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Complexes of Niobium(V) and Tantalum(V) with Phosphorus and Arsenic Ligands

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Complexation reactions between [M_2Cl_{10}] (M = Nb, Ta) and some phosphine, phosphite and arsine ligands have been investigated. Complexes [MCl_5L_2] {M = Nb, L_2 = (PMe_2Ph)$_2$, ($P(OPh)_3$)$_2$, (dmpe)$_2$, dppe and dpae; M = Ta, L_2 = (PMe_2Ph)$_2$, dmpe, dppe and dpae} have been isolated and characterised by analysis, IR and ^1H NMR spectroscopy and, in three cases, by ^{31}P NMR spectroscopy. Reactions of other phosphines ($PMePh_2$, PPh_3) and phosphites {$P(OEt)_3$, $P(OPh)_3$} with [M_2Cl_{10}] have also been studied. The nature of the phosphorus complexes appears to be sterically controlled and depends on the cone angles of the ligands.

Products [$M(C_6F_5)_xCl_{5-x}$] (x = 2–3, M = Nb, Ta) are formed by [M_2Cl_{10}] and pentafluorophenyllithium and these have been investigated by analysis, IR and ^{19}F NMR spectroscopy. A ditertiary arsine adduct, [$Nb(C_6F_5)_2Cl_3(dpae)$], has also been isolated and characterised.

Introduction

The ability of the chlorides of niobium(V) and tantalum(V) to form complexes with oxygen, sulphur and nitrogen donor ligands has been well documented [1–5], whereas complex formation with phosphorus and arsenic donors has been less well studied. Complexes [$NbCl_5L$] and [$Nb_2Cl_{10}L$] (L = PPh_3, $AsPh_3$) have been reported [6], although the nature of the dinuclear products is unknown. Similar 1:1 complexes, [MCl_5L] (M = Nb, Ta; L = PPh_3, PBu_3) have been described by other authors [5, 7] but complexes of PMe_3 with $TaCl_5$ were found to be unstable [4] at room temperature and an adduct of PPr^i_3 stable only at –60 °C in solution [4]. Complexes with 1,2-bis(diphenylphosphino)ethane (dppe) of basic formulae [MCl_5(dppe)] have been reported but these species were contaminated with approximately 1 mol of toluene which could not be removed [5]. No examples of complexes with phosphite ligands have been described.

The bidentate arsine ligand *o*-phenylenebis(dimethylarsine) (diars) was early reported to form species [MX_5(diars)] (X = Cl, Br) [8] although more recent X-ray analysis has shown that the alternative ionic species [$MX_4(diars)_2$]$^+$[MX_6]$^-$ exist [9] and hence the existence of a 7-coordinate, non-ionic complex is in doubt. Similar fluorinated ditertiary arsines with unsaturated chelate rings also form complexes of stoichiometry [MX_5(As–As)] but, although some of these were tentatively suggested to be non-ionic, 7 coordinate species, ionic structures were not conclusively ruled out [10].

Many simple alkyl derivatives of Nb(V) and Ta(V) have been prepared recently [11]. Compounds of the type [MR_xCl_{5-x}] (x = 1, 2, 3; R = Me [12, 13], $PhCH_2$ [14], Me_3CCH_2 [15], Me_3SiCH_2 [16]) and a number of adducts of these compounds with mono- and bi-dentate ligands (including PPh_3 and dppe) have been characterised. No examples of [MR_4Cl] compounds have been identified [14] and [MR_5] compounds decompose readily [14, 17], although [MMe_5] and [$Ta(CH_2Ph)_5$] have been prepared [18] and the complexes with 1,2-bis(dimethylphosphino)ethane (dmpe) are more stable, [MMe_5(dmpe)]. No simple, non-ionic aryl or fluoroaryl derivatives of Nb(V) or Ta(V) have been characterised. However, solutions which probably contain [$TaPh_xCl_{5-x}$] have been used to prepare cyclooctatetraene compounds of tantalum [19] and the anions [$TaPh_6$]$^-$ [20] and [$Ta(p\text{-}MeC_6H_4)_6$]$^-$ [21] have been reported.

We have investigated the complexes of several phosphine, phosphite and arsine ligands with the chlorides [M_2Cl_{10}] (M = Nb, Ta) and also the products of the reaction between pentafluorophenyllithium and these chlorides.

Results and Discussion

Complexes of MCl_5

By mixing [M_2Cl_{10}] (M = Nb, Ta) with the appropriate phosphorus or arsenic ligand in a suitable organic solvent (CCl_4, C_6H_6, cyclo-C_6H_{12} or n-C_6H_{14}) at ambient temperature adducts of MCl_5 are obtained. The complexes listed in Table I are isolable as microcrystalline solids or powders which, after purification, may be characterized by analysis, as shown, and by spectroscopic studies. Products with some other phosphorus ligands were found to be mixtures of com-

TABLE I. Analyses, Melting Points and Colours of Nb(V) and Ta(V) Complexes.

Complex	Colour	M.p./°C[a]	Analyses–found (calcd)%		
			C	H	Cl
[NbCl$_5$(dppe)][b]	salmon pink	200	46.9(46.7)	3.6(3.6)	26.4(26.6)
[NbCl$_5${P(OPh)$_3$}$_2$][c]	bright red	236	48.6(48.5)	3.7(4.1)	19.0(19.9)
[NbCl$_5$(PMe$_2$Ph)$_2$]	red	*ca.* 80	35.0(35.2)	4.1(4.1)	–
[NbCl$_5$(dmpe)$_2$]·½CH$_2$Cl$_2$	orange	d. 250	24.9(24.5)	5.7(5.4)	34.8(34.7)
[NbCl$_5$(dpae)][d]	red	d. 160–200	41.7(41.3)	3.2(3.2)	21.2(23.4)
[TaCl$_5$(PPh$_3$)][e]	lemon	195	34.8(34.8)	3.0(2.4)	29.1(28.6)
[TaCl$_5$(dppe)][f]	yellow	216	40.9(41.2)	3.4(3.2)	24.15(23.5)
[TaCl$_5$(dmpe)]	bright yellow	d. 320–335	14.2(14.2)	3.6(3.1)	35.3(34.9)
[TaCl$_5$(PMe$_2$Ph)$_2$]	pale yellow	d. 190	29.5(30.3)	3.7(3.5)	28.0(27.9)
[TaCl$_5$(dpae)][g]	yellow	d. 200	36.6(37.0)	2.7(2.9)	19.6(21.0)
[NbCl$_3$(C$_6$F$_5$)$_2$(dpae)]	red	–	44.6(44.8)	3.0(2.4)	10.4(10.4)
[NbCl$_{5-x}$(C$_6$F$_5$)$_x$], x = 2/3[h]	yellow	–	28.9–31.6	0.2	10.4–14.0
[TaCl$_{5-x}$(C$_6$F$_5$)$_x$], x = 2/3[j]	yellow	–	30.6	0.55	12.6–14.2

Abbreviations: dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$, dpae = Ph$_2$AsCH$_2$CH$_2$AsPh$_2$.

[a] *In vacuo*. [b] Reported previously but contaminated with toluene (ref. 5). [c] P% = 6.25(6.95). [d] As% = 21.0(19.8) – little excess dpae present. [e] Reported previously (ref. 5, 7). [f] Ta% = 23.6(23.9) – reported previously but contaminated with toluene (ref. 5). [g] Little excess dpae present. [h] F% = 39.1, results from several samples (see text). [j] F% = 34.5, results from several samples (see text).

plexes which were inseparable or to be intractable oily species which decomposed on attempted purification. Thus [PMePh$_2$] with [Ta$_2$Cl$_{10}$] gives an oily product in which two separate coordinated PMePh$_2$ groups, in varying concentrations, can be identified by ^{1}H NMR spectroscopy and this indicates the presence of at least two complexes (probably [TaCl$_5$(PMePh$_2$)] and [TaCl$_5$(PMePh$_2$)$_2$]). With [Nb$_2$Cl$_{10}$], partial reduction is observed with PMePh$_2$ but also an oily mixed product is formed. Although the complex [NbCl$_5${P(OPh)$_3$}$_2$] can be isolated the analogous tantalum complex is not obtained under similar conditions but a yellow solid is produced which analyses as a mixture of [TaCl$_5${P(OPh)$_3$}]: [TaCl$_5${P(OPh)$_3$}$_2$], *ca.* 1:1.5 (found C = 40.7%, H = 3.0%, Cl = 21.0%) even after repeated recrystallisation and shows complex ^{1}H NMR resonances in the region δ = 6.3–7.7 ppm. This evidence suggests the existence of 1:2 and 1:1 adducts – although it is possible that dinuclear or more complex species are present. It was found that P(OEt)$_3$ reacts with [M$_2$Cl$_{10}$] (M = Nb, Ta) to give oily, mixed products which show complex ^{1}H and ^{31}P NMR spectra, indicating that reactions other than simple adduct formation occur, probably involving P–OEt bond cleavage.

The complexes in Table I are all air unstable, especially in solution. The complexes with bidentate ligands dppe and dpae (1,2-bis(diphenylarsino)ethane) are most stable to air and appreciably more so than the monodentate species [MCl$_5$L] (L = PPh$_3$, AsPh$_3$). Complexes of dmpe are less stable than those of dppe, and complexes of PPh$_3$ and P(OPh)$_3$ are more stable than derivatives of PMe$_2$Ph and PMePh$_2$. They are all soluble in CHCl$_3$ and CH$_2$Cl$_2$ and some in benzene. The IR spectra snow typical ligand bands with small coordination shifts and exhibit low frequency ν(M–Cl) bands [22] (Table II). These low frequency bands are rather broad and hence the solid state spectra are unhelpful in assigning 6, 7 or 8 coordinate structures to the complexes.

The ^{1}H NMR spectra are consistent with the formulations and show significant coordination shifts from free ligand resonances. In 1:2 complexes both ligands appear equivalent and in [TaCl$_5$(PMe$_2$Ph)$_2$] the doublet resonance of P–*Me* shows that "virtual coupling" [23] of the two P atoms does not occur. The structural implications of these latter observations, however, may be invalidated by the occurrence of rapid exchange processes in solution.

The methylene proton resonances of dppe and dpae complexes occur as a single resonance, shifted 1.3–1.4 ppm to low field from the free ligand and the ^{31}P NMR spectra of [MCl$_5$(dppe)] also show a single resonance with large (55–58 ppm) low field coordination shifts. These results strongly support the presence of chelated ligands. It is of interest that in the ^{31}P NMR spectrum [NbCl$_5$(dppe)] shows a broad resonance whereas [TaCl$_5$(dppe)] shows a sharp singlet at ambient temperature and this is probably due to the higher nuclear electric quadrupole moment of ^{181}Ta compared to that of ^{93}Nb [24]. [TaCl$_5$(dmpe)] also shows a sharp ^{31}P NMR singlet with a large coordination shift (97 ppm), supporting chelation of dmpe and it is interesting that in [TaMe$_5$(dmpe)] the analogous resonance occurs at appreciably higher field (δ = 11.8 ppm) [18]. No ^{31}P

TABLE II. Some Spectroscopic Properties of Nb(V) and Ta(V) Complexes.

Complex	NMR Spectra[a]			UV–VIS nm[b] (> 300 nm)	IR cm^{-1}[b] (major bands 500–300 cm^{-1})
	^1H δ ppm[c] (assignment)	Solvent	^{31}P δ ppm[d]		
$[NbCl_5(dppe)]$	7.4 (C_6H_5), 3.5 br (CH_2CH_2)	$CDCl_3$	44.9 st.(br)	470 br, 340	500 w, 485 w, 414 w; {343 vs ν(NbCl)}
$[NbCl_5\{P(OPh)_3\}_2]$	7.1 complex (C_6H_5)	$CDCl_3$	–	340 br	467 s, 442 s, {359 vs, 345 sh ν(NbCl)}
$[NbCl_5(dmpe)_2]\cdot\frac{1}{2}CH_2Cl_2$	5.35 st. (free CH_2Cl_2), 1.7 v.br (dmpe)	$CDCl_3$	–	512, 452	451 w, {333 s, 305 m ν(NbCl)}
$[NbCl_5(dpae)]$	7.33 (C_6H_5), 3.40 st. (CH_2CH_2)	$CDCl_3$	–	518, 370 br	480 s, 461 m, 390 m, {339 vs ν(NbCl)}
$[TaCl_5(PPh_3)]$	7.75 (C_6H_5) – at 35 °C	CH_2Cl_2	–	–	360 m, 322 s, 310 sh ν(TaCl)
$[TaCl_5(dppe)]$	7.5 (C_6H_5), 3.5 d.br (CH_2CH_2)	$CDCl_3$	41.6 st.	410, 330 br	499 w, 482 w, 414 w, {326 vs ν(TaCl)}
$[TaCl_5(dmpe)]$	1.8 complex (dmpe) – at 35 °C	CH_2Cl_2	48.8 st.[e]	404, 365 br	323 vs (br) ν(TaCl)
$[TaCl_5(PMe_2Ph)_2]$	6.94 (C_6H_5), 1.38 d $^2J_{P-H}$ = 10 Hz (CH_3)	C_6D_6	–	–	470 m, 444 m, 404 m, {330 s ν(TaCl)}
$[TaCl_5(dpae)]$	7.37 (C_6H_5), 3.42 st (CH_2CH_2) – at 35 °C	CH_2Cl_2	–	404 br, 413	480 m, 459 m, 390 w, {327 s ν(TaCl)}
$[NbCl_3(C_6F_5)_2(dpae)]$	7.27 (C_6H_5), 3.45 st (CH_2CH_2) – at 35 °C	$CDCl_3$	–	–	479 s, 464 m, 391 w, {362 sh, 340 s ν(NbCl)}

Abbreviations: st = singlet, d = doublet, br = broad, w = weak, m = medium, s = strong, v = very.

[a] At ambient temperature unless marked. [b] Solid, nujol mull. [c] Relative to internal TMS. [d] Low field of H_3PO_4. [e] In $CDCl_3$.

NMR data were obtained for $[NbCl_5(dmpe)]$; the ^1H NMR indicates that CH_2Cl_2 is essentially free in solution so that it may be deduced that it is trapped in the lattice of the solid but not removed under vacuum even on warming. The dmpe resonance of $[NbCl_5(dmpe)_2]$ is very broad and the complex decomposes more readily than $[TaCl_5(dmpe)]$ so that it is possible that the ligands are either monodentate or less strongly bound in the niobium complex. It is to be noted that $[MH_5(dmpe)_2]$ (M = Nb, Ta) have been reported but these contain bidentate dmpe ligands (NMR, M = Nb; ^1H: δ = 1.43 ppm (broad), ^{31}P: δ = 39.5 ppm) [25].

The electronic spectra show bands in the visible or near UV. The energies of these bands follow the orders Nb < Ta and As < P for related complexes and the bands may be assigned as P (or As) to metal charge transfer. Similar bands have been observed for other Nb(V) and Ta(V) complexes [4].

The formulae of phosphorus ligand adducts indicate a tendency to increase in coordination from 1:1 to 1:2 (or more) in the series $PPh_3 < PPh_2Me < P(OPh)_3 < PMe_2Ph \sim dppe \leqslant dmpe$. Thus PPh_3 only forms 1:1 complexes, PMe_2Ph gives mixtures (probably 1:1 and 1:2), $P(OPh)_3$ gives 1:1 and 1:2 products with $TaCl_5$ but a 1:2 species with $NbCl_5$, PMe_2Ph gives 1:2 products, dppe chelates (1:2) and dmpe forms a chelated product with $TaCl_5$ whereas the coordination in $[NbCl_5(dmpe)_2]\cdot\frac{1}{2}CH_2Cl_2$ involves at least 2 and may even involve 3 or 4 phosphorus atoms. It is of interest that this series follows precisely the decrease in cone of angle of the ligands (145°–107°), as given by Tolman [26], so that the changes may be entirely due to steric effects. Also it appears that $NbCl_5$ seems more readily to accept an extra phosphorus ligand. The arsenic chelate with a saturated linkage, dpae, also forms a 1:2 species.

The actual structures have not been definitively established. Ionic structures could arise but the complexes are soluble in relatively non polar solvents. $[MCl_5L]$ complexes are probably octahedral. $[MCl_5L_2]$ could be ionic with 8 coordinate cations $[MCl_4L_4]^+[MCl_6]^-$ and it has been argued that a 7 coordinate structure with 5 chlorine ligands would be unstable due to Cl...Cl repulsions [9(a)]. The 8 coordinate structure, however, should be sterically crowded with the relatively bulky ligands L_2 = $(P(OPh)_3)_2$, $(PMe_2Ph)_2$, dppe or dpae. It is possible that such 8 coordinate dodecahedral cations are favoured only by planar, unsaturated chelating ligands such as diars [27] in $[TaX_4(diars)_2][TaX_6]$ and the 1:2 complexes described here are simple 7 coordinate species.

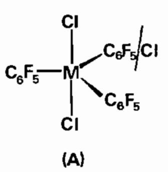
Pentafluorophenyl Derivatives

Reactions of $[Nb_2Cl_{10}]$ with pentafluorophenyllithium in hexane solution, using various ratios of $NbCl_5$: $Li(C_6F_5)$ (1:3–1:6) led to the isolation of yellow solids which analytical data (on several samples) show to have the stoichiometry $[Nb(C_6F_5)_xCl_{5-x}]$ (x = 2–3), *i.e.* intermediate between di- and tri-perfluoroaryl compounds. The molecular weight determined cryoscopically in benzene (647) is also intermediate between monomeric $[Nb(C_6F_5)_2Cl_3]$ (533) and $[Nb(C_6F_5)_3Cl_2]$ (665) and indicates a mononuclear species in solution. The IR spectrum (nujol) contains typical C_6F_5 bands [28] (*e.g.* 1630 m, 1058 s, 1457 s, 1072 s, 961 s) and frequencies in the ν(Nb–Cl) region (412 s, 372 w, 365 w). The ^{19}F NMR spectrum in C_6D_6 shows only *one* set of C_6F_5 resonances of correct relative intensities (δ ppm; −124.0 {(*ortho*-F)-broad complex doublet ~ 21 Hz}, −141.5 {(*para*-F)-triplet of triplets, $^3J_{F_3-F_4} = 21$ Hz, $^4J_{F_2-F_4}$ = 7 Hz}, −159.3 {(*meta*-F)-complex apparent triplet}). If, as suggested by analytical data, the product is a mixture then inequivalent C_6F_5 group resonances should have been expected (*cf.* methyl derivatives [11]) but these are not observed at ambient temperatures.

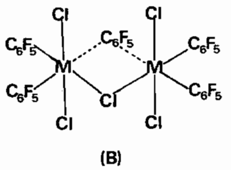
Attempts to separate the two aryl complexes by sublimation, chromatography or crystallisation were unsuccessful and addition of PPh_3 to the mixture only produced a similar mixture of 1:1 complexes $[Nb(C_6F_5)_xCl_{5-x}(PPh_3)]$ (x = 2–3). With dpae, however, a pure salmon-pink adduct, $[Nb(C_6F_5)_2Cl_3(dpae)]$, could be isolated after crystallisation. The formation of this complex supports the formulation of the yellow product as a mixture of $[Nb(C_6F_5)_2Cl_3$ and $[Nb(C_6F_5)_3Cl_2]$.

The reaction of $[Ta_2Cl_{10}]$ with pentafluorophenyllithium also gives a yellow solid which analytical data indicate to be a mixture $[Ta(C_6F_5)_xCl_{5-x}]$, (x = 2–3), but contaminated by a little organic impurity. The presence of traces of hydrocarbons is shown by analysis and ^1H NMR. ^{19}F NMR also indicates the presence of traces of C_6F_5Cl but only *one* set of resonances for metal bound C_6F_5 groups is observed (δ ppm (C_6D_6): −123.9 {(*ortho*-F)-broad doublet ~ 21 Hz}, −141.8 {(*para*-F)-triplet of triplets, $^3J_{F_3-F_4} = 21$ Hz, $^4J_{F_2-F_4} = 6$ Hz}, −159.0 {(*meta*-F) broad complex triplet}). The IR spectrum shows typical C_6F_5 bands and ν(Ta–Cl) bands (383 ms, 365 ms (KBr disc)).

The structures of these monomeric pentafluorophenyl compounds must be based on the trigonal bipyramid with electronegative Cl groups, presumably, in the axial positions (A). The ^{19}F NMR data, however, suggests either accidental equivalence of C_6F_5 groups in $[M(C_6F_5)_xCl_{5-x}]$ (x = 2 or 3) or, more likely, an exchange of C_6F_5 between species that is fast on the NMR time scale. This may occur via bridging C_6F_5 groups and an intermediate or transition state such as (B) may be formed. Such exchange would hamper any attempted separation of the two species. Although monomeric in solution it is also possible that Cl bridging may occur in the solid state to give 6 coordination, as found in $[M_2Cl_{10}]$, since the colour darkens on dissolution in benzene. The complex $[Nb(C_6F_5)_2Cl_3(dpae)]$ is probably 7 coordinate (*cf.* $[TaMe_3Cl_2(dipy)]$ [11]).



(A)



(B)

The ^{19}F NMR resonances for metal bound C_6F_5 groups throw some light on the bonding. *Para*-F resonances, δ = −141.5–−141.8 ppm, and *ortho-para*-F coupling constants, $^4J_{F_2-F_4}$ = 6–7 Hz, when correlated with other data for C_6F_5 compounds suggest that the pentafluorophenyl groups act as π-donors to the high oxidation state, M(V) metals [29]. This contrasts to C_6F_5 groups in low oxidation state complexes such as $[Mn(C_6F_5)(CO)_5]$ where they appear to act as π-acceptors (δ(*para*-F) = −158–−163 ppm, $^4J_{F_2-F_4} \leqslant 0.7$ Hz) [30].

Experimental

Operations were carried out under dry nitrogen or *in vacuo* using Schlenk type apparatus. All solvents were dried using $LiAlH_4$ (ethers and hydrocarbons), or P_4O_{10} (chlorinated solvents) and distilled before use. $[M_2Cl_{10}]$ (M = Nb, Ta) were purified by sublimation before use. Dmpe ($Me_2PCH_2CH_2PMe_2$) was prepared as described in the literature [31] and other ligands were purchased from Strem, B.D.H. or Maybridge Chemicals. IR spectra were recorded on a P.E. 457 spectrometer, ^1H NMR spectra on JEOL-MH-100 MHz (R.T.) or P.E. R12 (35 °C) 60 MHz spectrometers, ^{31}P NMR spectra on a Varian XL 100 FT spectrometer at 40.50 MHz with proton decoupling (at Edinburgh University) and ^{19}F NMR on a Brucker FT spectrometer at 84.68 MHz (at P.C.M.U., Harwell) using C_6F_6 as internal standard and corrected to $CFCl_3$ (δ C_6F_6 = −162.9 ppm). Downfield shifts are quoted as positive.

Analyses (C, H, Cl, F, As, P) were by B.M.A.C. Teddington, Herts., or A. Bernhardt, Germany. Ta was determined as Ta_2O_5.

Preparation of Complexes of MCl_5

$[NbCl_5(dppe)]$ A solution of dppe (0.85 g, 2.2 mmol) in benzene (60 ml) was added dropwise to a solution of $[Nb_2Cl_{10}]$ (0.58 g, 1.07 mmol) in benzene (100 ml) with stirring at R.T. A pink precipitate formed, was collected, washed well with benzene and hexane and dried *in vacuo* (10^{-4} torr). Yield

ca. 90%. A sample of this solid was recrystallised from dichloromethane.

[$TaCl_5$(dppe)] Prepared similarly from dppe (0.5 g, 1.26 mmol) and [Ta_2Cl_{10}] (0.5 g, 0.7 mmol) in benzene (*ca.* 80%).

[$NbCl_5$(dmpe)$_2$]·½CH_2Cl Dmpe (0.45 g, 3 mmol) in cyclohexane was added dropwise to solution of [Nb_2Cl_{10}] (0.8 g, 1.5 mmol) in cyclohexane (100 ml). Red precipitate was collected, washed with hexane and dried (this solid contained $NbCl_5$: dmpe = 1 :< 2, C = 20.5%, H = 4.3%). Recrystallisation from CH_2Cl_2–petroleum ether, washing with hexane and drying gave the product (30%).

[$TaCl_5$(dmpe)] Prepared similarly. Yield *ca.* 50%.

[$NbCl_5$(PMe_2Ph)$_2$] PMe_2Ph (0.41 g, 3 mmol) in hexane (50 ml) was added to [Nb_2Cl_{10}] (0.8 g, 1.5 mmol) in hexane (150 ml) with stirring. Some dark red solid precipitated and was filtered off (impure product). The filtrate was concentrated to low volume giving pure crystalline product (*ca.* 15%) which was washed with cold hexane and dried (10^{-4} torr).

[*$TaCl_5$(PMe_2Ph)$_2$*] Prepared analogously. Yield *ca.* 20%.

[$NbCl_5${P(OPh)$_3$}$_2$] P(OPh)$_3$ (5.2 g, 17 mmol) in CCl_4 (50 ml) was added dropwise to a slurry of [Nb_2Cl_{10}] (2.25 g, 4.1 mmol) in CCl_4 (100 ml) with stirring. Filtration and concentration of the filtrate gave orange, microcrystalline solid. Recrystallisation from CH_2Cl_2 as above gave pure product (85%).

Reaction of [Ta_2Cl_{10}] with P(OPh)$_3$ As above, using excess P(OPh)$_3$ and [Ta_2Cl_{10}] gave yellow solid which was a mixture (see text).

[$TaCl_5$(PPh_3)] PPh_3 (0.5 g, 1.9 mmol) in CCl_4 (50 ml) was added to [Ta_2Cl_{10}] (0.6 g, 0.85 mmol) in CCl_4 (100 ml). Pale lemon product precipitated, was washed and dried (10^{-4} torr). (80%).

Reactions with Other Phosphine Ligands

[M_2Cl_{10}] (M = Nb, Ta) with PPh_2Me 1:2, or with P(OEt)$_3$, 1:2–4, in hexane, after filtration, gave oily products (see text).

[$NbCl_5$(dpae)] [Nb_2Cl_{10}] (0.52 g, 0.96 mmol) and dpae (1.0 g, 2 mmol) stirred in benzene (40 ml) for 2d. Red solid collected, washed with benzene and recrystallised for CH_2Cl_2–hexane to give product (90%).

[$TaCl_5$(dpae)] Similarly, to give yellow product (90%).

Pentafluorophenyl Derivatives

[Nb(C_6F_5)$_x$$Cl_{5-x}$], x = 2–3 [$Nb_2Cl_{10}$] (8.7 g, 16 mmol) was added in small portions to [LiC_6F_5] {97 mmol, prepared from [$LiBu^n$] and C_6F_5Br} with stirring in hexane (150 ml at −78 °C. After 12 h the mixture was warmed to R.T. for 4 h, filtered and the green solid residue washed with hexane (*ca.* 50 ml). The combined filtrate and washings were evaporated to low volume and a yellow solid precipitated at −78 °C. This product was collected, washed with cold hexane and dried (10^{-4} torr). Yield *ca.* 15% (various other reactant ratios and reaction conditions were attempted with similar results).

[Ta(C_6F_5)$_x$$Cl_{5-x}$] (x = 2–3) was prepared similarly in low yields.

[Nb(C_6F_5)$_2$$Cl_3$(dpae)] [Nb($C_6F_5$)$_x$$Cl_{5-x}$] (x = 2–3) (0.2 g) and dpae (0.45 g) stirred in benzene, 18 h, at R.T. A red–pink precipitate formed which was collected and subsequently recrystallised from CH_2Cl_2–hexane.

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