Inorganica Chimica Acta, 36 (1979) 45–53
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Chemical Reactivity of Tris-(triphenylphosphine)chloroplatinum(II) Undecachlorotrititanate, $[(C_6H_5)_3P]_3PtCl^+Ti_3Cl_{11}^-$

S. WONGNAWA [1] and E. P. SCHRAM*

Evans Chemical Laboratory, 88 West 18th Avenue, The Ohio State University, Columbus, Ohio 43210, U.S.A.

Received November 14, 1978

Treatment of $[(C_6H_5)_3P]_3PtCl^+Ti_3Cl_{11}^-$, (I), with CH_3CN and pyridine, py, affords near quantitative yields of $TiCl_3(CH_3CN)_3$ and $TiCl_3(py)_3$ based on the presence of $2TiCl_3$ per $Ti_3Cl_{11}^-$. Oxidative hydrolysis of (I), (Ti(III) → Ti(IV) + $0.5H_2$) affords a maximum H_2 yield of 82% of that expected, similar to that described for the oxidative hydrolysis of α-$TiCl_3$ in the presence of cis-*$[(C_6H_5)_3P]_2PtCl_2$. Hydrogen chloride reacts with (I) to afford $\{[(C_6H_5)_3PtCl\}^+\{Ti_3Cl_{11}\cdot HCl\}^-$ while CO affords $[(C_6H_5)_3P]_2PtCOCl^+$. Both BF_3 and BCl_3 complex with (I) with the latter displacing the former. Ion exchange reactions between (I) and $(C_2H_5)_4NCl$ and $[(CH_3)_2CHCH_2CH_2]_4NI$ afford, as the only characterizable products,* cis-*$[(C_6H_5)_3P]_2PtCl_2$ and* trans-*$[(C_6H_5)_3P]_2PtI_2$ respectively. Reactions between (I) and $(C_2H_5)_4NPF_6$ yielded no identifiable exchange products.*

Introduction

Treatment of *tris*-(triphenylphosphine)platinum(0), $[(C_6H_5)_3P]_3Pt$, with excess titanium tetrachloride, $TiCl_4$, affords the emerald green salt, $[(C_6H_5)_3P]_3PtCl^+ Ti_5Cl_{19}^-$, which, on thermolysis, yields the brown salt, $[(C_6H_5)_3P]_3PtCl^+Ti_3Cl_{11}^-$, (I), and two equivalents of $TiCl_4$ [2]. Furthermore, the stoichiometry of the redox reaction affording these platinum complexes requires the anions contain two equivalents of Ti(III). The reactions of (I) herein reported were carried out to obtain additional information regarding the chemical nature of (I).

Results and Discussion

Reactions of $[(C_6H_5)_3P]_3PtCl^+Ti_3Cl_{11}^-$ with Lewis Bases

Acetonitrile

Treatment of (I) with CH_3CN effects decomposition of both the cation and anion and results in the formation of two equivalents of Ti(III) per (I), *i.e.*, $TiCl_3(CH_3CN)_3$. Furthermore, one equivalent of $(C_6H_5)_3P$ is replaced by Cl^- as determined by the isolation of *cis*-$[(C_6H_5)_3P]_2PtCl_2$. The displaced $(C_6H_5)_3P$ is believed to be associated with Ti in the complex, $TiCl_4\cdot CH_3CN\cdot P(C_6H_5)_3$. This chemical transformation is summarized by eqn. 1, while the associated data are contained in Table I.

$$[(C_6H_5)_3P]_3PtCl^+Ti_3Cl_{11}^- + 7CH_3CN \rightarrow \textit{cis-}[(C_6H_5)_3P]_2PtCl_2 + 2TiCl_3(CH_3CN)_3 + TiCl_4\cdot CH_3CN\cdot P(C_6H_5)_3 \qquad (1)$$

TABLE I. Stoichiometry Data Associated with the Reaction of (I) with CH_3CN.

Reaction	Amount of (I) Used		Amount of *cis*-$PtCl_2(PPh_3)_2$ Obtained		% Yield	Solid By-Products			
						$TiCl_3(CH_3CN)_3$		$TiCl_4\cdot P(C_6H_5)_3\cdot CH_3CN$	
	g	mmol	g	mmol		g	mmol	% yield	g
1	0.406	0.262	0.151	0.191	73.0	–	–	–	–
2	0.774	0.499	0.303	0.384	77.0	–	–	–	–
3	0.610	0.393	0.277	0.351	89.3	–	–	–	0.039
4	0.842	0.543	0.371	0.470	86.5	0.265	0.956	88.0	0.071

---

*Author to whom correspondence should be addressed.

TABLE II. Hydrogen Yields Associated with the Oxidative Hydrolyses of (I) and Other Ti(III)-Containing Derivatives.

Reaction	System	Mol Ratio of each Component Used	% Yield of H_2
1	(I)	–	82^a
2	α-$TiCl_3$	–	96
3	α-$TiCl_3$ + PPh_3	1:1	96
4	α-$TiCl_3$ + PPh_3 + *cis*-$PtCl_2(PPh_3)_2$	3:1:1	86
5	same as 4	3:1:1	84

^{a}Calculated based on the presence of two equiv. of Ti(III) per equiv. of (I).

Both *cis*-$[(C_6H_5)_3P]_2PtCl_2$ and $TiCl_3(CH_3CN)_3$ were characterized by comparison of their physical properties and infrared spectra with authentic samples. The characterization of $TiCl_4 \cdot CH_3CN \cdot P(C_6H_5)_3$ is tentative; however, the identical species results from treatment of $TiCl_4 \cdot P(C_6H_5)_3$ with CH_3CN and contains Ti(IV), as opposed to Ti(III), based on its chemical and magnetic properties. Furthermore, the infrared spectrum of this species contains a strong infrared absorption at 2425 cm^{-1} indicative of coordinated CH_3CN, while the presence of coordinated $P(C_6H_5)_3$ is confirmed by the characteristic weak bands at 1587 and 1573 cm^{-1}, the very strong absorptions in the region 750–690 cm^{-1}, and the very strong absorption at 500 cm^{-1} found in both $TiCl_4 \cdot P(C_6H_5)_3$ and $TiCl_4[P(C_6H_5)_3]_2$ [3]. Finally, $TiCl_4 \cdot P(C_6H_5)_3 \cdot CH_3CN$ is easily distinguished from $TiCl_4(CH_3CN)_2$ in that the latter contains a strong absorption at 398 cm^{-1} which is absent in the former [4]. Acetonitrile has been reported to reduce metal chlorides, *e.g.*, VCl_3, $CoCl_3$, $MoCl_5$ and WCl_6, however, we have demonstrated that $TiCl_4$ is not reduced by CH_3CN under the experimental conditions associated with the reaction described by eq. 1. Hence, the isolation of two equivalents of Ti(III) per (I), eq. 1, is consistent with $Ti_3Cl_{11}^+$ containing two equivalents of $TiCl_3$. In an analogous fashion, treatment of (I) with py was investigated.

Pyridine

Reaction of (I) with py at –78 °C, and subsequent warming of the reaction mixture at 0 °C, results in the formation of a dark green solution and pale green precipitate. Filtration of this product mixture results in an 89% yield of $TiCl_3(py)_3$ which is soluble in CH_3CN. Subsequent washing of the pale green precipitate with benzene results in the isolation of *cis*-$[(C_6H_5)_3P]_2PtCl_2$. Both of these species were characterized by comparison of their respective infrared spectra with those of authentic samples. Titanium tetrachloride has been reported to afford $TiCl_3(py)_3$, when treated with py [5]. However we have observed no reduction at 0 °C during a 10 hr reaction period although we have noted reduction within 30 min at 25 °C. The immediate appearance of green $TiCl_3(py)_3$, on treating (I) with py, further confirms the presence of Ti(III) in the anion, $Ti_3Cl_{11}^-$.

Oxidative Hydrolysis of (I)

Usually one may determine the amount of Ti(III) present in a sample by the base catalyzed oxidation of Ti(III) to Ti(IV) with accompanying reduction of H_2O to afford ½ mol H_2 per equivalent of Ti(III) [6]. We have found that when one carried out the base catalyzed oxidation of (I) and $[(C_6H_5)_3P]_3PtCl^+Ti_5Cl_{19}^-$ (II), the H_2 yields are dependent on the size of the sample hydrolyzed. For example, when one treats 0.07 mmol of (II) with aqueous base, a 11% yield of H_2 results, based on two equivalents of Ti(III) per mol (II). By increasing the sample size to 0.8 mmol (II), a 69% yield of H_2 was obtained. In a similar manner we have found the H_2 yield associated with the oxidative hydrolysis of (I) to vary with sample size. Table II summarizes H_2 yield data, associated with (I) as well as the affect of $(C_6H_5)_3P$ and a Pt(II) complex on the H_2 yield associated with the oxidative hydrolysis of α-$TiCl_3$. In all cases, Table II, samples contained *ca.* 1.5 meg of Ti(III). The H_2 yield for α-$TiCl_3$, in the presence or absence of $(C_6H_5)_3P$ is essentially quantitative, reactions 2 and 3, Table II, whereas the addition of *cis*-$[(C_6H_5)_3P]_2PtCl_2$ results in a decreased H_2 yield, reactions 4 and 5. A Pt(II) complex was added to α-$TiCl_3$ because (I) has been established to contain Pt(II) [2]. Apparently base catalyzed oxidation of Ti(III) is accomplished by reduction of Pt(II) in addition to reduction of H_2O. The infrared spectra of the control hydrolysis residue and that of (I), reactions 4 and 1 respectively, Table I, are identical and contain absorptions characteristic of $OP(C_6H_5)_3$ at 1182, 1155, 1120, 1070, 999, 748, 729, 695 and 540 cm^{-1} [7]. No platinum phosphine complexes survive the hydrolyses based on the fact that the ^{31}P NMR spectrum of both hydrolysis residues exhibit no ^{195}Pt–^{31}P coupling – a single absorption is found in both systems at –24.06 ppm (relation to 85% H_3PO_4) and is assigned to $OP(C_6H_5)_3$.

TABLE III. Data on the Reaction of (I) with Boron Trihalides.

Reaction		I		Reaction Temp. (°C)	Reaction Time (hr)	Boron Trihalide Absorbed (mmol)	mmol of Boron Trihalide per mmol of (I)
		g	mmol				
BF_3	1[a]	0.255	0.165	0	24	0.051	0.31
	2[b]	0.495	0.320	25	29	0.120	0.38
	3[b]	0.273	0.176	25	20	0.066	0.38
BCl_3	4[a]	0.339	0.218	0	15	–	–
	5[b]	0.371	0.240	0	20	0.166	0.69
	6[b]	0.443	0.286	0	37	0.261	0.91

[a]Reaction carried out in dichloromethane. [b]Solid state reaction.

Ion Exchange Reaction with (I), Attempted Isolation of New Salts of $Ti_3Cl_{11}^-$

In an effort to isolate salts of $Ti_3Cl_{11}^-$, free of complexed platinum, solutions of (I) were treated separately with $(C_2H_5)_4NCl$, $[(CH_3)_2CHCH_2CH_2]_4NI$, and $(C_2H_4)_4NPF_6$. In no case could new derivatives of $Ti_3Cl_{11}^-$ be isolated but rather halogen–$P(C_6H_5)_3$ exchange took place. Tetraethylammonium chloride afforded *cis*-$[(C_6H_5)_3P]_2PtCl_2$ while $[(CH_3)_2CHCH_2CH_2]_4NI$ resulted in the formation of *trans*-$[(C_6H_5)_3P]_2PtI_2$. Characterization of the former was based on the comparison of its infrared spectrum with that of an authentic sample while the latter was identified by its m.p. [8] and the fact that its infrared spectrum was identical to that of *trans*-$[(C_6H_5)_3P]_2PtCl_2$ except for the frequencies of the νPtX_2 absorptions [8]. The ease of obtaining *trans*-$[(C_6H_5)_3P]_2PtI_2$, by treatment of (I) with $[(CH_3)_2CHCH_2CH_2]_4NI$, is in contrast to the thermal rearrangement of *cis*-$[(C_6H_5)_3P]_2PtI_2$ [8].

Formation of *trans*-$[(C_6H_5)_3P]_2PtI_2$ from $[(C_6H_5)_3P]_4Pt$ and I_2 has also been reported to take place under reaction conditions which prevent formation of $(C_6H_5)_3P$ as the latter has been shown to catalyse *trans–cis* isomerizations of $[(C_6H_5)_3P]_2PtI_2$ [9]. In a similar fashion, in the reaction system $[(C_6H_5)_3P]_3PtCl^+$ and I^-, the Lewis acid $Ti_3Cl_{11}^-$ in present, $(2TiCl_3 + TiCl_4)$, hence displaced $P(C_6H_5)_3$ would be expected to be removed thereby eliminating *trans–cis* isomerization of $[(C_6H_5)_3P]_2PtI_2$.

In an effort to eliminate halide attack on $[(C_6H_5)_3P]_3PtCl^+$, (I) was treated with $(C_2H_5)_4NPF_6$ [12–14]. Unfortunately, no new crystallizable materials could be isolated from the resulting reaction mixture. In an attempt to abstract Cl^- from $Ti_3Cl_{11}^-$, (I) was treated with both BF_3 and BCl_3.

Reactions of (I) with Lewis Acids

Data associated with treatment of (I) with BF_3 and BCl_3, in solution and in the solid state, are summarized in Table III. The reaction ratios reported for BF_3, reactions 1, 2, and 3 (*ca.* (I): $0.4BF_3$), are based on initial uptake of BF_3. With respect to subsequent displacement of BF_3 by BCl_3, the combined reaction products, reactions 2 and 3, Table III (0.186 mmol BF_3) afforded 0.123 mmol BF_3 when treated with excess BCl_3. The non-stoichiometric nature of the reaction between (I) and BF_3 does not appear to be a consequence of the heterogeneous nature of the reaction, reaction 1, Table III, because only a slight increase of BF_3 uptake was observed during solution reactions, reactions 2 and 3, Table III. Furthermore, the observed stoichiometry is not due to an equilibrium concentration of BF_3 because (I)·$0.4BF_3$ is stable *in vacuo* at 25 °C.

Reaction of (I) with BCl_3 takes place to a greater extent than with BF_3 with a near 1:1 stoichiometry achieved under homogeneous reaction conditions, reaction 6, Table III. The ^{31}P NMR spectrum of this product, as well as the BF_3 reaction product, is that of $[(C_6H_5)_3P]_3PtCl^+$ and hence consistent with complex formation, *i.e.*, reaction between $Ti_3Cl_{11}^-$ and BCl_3 or BF_3. The infrared spectrum of the BCl_3 reaction product, reaction 6, Table III, is identical to that of (I). The presence of coordinated BCl_3 can often be detected by $\nu_{as}BCl_2$ in the range 1000–800 cm^{-1} and 800–650 cm^{-1} for three and four coordinated BCl_3 respectively [10, 11]. Unfortunately, the absorptions of (I), 692vs, 705vs(sh), 743vs, and 845w cm^{-1} mask the four coordinate regions of the infrared spectrum of (I)·BCl_3. In a similar fashion, ν_{as} BF_2 absorptions are masked in the four coordinate regions of BF_3 complexes, 1150–1000 cm^{-1} [12–14], by absorption at 999ms, 1022m, 1050m, 1092s, 1111m, and 1159 w cm^{-1} in (I).

We have previously demonstrated that treatment of $[(C_6H_5)_3P]_3PtCl^+Ti_3Cl_{11}^-$, (I), with the Lewis acid, $TiCl_4$, affords $[(C_6H_5)_3P]_3PtCl^+Ti_5Cl_{19}^-$ and observed that the latter is green in color while the former is brown [2]. The reaction product of (I) with BCl_3 was noted to be green-brown in color and furthermore, as previously mentioned, the ^{31}P NMR spectrum of (I)·BCl_3 is identical to $[(C_6H_5)_3P]_3PtCl^+$. On the basis of the cited data, (I)·BCl_3 is

TABLE IV. Reaction of (I) with Hydrogen Chloride.

Reaction	Amount of (I)		Reaction Temp. (°C)	Reaction Time (hr)	Amount of HCl reacted (mmol)	Mol Ratio of (I)/HCl
	g	mmol				
1[a]	0.476	0.307	0	26	0.295	1:0.96
2[b]	0.662	0.427	25	14	0.471	1:1.10

[a]Reactions carried out in dichloromethane. [b]Solid state reaction.

formulated as $[(C_6H_5)_3P]_3PtCl^+Ti_3Cl_{11}\cdot BCl_3^-$ while the nature of the reaction product between (I) and BF_3 remains unknown.

Reactions of (I) with HCl

Treatment of (I) with HCl was carried out in an effort to prepare $Ti_3Cl_{11}H$ with possible by-products including *cis*-$[(C_6H_5)_3P]_2PtCl_2$ and $P(C_6H_5)_3$. The data associated with this reaction are contained in Table IV and are interpreted to indicate formation of a complex with the stoichiometry, (I)•HCl. The ^{31}P NMR spectrum of I•HCl is identical to that of (I) consistent with reactions of HCl with $Ti_3Cl_{11}^-$ rather than $[(C_6H_5)_3P]_3PtCl^+$. This lack of reactivity between the cation and HCl is in contrast to reactions between $[(C_6H_5)_3P]_3RhCl$ or $[(C_6H_5)_3P]_3IrCl$ with HCl to afford $[(C_6H_5)_3P]_3RhHCl_2$ and $[(C_6H_5)_3P]_3IrHCl_2$, respectively [15, 16]. Hydrogen chloride has been reported to reversibly react with *trans*-$[(C_2H_5)_3P]_2PtHCl$ to afford $[(C_2H_5)_3P]_2PtH_2Cl_2$ but the latter is only stable in the presence of excess HCl.

The infrared spectrum of I•HCl is identical to that of (I) and chloride ion has not been abstracted from (I) to afford $ClHCl^-$, based on the absence of strong antisymmetric and bending infrared absorptions in the reaction product, which have been attributed to $ClHCl^-$ (1565 and 1180 cm^{-1}) [17, 18]. Most likely, I•HCl contains the new anion, $Ti_3Cl_{12}H$ with νH–Cl masked by the infrared absorptions of (I).

Reactions of (I) with Unsaturated Ligands

Treatment of (I) in solution, −78° to 25 °C, with ethylene at 800 torr for 22 hr resulted in no uptake of ethylene. Both reactants were quantitatively recovered. This lack of reactivity of (I) with C_2H_4 is in contrast to that with CO; data associated with the latter are summarized in Table V. In no case was a 1:1 stoichiometry achieved with CO; however, a reproducible ratio of 2(I):1(CO) was obtained at 1 atm CO pressure, reactions 1–3 as compared to reactions 4–6, Table V. The infrared spectrum of the product in all cases contain a strong absorption in the carbonyl region at 2108 cm^{-1}. Subsequent pyrolysis of the reaction product at 160 °C results in complete removal of CO as evidenced by loss of the 2108 cm^{-1} absorption.

TABLE V. Stoichiometry for the Reaction of (I) with CO.

Reaction[a]	(I)		CO Complexed[b] mmol	Mol Ratio of (I)/CO
	g	mmol		
1	0.190	0.123	0.03	4:1
2	0.472	0.304	0.09	3.5:1
3	1.860	1.199	0.31	4:1
4	1.098	0.708	0.34	2:1
5	0.715	0.461	0.23	2:1
6	0.472	0.304	0.14	2:1

[a]The first three reactions were carried out under *ca.* 100 torr of CO pressure while the last three reactions were under 1 atm CO. [b]Determined as CO recovered during thermolysis.

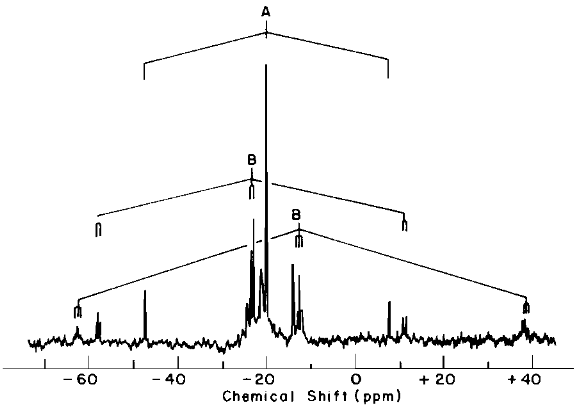


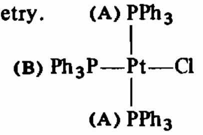
Fig. 1. FT ^{31}P NMR spectrum of the reaction mixture resulting from treatment of (I) with CO. A) Due to *trans*-$[(C_6H_5)_3P]_2Pt(CO)Cl^+$, B) Due to $[(C_6H_5)_3P]_3PtCl^+$.

The ^{31}P NMR spectrum, obtained in CH_2Cl_2, for the reaction product produced under the reaction conditions identical to reaction 6, Table V, is reproduced in Fig. 1 and the data summarized in Table VI. Although several unidentified phosphorus containing species are present, *i.e.*, associated with the absorptions at −13.68, −20.99 and −23.98 ppm, only two Pt–P complexes are present. Unreacted $[(C_6H_5)_3$-

TABLE VI. ^{31}P NMR Data on the Reaction Mixture Resulting from Treatment of (I) with CO.

Species	Chem. Shift[a] (ppm)	$^1J_{Pt-P}$ (Hz)	$^2J_{P_A-P_B}$ (Hz)	Relative Intensity[c]
trans-$Pt(PPh_3)_2(CO)Cl^+$	−19.6	1975	–	2.04
trans-$Pt(PPh_3)_3Cl^+$	$-12.2(P_B)^b$	$3642(P_B)$	18	$1.00(P_B)^c$
	$-22.9(P_A)$	$2481(P_A)$	18	$1.61(P_A)^c$

[a] Negative sign indicates downfield shift relative to 85% H_3PO_4. [b] Subscript A and B refer to the designated position of phosphorus atoms in the geometry.



$$\begin{array}{c} (A)\ PPh_3 \\ | \\ (B)\ Ph_3P\text{—}Pt\text{—}Cl \\ | \\ (A)\ PPh_3 \end{array}$$

[c] Relative to that of P_B in $Pt(PPh_3)_3Cl^+$.

$P]_3PtCl^+$ is positively identified by the absorptions at −12.2 ppm and 22.9 with $^1J_{Pt-P}$ coupling constants, 3642 Hz and 2481 Hz, respectively [2]. The new PtP complex exhibits a ^{31}P chemical shift at −19.6 ppm, and $^1J_{Pt-P}$ 1975 Hz. *Trans*-$Cl(CO)Pt(PCl_3)_2^+$ BF_4^- has been reported to exhibit νCO at 2120 cm^{-1} (in solution) [19] as compared to 2108 cm^{-1} (solid state) observed for the reaction product of (I) and CO. Based on the combined ^{31}P NMR and infrared data, the platinum–phosphine–carbonyl complex present in solution is tentatively characterized as *trans*-$ClCOPt(PCl_3)_2^+$. With regard to $P(C_6H_5)_3$ displaced from Pt, we have observed $TiCl_4 \cdot P(C_6H_5)_3$ to exhibit a ^{31}P NMR absorption at −18 ppm. The singlet observed at −20.99 is most likely associated with $P(C_6H_5)_3$ complexed to $Ti_3Cl_{11}^-$ or its components.

Experimental

The high vacuum equipment and techniques employed during syntheses and investigation of chemical species have been previously described [3]. Reactions were carried out either in a 10 or 50 ml bulb containing a teflon coated spin bar and the bulb attached via O-ring joints and a teflon stopcock to the manifold of the vacuum line. Air and moisture sensitive materials, soluble *vs.* insoluble in a particular solvent, were separated by filtration *in vacuo* employing a medium porosity glass frit.

Qualitative Test for Ti(III). Ammonia

The determination of the presence of Ti(III) in a sample was carried out after treatment with 3*M* H_2SO_4 and removing any residue by filtration. The presence of Ti(III) was indicated by the violet color of the resulting solution and subsequent addition of ammonia to the solution resulted in precipitation of black Ti_2O_3. This precipitate affords white TiO_2 after heating to 100 °C for 30 min. The presence of Ti(IV) is indicated by the immediate formation of TiO_2 with addition of NH_3. Titanium(IV) can be qualitatively detected at a low limit of *ca.* 5 X 10^{-3} *M* Ti. For Ti(III) the limit was not determined, however it is less than 5 X 10^{-3} *M* due to the obvious formation of black Ti_2O_3. When a sample contained both Ti(III) and Ti(IV) in comparable amounts, it was not possible to detect Ti(IV) because the black precipitate of Ti_2O_3 completely masks the white precipitate of TiO_2.

Peroxide Test

After sample treatment with 3*M* H_2SO_4, 30% hydrogen peroxide was added to the filtrate. The initial presence of Ti(III) or (IV) results in the formation of a clear yellow solution. This test easily detects Ti(III) or (V) at 3 X 10^{-4} *M* Ti; however, it does not distinguish between the two oxidation states.

Reagents

Acetonitrile, Fisher Scientific Co., was dried over calcium hydride and fractionated through a −35° trap into a −78° trap. The condensate in the −78° trap, acetonitrile, had a vapor pressure of 25.5 torr at 0° (lit. 25.0 torr [20]). *Ammonium hexafluorophosphate*, PCR, Inc., was used as received. *Benzene*, Anal. Reagent, J. T. Baker Co., was dried over lithium aluminum hydride. *Benzene-d_6*, 99.5%, ICN Corp., was used as received. *Boron trichloride*, Matheson Co., was purified through a −45° trap into a −126° trap. Boron trichloride, collected from the −126° trap, had a vapor pressure of 4.2 torr at −78° (lit. 3.9 torr [20]). *Boron trifluoride*, The Matheson Co., was purified through a −126° trap. *Carbon monoxide*, The Matheson Co., was purified by circulation through a −126° trap. *Cyclopentane*, 99%, Chemical Samples Co., was dried over lithium aluminum hydride and fractionated through a series of −46°, −78°, and −196° traps and collected from the −78° trap. *1,2-Dichlorobenzene,* Anal. Reagent, J. T. Baker Co., was dried over lithium aluminum hydride and purified further by distilling in a Nester Faust spinning band column at 59.5° under 10 torr of inert gas (lit. = 59.1°, 10 torr [20]). *Dichloromethane,* Anal. Reagent, Mallinckrodt Chemical Works, was dried over lithium aluminum hydride and fractionated through a −22° trap into a −78° trap; the −78° trap fraction had a vapor pressure of 41.5 torr at −22° (lit. 40.0 torr [21]). *Dichloromethane-d_2,* 99%, Merck Co., Inc., was used as received. *Ethanol,* 95%, Commercial Solvents Corp., was used as received. *Ethylene,* The Matheson Co., was purified through a −78° trap into a −196° trap. *Hydrogen chloride,* The Matheson Co., was purified by functional condensation through a −126° trap, the −196° fraction was used. *Hydrogen peroxide,* 30%, Mallinckrodt Chemical Works, was used as received. *Pyridine,* py, Fisher Scientific Co., was dried by refluxing over calcium hydride for 24 hr and distilled *in vacuo.* Pyridine dried in this manner reacts with $TiCl_4$ to yield a red rather than a green solution. Pyridine was further dried by treatment with a small amount of $TiCl_4$, prior to distillation. *Tetraethylammonium chloride,* Eastman Organic Chemicals, was dried by heating to 95°, *in vacuo,* for *ca.* 10 h. *Tetraethylammonium hexafluorophosphate,* was prepared by dissolving equimolar amounts of NH_4PF_6 and NEt_4Cl in water. The resulting white solid was washed repeatedly with distilled water until the filtrate indicated the absence of Cl^- when treated with $AgNO_3$. After rinsing with EtOH it was dried, *in vacuo,* at 25° for 24 h. *Tetraisopentylammonium iodide,* $(CH_3)_2CHCH_2CH_2)_4NI$, Eastman Organic Chemicals, was dried by heating to 70°, *in vacuo,* for 6 h. *Titanium tetrachloride,* 99.9%, Alfa Products, was purified immediately before use by fractionating into a −15° trap while other more volatile components passed through this trap into a −196° trap. *α-Titanium trichloride,* >98%, Alfa Products, was heated at 200°, *in vacuo,* for *ca.* 2 h before use. Triphenylphosphine, Chemical Samples Co., was used as received. *Potassium hexachloroplatinate(IV)* was prepared as described in the lit. [22]. *Potassium tetrachloroplatinate(II)* was prepared from K_2PtCl_6, using hydrazine dihydrochloride, as described in the lit. [23]. *cis-Dichlorobis(triphenylphosphine)platinum(II)* was prepared from K_2PtCl_4 by the method described in the lit. [24]. Ir data: 3060w, 1585w, 1570w, 1480s, 1432vs, 1312m, 1185w, 1165w, 1155w, 1105s, 1099s, 1090s, 1063w, 1029w, 1000m, 758s, 747s, 718m, sh, 707s, 699vs, 690s, sh, 620vw, 550s, 529vs, 518s, 500s, 465w, 450vw, 440vw, 420w, 320ms, and 292ms, cm^{-1}. *Tetrachlorobis(acetonitrile)titanium(IV),* $TiCl_4(CH_3CN)_2$, was prepared by condensing excess acetonitrile onto 0.015 mol (2.772 g) of titanium tetrachloride at −78°. After warming to 25° and removal of excess CH_3CN, the yellow solid was pumped to dryness and the weight increase was equivalent to 0.027 mol of CH_3CN corresponding to $TiCl_4(CH_3CN)_{1.8}$. The ir spectrum of this compound was identical to that reported for $TiCl_4(CH_3CN)_2$ [4]. When $TiCl_4(CH_3CN)_2$ is allowed to contact liquid acetonitrile for 36 hr at 25°, no change takes place in the product. *Tetrachlorobis(pyridine)titanium(IV),* $TiCl_4(py)_2$, was prepared by condensing an excess pyridine, py, with $TiCl_4$ at −78°. The reaction flask was allowed to warm up to 0° and maintained at this temperature with stirring to avoid reduction to Ti(III) by py [5]. This reaction was exothermic yielding a yellow solid. After 15 m at 0° the excess py was removed and the ir spectrum of the yellow product had absorptions at: 3100vw, 1912w, 1662w, 1638w, 1612vs, 1572w, 1538m, 1490s, 1450vs, 1310m, 1240w, 1220vs, 1161w, 1132w, 1090w, 1072vs, 1050s, 1024vs, 950m, 69w, 763vs, 708m, 692vs, 650vs, 610w, 445vs, 378vvs, and 292s, cm^{-1}. When the reaction was carried out at 25° reduction of Ti(IV) to Ti(III) by pyridine occurred in 30 m as evidenced by the small amount of green color indicating the presence of $TiCl_3(py)_3$. At 0° this reduction was much slower: *ca.* 10 h was required for the green color to be observed. *Trichlorotris(pyridine)titanium(III),* $TiCl_3(py)_3$, was prepared by distilling pyridine into a flask containing α-$TiCl_3$ at −78°. During a subsequent warm-up period, the liquid turned to greenish brown, then clear green, with precipitation of microcrystalline green $TiCl_3(py)_3$. Ir data: 1600s, 1583m, 1570w, sh, 1484s, 1441vs, 1228m, 1211s, 1161w, 1152w, sh, 1149m, 1068s, 1042s, 1033w, 1010s, 995m, 990vw, 779w, 764s, 743ms, 696vs, 635s, 628m, 605w, 430s, ms, 400vs, 350s, 320s, and 280m, cm^{-1}. $\{[(C_6H_5)_3P]_2PtCl\}^+Ti_5Cl_{19}^-$, (II), was prepared by the lit. method [2, 3].

Detection and Measurements of Ti(III) in (II)

Qualitative tests for the presence of Ti(III) in (II) were positive using the ammonia test. The amount of Ti(III) was measured indirectly by measuring the amount of H_2 produced when (II) was hydrolyzed in basic solution. 25 ml of 1 *M* KOH was added to a flask containing 1.601 g (0.813 mmol) of (II). Titanium trioxide formed under these conditions was oxidized further by water to afford H_2 and TiO_2. During the first 40 hr, this oxidation proceeded rather vigorously affording 0.463 mmol of H_2. After this period of time, oxidation of Ti(III) was extremely slow; heating at 48° with stirring for 20 hr afforded 0.070 mmol H_2. At this point the reaction residue was pale blue indicating only small amounts of Ti_2O_3. Another heating period at 60° for 60 hr yielded an additional 0.28 mmol of H_2. This second heating period changed the residue drastically to a heterogeneous mixture of orange and white solids. No trace of bluish residue could be seen in the mixtury indicating that it was relatively free of Ti_2O_3. However, to assure completeness of the reaction it was heated at 70° for an additional 15 hr during which no additional H_2 formed. The total amount of H_2 collected was 0.561 mmol and it was characterized by oxidation to water with CuO at 300 °C. The residue, a mixture of orange and white solids, was filtered and dried. Ir data: 3050w, 1677m, 1625w,sh, 1587w, 1565w, 1439vs, 1310w, 1200m,sh, 1182ms, 1155m,sh, 1120s, 1096ms, 1070w, 1028w, 999w, 970vw, 925vw, 758m,sh, 748ms, 720s, 695vs, 540vs, 528s,sh, 518s,sh, 500ms,sh, 460m, and 290w, cm^{-1}.

Detection and Measurements of Ti(III) in (I)

The qualitative test for the presence of Ti(III) in (I) was carried out by the method previously described and resulted in formation of black Ti_2O_3. Treatment of (I), 0.860 g (0.555 mmol), with 15 ml of 1 *M* KOH afforded 0.458 mmol of H_2 after heating at 60° for 20 hr. The residue obtained from this hydrolysis was identical in appearance and its ir spectrum was identical to that of hydrolyzed (II).

Reaction of (I): Acetonitrile

Excess CH_3CN was condensed onto 0.842 g (0.543 mmol) of (I) at –78°. The solution was allowed to warm slowly to 25° with stirring to afford a white precipitate and a clear blue solution. The white precipitate was separated by filtration and dried to afford 0.371 g of the *cis*-$[(C_6H_5)_3P]_2PtCl_2$ which was characterized by comparison of its ir spectrum with that of the authentic compound. An equivolume of cyclopentane was added to the clear blue filtrate affording a greenish-blue solution and a small amount of yellow precipitate, 0.071 g. This yellow material was diamagnetic (Faraday method) and contained Ti(IV), ammonia test, m.p. 201–203°. Ir data: 3080w, 2425s, 1910w, 1825w, 1680w, 1587w, 1573w, 1485s, 1440vs, 1338w, 1320w, 1168s, 1150w, 1113vs, 1070w, 1028w, 995w, 869vs, 760vs, 722vs, 692vs, 540w, 500vs, 430m, and 318vs, cm^{-1}. The filtrate was reduced in volume and cyclopentane added to afford a blue precipitate and a slightly greenish-blue filtrate. This procedure was repeated to afford an additional small amount of blue precipitate and a blue filtrate. The total mass of blue solid was 0.265 g and identified by its ir spectrum as $TiCl_3(CH_3CN)_3$.

Preparation of $TiCl_4\cdot P(C_6H_5)_3\cdot CH_3CN$

$TiCl_4\cdot P(C_6H_5)_3$, was refluxed in CH_3CN at 85° under dry nitrogen for 72 hr to afford a green solution. At 25° this reaction system consisted of a mixture of blue, red and grey solid material and a yellow solution. Filtration and solvent removed, *in vacuo,* affords a yellow crystalling solid identical in ir spectrum and m.p. to that produced by the reaction of (I) and CH_3CN, *i.e.*, $TiCl_4\cdot P(C_6H_5)_3\cdot CH_3CN$.

Reaction of (I) with Pyridine

An excess of py was condensed onto 0.40 g (0.26 mmol) of (I) at –78° and allowed to warm to and maintained at 0° for 1 hr. The green precipitate was dissolved in CH_3CN and filtered to afford *ca.* 0.3 g of yellow-green solid after removal of CH_3CN. This solid contained a trace amount of *cis*-$((C_6H_5)_3P)_2PtCl_2$ which was identified by its ir spectrum. The insoluble material was washed with CH_3CN and benzene and identified as pure *cis*-$((C_6H_5)_3P)_2PtCl_2$ by its ir spectrum. Redissolving of the yellow-green solid, in a *minimum* of CH_3CN, afforded a green solution which was separated from a white precipitate by filtration to afford *ca.* 0.18 g $TiCl_3(py)_3$. The white precipitate was washed with benzene and identified as *cis*-$Cl_2Pt(P(C_6H_5)_3)_2$ by its ir spectrum.

Reaction of (I) with $(C_2H_5)_4NCl$

Dichloromethane was condensed onto a mixture of excess $(C_2H_5)_4NCl$ and (I), 0.3 g (0.2 mmol), at –78° and warmed to 25° with gentle stirring. An orange solid and a yellow solution resulted within one hr and were separated by filtration to afford an orange solid and a clear yellow solution. The orange solid was air sensitive turning yellow. It dissolved completely in 3*M* H_2SO_4 to afford a violet solution which yielded Ti_2O_3 when treated with ammonia, an indication of Ti(III). The orange solid has ir absorptions at: 1400ms, 1308m, 1270w, 1184s, 1175m, sh, 1120w, 1080w, 1033s, 1009s, 969m, 895w, 792s, 742w, sh, 720m, and 322vs, cm^{-1}. After solvent removal, the light yellow precipitate was determined to be free from Ti by the peroxide test. Ir data for the yellow solid: 3050w, 1585w, 1570vw, 1480vw, 1473vs, 1409w, 1312w, 1182ms, 1155m, 1119m, 1096s, 1090s, 1071w, sh, 1028m, 1000m, 968w, 804m, 754s, 744vs, 720s, sh, 693vs, 615vw, 548vs, 527vs, 514vs, 498s, 464w, 420w, 318ms, and 292m cm^{-1}.

When the reactants were used in equimolar amounts, a dark brown solid and a clear brown solution were obtained. The solid contained Ti(III) as indicated by the ammonia test. Ir data: 1483vs, 1440vs, 1392m, 1185w, sh, 1171m, 1120m, 1090w, 1060w, 1000m, 783m, 745m, 720m, 690m, 538m, 520m, 496w, 391vs, 370vs, 316w, 260ms, sh, and 258s, cm^{-1}. The filtrate, after solvent removal, yielded a light brown solid which gave negative ammonia and peroxide tests for Ti(III) and Ti(IV), respectively. Ir data on the light brown solid: 3050w, 1583w, 1570w, 1477vs, 1433vs, 1310w, 1180w, 1160w, 1120ms, 1090vs, 1025m, 1000ms, 920vw, 845w, 780w, 743vs, 690vs, 615w, 545ms, 520vs, 495s, 460vs, 420ms, 365ms, 345ms, 320ms, and 290w, cm^{-1}.

Reaction of (I) with Tetraisopentylammonium Iodide, $[CH_3CH_2CH(CH_3)_2]_4NI$

Equal molar quantities of (I), 0.3 g (0.2 mmol), and the iodide salt were treated with several ml CH_3Cl_2 at −78°. A brown solution was immediately obtained and the reaction mixture warmed to 25° to afford a clear brown solution. Reduction of the solution volume resulted in precipitation of an orange, microcrystalline solid which was separated by filtration. This material was air stable, gave a negative peroxide test for Ti, and was identified as *trans*-$(C_6H_5)_3P)_2PtI_2$ by its m.p. and ir spectrum. Ir data: 3050w, 1582w, 1570w, 1470vs, 1432vs, 1309m, 1269m, 1180m, 1158m, 1098vs, 1092vs, sh, 1070m, 1028m, 999m, 970vs, 855vs, sh, 840w, 755s, 742s, 703s, 693vs, 617w, 523vs, 512vs, 499s, 461m, 430m, and 422m, sh, cm^{-1}. The filtrate, after solvent removal, afforded a solid which appeared to be a mixture of brown and yellowish solids. The ammonia test indicated that this solid contained Ti(III). Ir data: 3050w, 1585w, 1570vs, 1370vs, 1350m, 1295w, 1170s, sh, 1160s, 1122m, 1096w, 1090w, 1070vs, 1045w, 1029w, 999w, 950w, 929m, 880m, 834w, 768m, 745m, 720m, 692s, 540m, 520m, 510m, 498m, 428w, 330vs, and 305vs, cm^{-1}.

Reaction of (I) with $(C_2H_5)_4NPF_6$

(I), 0.5 g (0.3 mmol), was treated with excess $(C_2H_5)_4NPF_6$ and several ml of CH_2Cl_2 at −78°. The solution mixture was warmed and stirred for 1 hr at 25°, yielding a light yellow solution and a dark colored residue. The unreacted $(C_2H_5)_4NPF_6$ was also observed as a colorless solid. The mixture was separated by filtration to afford a greyish black and white precipitate, and a clear yellow solution. The precipitate was repeatedly washed with the original solvent and unreacted NEt_4PF_6 successfully removed from the residue. The dark brown solid tested positive for Ti(III) with ammonia, and contained ir absorptions at: 1485vs, 1440s, 1393s, 1186m, 1175s, 1098w, 1060w, 1030w, sh, 1000m, 850ms, 840s, 785ms, 745w, 725w, 693w, 560m, 550m, 530w, 518vw, 390vs, 370vs, 360vs, 315w, 285m, sh, 270s, and 257vs, cm^{-1}. The yellow filtrate, after solvent removal, yielded a pale yellow solid which seemed to be a heterogeneous mixture of yellow and white solids. The peroxide test indicated only traces of titanium. Ir data: 1588w, 1575w, 1482s, 1441s, 1410m, 1313m, 1189ms, 1095m, 1080m, 1032m, 1010ms, 880s, sh, 840v, vs, 798ms, sh, 790ms, 745m, 732w, sh, 705ms, sh, 695ms, 560vs, 525s, 518s, sh, and 498m, cm^{-1}.

Reaction of (I) with BF_3

Boron trifluoride, 1.80 mmol, was condensed onto 0.255 g (0.165 mmol) (I) and CH_2Cl_2 at −196°, and the reaction mixture warmed and maintained with stirring at 0° for 24 h, P_{BF_3} = 600 torr. The solvent and BF_3 were removed and fractionated through a −112° trap into a −196° trap. The condensate in the −112° trap was characterized as the solvent, CH_2Cl_2, by its ir spectrum. The condensate in the −196° trap was BF_3, 1.75 mmol, and characterized by ir spectroscopy. The infrared spectrum of the brown solid reaction product obtained was identical to that of (I). This reaction was also carried out in the absence of the solvent. The reaction conditions were similar to those above except for the reaction temperature which was 25°.

Reaction of (I) with BCl_3

Boron trichloride, 1.78 mmol, was condensed onto (I), 0.339 g (0.218 mmol) (I) and CH_2Cl_2 at −196°, and the reaction mixture warmed to and maintained at 0° throughout the course of the reaction. The reaction mixture was stirred for 15 h without noticeable change. The solvent and unreacted BCl_3 were removed but quantitative separation was not achieved due to their similar vapor pressures. For the solid state reaction, a large excess amount of BCl_3, 16.343 mmol, was condensed into a flask containing (I), 0.371 g (0.24 mmol), at −196° and the reaction mixture stirred with liquid BCl_3 at 0° for 18 h. The recovered BCl_3 was fractionated through −45° and −78° traps; no other gaseous products were obtained, and the amount of BCl_3 recovered determined 16.18 mmol. The solid reaction residue was greenish-brown in color but its ir spectrum was identical to that of (I).

Reaction of (I) with HCl

Hydrogen chloride, 1.615 mmol, was condensed onto (I), 0.479 g (0.307 mmol), and CH_2Cl_2 at −196°. The reaction mixture was warmed to and maintained with stirring at 0° for 26 h, $P_{HCl} \sim 1$ atm. Unreacted HCl recovered, after purification through a −126° trap to remove CH_2Cl_2, was 1.323 mmol. The condensate in the −126° trap was characterized as pure CH_2Cl_2 by its ir spectrum and vapor pressure. The brown solid remaining in the flask had an ir spectrum identical to that of (I). Similar results were obtained when the reaction was carried out in the absence of solvent under *ca.* 1 atm of HCl at 25°, for 14 h.

Reaction of (I) with CO

I), 0.472 g (0.304 mmol) was dissolved in ODCB with CO above the solution, 700 torr. The reaction mixture was stirred at 25° for 13 h after which a clear brown solution was obtained. Unreacted CO and the solvent were removed at 35° and the solvent determined to be pure ODCB by ir spectroscopy. The amorphous greenish-brown product contained ir absorptions at: 3050w, 2108ms, 1582w, 1569w, 1475s, sh, 1440vs, 1310w, 1180w, 1159w, 1120s, 1092s, 1060m, 1035m, 1025m, 998m, 889w, 845w, 748vs, 703s, sh, 690vs, 659w, 618vw, 544w, sh, 534m, 520vs, 511vs, 495m, 460w, 390s, br, 320w, 285m, and 257m, cm^{-1}. Pyrolysis of this product, 140° for 3 h affords CO, 0.088 mmol. The ir spectrum of the pyrolysis residue contains absorptions at: 3060w, 2110vw, 1590w, 1575vw, 1480s, 1440vs, 1310w, 1189m, 1162w, 1120s, 1095s, 1065m, 1025m, 999s, 970vw, 880w, 845w, 743s, 728s, 703vs, sh, 690vs, 618vw, 540m, 522vs, 499m, 460w, 390ms, 360ms, and 270w, cm^{-1}. A ^{31}P nmr spectrum of the product from (I) and CO indicates the presence of *trans*-$[(C_6H_5)_3P]_2PtCOCl^+$; δ = 19.6 ppm from 85% H_2PO_4; $^1J_{Pt-P}$ = 1975 Hz; $[(C_6H_5)_3P]_3PtCl^+$; $\delta = -22.9$ ppm, (P_A), $^1J_{Pt-P_A} = 2481$, $^2J_{P_AP_B}$ 18 Hz; δ = 12.2 ppm (P_B), $^1J_{Pt-P}$ = 3642 Hz, $^2J_{P_AP_B}$ = 18 Hz.

Reactions of (I) and C_2H_5

Ethylene, 0.971 mmol, was condensed onto (I), 0.526 g (0.340 mmol), and CH_2Cl_2 at −196°. The reaction mixture was stirred at room temperature for *ca.* 22 h, $P_{ethylene}$ = 400 torr. Ethylene, 0.968 mmol, was recovered and the spectrum of the residue was identical to (I).

References

1 In partial fulfillment of the Ph.D. degree, The Ohio State University (1976).

2 S. Wongnawa and E. P. Schram, *Inorg. Chem., 16,* 1001 (1977).

3 J. F. Plummer and E. P. Schram, *Inorg. Chem., 14,* 1505 (1975).

4 G. S. Rao, *Z. Anorg. Allg. Chem., 304,* 351 (1960).

5 G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.,* 33 (1963).

6 G. S. Kyker and E. P. Schram, *Inorg. Chem., 8,* 2306 (1969).

7 'The Aldrich Library of Infrared Spectra', Aldrich Chemical Co., Inc. (1970) p. 873.

8 R. D. Gillard and M. F. Pilbrow, *J. Chem. Soc. Dalton,* 2320 (1974).

9 Tong-Wai Lee and R. Stoufer, *J. Am. Chem. Soc., 97,* 195 (1975).

10 G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds', Vol. 1, Methuen, London (1967) p. 293.

11 T. R. Durkin and E. P. Schram, *Inorg. Chem., 11,* 1054 (1972).

12 R. L. Amster and R. C. Taylor, *Spectrochim. Acta, 20,* 1487 (1964).

13 R. N. Scott, D. F. Shriver and L. Vaska, *J. Am. Chem. Soc., 90,* 1079 (1968).

14 M. Fishwick, H. Noth, W. Petz, and M. G. H. Wallbridge, *Inorg. Chem., 15,* 490 (1976).

15 M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Comm.,* 129 (1966).

16 M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc., 91,* 6983 (1969).

17 T. C. Wallington, *J. Phys. Chem., 70,* 11 (1966).

18 J. C. Evans and G. Y-S. Lo, *J. Chem. Soc.,* 1708 (1968).

19 H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc., 90,* 2259 (1968).

20 D. R. Stull, *Ind. and Eng. Chem., 39,* 519 (1947).

21 D. F. Shriver, 'The Manipulations of Air-Sensitive Compounds', McGraw-Hill, N.Y. (1969) p. 270.

22 R. N. Keller, *Inorg. Syn., 2,* 247 (1946).

23 G. B. Kauffman and D. O. Cowan, *Inorg. Syn., 7,* 239 (1968).

24 L. Malatesta and C. Cariello, *J. Chem. Soc.,* 2323 (1968).