Some Coordination Compounds of Titanium and Zirconium Halides with Tertiary Phosphines and Related Ligands

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Abstract

Various new adducts of $TiCl_4$, $(PhO)_2TiCl_2$, $TiCl_3$ and $ZrCl_4$ with phosphine and amine ligands are reported including, $(PhO)_2TiCl_2\cdot 2L$ (or L′) (L = PMe_3, PPh_3; L′ = dmpe, dbpe, tmed); $MCl_4\cdot L$ (M = Ti, Zr; L = dbpe): $TiCl_3\cdot L$ (L = dmpe, dbpe, tmed): $TiCl_3\cdot$tmed$\cdot$THF and $ZrCl_4\cdot 1.5$tmed. The solution properties of some of the $TiCl_4$ adducts are discussed, as deduced from ^{31}P NMR spectra.

Introduction

In comparison with the amount of information available on the coordination chemistry of the Group IVA elements (Ti, Zr, Hf) with ligands having nitrogen or oxygen as the donor atoms, much less is known of systems with tertiary phosphine ligands. This is especially true when the metal centre does not carry a C_5H_5 or C_5Me_5 ligand, which often moderates reactions. It is of interest to see to what extent the 'soft' phosphine ligand is compatible with the 'hard' metal centre in $M^{4+/3+}$ derivatives, and to devise convenient preparative routes to such adducts.

Earlier reports have established that adducts of the type $TiCl_4\cdot 2PR_3$ (R = H [1], Me [2], Et [3], Ph [3, 4], cyclo-C_6H_{11} [2]), $TiCl_4\cdot PR_3$ (R = H [1], Me [2], Ph [4], cyclo-C_6H_{11} [2]), and compounds with the bidentate ligands $R_2P(CH_2)_2PR_3$ [(dppe (R = Ph), dmpe (R = Me), depe (R = Et)], and o-$C_6H_4(PEt_2)_2$, are known, namely $TiCl_4\cdot L$ (L = dppe [4], dmpe, depe, o-$C_6H_4(PEt_2)_2$ [1]], as well as $(TiCl_4)_2\cdot 3$dppe and $(TiCl_4)_3\cdot 2$dppe [4]. With $ZrCl_4$ adducts of the type $ZrCl_4\cdot 2L$ (L = PR_3; R = Et, Pr, Bu) have been mentioned but are not well characterised [5], and with the chelating phosphines only the 1:1 ($ZrCl_4\cdot$dppe) [6] and 1:2 ($ZrCl_4\cdot 2$dmpe) [7] adducts are known. In the case of the trihalide derivatives, with titanium the compounds $TiCl_3\cdot 2PR_2$ (R = Me, Et; R_3 = Me_2H, MeH_2) have been obtained directly from $TiCl_3$ [8], as has the $TiCl_3\cdot$depe adduct [3]. In the case of zirconium the corresponding $[ZrCl_3\cdot 2PR_3]_2$ (R = Et, Pr, Bu) compounds, have been prepared from the $ZrCl_4\cdot 2PR_3$ compounds by reduction with sodium amalgam [5].

In this paper we report some new phosphine adducts of MCl_4 (M = Ti, Zr), and $(PhO)_2TiCl_2$, including some with the new ligand dbpe [n-$Bu_2P(CH_2)_2P$n-Bu_2], together with convenient preparations of some $TiCl_3$ derivatives. Related new adducts with $Me_2N(CH_2)_2NMe_2$ (tmed) are also discussed.

Results and Discussion

Previous detailed investigations using ^1H and ^{31}P NMR spectroscopy have shown that, while discrete solid adducts of $TiCl_4$ and tertiary phosphines can be isolated, the behaviour of the adducts in solution is complex [2]. Various equilibria exist, depending on the molar ratios of the reactants used:

$$TiCl_4\cdot PR_3 + TiCl_4 \rightleftharpoons (TiCl_4)_2\cdot PR_3$$

$$TiCl_4\cdot PR_3 + PR_3 \rightleftharpoons TiCl_4\cdot 2PR_3$$

$$TiCl_4\cdot 2PR_3 + TiCl_4 \rightleftharpoons 2TiCl_4\cdot PR_3$$

(PR_3 = PMe_2Ph)

Our results using PEt_3 and Pn-Bu_3 as the ligands are consistent with these conclusions. However, we find that in contrast to the above results where only one signal was observed in the ^{31}P NMR spectra of the mixtures due to rapid exchange between the different species, in our mixtures two or three resonances are obtained, in addition to that of the free phosphine (^{31}P δ values for PEt_3 and PBu_3 in C_6D_6 are −20.0 and −32.2 ppm respectively, relative to 85% H_3PO_4, negative values being to high-field of standard). Thus for molar ratios $TiCl_4:PR_3 > 2:1$ three resonances at +21.1, +22.3 and +25.3 ppm (PEt_3), and +11.7, +15.9, and +25.7 ppm (PBu_3), but no free phosphine, are observed in C_6D_6 solution. As the ratio of phosphine is increased from 2:1 to 1:10 the resonances at +25.3 (PEt_3) and +25.7 (PBu_3) decrease and are eventually replaced

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by slightly broadened resonances from the free phosphine. It appears therefore as if two species, presumably $TiCl_4 \cdot PR_3$ and $TiCl_4 \cdot 2PR_3$, are always present, but species of the type $(TiCl_4)_2 \cdot PR_3$ only exist at high $TiCl_4$:PR_3 ratios.

Based on the ^{31}P NMR spectrum of $TiCl_4 \cdot 2PEt_3$, which we have isolated, we assign the resonance at +21.1 ppm to this compound, the resonances at 22.3 (PEt_3) and 15.9 ppm (PBu_3) to the species $TiCl_4 \cdot PR_3$ and the two lowest field resonances [25.3 (PEt_3) and 25.7 ppm (PBu_3)] to the $(TiCl_4)_2 \cdot PR_3$ compounds. In addition to the above equilibria two further reactions may be required to give a more complete description of the system, namely:

$$TiCl_4 + PR_3 \rightleftharpoons TiCl_4 \cdot PR_3$$

$$(TiCl_4)_2 \cdot PR_3 + PR_3 \rightleftharpoons 2TiCl_4 \cdot PR_3$$

Thus when the concentration of $TiCl_4$ is high no free phosphine is observed, and similarly when excess phosphine is present the species $(TiCl_4)_2 \cdot PR_3$ is not observed.

It is interesting that when the spectra were recorded at higher frequency (162.0 MHz instead of 36.4 MHz), the signals assigned to the $TiCl_4 \cdot 2PR_3$ species in a 1:1 molar ratio mixture were resolved into two signals at +19.1, +21.2 ppm (PEt_3), and +11.7 and + 11.9 ppm (PBu_3), and we tentatively assign these to the *cis*- and *trans*-isomers of the adducts.

We were unable to assign accurately the relative amounts of the individual species present in solution since all the resonances are broadened, and for the free phosphine in particular the width of the resonance at half height was typically ~200 Hz. Since the spectra showed little change at –70 °C we believe this effect arises in part from the presence of paramagnetic impurities. We have found that the ESR spectrum of a solution of $TiCl_4$ and PBu_3 (1:1 molar ratio) at –196 °C shows a triplet at 2.95 G, which is very similar to that reported for $TiCl_3 \cdot 2PMe_3$ [8]. Reduction of Ti(IV) to Ti(III) species by phosphines has been proposed previously, though no direct evidence was presented [4], but we find that even when dilute (0.1 M) solutions of $TiCl_4$ and PBu_3 are mixed slowly at –50 °C, some reduction occurs, and we deduce that in such mixtures Ti(III) species are invariably present.

With $ZrCl_4$ on the other hand no reduction occurs, and the addition of 2 mol of PEt_3 to a benzene suspension of 1 mol of $ZrCl_4$ causes the halide to dissolve, and after removal of some of the solvent the adduct $ZrCl_4 \cdot 2PEt_3$ deposits on standing. The ^{31}P NMR (decoupled) spectrum in benzene shows only one sharp singlet at +21.8 ppm. A similar procedure using PBu_3 afforded only a viscous yellow oil whose ^{31}P NMR spectrum showed a single resonance at +10.8 ppm, but no solid adduct could be isolated.

With the chelating phosphine dbpe [n-$Bu_2P(CH_2)_2Pn$-Bu_2], the adducts with MCl_4 (M = Ti, Zr) are easily prepared by adding the ligand to a stirred solution of the halide in toluene.

The adduct with $ZrCl_4$ shows a composition $ZrCl_4 \cdot$dbpe, in contrast to the 1:2 adduct found in $ZrCl_4 \cdot$2dmpe. It is noteworthy that in spite of the longer alkyl chains $ZrCl_4 \cdot$dbpe is much less soluble in common organic solvents than is $ZrCl_4 \cdot$2dmpe. The ^{31}P NMR spectra of $MCl_4 \cdot$dbpe in benzene solution show singlets at 39.0 (M = Ti), and 37.8 ppm (M = Zr), and they appear therefore to be simple 1:1 adducts with the ligand atoms in *cis*-positions around a 6-co-ordinate metal atom.

The 1:1 complexes, $MCl_4 \cdot$tmed (M = Ti [9], Zr [6]), were prepared as previously described, but in the case of the zirconium compound when ethyl acetate is used as the solvent instead of benzene the adduct obtained is $ZrCl_4 \cdot$1.5tmed. This complex gives a different infrared spectrum from the 1:1 adduct, with the Zr–Cl stretching frequency moving from 340 cm^{-1} (in the 1:1 adduct) to 300 cm^{-1}. The adduct is insoluble in the common organic solvents, and therefore appears to be polymeric in nature.

The only reported adduct of $TiCl_3$ with a chelating phosphine, $TiCl_3 \cdot$depe, was formed by a prolonged interaction of the two reagents in benzene [3]. We have prepared the 1:1 adducts with dmpe and dbpe conveniently by adding the ligand to an ethyl acetate solution of $TiCl_3$ (see Experimental) and the infrared spectra show characteristic absorptions from Ti–Cl bonds as 380 and 350 cm^{-1} respectively. The same compounds can also be obtained in high yield by reduction of the corresponding $TiCl_4$ adducts using equimolar amounts of $LiBH_4$ or sodium amalgam in THF solution, and surprinsingly with the former reagent no hydride or tetrahydroborate species were detected among the products.

When $TiCl_4 \cdot$tmed is treated with one mole equivalent of $LiBH_4$ in THF, the blue solid obtained, after removal of the solvent and extraction with hot toluene, is $TiCl_3 \cdot$tmed$\cdot$THF. This solid is different from that previously obtained by adding tmed to $TiCl_3 \cdot$3THF in benzene, which was formulated as $TiCl_3 \cdot$2tmed$\cdot$THF [10]. The infrared spectra of the two compounds are different, the $TiCl_3 \cdot$tmed$\cdot$THF compound showing bands at 1165 and 1065 cm^{-1} from the co-ordinated tmed, and 1020 and 870 cm^{-1} from the THF. When $TiCl_3 \cdot$tmed$\cdot$THF is pumped for four hours under vacuum the resulting grey solid did not show the bands at 1020 and 870 cm^{-1}. The solid analysed as $TiCl_3 \cdot$tmed, and is therefore also different to the $TiCl_3 \cdot$1.5tmed reported previously [11], but due to its insolubility was not further characterised.

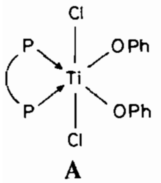
We have also prepared various phosphine derivatives of $(PhO)_2TiCl_2$ as $(PhO)_2TiCl_2 \cdot 2PR_3$ (R = Me,

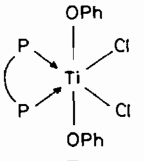
TABLE I. Analytical Data (Found (Calcd)%)

Compound (colour)	C	H	N	Cl	Ti
$ZrCl_4 \cdot 2PEt_3$	30.43	6.35		30.40	
(colourless)	(30.69)	(6.43)		(30.24)	
$TiCl_4 \cdot$dbpe	42.67	7.98			9.25
(orange)	(42.54)	(7.93)			(9.43)
$ZrCl_4 \cdot$dbpe	39.95	7.50		25.43	
(colourless)	(39.20)	(7.31)		(25.71)	
$ZrCl_4 \cdot 1.5$tmed	27.13	6.14	10.35	35.3	
(colourless)	(26.54)	(5.95)	(10.31)	(34.8)	
$TiCl_3 \cdot$dbpe	45.97	8.62			9.96
(green)	(45.73)	(8.53)			(10.13)
$TiCl_3 \cdot$dmpe	23.52	5.23		34.7	15.65
(brown)	(23.67)	(5.30)		(35.0)	(15.74)
$TiCl_3 \cdot$tmed$\cdot$THF	35.91	7.21	8.04		14.12
(blue)	(35.05)	(7.07)	(8.18)		(13.99)
$TiCl_3 \cdot$tmed	26.47	5.88	10.24		17.95
(grey)	(26.65)	(5.95)	(10.35)		(17.71)
$(PhO)_2TiCl_2 \cdot 2PMe_3$	47.05	6.09			10.51
(orange)	(47.25)	(6.17)			(10.47)
$(PhO)_2TiCl_2 \cdot$dmpe	48.36	5.75			10.61
(orange)	(47.52)	(5.72)			(10.53)
$(PhO)_2TiCl_2 \cdot 2PPh_3$	70.32	4.91			5.66
(yellow)	(69.53)	(4.86)			(5.78)
$(PhO)_2TiCl_2 \cdot$dppe	66.01	4.95		9.87	6.71
(yellow)	(64.87)	(4.88)		(10.09)	(6.81)
$(PhO)_2TiCl_2 \cdot$tmed	51.25	6.26	6.75		11.47
(orange)	(51.33)	(6.23)	(6.65)		(11.38)

Ph), and $(PhO)_2TiCl_2 \cdot L$ [L = $Ph_2P(CH_2)_2PPh_2$, dppe; dmpe]. When two reagents are mixed in Et_2O or C_6H_6 the adducts can be recovered from the solution by the addition of petroleum ether as orange (PMe_3, dmpe adducts) or yellow (PPh_3, dppe adducts) crystals, although the compound with PMe_3 forms only very slowly over several days.

The ^{31}P NMR spectra of the PMe_3 and PPh_3 adducts in $CDCl_3$ show singlets at 65.6 and 1.8 ppm respectively (rel. to 85% H_3PO_4), indicating that the phosphine ligands are equivalent, and a trans geometry seems more likely, at least for the relatively bulky PPh_3. The dmpe adduct also shows only a singlet at –5.5 ppm under similar conditions, which is consistent with the adduct existing as one of the two possible isomers (**A**) or (**B**).


A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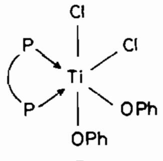
C

(P–P = chelating phosphine)

However, the dppe compound shows two rather broad (~25 Hz wide at half height) singlets at 3.7 and 14.5 ppm with relative intensities 60:40 respectively. Although the resonances narrow slightly on cooling to –30 °C, no P–P coupling was observed. It appears therefore as though the two isomers (**A**) and (**B**) are present but in slightly different amounts, and the presence of the isomer (**C**) seems less likely. Not unexpectedly dppe is a more labile ligand than dmpe under these circumstances, and rearrangement processes between the different isomers therefore becomes more facile.

The presence of several isomers in the orange adduct $(PhO)_2TiCl_2 \cdot$tmed is also indicated from the complex ^1H NMR spectrum, which shows at least fifteen different resonances in the region 1.9–3.1 ppm (relative to $SiMe_4$), where resonances due to the protons of tmed would be expected.

The ligands are not so strongly bound to $(PhO)_2TiCl_4$ as they are to $TiCl_4$ as might be expected, since on attempted reduction of the adducts with either $LiBH_4$ or sodium amalgam in THF or Et_2O, much of the free ligand could be recovered from the solutions. Although some reduction of the Ti(IV) species did occur as shown by a colour change from orange to blue–green, no lower valent metal species could be identified from the reactions.

These results therefore extend the type of complexes known for Ti(IV) and Zr(IV) compounds with phosphine ligands in particular. The complexes show a strong preference for 6-coordination around the metal centre in the 4+ oxidation state, even in the case of zirconium, and it may well be that the previously reported 8-coordinate centre in $ZrCl_4 \cdot 2dmpe$ is an exception to the general rule. It would also be of interest to establish further, even by simple displacement reactions, the relative binding ability of similar ligands containing N, P, O and S atoms as the donor centre, towards the so-called 'hard' centres found in M(IV) (M = Ti, Zr, Hf) compounds.

Experimental

All operations were carried out under dry nitrogen, either in conventional Schlenk apparatus, or in a glove box. All solvents were dried and distilled prior to use, titanium tetrachloride was used as supplied by B.D.H. Ltd., zirconium tetrachloride was freshly prepared by passing chlorine over metal turnings at 450 °C, and $(PhO)_2TiCl_2$ was obtained by refluxing phenol (2 mol) with $TiCl_4$ (1 mol) in CCl_4 for 4 h. The ligands PPh_3 and dppe were supplied by B.D.H. Ltd., and PEt_3 and $Pn\text{-}Bu_3$ by Strem Chemicals Inc. PMe_3 was prepared by the literature method [12]. The ligands dmpe and dbpe were prepared from $Cl_2P(CH_2)_2PCl_2$, which was in turn prepared by the published method [13], with modifications suggested by Dr. M. L. H. Green (University of Oxford). Treatment of $Cl_2P(CH_2)_2PCl_2$ with the appropriate Grignard reagent in Et_2O, hydrolysis of the excess Grignard, and removal of the ether layer yielded after distillation dmpe (b.p. 66 °C/10 mm Hg, ^{31}P NMR resonance at −47.9 ppm), and dbpe (b.p. 130 °C/0.25 mm Hg, ^{31}P NMR resonance at −27.9 ppm). The analytical data for the various compounds reported are given in Table I.

Syntheses of Adducts

$ZrCl_4 \cdot 2PEt_3$

The PEt_3 (0.83 cm^3, 5.7 mmol) was added dropwise to a stirred suspension of $ZrCl_4$ (1.30 g, 5.6 mmol) in benzene (30 cm^3). The solid dissolves immediately and after filtering through celite the solution was reduced to half its volume by pumping, and on standing crystals of the product are deposited (1.4 g, 75%). The IR (nujol mull) shows major bands at 1460, 1380, 1050, 875, 780, 760, 725 and 300 cm^{-1}.

$MCl_4 \cdot dbpe$ (M = Ti, Zr)

Both compounds are prepared by essentially the same method. Thus dbpe (7.1 cm^3, 19.0 mmol) was added to a stirred suspension of $ZrCl_4$ in toluene at 0 °C, and the solid dissolved after heating to 80 °C for 2 h. After filtering through celite the solid product precipitates initially, but removal of the solvent and the addition of petroleum ether, produces a free flowing solid $ZrCl_4 \cdot dbpe$. The IR shows major bands at 1460, 1370, 770, 720 and 300 cm^{-1}, and 1460, 1380, 1225, 1090, 800, 720 and 350 cm^{-1}, for the zirconium and titanium compounds respectively.

$ZrCl_4 \cdot 1.5tmed$

The tmed (1.7 cm^3, 11.5 mmol) was added to a stirred solution of $ZrCl_4$ (1.34 g, 5.75 mmol) in EtOAc (50 cm^3). A precipitate formed immediately, and was dried under vacuum for 4 h (2.1 g, 90%). The product showed major bands in the IR spectrum at 1460, 1380, 1310, 1150, 1020, 1000, 970, 860, 725, 525 and 300 cm^{-1}.

$TiCl_3 \cdot L$ (L = dmpe, dbpe)

Both procedures were similar but the dbpe adduct was the more soluble. Thus dbpe (5.6 cm^3, 15.0 mmol) was added to a solution of $TiCl_3$ (2.3 g, 14.9 mmol) in EtOAc (30 cm^3). After stirring for 16 h the solvent was removed leaving a brown oil. After stirring the oil with petroleum ether (b.p. 60–80 °C) (50 cm^3) for 24 h the product remained as a green powder (5.6 g, 80%), with IR bands at 1460, 1380, 1100, 1020, 725, and 350 cm^{-1}. The dmpe adduct was prepared in a similar manner, but in this case the solid $TiCl_3 \cdot dmpe$ precipitated as the solvent was removed. The IR spectrum showed bands at 1460, 1390, 1240, 1145, 950, 930, 720, 640, 380, 300 and 280 cm^{-1}.

$TiCl_3 \cdot tmed \cdot THF$

$LiBH_4$ (0.28 g, 10.3 mmol) was added to a stirred yellow solution of $TiCl_4 \cdot tmed$ (3.1 g, 10.5 mmol) in THF (40 cm^3). The solution quickly turns green, and after stirring for 12 h, filtering through celite, and standing at −20 °C for 16 h, blue crystals had formed in the solution. After drying under vacuum the solid (0.93 g, 25%) showed IR bands at 1010, 860, 800, 355 and 320 cm^{-1}. After heating this solid (1.4 g) to 60 °C for 4 h under vacuum the weight loss was 0.24 g (17.6%) indicating the solid was $TiCl_3 \cdot tmed$, as confirmed by analysis. This adduct showed major IR bands at 1100, 1070, 800, 350 and 320 cm^{-1}.

Adducts of $(PhO)_2TiCl_2$ with PMe_3, dmpe, PPh_3, dppe and tmed

The method used was similar in each case, the solvents used were Et_2O(PPh_3, dppe, tmed) and benzene (PMe_3, dmpe). Thus dmpe (1.17 cm^3, 7.4 mmol) was added to a stirred solution of $(PhO)_2TiCl_2$ in C_6H_6 (30 cm^3). The red solution turned orange over 10 min, and a yellow precipitate formed as the volume of the solution was reduced by pumping. The addition of petroleum ether assists the precipitation. The solid was dried by pumping under vacuum. Yields of the adducts were 50–80%. The main infrared absorptions are as follows: $(PhO)_2TiCl_2 \cdot 2PMe_3$: 1585, 1380, 1250, 760, 365, 320 cm^{-1}. $(PhO)_2TiCl_2 \cdot dmpe$: 1590, 1380, 890, 760, 460, 390, 350 cm^{-1}. $(PhO)_2TiCl_2 \cdot 2PPh_3$: 1590, 1380, 900, 725, 690, 340 cm^{-1}. $(PhO)_2TiCl_2 \cdot dppe$: 1590, 1380, 890, 740, 725, 690, 380 cm^{-1}. $(PhO)_2TiCl_2 \cdot tmed$: 1590, 1250, 880, 800, 690, 400, 360, 345 cm^{-1}.

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