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Triphenylphosphine Adducts of Titanium(IV) Bromide

C. M. F. RAE and K. R. SEDDON

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, U.K.

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Although a number of phosphine complexes of titanium(IV) chloride have been characterized,[1-10] there are no known phosphine adducts of titanium (IV) bromide. Previous attempts to prepare these complexes have resulted in the titanium being reduced to the tervalent state.[4,5] We report here the preparation of $TiBr_4(PPh_3)_2$ and $TiBr_4(PPh_3)$, and discuss the possible structures of these complexes.

Results and Discussion

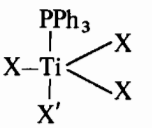
The room temperature reaction between titanium (IV) bromide and triphenylphosphine in hexane resulted in products with low Ti:Br ratios (typically, 1:3.28). This is consistent with a report[5] that triphenylphosphine reduces $TiBr_4$ in benzene solution. However, if the reaction is allowed to occur at low temperature, no reduction is observed. With a six-fold molar excess of phosphine:titanium, the dark brown diamagnetic powder, $TiBr_4(PPh_3)_2$, was isolated. With a six-fold molar excess of titanium: phosphine, a dark maroon diamagnetic powder, $TiBr_4(PPh_3)$, was isolated. Both these products were extremely moisture sensitive, and were hydrolysed by dilute acid to yield pure triphenylphosphine. Reactions in which only a 2 or 3-fold excess of ligand were used resulted in the formation of mixtures of $TiBr_4(PPh_3)_2$ and $TiBr_4(PPh_3)$.

Analogous low temperature reactions were carried out using $TiCl_4$ in hexane. With a 6:1 excess of phosphine, the well established $TiCl_4(PPh_3)_2$[3,5,6,10] was formed. With a 6:1 excess of $TiCl_4$, $TiCl_4(PPh_3)$ was isolated. This has been reported in Westland and Westland[6] and by Calderazzo *et al.*[10] However, the infrared data reported by these authors are at variance. We confirm the results of Calderazzo *et al.* A spectrum similar to that reported by Westland was obtained by using only a 2:1 excess of $TiCl_4$, which resulted in the formation of a mixture of $TiCl_4(PPh_3)_2$ and $TiCl_4(PPh_3)$.

The metal–halogen stretching frequencies for $TiX_4(PPh_3)_n$ [X = Cl, Br; n = 1, 2] are reported in the Table. The six-coordinate complexes have been assigned assuming a *cis*-octahedral configuration;[5,10] the five-coordinate complexes have been assigned assuming a C_{3v} structure.[8,10]

TABLE. Metal–Halogen Stretching Frequencies (Units of cm^{-1}).

		X = Cl	X = Br	ν(TiBr)/ν(TiCl)
$TiX_4(PPh_3)$	$\nu(TiX_3)_{as}$	467 s	352 s	0.77
	ν(TiX')	453 s		
	$\nu(TiX_3)_{sym}$	378 vs, br	306 s, br	0.81
$TiX_4(PPh_3)_2$		381 vs	308, 301 vs	0.80
		355 sh	279 w	0.79
		325 m, br	256 m, br	0.79



The consistency of the ν(TiBr)/ν(TiCl) ratio corroborates the assumption that the chloride and bromide complexes are isostructural.[11]

Both $TiBr_4(PPh_3)_2$ and $TiBr_4(PPh_3)$ are extremely soluble in dichloromethane, and a variable temperature ^{31}P nmr study of these and related complexes is in progress.

Experimental

Preparation and Purification of Starting Materials

Titanium(IV) bromide (prepared by the reaction of titanium metal with liquid bromine[12]) and titanium(IV) chloride (*ex* B.D.H.) were distilled *in vacuo* prior to use. Triphenylphosphine (*ex* B.D.H.) was dried *in vacuo*, and hexane was dried by refluxing over phosphorus pentoxide.

All manipulations were performed under dry nitrogen or *in vacuo*.

Physical Methods and Analyses

Infrared spectra were measured on Perkin–Elmer 457 and 577 spectrophotometers. Magnetic susceptibility measurements were made at room temperature by the Gouy method. Titanium was determined gravimetrically as TiO_2, and halide as silver halide. C, H, P and Br analyses were performed by the Butterworth Microanalytical Consultancy, Ltd.

Preparation of Tetrabromobis(triphenylphosphine) titanium(IV)

Titanium(IV) bromide (2.81 g) was condensed on to a frozen solution of triphenylphosphine (12.03 g) in hexane (500 cm^3) at −196 °C, and then the mixture was slowly allowed to warm up to room temperature. The mixture was well shaken and filtered *in vacuo* to yield a dark solid and a pale orange filtrate. The solid was washed with hexane (500 cm^3), in which it was slightly soluble (giving a red solution), and dried *in vacuo* for twenty-four hours. The product was a dark brown, diamagnetic powder. Found: C, 48.3; H, 3.50; Br, 36.0; P, 7.08; Ti, 5.4%. $C_{36}H_{30}Br_4P_2Ti$ requires: C, 48.47; H, 3.39; Br, 35.83; P, 6.94; Ti, 5.37%.

Preparation of Tetrabromo(triphenylphosphine) titanium(IV)

Titanium(IV) bromide (18.60 g) was condensed on to a frozen solution of triphenylphosphine (2.21 g) in hexane (250 cm^3) at −196 °C, and then the mixture was slowly allowed to warm up to room temperature. The dark maroon, diamagnetic powder was isolated, washed and dried as described above. Found: C, 34.1; H, 2.42; Br, 51.1; P, 4.87; Ti, 7.66%. $C_{18}H_{15}Br_4PTi$ requires: C, 34.29; H, 2.40; Br, 50.75; P, 4.92; Ti, 7.60%.

Preparation of Tetrachloro(triphenylphosphine) titanium(IV)

Titanium(IV) chloride (6.38 cm^3) was condensed on to a frozen solution of triphenylphosphine (2.54 g) in hexane (250 cm^3) at −196 °C, and then the mixture was slowly allowed to warm up to room temperature. The dark aubergine, diamagnetic powder was isolated, washed and dried as described above. Found: C, 47.6; H, 3.47; Cl, 31.2; P, 7.01; Ti, 10.7%. $C_{18}H_{15}Cl_4PTi$ requires: C, 47.83; H, 3.34; Cl, 31.37; P, 6.85; Ti, 10.60%.

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