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THE REACTION OF $RTiBr_3$ (R = METHYL, PHENYL AND *p*-TOLYL) WITH SOME MONODENTATE AND BIDENTATE LIGANDS

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Summary

$RTiBr_3$ ($R = CH_3$, C_6H_5 and $(4\text{-}CH_3)C_6H_4$) forms 1/2 adducts, $RTiBr_3,2L$, with a number of monodentate ligands containing nitrogen, oxygen and sulphur donor atoms. Bidentate ligands normally give 1/1 adducts, as do the bulky monodentate ligands $(C_6H_5)_3P$ and $(C_6H_5)_3PO$. Dioxan gives 1/1 adducts with CH_3TiBr_3 and $C_6H_5TiBr_5$ but a 1/2 adduct with $(4\text{-}CH_3)C_6H_4TiBr_3$.

Structures are assigned on the basis of IR and NMR data.

Introduction

The chemistry of CH_3TiCl_3 is well documented [1—8], but comparatively little is known of the analogous bromo compound, the only reported coordination compounds being CH_3TiBr_3, bipy [9] and such anonic complexes as $[(CH_3)_2Ti_2Br_7]^-$, $[(CH_3)_2Ti_2Br_8]^{2-}$ and $[CH_3TiBr_5]^{2-}$ [8]. The aryl analogues are even less investigated, although $C_6H_5TiCl_3$ is said to be explosive and an attempted preparation of $C_6H_5TiBr_3$ from $(C_6H_5)_2Zn$ and $TiBr_4$ was unsuccessful [9].

We have now prepared the two aryl compounds $C_6H_5TiBr_3$ and $(4\text{-}CH_3)C_6H_4TiBr$ by the reaction of the appropriate aryllithium with titanium(IV) bromide, and studied their reactions (and that of CH_3TiBr_5) with a variety of monodentate and bidentate ligands.

Experimental

All the compounds were extremely sensitive to moisture and accordingly great care was taken to rigorously dry all solvents, reagents and gases. An all-glass vacuum line was used to isolate and handle the products.

Physical measurements. Spectra were measured as previously described [6]. Molecular weight determinations were made cryoscopically on benzene solutions.

Preparation of CH_3TiBr_3. Titanium(IV) bromide was allowed to react with $Zn(CH_3)_2$, and CH_3TiBr_3 was isolated at 195 K as red crystals [8,9].

Preparation of $C_6H_5TiBr_3$ and $(4\text{-}CH_3)C_6H_4TiBr_3$. Titanium(IV) bromide (0.1 mol) was added to n-pentane (150 cm^3) in a three-necked flask cooled to 195 K, and the aryllithium (0.11 mol) added dropwise as an n-pentane solution. The reaction mixture was stirred for 4 h at 195 K and the precipitated lithium bromide was removed by filtration in vacuo; partial removal of solvent from the filtrate by evaporation at room temperature resulted in the deposition of red crystals of $ArTiBr_3$ (Ar = C_6H_5 or $(4\text{-}CH_3)C_6H_4$) when the solution was again cooled to 195 K.

Preparation of coordination compounds of $RTiBr_3$. n-Pentane solutions of CH_3TiBr_3 and $C_6H_5TiBr_3$, and a toluene solution of $(4\text{-}CH_3)C_6H_4TiBr_3$, were used in the preparation of complexes. Solid ligands were used as toluene solutions except for 2,2'-bipyridyl which was dissolved in ether; liquid ligands were dissolved in either n-pentane or toluene to match the solvent used for $RTiBr_3$. The reactions were carried out at room temperature, the solutions of $RTiBr_3$ being added to that of the ligand, with constant stirring. Molar ratios of ligand/$RTiBr_3$ = 2.2/1 were used for all unidentate ligands, 1,4-dioxan and 1,4-thioxan, 1.1/1 for the remaining ligands. The complexes normally precipitated after 1 h and were isolated by vacuum filtration; $RTiBr_3$, 2thf, $RTiBr_3$, $2CH_3CN$ and $(4\text{-}CH_3)C_6H_4TiBr_3$, PPh_3 were more soluble and some solvent was removed at the pump to encourage precipitation.

Results and discussion

From the information given in Table 1 it can be seen that in almost every instance the stoichiometries of complexes formed by $RTiBr_3$ (R = CH_3, C_6H_5 and $(4\text{-}CH_3)C_6H_4$) are the same as those of the analogous CH_3TiCl_3 complexes. Most monodentate ligands gave 1/2 complexes, and the bidentate ligands bipy, phen, dppm, ete and pte give 1/1 complexes, suggesting six-coordinate titanium. Molecular weight studies on the thf and CH_3CN complexes, which are soluble enough for such measurements to be made, show the compounds to be monomeric thus confirming six-coordination. The 1/1 complexes formed by PPh_3 and $OPPh_3$ are dimeric (apart from $CH_3TiBr_3PPh_3$, see later) so it appears that these compounds are bromide bridged. The infrared spectra (200—400 cm^{-1}) of these six-coordinate complexes show bands that may be assigned to Ti—Br stretching modes, and comparison with the spectra of the analogous chloro complexes shows that the ration ν(Ti—Br)/ν(Ti—Cl) is close to the expected value of 0.75 [8,10]. The infrared spectra of all the compounds shows a Ti—C stretching mode in a position similar to that reported previously, as does the occurrence of the CH_3—Ti resonance in the NMR spectrum [6].

The NMR spectrum of the complex CH_3TiBr_3, dppe showed a methyl resonance at τ 8.77 ppm as a symmetrical triplet, showing that it is split by two equivalent phosphorus atoms; this indicates that the methyl group is *cis* to the two phosphorus atoms. The dppe complexes formed by the aryltitanium bromides which have the stoicheiometry $2RTiBr_3$,dppe are too insoluble for either molecular weight or NMR measurements to be made, so suggestions of structures would be speculative.

TABLE 1

ADDUCTS OF $RTiX_3$

L	Ratio $RTiX_3/L$			
	CH_3TiCl_3	CH_3TiBr_3 [a]	$C_6H_5TiBr_3$ [a]	$(4\text{-}CH_3)C_6H_4TiBr_3$ [a]
Acetonitrile	1/2 [6]	1/2	1/2	1/2
Pyridine (py)	1/2 [6]	1/2	1/2	1/2
3-Cyanopyridine (3-cpy)	—	1/2	—	—
4-Cyanopyridine (4-cpy)	—	1/2	1/1	1/2
2,2'-Bipyridyl (bipy)	1/1 [2,6]	1/1	1/1	—
1,10-Phenanthroline (phen)	1/1 [6a]	1/1	1/1	1/1
Triphenylphosphine (tpp)	1/1 [1,6]	1/1	1/1	1/1
1,2-Bis(diphenylphosphino)-ethane (dppe)	1/1 [5,6]	1/1	2/1	2/1
1,2-Bis(diphenylphosphino)-methane(dppm)	—	1/1	—	—
Tetrahydrofuran (thf)	1/1 [6] 1/2 [6]	1/2	1/2	1/2
Triphenylphosphine-oxide (tppo)	—	—	1/1	1/1
Dioxan (diox)	1/1 [1,6]	1/1	1/1	1/2
Tetrahydrothiophen (tht)	1/2 [6]	1/2	—	—
1,2-Bis(ethylthio)ethane (ete)		1/1	—	—
1,2-Bis(phenylthio)ethane (pte)	1/1 [6a]	1/1	—	—
Thioxan (thiox)	1/1 [6a] 1/2 [3,6]	1/2	—	—

[a] This work.

The 1/1, 1.4-dioxan adducts formed by $RTiBr_3$ ($R = CH_3$, or C_6H_5) have infrared spectra that show both oxygen atoms of the dioxan molecules are coordinated, since the symmetric and asymmetric COC stretching frequencies occur at appreciably lower values than those found in the spectrum of the free ligand [6]; thus, in these complexes dioxan behaves as a bidentate bridging ligand. With the complex $(4\text{-}CH_3)C_6H_4TiBr_3$, 2 diox, on the other hand, the dioxan ligand bonds through one oxygen atom only, since the infrared spectrum shows bands of both modified and unmodified COC stretching frequencies.

A 1/2 complex is also formed between CH_3TiBr_3 and thioxan and the spectroscopic evidence again favours a structure with a monodentate ligand, but in this case, with the link through sulphur rather than oxygen. Thus the infrared spectrum shows the COC stretching frequencies to be the same as in the free ligand, which rules out coordination by the oxygen atom; furthermore there is a shift of 14 cm^{-1} in the CSC stretching mode (compared to the peak position for the free ligand) [11]. Convincing evidence for sulphur coordination comes from the NMR spectra, where the resonances arising from the methylene groups adjacent to the oxygen atom are shifted by only τ 0.15 ppm on coordination, whereas the corresponding resonances for the methylene group adjacent to sulphur are shifted by τ 0.33 ppm. In the NMR spectra of the three thf complexes the corresponding shift of the α-methylene protons ranges from τ 0.56 to 0.78 ppm.

It was stated earlier that in benzene solution, CH_3TiBr_3, tppo is monomeric,

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TABLE 2

ANALYTICAL AND SPECTROSCOPIC DATA

Ligand	Adduct	Analysis (Found (calcd.) (%))			Mol. weight (found (calcd.))	Decomp. temp. (K)	NMR R—Tl [a] resonance (τ, ppm)	Infrared spectra (550—300 cm^{-1})	
		Tl	Br	N (or P or S)				ν(M—C) (cm^{-1})	Other peaks
CH$_3$CN	CH$_3$TlBr$_3$,2CH$_3$CN	12.2 (12.5)	62.0 (62.3)	—	342 (385)	392	8.71	450	330—280v (br) [b, c]
	C$_6$H$_5$TlBr$_3$,2CH$_3$CN	10.5 (10.7)	53.3 (53.7)	—	—	362	2.67	462	391m(br), 298ms(br) [b]
	(4-CH$_3$)C$_6$H$_4$TlBr$_3$,2CH$_3$CN	10.1 (10.14)	51.2 (52.1)	—	409 (461)	343	2.74; 7.57	461	[c]
py	CH$_3$TlBr$_3$,2py	10.1 (10.4)	52.0 (52.0)	6.3(6.1)	—		2.63	450	300s,br [b]
	C$_6$H$_5$TlBr$_3$,2py	9.1 (9.2)	45.8 (45.9)	5.0(5.4)	—	327	2.63	465	388m(br), 300m(br) [b]
	(4-CH$_3$)C$_6$H$_4$TlBr$_3$,2py	8.6 (8.9)	44.6 (44.7)	4.8(5.2)	—	314	—	478	389w, 309(sh) [b], 205vs(br) [b]
3-cpy	CH$_3$TlBr$_3$,2(3-cpy)	9.3 (9.4)	46.6 (47.0)	10.9(11.0)	—	—	8.70	464	395w, 365w, 290s(br) [b]
4-cpy	CH$_3$TlBr$_5$,2(4-cpy)	9.4 (9.4)	46.9 (47.0)	11.1(11.0)	—	395	—	460	390w, 292ms(br) [b]
	C$_6$H$_5$TlBr$_3$,(4-cpy)	10.1 (10.2)	50.9 (51.2)	6.0(6.0)	—	353	2.66	460	390m(br), 312ms [b], 303ms [b], 290ms [b]
	(4-CH$_3$)C$_6$H$_4$TlBr$_3$,2(4-cpy)	8.1 (8.12)	39.8 (40.9)	—	—	351	2.80; 7.67	461	380(sh), 318s(br) [e], 280s(br) [b]
bipy	CH$_3$TlBr$_3$,bipy	10.4 (10.4)	51.8 (52.3)	6.1(6.1)	—	457	8.75	475	359ms, 323(sh) [b], 300(sh) [b], 280vs [b]
	C$_6$H$_5$TlBr$_5$,bipy	9.0 (9.2)	46.1 (46.1)	5.2(5.4)	—	407	—	470	385m(br), 358m, 325m [b], 300m [b], 280ms [b]
phen	CH$_3$TlBr$_3$, phen	9.9 (9.9)	49.6 (49.7)	5.9(5.8)	—	459	—	481	330vs [b], 314vs [b], 283vs [b], 240m, 227(sh)
	C$_6$H$_5$TlBr$_3$,phen	8.6 (8.8)	43.1 (44.0)	4.9(5.1)	—	412	—	482	395ms(br), 330(hs) [b], 318ms [b], 280ms [b]
	(4-CH$_3$)C$_6$H$_4$TlBr$_3$,phen	8.6 (8.6)	42.5 (42.9)	5.0(5.0)	—	377	2.80; 7.67	482	376w, 320ms(br) [b], 283ms(br) [b]
tpp	CH$_3$TlBr$_3$,tpp	8.4 (8.5)	42.5 (42.5)	5.6 (5.5) [b]	517 (565)	391	7.50; 8.70	511	350ms(br), 280s, nr [b]

	$\mathrm{C_6H_5TiBr_3}$,tpp	7.3 (7.7)	38.2 (38.3)	4.7(5.0) ^{b}	1056 (617) ^{d}	389	^{c}	512	388m(br), 321m ^{b}, 308m ^{b}, 278m(br) ^{b}
	(4-$\mathrm{CH_3}$)$\mathrm{C_6H_4TiBr_3}$,tpp	7.3 (7.5)	37.4 (37.4)	4.8(4.8) ^{b}	1125 ^{d} (641) ^{d}	374	2.80; 7.67	535	390w, 314m ^{b}, 280(sh) ^{b}, 255ms(br)
dppe	$\mathrm{CH_3TiBr_3}$,dppe	6.7 (6.8)	34.2 (34.2)	8.6(8.8) ^{b}	—	—	8.77 (triplet)	480	345m, 295s(br) ^{b}
	2$\mathrm{C_6H_5TiBr_3}$,dppe	8.2 (8.5)	42.3 (42.6)	5.2(5.5) ^{b}	—	—	—	480	395m(br), 304(sh) ^{b}, 298vs ^{b}, 278m ^{b}
	2(4-$\mathrm{CH_3}$)$\mathrm{C_6H_4TiBr_3}$,dppe	8.2 (8.3)	41.3 (41.5)	5.2(5.4) ^{b}	—	—	—	479	
dppm	$\mathrm{CH_3TiBr_3}$, dppm	6.8 (7.0)	34.5 (34.9)	8.7(9.0) ^{b}	—	429	8.70	468	360m, 349m, 290ms(br) ^{b}
thf	$\mathrm{CH_3TiBr_3}$,2thf	10.4 (10.7)	52.7 (53.7)	—	427 (447)	—	8.69	480	318s(br) ^{b}
	$\mathrm{C_6H_5TiBr_3}$,2thf	9.1 (9.4)	47.5 (47.2)	—	479 (509)	360	2.67	482	385m(br), 295ms(br) ^{b}
	(4-$\mathrm{CH_3}$)$\mathrm{C_6H_4TiBr_3}$,2thf	9.0 (9.1)	45.9 (46.1)	—	457 (521)	338	2.80; 7.67	—	^{c}
tppo	$\mathrm{C_6H_5TiBr_3}$,tppo	7.1 (7.5)	37.5 (37.3)	4.6(4.8)	1084 (643) ^{d}	—	^{c}	485	355m, 309(sh) ^{b}, 285m ^{b}
	(4-$\mathrm{CH_3}$)$\mathrm{C_6H_4TiBr_3}$,tppo	7.1 (7.3)	36.8 (36.5)	4.8(4.7)	1034 (657) ^{d}	361	^{c}; 7.64	490	380w, 309m(br) ^{b}, 250ms(br)
diox	$\mathrm{CH_3TiBr_3}$,diox	12.1 (12.3)	61.0 (61.4)	—	—	463	—	490	338ms, 320(sh) ^{b}, 292s ^{b}
	$\mathrm{C_6H_5TiBr_3}$,diox	10.2 (10.0)	53.3 (53.0)	—	—	426	—	460	385m, 330m ^{b}, 285m ^{b}
	(4-$\mathrm{CH_3}$)$\mathrm{C_6H_4TiBr_3}$,2diox	8.5 (8.6)	42.8 (43.2)	—	—	339	—	465	380(sh), 340(br) ^{b}, 320(sh) ^{b}
tht	$\mathrm{CH_3TiBr_3}$,2tht	10.0 (10.0)	50.3 (50.1)	—	—	—	—	480	318vs(br) ^{b}
ete	$\mathrm{CH_3TiBr_3}$,ete	10.4 (10.6)	52.9 (53.0)	—	—	—	8.83	450	379m, 308(sh) ^{b}, 292vs ^{b}, 257(sh)
pte	$\mathrm{CH_3TiBr_3}$,pte	8.9 (8.7)	43.8 (43.7)	11.5(11.7)	—	394	8.90	470	380m, 323m ^{b}, 301m ^{b}, 280(sh) ^{b}
thiox	$\mathrm{CH_3TiBr_3}$,2thiox	9.2 (9.4)	46.7 (47.0)	—	—	362	8.72	452	369m, 309(sh) ^{b}, 292s(br) ^{b}, 286(sh) ^{b}, 240(sh)

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[a] Spectra measured on $\mathrm{CH_2Cl_2}$ solutions. [b] Bands provisionally assigned to ν(Ti—Br) stretching modes. [c] Broad ill-defined absorption. [d] Calculated weight for monomers.

and evidently contains five-coordinate titanium. This does not appear to be the case with the solid, however, since the mull infrared spectrum shows a strong peak at 280 cm^{-1}, which is a typical Ti—Br stretching frequency for six-coordinate species. Accordingly, we suggest that the solid has a dimeric structure, which is broken down upon dissolution in benzene. The NMR spectrum of a CH_2Cl_2 solution of the compound shows the presence of two resonances that can be attributed to the methyl group, which rules out a single monomeric species. One explanation is the possible existence of a monomer—dimer equilibrium similar to that postulated for $TiCl_4$, tppo [12].

Table 2 records the temperature at which the adducts show visible signs of decomposition. These temperatures are very much higher than the corresponding ones for the parent organometallic compounds, all of which decompose quite readily at room temperature. In NMR experiments on solutions of $C_6H_5TiBr_3$ and $(4\text{-}CH_3)C_6H_4TiBr_3$, decomposition was observed with the formation of benzene and toluene, respectively rather than biphenyl and 4,4′-biphenyl.

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