ADDITION COMPOUNDS OF TITANIUM(IV) CHLORIDE CONTAINING ELEMENTS OF GROUPS V AND VI AS DONOR ATOMS

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ABSTRACT

Complexes $TiCl_4.L$ where L is a mono- or bi-dendate ligand having P, As, S, or Se as donor atom were prepared. Triphenylphosphine and dialkyl sulfide also form complexes $TiCl_4.2L$. Far infrared data are presented for certain of the complexes.

Organo derivatives of the heavier elements of groups V and VI, that is, phosphorus, arsenic, antimony, sulfur, selenium, and tellurium serve frequently as ligands in addition complexes with transition elements in low valence states. Few complexes of these elements have been reported in which the central atom is a transition element from one of the earlier groups in its highest valence state. However, H. Rose (1) reported over a century ago that phosphine forms an adduct with titanium(IV) chloride and hydrogen sulfide is known to form an adduct at low temperatures (2). Challenger and Pritchard (3) reported in 1924 that triphenylarsine forms an addition compound with $TiCl_4$ but they did not identify the resulting substance. In recent years, Clarke and co-workers (4) have shown that *o*-phenylenebisdimethylarsine forms the complexes $MCl_4.$dias and $MCl_4.2$dias where M = Ti, Zr, Hf. Fairbrother and Nixon (5) have shown that alkyl sulfides, R_2S, where R = CH_3, C_2H_5, will form complexes with pentahalides of niobium and tantalum. Chatt and Hayter (6) have prepared a few complexes of titanium(IV) chloride and mono- and di-tertiary phosphines. We have extended the list of known adducts formed by tertiary phosphines and arsines with tetrahalides of group IV elements and have shown that even the very weak Lewis bases, dialkyl sulfide and dialkyl selenide, form stable complexes with these elements. The present paper deals with complexes of titanium(IV) chloride.*

RESULTS AND DISCUSSION

All of the alkyl and aryl compounds of the elements N, P, As, Sb, O, S, Se, and Te which were tested were found to react with $TiCl_4$. Fowles has reported an investigation of the reaction of tertiary amines with $TiCl_4$ (7). We shall restrict ourselves here to the behavior of tertiary phosphine, arsine, and stibine and organo-sulfide, -selenide, and -telluride.

When pure components were allowed to react, fairly exothermic reactions occurred. The reaction of $TiCl_4$ with pure triethylphosphine is violent. For preparative purposes, the components were dissolved in dry benzene and allowed to react. In all cases, a yellow or deep-red coloration appeared. In one case studied more closely, that of triphenylarsine, the red color did not obey Beer's law indicating that the equilibrium,

$$TiCl_4 + AsPh_3 \rightleftharpoons TiCl_4.AsPh_3,$$
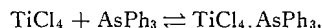
does not lie strongly to the right at low concentrations. It follows that the complex formed is not particularly stable with respect to the solvating effect of benzene upon the

*Note added in proof: Professor G. W. A. Fowles described the dialkyl sulfide complexes at the 8th International Conference on Coordination Chemistry, Vienna, September 1964.

component substances. This solvation energy is presumably not large in the case of each component as there is no sensible heat effect when they are dissolved alone. However, Elliot, Evans, and Owen (8) report that $TiCl_4$ forms a 1:1 complex with benzene but it is a very weak one.

The compounds which were prepared are listed with colors, melting points, and analyses in Table I. It may be seen that 1:1 complexes only are found with monodentate arsine and selenide while triphenylphosphine and alkylsulfide formed 2:1 addition compounds. We have found a 1:1 complex as well with triphenylphosphine. This gave a Debye–Scherrer X-ray pattern which was almost identical with that of the corresponding arsine but which differed from that of the 2:1 complex. The 2:1 phosphine complex has been reported by Chatt and Hayter (6).

TABLE I
Properties and analyses of complexes of $TiCl_4$

Compound	Color	Melting point (°C)	Found		Calcd.	
			Ti	Cl	Ti	Cl
$(Ph_3P)TiCl_4$	Red–violet	147.5–149	11.2	31.1	10.6	31.4
$(Ph_3P)_2TiCl_4$	Red–black	149–151	6.77	19.4	6.75	19.8
$(Ph_4P_2C_2H_4)_2Ti_3Cl_{12}$	Dark red	139–143	9.84	29.2	10.5	31.1
$(Ph_4P_2C_2H_4)TiCl_4$	Red	178 (decomp.)	7.97	25.2	8.14	24.1
$(Ph_4P_2C_2H_4)_3Ti_2Cl_8$	Red	138–140	6.38	19.0	6.08	18.0
$(Ph_3As)TiCl_4$	Red–black	126–128	9.67	28.4	9.66	28.6
$(Ph_4As_2C_2H_4)_3Ti_2Cl_8$	Red–orange	145–149	5.60	15.4	5.21	15.4
$(Me_2S)_2TiCl_4$	Orange	95–99	15.4	44.1	15.3	45.2
$(Et_2S)_2TiCl_4$	Bright red	55–57	13.2	37.9	12.9	38.3
$(Ph_2S_2C_2H_4)TiCl_4$	Bright red	69.5–70	11.3	32.0	11.0	32.5
	Dark	122–132	11.1	32.1	11.0	32.5
$(Et_2Se)TiCl_4$	Red–black	55 (decomp.)	14.7	42.6	14.7	43.4
$(Ph_2Se_2C_3H_6)TiCl_4$	Red–black	83 (decomp.)	8.20	25.3	8.81	26.1

Triphenylstibine and diethyltelluride reacted with $TiCl_4$ in two stages. A deep-violet color was observed in each case, upon mixing benzene solutions of the components. After some seconds or minutes a black, somewhat gummy solid appeared. Evaporation of the mother liquor yielded a gum which crystallized poorly upon standing for a few days. Benzene solutions of these gums were brown rather than violet. Although the chlorine to titanium ratio in these residues was 4:1, the products were thought to consist of a complex or mixture of $TiCl_2$ and dichlorinated diethyltelluride. That it was not a simple mechanical mixture was indicated by the failure to remove tellurium, e.g. as dichlorodiethyltellurium, by extraction with carbon tetrachloride.

The possibility that all of the compounds contained titanium in a reduced valence state was considered, for all of the ligand substances are reducing agents to some degree. The molar magnetic susceptibility of one of the compounds, $TiCl_4 \cdot AsPh_3$, was found to be $\chi_M = -0.26 \times 10^{-3}$ c.g.s. units. The estimated value for the compound assuming an oxidation state of $+4$ for the titanium is -0.27×10^{-3}. The similar color and behavior of the remaining compounds allows us to extend analogous formulations to them.

Attempts were made to discover compounds with apparently different coordination numbers. The use of a ditertiary arsine and a selenodiether allowed us to produce complexes with two donor atoms in the coordination shell. Variation of the proportions of the components in the reaction mixture led to the formation of more than one product in

the cases of triphenylphosphine and the ditertiary phosphine. As Clarke and co-workers (4) were successful in preparing an eight-coordinate complex of $TiCl_4$ with $o\text{-}C_6H_4(AsMe_2)_2$, similar complexes with $C_2H_4(PPh_2)_2$ and $C_2H_4(AsPh_2)_2$ were sought. However, addition occurred in each case only to the extent of 3 moles of ligand to 2 moles of $TiCl_4$ which, if the compounds are not molecular mixtures, indicates a coordination greater than six. The 3:2 phosphine compound was formed when a benzene solution containing n moles of $TiCl_4$ was mixed with a solution containing $5n$ moles of the base. The 3:2 and the 2:3 adducts appear from the analyses to be somewhat contaminated with the 1:1 compound. The ditertiary arsine formed only the 3:2 complex.

It remains undecided whether the 1:1 complexes are five-coordinate monomers or more highly coordinated polymers. Many of the complexes are not sufficiently stable to yield definitive results from molecular weight determinations. It is likely that both 1:1 and 2:1 complexes occur in varying proportions in solution. Attempts to detect spectrophotometrically the existence of a 2:1 complex in the system $Ph_3As\text{-}TiCl_4$ were limited, because of the intense color, to work on systems containing very low concentrations of the components and perhaps for this reason were unsuccessful.

The dialkyl sulfide complexes were sufficiently soluble in benzene to measure depression of the freezing point. Good agreement with the molecular weights indicated that these complexes are stable monomers in benzene solution. The chelated compounds were all too sparingly soluble to afford sufficient accuracy in freezing point determinations.

An examination of far infrared spectra provided values of various metal–ligand stretching frequencies and thereby some comparison of the bonding was possible. Sulfide and selenide complexes gave broad absorptions of little interpretive value. About all that could be seen with certainty was the fact that this absorption reached a maximum at ca. 410 cm^{-1} for sulfur compounds and continued to lower frequencies while the maximum was reached at 395 cm^{-1} for the ethyl selenide complex. The upper limit is certainly associated with sulfur and selenium stretching rather than chlorine stretching.

TABLE II

Infrared absorption frequencies for complexes of $TiCl_4$ in the region 525–260 cm^{-1}

Compound									
$(Ph_3P)TiCl_4$	514w	499.5s	*463*s	426w		393sh	380sh	357vs	
$(PhP_3)_2TiCl_4$	516s	496s	489sh	*445*s		*434*s	431s	418w	381s, b	365–302s, b
$(Ph_4P_2C_2H_4)TiCl_4$	506sh	499s	479s	*453*w	*414*w		343vs	325vs	313vs
$(Ph_4P_2C_2H_4)_3Ti_2Cl_8$	447w	*435.5*w	*416*s	393vs	389vs		374vs	363vs	359sh	312sh
$(Ph_4P_2C_2H_4)_2Ti_3Cl_{12}$	514s	499.5s	493.5s	465s					
$(Ph_3As)TiCl_4$	470s	452sh	396sh	383s, b		322vs			
$(Ph_4As_2C_2H_4)_3Ti_2Cl_8$	477s	457w	400sh	391s		381.5s	375s	350s	345s	316.5w

Titanium–phosphorus stretches, where identifiable, are shown in italics.
Abbreviations: s, strong; vs, very strong; w, weak; sh, shoulder; b, broad.

It was possible to identify stretching bands with reasonable certainty in the case of the simpler phosphine complexes. A summary of frequencies in the region 260–520 cm^{-1} is given in Table II and where possible titanium–phosphorus stretching frequencies are shown in italics. These were assigned easily because of their relative isolation in compounds of various transition metals.* A sample spectrum is shown in Fig. 1. A single phosphorus stretch appears in the spectrum of $(Ph_3P)TiCl_4$ as expected but two bands are found for $(Ph_3P)_2TiCl_4$. The conclusion drawn is that these are symmetric and antisymmetric

*Unpublished work.
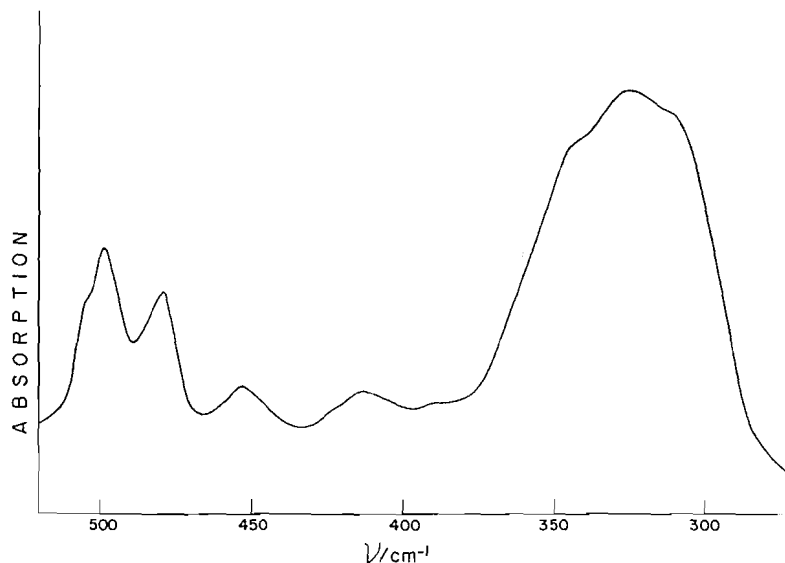
FIG. 1. Infrared spectrum of the compound $(Ph_4P_2C_2H_4)TiCl_4$.

modes which arise in the case of complexes having the *cis* configuration. The frequency values reported by Coates and Parkin (9) for the bonds formed between phosphorus and palladium, platinum, and gold are comparable with those found here. A force constant calculation which takes account only of the two atoms forming the bond shows that the values for the Ti—P bond in $(Ph_3P)_2TiCl_4$ are just about the same as for the Pt—P bond in *cis*-$(Me_3P)_2PtCl_2$, a typical phosphine complex of high stability. Table III presents the force constants so estimated for the symmetric and antisymmetric modes of these compounds. The force constants are designated k_1 and k_2 because it is not certain which belongs to the symmetric and which to the antisymmetric mode. The comparison

TABLE III

Comparison of force constants

	Force constants (dyne $cm^{-1} \times 10^{-5}$)	
Compound	k_1	k_2
$(Ph_3P)_2TiCl_4$	2.18	2.07
$(Ph_4P_2C_2H_4)TiCl_4$	2.27	1.90
cis-$(Me_3P)_2PtCl_2$	2.22	2.05
$(Ph_4P_2C_2H_4)PtCl_4$	2.96	2.87

shows that $TiCl_4$ is just as effective as an acceptor toward a phosphine as $PtCl_2$. It will be remembered that platinum is regarded as one of the most strongly bonding elements towards phosphines. However, it is seen that when the valence state of the platinum is made to equal that of the titanium, platinum is then the better acceptor.

It is interesting to observe that the Ti—P stretching frequency is greater for (Ph_3P) $TiCl_4$ than for either mode of the 2:1 adduct. A similar but rough comparison can be made for the 2:3 and the 3:2 complexes. Although it is not certain how many bands in each case should be attributed to metal–phosphorus and metal–chlorine stretching, it is at

least likely that the band at 465 cm^{-1} for $L_2Ti_3Cl_{12}$ is due to Ti—P stretching and this is higher than the highest corresponding frequency, 436 cm^{-1}, for $L_3Ti_2Cl_8$. In the latter compound, additional bands, e.g. at 416 and 393 cm^{-1} are evidently due to Ti—P stretching, which indicates the complexity of the compound structure. A similar complexity is observed for the arsine $(Ph_4As_2C_2H_4)_3Ti_2Cl_8$.

EXPERIMENTAL

Infrared spectra of Nujol mulls between caesium iodide plates were obtained with a Perkin–Elmer Model 13G spectrometer set for double beam operation and fitted with a 30 micron grating. The fore-prism index was adjusted continuously throughout the spectral range. Analyses of complexes were carried out gravimetrically following preparation of the sample by Parr bomb combustion.

Titanium(IV) chloride was purified by the method of Clabaugh and co-workers (10). Triphenylphosphine, triphenylarsine, and triphenylstibine, obtained from M and T Chemicals, Inc., were recrystallized from ethanol until the melting points were constant. Dimethylsulfide and diethylsulfide, supplied by Distillation Products Industries, were distilled prior to use. The compounds 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylarsino)ethane were prepared by the method of Chatt and Hart (11).

1,3-Bis(phenylseleno)propane.—Phenylselenol (55.4 g) was added to a solution prepared by adding sodium (8.18 g, 1 mole) to ethanol (50 cc). To this, 1,3-dibromopropane (71.6 g, 0.5 mole) dissolved in ethanol (50 cc) was added dropwise with stirring. The solution was heated under reflux in a nitrogen atmosphere for 2 h. The solution was separated from sodium bromide by filtration and the alcohol removed by distillation. The resulting brown oil was distilled at 0.1 mm Hg pressure to yield an amber oil (37.2 g, 59%) with b.p. 185–188 °C.

Anal. Found: C, 50.7; H, 4.32. Calcd. for $C_{15}H_{16}Se_2$: C, 50.9; H, 4.55.

Preparation of complexes.—The addition complexes were all prepared by essentially the same procedure of which the following is representative.

Tetrachlorotriphenylphosphinetitanium.—The content of an ampoule of titanium(IV) chloride (3.84 g) was introduced to a nitrogen-filled Schlenk tube containing carefully dried, sulfur-free benzene (8 cc). To this solution was added triphenylphosphine (2.7 g, 0.5 mole) dissolved in benzene (10 cc). There was immediate appearance of a dark-red coloration with the formation of dark crystals. These were removed by filtration in an apparatus similar to that described by Fritz and co-workers (12). The product (2.3 g) was washed on the filter with a small quantity of benzene and dried at room temperature under vacuum. As the compound was attacked by moist air, it was stored in ampoules. This was true of all other complexes as well.

The other complexes were best prepared from stoichiometric quantities of the components except in the cases of the 3:2 and 2:3 compounds of the diphosphine. For the former, a fivefold excess of diphosphine was used and for the latter, a fivefold excess of TiCl$_4$.

It was possible to recrystallize the compounds prepared from monodentate ligands by dissolving in benzene and removing the solvent by distillation under reduced pressure. The bidentate ligands formed compounds which were only sparingly soluble. However, the analyses reported in Table I refer to preparations which had not been recrystallized.

One compound, $(Ph_2S_2C_2H_4)TiCl_4$, appeared as a mixture of bright-red needles and darker-red granules. As shown in Table I these forms when separated melt at different temperatures, the darker one under non-equilibrium conditions, of course.

ACKNOWLEDGMENTS

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