σ-Bonded Early Transition Metal–Carbon Derivatives. Part II.[1] Methylniobium(V) and Methyltantalum(V) Oxohalide Complexes

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A range of methylniobium(V) and methyltantalum(V) oxohalide complexes of formula $MeMOX_2,2L$ have been synthesised, most of them in good yields, (i) by the action of MeMgI on $NbOCl_3$ in toluene–ether [L = $OSMe_2$, $OP(NMe_2)_3$, $OP(OMe)_3$, and PPh_3], (ii) by reaction of $MeMX_4$ with an excess of the ligand in the case of oxo-type ligands (M = Nb, X = Cl, L = $OSMe_2$, $ONMe_3$, ONC_5H_5, $OPMe_3$, $OPPh_3$, $OP(NMe_2)_3$, $O[OP(NMe_2)_2]_2$, and $OAsPh_3$; M = Nb, X = Br, L = $OPPh_3$; M = Ta, X = Cl, L = $OPPh_3$). The reaction of $MeNbCl_4$ with acetone and the reaction of $MeTaCl_4$ with $OP(NMe_2)_3$ gave only the $MeMCl_4,L$ adducts. The new compounds were thermally fairly stable. The acceptor character is weaker for $MeNbOCl_2$ than for $NbOCl_3$. The fundamental role of ether in the direct alkylation of $NbOCl_3$ is shown. Evidence for the existence of an $NbOCl_3,2OEt_2$ adduct is given and the formation of an analogous $MeNbOCl_2,2OEt_2$ intermediate is suggested. The fact that the 'labile' metal–carbon bond remains unaffected throughout the oxygen abstraction–halogen exchange reaction is stressed.

As yet no σ-alkyl oxohalide derivatives of the early transition metals have been reported in the literature to our knowledge. One aryl derivative, $PhVOCl_2$,[2] has recently been obtained and the compound $OV(CH_2SiMe_3)_3$ seems to be the only σ-alkylated metal oxo-derivative at present known.[3] Attempts to alkylate $VOCl_3$ by organoaluminium[4] or organoboron[5] compounds resulted, in the first case, in the reduction of the vanadium, during which process no alkylated compounds were isolated, while in the second case alkoxides were formed. On the other hand, several organometallic π-bonded oxo-derivatives were isolated, namely $(\pi\text{-}C_5H_5)_3VO$,[6] $(\pi\text{-indenyl})_3VO$,[6] $(\pi\text{-}C_5H_5)VOCl_2$,[7] and $(\pi\text{-}C_5H_5)_2NbOCl$.[8]

We now report the preparation of a series of methylniobium(V) and methyltantalum(V) oxodihalide derivatives which were obtained both by direct reaction

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[1] C. Santini-Scampucci and J. G. Riess, *J.C.S. Dalton*, 1973, 2436.

[2] K. H. Thiele, W. Schuman, S. Wagner, and W. Brüser, *Z. anorg. Chem.*, 1972, 390.

[3] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

[4] S. Jaroslav and H. Zdenek, *Chem. průmysl.*, 1973, **23**, 25 (*Chem. Abs.*, 1973, **79**, 42890); *ibid.*, p. 302 (*Chem. Abs.*, 1973, **79**, 78914).

[5] P. E. Matkovskii, N. M. Chirkov, I. D. Leonov, G. A. Beikhol'd', and A. D. Pomogailo, *Zhur. priklad. Spectroskopii*, 1969, **11**, 903.

[6] S. Kapur, B. L. Kalsotra, and R. K. Multani, *Indian J. Chem.*, 1972, **10**, 947.

[7] E. O. Fisher and S. Vigoureux, *Berichte*, 1958, **91**, 1342.

[8] P. M. Treichel and G. P. Werber, *J. Amer. Chem. Soc.*, 1968, **90**, 1753.

of methylmagnesium iodide on niobium oxochloride and by reaction of oxo-ligands on the metal pentahalides. This paper is a further contribution to the syntheses and knowledge of the properties of 'unstabilised' σ-bonded early transition metal–carbon derivatives.[9]

RESULTS

Direct Alkylation of Niobium(V) *Oxotrichloride.*—Niobium oxotrichloride reacts readily with an equivalent amount of methylmagnesium iodide in ether but the reaction results in extensive reduction of the metal, the niobium(IV) oxodichloride $NbOCl_2$ being the main reaction product (*ca.* 80%), characterised by its elemental analysis even if the reaction is performed at −78°. Thiele similarly observed the reduction of $VOCl_3$ in an attempt to alkylate it with $SnMe_4$.[2]

We have found that it is possible to control this reaction and to avoid extensive reduction by employing mixtures of ether and toluene as solvent. Convenient reaction conditions and good results were obtained with toluene–ether (2 : 1); the reaction with a little less than one equivalent of MeMgI then lasted *ca.* 4 h at −15°, and the magnesium salts could be filtered at 0° without noticeable reduction. The clear yellow solution contained about 75% of the niobium, and some unreacted MeMgI ($\delta = -0{\cdot}5$ p.p.m.).

When treated with stronger donors, such as $OSMe_2$, $OP(NMe_2)_3$, $OP(OMe)_3$, or PPh_3, all the niobium present in the solution was converted into the corresponding alkylniobium(V) oxochloride complexes $MeNbOCl_2,2L$ which were isolated and characterised as described below.

On the other hand, evidence for the existence of a weak $NbOCl_3,2OEt_2$ adduct was provided by an experiment in which ether was added stepwise to a suspension of $NbOCl_3$ in methylene chloride. The complexed ether ($\delta_{Me} = 1{\cdot}208$ p.p.m.) can clearly be distinguished from the uncomplexed ether ($\delta_{Me} = 1{\cdot}184$ p.p.m.) in the n.m.r. spectra. The formation constant for this complex, as evaluated from the peak area ratios, was found to be $K_c = [NbOCl_3][OEt_2]^2/[NbOCl_3,2OEt] = 10{\cdot}2$. It is very likely that a comparable situation exists for $MeNbOCl_2$.

Higher toluene : ether ratios slow down the reaction rate, which results in over-long reaction times, during which side reactions occur, lowering conversion to the expected alkylated, non-reduced, product. This once more illustrates the view that, in this series of compounds, long reaction times should be avoided, and furthermore establishes the fundamental role of ether during the alkylation. It appears likely that ether partially dissolves the polymeric $NbOCl_3$ to form $NbOCl_3$–Et_2O as evidenced by the appearance of the ν(Nb=O) vibration at 965 cm^{-1} when ether is added to a suspension of $NbOCl_3$ in CH_2Cl_2. In consideration of the well established tendency of niobium to achieve six-co-ordination and of the existence of a wide range of stable $NbOCl_3,2L$ complexes,[10] we suggest that this adduct is also a monomeric octahedral $NbOCl_3,2OEt_2$ complex. This adduct in turn reacts with the Grignard reagent.

Our attempts to isolate the uncomplexed methylniobium oxochloride from its ether–toluene solution have failed so far. If one tries to evaporate the solution at −78° then the reduction to $NbOCl_2$ is observed once the molar ratio Et_2O : Nb becomes lower than 4.

When acetone, acetonitrile, or γ-picoline were used as ligands decomposition of the reaction products occurred before they could be isolated, possibly because of the presence of trace amounts of MeMgI in the solution.

Smoother, less powerful, reducing agents,[1] such as $HgMe_2$ or $SnMe_4$, were found to be inactive with respect to the direct alkylation of $NbOCl_3$ under a range of experimental conditions: solvents (toluene, methylene chloride, light petroleum, trichlorofluoromethane, and acetonitrile); temperatures (−78° to +30°); and reaction times (up to a week).

Synthesis of the Methylniobium(V) *Oxohalide Complexes from the Methylniobium Tetrahalides through an Oxygen Abstraction–Halogen Exchange Reaction.*—An alternate route to the synthesis of the methylniobium and methyltantalum oxodihalide complexes was provided by an oxygen abstraction–halogen exchange reaction between both the complexed and the uncomplexed methylniobium and methyltantalum halides and a variety of ligands of the nitrogen oxide, phosphorus oxide, arsenic oxide, or sulphur oxide type. Such reactions were already known to occur with the metal pentahalides.[11]

Thus, $MeNbCl_4$ was found to react with an excess of the following ligands (L); $ONMe_3$, ONC_5H_5, $OPMe_3$, $OPPh_3$, $OP(NMe_2)_3$, $OP(NMe_2)_2(OMe)$, $OP(NMe_2)(OMe)_2$, $OP(OMe)_3$, $O[OP(NMe_2)_2]_2$, $OAsPh_3$, and $OSMe_2$ according to the equation.

$$MeNbCl_4 \xrightarrow[-35^\circ]{\text{excess of ligand}} MeNbCl_4,L^{a} \xrightarrow[\text{Room temp.}]{} MeNbOCl_2,2L$$

[a] not identified for $L = OSMe_2$

N.m.r. monitoring of the reaction shows that, in the presence of an excess of the oxo-ligand, $MeNbCl_4$ is immediately and quantitatively converted, at −35°, to the 1 : 1 adduct $MeNbCl_4,L$ with characteristic deep red or purple colouration.[1] The oxygen *vs.* chlorine exchange reaction occurs much more slowly (30 min to 15 h at room temperature) except in the case of $L = OSMe_2$ where it occurs immediately even at −35°, preventing the n.m.r. detection of the 1 : 1 adduct although the transient deep red colour indicates its formation. It is worth noting that in the case of the formation of $NbOCl_3,2OSMe_2$, likewise, no intermediate $NbCl_5,OSMe_2$ adduct could be detected, even at −45°.[12]

In the case of the phosphoryl ligands the reaction rates exhibit a marked dependence upon the π character of the phosphoryl bond [13] except for $L = OPPh_3$ (Table 1).

The conversion of the alkylmetal halide into its oxohalide complex was quantitative. The yields in the isolated compounds generally reached 70—90% (Table 2). A lower

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[9] G. Wilkinson, *Chimia*, 1973, **27**, 165; P. S. Braterman and R. J. Cross, *J.C.S. Dalton*, 1972, 657.

[10] D. L. Keppert, 'The Early Transition Metals,' Academic Press, London, 1972.

[11] (*a*) D. B. Copley, F. Fairbrother, K. H. Grundy, and A. Thompson, *J. Less-Common Metals*, 1964, **6**, 407; (*b*) D. B. Copley, F. Fairbrother, and A. Thompson, *ibid.*, 1965, **8**, 256; (*c*) D. Brown, J. Hill, and C. E. F. Richard, *ibid.*, 1970, **20**, 57; (*d*) J. R. Dorschner, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2665.

[12] J. G. Riess, R. Muller, and M. Postel, *Inorg. Chem.*, in the press.

[13] E. L. Wagner, *J. Amer. Chem. Soc.*, 1963, **85**, 161; P. Mauret and J. P. Fayet, *Bull. Soc. chim. France*, 1969, 2363; M. C. Labarre and J. F. Labarre, *J. Chim. phys.*, 1971, **68**, 540.

yield with L = $OP(NMe_2)_3$ was caused by difficulties in eliminating trace amounts of excess of ligand. In the case of the mixed $OP(NMe_2)_x(OMe)_{3-x}$ ligands the adducts could not be entirely freed from traces of the ligand but were identified by their i.r. and n.m.r. spectra.

TABLE 1

Ligand	$P_{\pi\pi'}$ Character[13]	ν(P=O)	Reaction time in CH_2Cl_2/min
$OPMe_3$	0	1182	30
$OP(NMe_2)_3$	0·2	1210	30
$O[OP(NMe_2)_2]_2$		1230	30
$OPPh_3$	0·370	1195	180
$OP(OMe)_2(NMe_2)$	0·390	1220	60
$OP(OMe)_2(NMe_2)$	0·77 [a]	1260	180
$OP(OMe)_3$	1·079	1278	*b*

[a] Estimated by interpolation. [b] No apparent reaction after 6 months in pure CH_2Cl_2, 15 h in a 1 : 1 mixture of CH_2Cl_2 and CH_3CN.

The same oxygen abstraction–chlorine exchange reaction was obtained in an experiment with L = $OP(NMe_2)_3$, where the isolated 1 : 1 adduct[1] was used as a starting material.

TABLE 2

Physical and analytical properties of $MeMOX_2$,2L

					Found (%)			Calc. for (%)		
Formula	Colour	Decomp. point	I.r. spectrum ν(E=O)/cm^{-1}	Yields	C	Cl or Br	Nb or Ta	C	Cl or Br	Nb or Ta
$MeNbOCl_2$,$2OSMe_2$	White	140	1025, 990	90,[a] 70 [b]	16·8	19·7	26·8	17·0	20·0	26·8
$MeNbOCl_2$,$2OPMe_3$	White	115	1130, 1070	72 [a]	21·0	19·0	24·5	22·4	19·0	24·8
$MeNbCl_2$,$2OPPh_3$	Yellow	105	1165—1160	80 [a]	57·2	9·4	12·4	58·0	9·4	12·4
$MeTaOCl_2$,$2OPPh_3$	Clear yellow	80	1160	43 [a]	52·5	8·4	22·5	53·0	8·4	22·5
$MeNbOBr_2$,$2OPPh_3$	Orange	90	1115—1110	60 [a]	52·5	19·0	11·2	53·0	19·0	11·2
$MeNbOCl_2$,$2OP(NMe_2)_3$	Clear orange	152	1052, 1130	20,[a] 60 [b]	26·8	12·8	16·8	28·0	12·8	16·8
$MeNbOCl_2$,$2OP(OMe)_3$	Yellowish	135	1235, 1200	56 [b]	29·6	30·0	19·5	30·4	30·0	19·5
$MeNbOCl_2$,$2OP(OMe)_2(NMe_2)$			1170, 1150	*a, c*						
$MeNbOCl_2$,$2OP(OMe)(NMe_2)_2$			1165, 1100	*a, c*						
$MeNbOCl_2$,$2OAsPh_3$	Yellowish	145	890, 850	77 [a]	58·0	8·3	11·0	58·5	8·4	11·0
$MeNbOCl_2$,$2PPh_3$	Yellowish	105		70 [b]	61·0	10·0	13·0	61·8	10·0	13·0
$MeNbOCl_2$,$2ONMe_3$	White	110	1245, 1170	80 [a]	22·8	20·8	27·0	23·2	20·8	27·0
$MeNbOCl_2$,$2ONC_5H_5$	Yellow	125	1195, 1168	85 [a]	33·6	18·2	24·4	34·2	18·5	24·4
$MeNbOCl_2$,$O\{OP(NMe_2)_2\}_2$	Bright yellow	158	1180, 1165	68 [a]	21·7	14·0	19·0	22·0	14·5	19·2

[a] Preparation of $MeMOX_2$,2L adducts from $MeMX_4$. [b] Direct alkylation by Grignard reagent. [c] Compound not isolated.

The dichloro-compounds Cl_2PPh_3, $Cl_2P(NMe_2)_3$, $Cl_2P(OMe)_3$, $Cl_2P(NMe_2)_x(OMe)_{3-x}$, and Cl_2AsPh_3 were isolated from the mother liquors and characterised through their m.p.s, n.m.r. and i.r. spectra, and by hydrolysis and subsequent identification of their oxides.[11,14] In the case of L = $OSMe_2$ compound $ClCH_2SCH_3$ was isolated.[11a]

Where acetone was used as a ligand only the 1 : 1 adduct $MeNbCl_4$,$OCMe_2$ formed and no subsequent oxygen *vs.* chlorine exchange was observed, even with a large excess of ligand and after standing for a long time. When $OSMe_2$ or $OAsPh_3$ were added to this adduct, the oxygen *vs.* chlorine exchange reaction occurred. The initial ligand was then displaced to give the $MeNbOCl_2$,$2OSMe_2$ and $MeNbOCl_2$,$2OAsPh_3$ compounds respectively.*

$MeNbBr_4$ reacted with $OPPh_3$ to give the $MeNbOBr_2$,2L compound. $MeTaCl_4$ reacted in a similar manner with L = $OPPh_3$ to give $MeTaOCl_2$,2L. However, with $OP(NMe_2)_3$ only the $MeTaCl_4$,L adduct was formed in methylene chloride or methylene chloride–acetonitrile.

Characterisation and Stability of the Methylniobium Oxochloride Adducts.—The characterisation of the new compounds includes analysis, melting and decomposition points (Table 2), i.r. (Table 2) and n.m.r. (Table 3) spectroscopy, and, in some cases, mass spectra measurements.

The osmometric molecular weight determinations performed on two samples [L = $OSMe_2$ and $OP(NMe_2)_3$] show the compounds to be monomeric in acetonitrile solutions. These complexes were recovered unchanged by evaporating their acetonitrile solutions.

The n.m.r. spectra are often difficult to read due to frequent overlap of the *Me*Nb resonance with those of the ligands. The high temperature spectra (25—40°) generally exhibit two separate signals for the *Me*Nb and the ligand protons. Where the data were available [L = $OSMe_2$ and $OP(NMe_2)_3$] the ligand shifts were found at higher fields than for their $NbOCl_3$ adducts: this indicates that the methyl group lowers the acceptor ability of the metal. At lower temperatures (0 to −45°) the ligand signals split into several peaks or doublets, which is consistent with the presence of several monomeric octahedral isomers in dynamic equilibrium in the solution as was found for $NbOCl_3$,2L complexes.[12]

The ν(P=O), ν(As=O), and ν(S=O) stretching vibrations could generally be identified precisely (Table 2). The increase in their frequencies with respect to those found for the corresponding $NbOCl_3$,2L derivatives further supports the rationale that the methylniobium derivatives are weaker acceptors than the related halides.[1] There is always a broad complex band extending from 950 to 910 cm^{-1} in the region where the ν(Nb=O) vibrations are expected to be found; thus no precise assignment of this vibration was attempted.[12] The same is true for the ν(M–C) vibration in the region between 420 and 580 cm^{-1}.

Generally the mass spectra were of little use for the

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* Similarly, only $NbOCl_3$,$2OSMe_2$ was observed to form when $NbCl_5$,$OCMe_2$ was allowed to react with $OSMe_2$.

[14] S. R. Jain, L. K. Krannich, R. E. Highsmith, and H. H. Sisler, *Inorg. Chem.*, 1967, **6**, 1058; H. Noth and H. J. Vetter, *Chem. Ber.*, 1965, **98**, 1981.

characterisation of the $MeMOX_2$,2L adducts due to their poor volatility. At the temperature at which the mass spectra were measured (300°) only the MOX_2^+ fragment and the fragmentation patterns of the ligands were recognised. Mass spectral analysis was however conclusive for the identification of the more volatile $MeTaCl_4$,$OP(NMe_2)_3$ and $MeNbCl_4$,$OCMe_2$ adducts in which, among others, the characteristic isotopic chlorine patterns were observed (see Experimental section).

TABLE 3

N.m.r. spectral data on the adducts of $MeMOX_2$,2L at room temperature

Compound	Nb–Me	Co-ordinated ligand resonances
$MeNbOCl_2$,$2OSMe_2$ [a]	3·01	2·8 to 2·86
$MeNbOCl_2$,$2OPMe_3$ [a]	3·01	2·28 to 1·784
$MeNbOCl_2$,$2OPPh_3$ [a]	*c*	7·52, 7·35
$MeTaOCl_2$,$2OPPh_3$ [a]	*c*	7·5, 7·35
$MeNbOBr_2$,$2OPPh_3$ [a]	*c*	7·4
$MeNbOCl_2$,$2OP(NMe_2)_3$ [a]	30·1	2·8 to 2·5 doublets *J*(PH) 12 Hz
$MeNbOCl_2$,$2OP(OMe)_3$ [b]	2·98	4·2 to 3·4 doublets *J*(PH) 9 Hz
$MeNbOCl_2$,$2OP(OMe)_2(NMe_2)$ [b]	3	(P–OMe) 4·1 to 3·6 doublets *J*(PH) 9 Hz P–NMe_2 3 to 2·55 doublets *J*(PH) 12 Hz
$MeNbOCl_2$,$2OP(OMe)(NMe_2)_2$	*d*	P–OMe 3·68 to 3·42 doublets *J*(PH) 9 Hz P–NMe_2 3·1 to 2·55 doublets *J*(PH) 12 Hz
$MeNbOCl_2$,$2OAsPh_3$ [a]	2·95	7·92, 7·6, 7·45
$MeNbOCl_2$,$2PPh_3$ [a]	2·95	7·85 H_o, 7·73 H_m, 7·63 H_p, 7·43
$MeNbOCl_2$,$2ONC_5H_5$ [a]	3	8 to 8·85
$MeNbOCl_2$,$O[OP(NMe_2)_2]_2$	*d*	3 to 2·62

Values were calculated assuming solvent methylene chloride resonates at $\delta = 5·3$ p.p.m. and acetonitrile at $\delta = 2$ p.p.m.

[a] MeCN as solvent. [b] CH_2Cl_2 as solvent. [c] Accurate data precluded by low solubility. [d] Obscured by ligand resonances.

The isolated methylniobium and methyltantalum oxohalide complexes are indefinitely stable at room temperature under nitrogen. Their decomposition temperatures range from 80 to 158° which makes them even more stable than the corresponding methylmetal tetrahalide adducts. The comparatively lower stability of the $OPPh_3$ adduct, especially with respect to that of the $OAsPh_3$ adduct, could mean that the former adopts a *trans* disposition of the ligands due to steric hindrance, instead of the *cis* configuration which is generally admitted to be the most stable for this type of compound.[15] This would be supported also by the fact that the $OPPh_3$ adduct exhibits only one broad band at 1165—1160 cm^{-1} in the i.r. while the other phosphoryl vibrations are split into two well separated signals as observed when the two ligands are *cis* in an octahedral compound.[16] A similar splitting is found for the ν(As=O) vibration in $MeNbOCl_2$,$2OAsPh_3$.

DISCUSSION

Both the direct alkylation route by the Grignard reagent, and the oxygen abstraction–chlorine exchange reaction between the methylniobium tetrahalide and an excess of ligand, provide access to the methylniobium(v) oxochloride complexes. Although the second method is obviously restricted to ligands of the oxo-type, with the exception of the carbonyl compounds, we found it to be more convenient: the conversion is quantitative and the products can generally be isolated in higher purity and with better yields. No side reactions were observed. In the first route, the necessity of the presence of ether during the alkylation step was demonstrated. The reaction could be tamed by using ether–toluene mixtures; thus experimental conditions could be defined in which only monoalkylation occurred. The elimination of trace amounts of MgI_2 or unreacted MeMgI is less easy and may be responsible for the triggering of the reduction processes which prevented us from isolating the amine complexes.

The fair stability of new compounds, and the fact that the carbon–metal bond remains unaffected during the oxygen abstraction–halogen exchange reaction, further 'dispose of the myth' that transition metal alkyl derivatives are inherently unstable.[9]

EXPERIMENTAL

All the reactions and manipulations were carried out in an atmosphere of oxygen-free dry nitrogen, using Schlenk-tube techniques.[17] Niobium oxotrichloride was prepared according to the literature.[18] Monomethylniobium(v) and tantalum(v) halides were prepared and purified as previously described.[1] Acetonitrile and methylene chloride were distilled from phosphorus pentoxide under nitrogen prior to use. Triphenylphosphine, triphenylphosphine oxide, and triphenylarsine oxide were dried by heating at 80° *in vacuo* for 24 h. Dimethyl sulphoxide was repeatedly distilled over calcium hydride. Trimethyl phosphate (Fluka), hexamethylphosphoramide (gift from Pierrefitte), and octamethylpyrophosphoramide (gift from Murphy Co.) were dried with phosphorus pentoxide, distilled, and stored over molecular sieves (4 Å). Trimethylphosphine oxide,[19] dimethyl *N*-dimethylamidophosphate,[20] and methyl *NN'*-dimethylamidophosphate [20] were prepared in accordance with the literature. Acetone was dried over anhydrous potassium carbonate and distilled repeatedly. Pyridine *N*-oxide was distilled before use.

N.m.r. spectra were recorded on a Jeol C-60 HL spectrometer. I.r. spectra were measured on a Perkin-Elmer 557 instrument. Mass spectra were obtained at 70 eV on a C.E.C. 21—130 spectrometer. Elemental analyses were carried out by the Service Central de Microanalyses du C.N.R.S. Niobium and tantalum were determined gravimetrically by ignition to the oxides. Chlorine and bromine were determined by titration with a silver nitrate solution in the presence of potassium dichromate.

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[15] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082; O. A. Osipov and V. B. Kretenik, *J. Gen. Chem. U.S.S.R.*, 1957, **27**, 2955; 1502; E. Le Caz and J. E. Guerchais, *Bull. Soc. chim. France*, 1971, 80; R. G. Garvey, J. H. Nelson, and R. O. Radsgale. *Co-ordination Chem. Rev.*, 1968, **3**, 375.

[16] D. J. Phillips and S. Y. Tyree, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 1806; F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 1966, 2199.

[17] D. F. Shriver, 'The Manipulation of Air Sensitive Compounds,' McGraw-Hill, London, 1969.

[18] M. Chaigneau, *Compt. rend. Ser. C*, 1956, **243**, 957.

[19] J. G. Evans and P. L. Goggin, *J. Chem. Soc.* (*A*), 1968, 467.

[20] K. Sasse, 'Organische Phosphore Verbindungen,' Georg Thieme, Stuttgart, 1963.

Direct Alkylation by Grignard Reagent.—MeNbOCl$_2$,2OSMe$_2$. A solution of methylmagnesium iodide (2·1 mmol) in diethyl ether (10 cm^3) was added dropwise, at −25°, to a suspension of NbOCl$_3$ (2·35 mmol, 0·5 g) in toluene (30 cm^3) and diethyl ether (5 cm^3). The reaction mixture was warmed to −15° and stirred for 4 h. The excess of Grignard reagent was removed by the addition of light petroleum (2×5 cm^3). The mixture was filtered at 0° and OSMe$_2$ (3·0 mmol, 0·22 cm^3) was added to the filtrate at −10°. The formation of finely divided white crystals was observed. The product was filtered off, washed with diethyl ether (5 cm^3) and light petroleum (2×5 cm^3), dried under reduced pressure for 48 h at room temperature, and stored under nitrogen.

MeNbOCl$_2$,2OP(NMe$_2$)$_3$ and MeNbOCl$_2$,2OP(OMe)$_3$ were prepared by the same procedure.

MeNbOCl$_2$,2PPh$_3$. A solution of PPh$_3$ in toluene was added as above to give a yellowish powder.

Preparation of MeMOX$_2$,2L *Adducts from* MeMX$_4$. *General Procedure*.—One equivalent of the oxo-ligand (1 mmol) was injected through a serum cap into an orange solution of MeNbCl$_4$ (0·25 g, 1 mmol) in CH$_2$Cl$_2$ (50 cm^3), at −35°. The solution turned deep red. The reaction mixture containing MeMX$_4$,L adduct, was allowed to reach room temperature. Two more equivalents (2·3 mmol) of the ligand were then added dropwise. The solution was stirred until the colouration disappeared (Table 1).

In the case of OP(OMe)$_3$ the reaction solvent was a 1 : 1 mixture of CH$_2$Cl$_2$ and CH$_3$CN; for OAsPh$_3$ it was a 2 : 1 mixture of CH$_2$Cl$_2$ and OCMe$_2$.

The isolation of complexes MeMOX$_2$,2L was achieved in several ways: (i) by addition of light petroleum and crystallisation at −40° {for L = OSMe$_2$ and O[OP(NMe$_2$)$_2$]$_2$}; (ii) by removal of the solvent *in vacuo* and of the excess of ligand and dichloro-compounds by washing with benzene (for L = OPPh$_3$, OPMe$_3$, and OAsPh$_3$); (iii) by evaporation of the solvent to a smaller volume; the product then crystallises over a storage period of several days at −40° [for L = OP(NMe$_2$)$_3$]; (iv) by spontaneous precipitation of Cl$_2$NC$_5$H$_5$ or Cl$_2$NMe$_3$, in the case of ONC$_5$H$_5$ or ONMe$_3$ respectively; after filtration the product precipitated from the filtrate within one day at −40°.

Preparation of MeNbOCl$_2$,2L *Adduct from* MeNbCl$_4$,L.—To a solution of MeNbCl$_4$,OP(NMe$_2$)$_3$ (0·5 mmol, 0·21 g) in CH$_2$Cl$_2$ (20 cm^3) was added dropwise OP(NMe$_2$)$_3$ (1·3 mmol, 0·23 g) at room temperature. The solution was stirred for 30 min. The isolation of this complex was achieved as in (iii).

These compounds were insoluble in toluene, only sparingly soluble in methylene chloride, and soluble in complexing solvents.

MeMCl$_4$,L *Adducts*.—MeNbCl$_4$,OCMe$_2$. Acetone (0·07 cm^3, 1 mmol) was injected through a serum cap into an orange solution of MeNbCl$_4$ (0·25 g, 1 mmol) in CH$_2$Cl$_2$ (50 cm^3) at −35°. The solution became deep red. It was evaporated to a smaller volume (20 cm^3), and stored for two days at −40°. At the end of this time brass-coloured crystals had formed. The crystals were filtered off, washed with cold light petroleum (2×10 cm^3), and dried under reduced pressure for 48 h at 0°; yield 90%, m.p. 80° (decomp.) (Found: C, 15·48; Cl, 33·1; Nb, 30·0. Calc. for C$_4$H$_9$Cl$_4$ONb: C, 15·5; Cl, 33·0; Nb, 30·0%). The product is soluble in CH$_2$Cl$_2$, and in acetone, and slightly in toluene. The product is highly sensitive to moisture and oxygen. I.r. spectrum: ν(C=O) 1640 and 1550 cm^{-1}. N.m.r. spectrum; δ(Nb*Me*) = 2·85 and δ(Me$_2$CO) = 2·5 p.p.m. Mass spectrum (at 130°): NbCl$_4$OCMe$_2^+$ (4%); NbCl$_4$Me$^+$ (100%); NbCl$_4^+$ (43%); NbCl$_3^+$ (55%); NbCl$_2^+$ (2%); NbCl$^+$ (5%); Nb$^+$ (10%); MeCOCl$^+$ (5%); Me$_3$CO$^+$ (3%); Me$_2$CO (11%); MeCl$^+$ (16%); MeCOH (2%).

MeNbCl$_4$,OP(OMe)$_3$. The same procedure as above gave red-purple crystals; yield 90%, m.p. 78° (decomp.) (Found: C, 11·8; Cl, 36; Nb, 23·8. Calc. for C$_4$H$_{12}$Cl$_4$O$_4$PNb: C, 12·0; Cl, 36·2; Nb, 23·8%). The product is soluble in CH$_2$Cl$_2$ and all complexing solvents. I.r. spectrum: ν(P=O) 1250 cm^{-1}. N.m.r. spectrum: δ(Nb*Me*) = 2·92, δ_L = 4·1 doublet *J*(PH) 12 Hz.

MeTaCl$_4$,OP(NMe$_2$)$_3$. The same procedure as above gave clear yellow crystals soluble in dichloromethane, acetonitrile, toluene, and hexamethylphosphoramide; yield 63%, m.p. 90° (decomp.) (Found: C, 16·5; Cl, 28·7; P, 6·4; Ta, 35. Calc. for C$_7$H$_{21}$Cl$_4$N$_3$OPTa: C, 16·4; Cl, 28·7; P, 6; Ta, 35%). I.r. spectrum: ν(P=O) 1090 cm^{-1}. Mass spectrum (at 150°): TaCl$_4$OP(NMe$_2$)$_3^+$ (100%); TaCl$_4$OP(NMe$_2$)$_2$(NMe)$^+$ (20%); TaCl$_4$OP(NMe$_2$)$_2$N$^+$ (10%); TaCl$_4$,OP(NMe$_2$)$_2^+$ (10%); TaCl$_4^+$ (60%); TaCl$_3^+$ (20%); TaCl$_2^+$ (20%); Ta$^+$ (66%); OP(NMe$_2$)$_3^+$ (80%); OP(NMe$_2$)$_2^+$ (100%); OP(NMe$_2$)$^+$ (60%); Me$_3$N$^+$ (10%); MeCl$^+$ (10%).

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