⁸ the antisymmetric deformation vibration of the group at 1390 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.

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 ($\delta 0.63 \text{ p.p.m.}$)¹⁰ was formed as a by-product, which could be separated from MeNbCl_4 or MeTaCl_4 by solubility differences.

⁶ C. Lalau, *Rec. Trav. chim.*, 1965, **84**, 429.

⁷ H. H. Eysel, H. Seibert, H. J. Berthold, and G. Groh, *Spectrochim. Acta*, 1970, **26A**, 1595.

⁸ L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1966.

⁹ R. D. Werder, R. A. Frey, and Hs. H. Gunthard, *J. Chem. Phys.*, 1967, **47**, 4159.

¹⁰ C. R. McCoy and A. L. Allred, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1219.

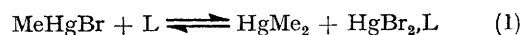
Adducts of MeNbCl₄.—The reaction of MeNbCl₄ with a range of common monodentate and with a few bidentate ligands was investigated by low-temperature n.m.r. spectroscopy (Table 1). Several adducts were isolated and further characterized by elemental analysis and i.r. spectroscopy. The compound MeNbCl₄ gave only 1:1 adducts, even in the presence of an excess of most of the ligands which were tested [MeCN, NMe₃, SMe₂, $\begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$, P(NMe₂)₃, PPh₃, and AsPh₃], as evidenced by a single peak in the n.m.r. spectra for CH₃-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 MeTiCl₃ complexes (δ 2.19–3.0 p.p.m.).^{11–13} An ebulliometric molecular-weight determination on the isolated adduct [MeNbCl₄],-PPh₃ shows it to be monomeric, which implies that the niobium atom is six-co-ordinated. Two CH₃-Nb signals were however observed for L = OMe₂ 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 = OPMe₃, OPPh₃, and OP(NMe₂)₃ and resulted in the formation of oxo-species [$\nu(\text{Nb}=\text{O})$ 935 cm⁻¹].¹⁴ Addition of amines to the compound MeNbCl₄ generally resulted in immediate decomposition at room temperature. However a 1:1 adduct with NMe₃ 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 MeNbCl₄· 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 NbCl₅¹⁵ and for Me₂NbCl₃.³ 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. $J_{\text{H-P}}$ 13 Hz) for the methylene groups down to –65 °C. This implies that the niobium atom is seven-co-ordinate in this complex.

Reaction of Niobium(v) Pentabromide with Dimethylmercury and with Tetramethyltin.—*Preparation of tetra-bromomethylniobium and some of its adducts.* The reaction of dimethylmercury with NbBr₅ differs appreciably from its reaction with NbCl₅. (i) It takes a two-fold excess of the alkylating agent to complete the reaction and the HgMe₂ is converted into MeHgBr instead of HgBr₂, which makes the isolation of the compound MeNbBr₄ 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 [MeNbBr₄],-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 MeNbBr₄ 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 MeNbBr₄ in a pure state.



The reaction of NbBr₅ with an equivalent amount of tetramethyltin is initially faster, with ca. 50% of the metal halide converted into the compound MeNbBr₄ at 0 °C in 1 h compared to ca. 10% only with HgMe₂ under the same conditions. The reaction later slows down and stops after ca. 2 h at 0 °C with only 70% of the expected MeNbBr₄ 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: Me₃SnBr remains generally unreacted and uncomplexed with bidentate ligands.^{17,18}

Adducts of MeNbBr₄. Adducts of MeNbBr₄ 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 SnMe₄ as an alkylating agent. The compound BrSnMe₃ 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 co-ordination.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 HgMe₂ or SnMe₄ were added to NbF₅, Nb(OMe)₅, [NbCl(OMe)]₃, [NbCl₂(OMe)]₃, [Nb(O)Cl₃], and NbCl₄ 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

¹¹ G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J. Chem. Soc. (A)*, 1971, 1920.

¹² R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. (A)*, 1970, 2026.

¹³ R. J. H. Clark and A. J. McAlees, *Inorg. Chem.*, 1972, **11**, 342.

¹⁴ D. B. Copley, F. Fairbrother, and A. Thompson, *J. Less-Common Metals*, 1965, **8**, 256.

¹⁵ K. Feenan and G. W. A. Fowles, *J. Chem. Soc.*, 1965, 2449.

¹⁶ G. W. Parshall and J. J. Mrowca, *Adv. Organometallic Chem.*, 1968, **7**, 157.

¹⁷ I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1963, 1519.

¹⁸ M. Gielen and N. Sprecher, *Organometallic Chem. Rev.*, 1966, **1**, 455.

¹⁹ S. Castellano, H. Gunther, and S. Ebersole, *J. Phys. Chem.*, 1965, **69**, 4166.

with the slow, complex reaction of dimethylzinc with niobium pentachloride: with HgMe_2 and SnMe_4 the reaction product is solely the monomethylniobium 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 expeditious. 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 $\nu(\text{P}=\text{O})$ frequencies in the substitution series $\{\Delta\nu \text{ from free } \text{OP}(\text{NMe}_2)_3: \text{NbCl}_5, \text{L}, -230; [\text{MeNbCl}_4], \text{L}, -195; * \text{ and } [\text{Me}_2\text{NbCl}_3], \text{L}, -150 \text{ cm}^{-1}\}$ 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 $\{\Delta\delta \text{ from the free ligand for } -\text{CH}_2-\text{S}-: \text{NbCl}_5, \text{L}, -0.7; [\text{MeNbCl}_4], \text{L}, -0.5; [\text{Me}_2\text{NbCl}_3], \text{L}, -0.3 \text{ p.p.m.}\}$.

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 chlorination²⁴ or bromination²⁵ of the metal. Niobium(v) fluoride and tantalum(v) chloride were commercial products (Fluka). Dimethylmercury²⁶ and tetramethyltin²⁷ 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

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

²⁰ P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657.

²¹ G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *Chem. Comm.*, 1970, 1369; *J.C.S. Dalton*, 1972, 533.

²² C. Beerman, R. Graf, and H. Bestian, *Ger. 1,023,766/1958*.

²³ D. F. Shriver, 'The Manipulation of Air-sensitive Compounds,' McGraw-Hill, London, 1969.

²⁴ K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, 1949, 223.

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, 5.5 mm) was added dropwise, at -35°C , to a suspension of NbCl_5 (2.7 g, 10 mm) in dichloromethane (50 cm³) 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 $\rho(\text{CH}_3)$; 530m, 510m $\nu(\text{Nb}-\text{Cl})$; and 400s, 395s, 375s cm^{-1} $\nu(\text{Nb}-\text{Cl})$.

Tetrachloromethyltantalum from Tantalum Pentachloride and Dimethylmercury.—The same procedure, using TaCl_5 (0.72 g, 2 mm) 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 $\rho(\text{CH}_3)$; 542m, 520m $\nu(\text{Ta}-\text{Cl})$; and 400s cm^{-1} $\nu(\text{Ta}-\text{Cl})$.

Tetrachloromethylniobium by treating Niobium Pentachloride with Tetramethyltin.—A solution of SnMe_4 (0.9 g, 5 mm) in dichloromethane (50 cm³) was added dropwise, at -35°C , to a suspension of NbCl_5 (1.37 g, 5 mm). Chlorotrimethyltin was precipitated by the addition of light petroleum (b.p. $45-60^\circ\text{C}$, 5 cm³) 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, 2 mm) in dichloromethane (20 cm³) was added to a solution of MeNbCl_4 (0.48 g, 2 mm) in the same solvent (50 cm³) at -30°C . The purple solution was concentrated to 30 cm³. 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 $\text{C}_{19}\text{H}_{18}\text{Cl}_4\text{PNb}$: 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 $\rho(\text{CH}_3)$; 740s $\nu_{\text{asym}}(\text{P}-\text{Ph})$; 685s $\nu_{\text{sym}}(\text{P}-\text{Ph})$; 525m, 500m $\nu(\text{Nb}-\text{Cl})$; and 450m, 430m, 355s, 330s cm^{-1} $\nu(\text{Nb}-\text{Cl})$.

Tetrachloromethylniobium-1,2-Bis(diphenylphosphino)ethane.—The same procedure as above gave 1.27 g of the complex $[\text{MeNbCl}_4]_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ as red crystals, soluble in dichloromethane and acetonitrile, m.p. 105°C (Found: C, 49.5; H, 3.9; Cl, 21.2. Calc. for $\text{C}_{27}\text{H}_{27}\text{Cl}_4\text{NbP}_2$: C, 50.0; H, 4.15; Cl, 22.0%). I.r. spectrum: 855s, 820s

²⁵ A. H. Cowley, F. Fairbrother, and N. Scott, *J. Chem. Soc.*, 1958, 3133.

²⁶ C. S. Marvel and V. L. Gould, *J. Amer. Chem. Soc.*, 1922, 44, 153.

²⁷ G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' Academic Press, London, 1963, 744.

$\rho(\text{CH}_3)$; 500 $\nu(\text{Nb}-\text{C})$; 450m, 430m $\nu(\text{Nb}-\text{P})$; ²⁸ and 345s, 335s, 310s cm^{-1} $\nu(\text{Nb}-\text{Cl})$.

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 $\rho(\text{CH}_3)$; 500m $\nu(\text{Nb}-\text{C})$; and 470w, 450w, 425w cm^{-1} .

Tetrabromomethylniobium by Treating Tetramethyltin with Niobium Pentabromide.— SnMe_4 (0.38 g, 2.2mm) was syringed through a serum 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 pre-

cipitated 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 $\text{C}_{27}\text{H}_{27}\text{Br}_4\text{NbP}_2$: C, 39.2; H, 3.3; Br, 38.7%). I.r. spectrum: 785s, 750s $\rho(\text{CH}_3)$; 735s $\nu_{\text{asym}}(\text{P}-\text{Ph})$; 685s $\nu_{\text{sym}}(\text{P}-\text{Ph})$; 490m $\nu(\text{Nb}-\text{C})$; 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 $\text{C}_{11}\text{H}_{11}\text{Br}_4\text{N}_2\text{Nb}$: C, 22.5; H, 1.9; Br, 54.8; N, 4.8%). I.r. spectrum: 1600s $\nu(\text{C}=\text{C})$; 760s, 725s $\rho(\text{CH}_3)$; 470m $\nu(\text{Nb}-\text{C})$; and 415s, 360s cm^{-1} .

This work was supported by the Centre National de la Recherche Scientifique. We wish also to thank Dr. Meyer (Marseille) for the cryoscopic molecular-weight measurements.

[3/166 Received, 24th January, 1973]

²⁸ A. D. Westland and L. Westland, *Canad. J. Chem.*, 1965, **43**, 426.