Reactions of Trimethylsilylcyclopentadiene Derivatives with Titanium, Niobium, and Tantalum Halides

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The use of trimethylsilyl derivatives as effective reagents for the new or improved syntheses of complexes of the early transition metals is described. Improved routes, involving the use of trimethylsilylcyclopentadiene, are described for the syntheses of $[TiCl_3(cp)]$, $[TiBr_3(cp)]$, $[TiI_3(cp)]$, $[NbCl_4(cp)]$, and $[TaCl_4(cp)]$ (cp = cyclopentadienyl). Routes, involving the use of bis(trimethylsilyl)cyclopentadiene, are described for the syntheses of the analogous complexes $[TiX_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$, where X = Cl, Br, or I. The reactions of $[TiCl_3(cp)]$, $[TiBr_3(cp)]$, and $[TiCl_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$ with a variety of bidentate ligands are described. The Lewis acidity of these titanium compounds is much reduced from that of the parent tetrahalides and only two adducts have been positively identified: these are $[TiCl_3(cp)]\cdot$phen (phen = *o*-phenanthroline) and $[TiCl_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]\cdot$pdma (pdma = *o*-phenylenebisdimethylarsine).

THE organometallic chemistry of titanium which, in 1968 [1] and even in the early 1970's was relatively poorly developed,[2] has recently been recognized (along with that of other early transition metals) as being a fertile area for new synthetic studies.[3] Cyclopentadienyl chemistry in particular has developed rapidly since the unravelling of the controversies concerning the structure of 'titanocene'.[4-7] Since further synthetic studies in this area are likely to lead to increased understanding of the chemistries of the early transition elements, and to the factors governing their reactivities towards hydrocarbon ligands, we have embarked on a study of the reactions of trimethylsilylcyclopentadiene and bis(trimethylsilyl)cyclopentadiene with halides of Groups 4 and 5. This has led to the discovery of improved synthetic routes to, and the synthesis of, a number of cyclopentadienyl derivatives of the early transition elements; the properties of the complexes are described. The new routes to the niobium and tantalum complexes complement the related ones, reported independently by Bunker *et al.*,[8] involving the use of trialkylcyclopentadienyltin compounds, and Burt *et al.*[9] involving the use of $Mg(C_5H_5)_2$ or $Sn(CH_3)_3(C_5H_5)$.

We have also investigated further [10] the Lewis acidity of $[TiCl_3(cp)]$ and $[TiBr_3(cp)]$ (cp = cyclopentadiene) with a variety of bidentate ligands and demonstrated that this is much reduced over that established for the parent halides.

EXPERIMENTAL

All solvents were dried immediately before use according to standard procedures.

Titanium tetrachloride, titanium tetrabromide, niobium pentachloride, and tantalum pentachloride were commercial products and used as such. Titanium tetraiodide was purified by vacuum sublimation at 140—150 °C (10^{-2} Torr).†

o-Phenanthroline was obtained by dehydration of the monohydrate using a Dean-and-Stark head and was then purified by vacuum sublimation at 110—120 °C (10^{-2} Torr).

NNN'N'-Tetramethylethylenediamine, 2,5-dithiahexane, and 1,2-dimethoxyethane were dried over calcium hydride.

o-Phenylenebis(dimethylarsine) was prepared by the staff of the Synthetic Chemicals Laboratory of this Department.

Trimethylsilylcyclopentadiene was prepared by treating sodium cyclopentadienide (1 mol) with chlorotrimethylsilane (1 mol). Distillation at 36 °C (13 Torr) afforded pure trimethylsilylcyclopentadiene. Further distillation at 40 °C (0.1 Torr) afforded pure bis(trimethylsilyl)cyclopentadiene.

Preparations of Complexes.—*Reaction of trimethylsilylcyclopentadiene with titanium tetrachloride.* To titanium tetrachloride (12.5 g, 66 mmol) in 40 cm³ of benzene, was slowly added trimethylsilylcyclopentadiene (9.17 g, 66 mmol) with stirring. The reaction is rather violent with evolution of heat and precipitation of a yellow solid is virtually immediate. The reaction mixture was stirred for a further 30 min. The product was filtered off, washed with two 20-cm³ portions of benzene, and dried. Sublimation at 120—130 °C (10^{-1} Torr) yielded yellow crystals of cyclopentadienyltitanium trichloride (13.3 g, 92%), m.p. 198—201 °C (lit. 208—211 °C).[11]

Reaction of trimethylsilylcyclopentadiene with titanium tetrabromide. To titanium tetrabromide (17.2 g, 47 mmol) in 75 cm³ of dichloromethane, was added trimethylsilylcyclopentadiene (6.47 g, 47 mmol). The reaction mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure, leaving an orange-brown residue. After removing any trace of unreacted titanium tetrabromide by sublimation onto a −80 °C probe at 90 °C (10^{-1} Torr), cyclopentadienyltitanium tribromide (13.6 g, 82%) was then isolated as orange crystals by further sublimation at 130 °C (10^{-1} Torr), m.p. 179—181 °C (lit. 197—199 °C).[11]

Reaction of trimethylsilylcyclopentadiene with titanium tetraiodide. To titanium tetraiodide (5.98 g, 11 mmol) in 150 cm³ of benzene was added trimethylsilylcyclopentadiene (1.50 g, 11 mmol) and the reaction maintained under reflux for 1 h, affording a deep red solution. The solvent was removed under reduced pressure and the product, cyclopentadienyltitanium tri-iodide (3.71 g, 70%), was sublimed onto a cold water probe as black crystals, m.p. 148—150 °C (lit. 148—150 °C).[11]

Reaction of trimethylsilylcyclopentadiene with niobium pentachloride. To a rapidly stirred suspension of niobium pentachloride (4.87 g, 18 mmol) in 200 cm³ of dichloromethane, trimethylsilylcyclopentadiene (2.50 g, 18 mmol) was added slowly. The reaction mixture was maintained

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

under reflux for 10 min. On cooling to room temperature the red crystals of cyclopentadienylniobium tetrachloride (4.98 g, 93%) were filtered off and washed with 50 cm^3 of dry dichloromethane, m.p. (decomp.) 180 °C (Found: C, 19.8; H, 1.75; Cl, 47.2. $C_5H_5Cl_4Nb$ requires C, 20.0; H, 1.70; Cl, 47.3%). The major metal-containing fragments in the mass spectrum occur at *m/e* (*I*) values of: $NbCl_3(cp)^+$ 263 (60), $NbCl_2(cp)^+$ 228 (21), $NbCl_4^+$ 233 (20), $NbCl_3^+$ 198 (45), $NbCl_2^+$ 163 (76), $NbCl^+$ 128 (57), Nb^+ 93 (17), together with some fragments arising from oxygen-containing impurities formed in the mass spectrometer.

Reaction of trimethylsilylcyclopentadiene with tantalum pentachloride. To tantalum pentachloride (25 g, 70 mmol) in 500 cm^3 of dichloromethane was added slowly trimethylsilylcyclopentadiene (9.64 g, 70 mmol). The reaction mixture was heated under reflux for 10 min. On cooling to room temperature, the yellow-green crystals of cyclopentadienyltantalum tetrachloride (25.6 g, 95%) were filtered off and washed with dichloromethane, m.p. (decomp.) 190 °C (Found: C, 15.9; H, 1.60; Cl, 36.4. $C_5H_5Cl_4Ta$ requires C, 15.5; H, 1.3; Cl, 36.6%). The major metal-containing fragments in the mass spectrum occur at *m/e* (*I*) values of $TaCl_3(cp)^+$ 351 (100), $TaCl_4^+$ 321 (95), $TaCl_3^+$ 286 (70), $TaCl_2^+$ 251 (24), $TaCl^+$ 216 (7.5), and Ta^+ 181 (1.5).

Reaction of bis(trimethylsilyl)cyclopentadiene with titanium tetrachloride. A mixture of titanium tetrachloride (7.35 g, 39 mmol) and bis(trimethylsilyl)cyclopentadiene (8.10 g, 38 mmol) in 30 cm^3 of benzene was stirred for 5 min. The solvent was evaporated from the solution leaving a brown solid. Sublimation of the residue at 100—120 °C (10^{-1} Torr) afforded yellow crystals of trimethylsilylcyclopentadienyltitanium trichloride (9.16 g, 82%), m.p. 64—64.5 °C (Found: C, 32.6; H, 4.55; Cl, 36.6. $C_8H_{13}Cl_3SiTi$ requires C, 32.9; H, 4.50; Cl, 36.5%).

Reaction of bis(trimethylsilyl)cyclopentadiene with titanium tetrabromide. A mixture of titanium tetrabromide (2.28 g, 6 mmol) and bis(trimethylsilyl)cyclopentadiene (1.31 g, 6 mmol) in 30 cm^3 of dichloromethane was stirred for 30 min. The solvent was removed under reduced pressure and the brown residue sublimed at 110—120 °C (10^{-1} Torr) to yield orange crystals of trimethylsilylcyclopentadienyltitanium tribromide (1.50 g, 59%), m.p. 75—76 °C (Found: C, 23.3; H, 3.55; Br, 56.3. $C_8H_{13}Br_3SiTi$ requires C, 22.6; H, 3.10; Br, 56.4%).

Reaction of bis(trimethylsilyl)cyclopentadiene with titanium tetraiodide. To titanium tetraiodide (4.75 g, 8 mmol) in 150 cm^3 of benzene, was slowly added bis(trimethylsilyl)-cyclopentadiene (1.80 g, 8 mmol). The reaction mixture was heated and maintained under reflux for 1 h. Removal of the solvent under reduced pressure was followed by sublimation of the residue at 140 °C (10^{-1} Torr). This afforded the black trimethylsilylcyclopentadienyltitanium tri-iodide (1.90 g, 42%), m.p. 97—98 °C (Found: C, 17.1; H, 2.50; I, 67.1. $C_8H_{13}I_3SiTi$ requires C, 17.0; H, 2.30; I, 67.3%).

Redistribution reaction of monocyclopentadienyltitanium trichloride with monocyclopentadienyltitanium tribromide. A mixture of cyclopentadienyltitanium tribromide (2.11 g, 6 mmol) and cyclopentadienyltitanium trichloride (2.61 g, 12 mmol) in 20 cm^3 of benzene was sealed in an evacuated tube and heated at 80 °C for two days. On opening the tube the solvent was removed under reduced pressure leaving a yellow-orange solid, which was shown to be a mixture of redistribution products.

Reaction of cyclopentadienyltitanium trichloride with o-*phenanthroline.* To cyclopentadienyltitanium trichloride (1.50 g, 7 mmol) in 40 cm^3 of toluene, was added a solution of *o*-phenanthroline (1.26 g, 7 mmol) in 30 cm^3 of toluene. Precipitation of a dark pink solid was immediate. The reaction mixture was stirred for 20 min and the product isolated by filtration, washed with toluene, and dried, m.p. (decomp.) 165 °C (Found: C, 51.8; H, 4.00; Cl, 26.4; N, 7.75. $C_{17}H_{13}Cl_3N_2Ti$ requires C, 51.1; H, 3.30; Cl, 26.6; N, 7.00%).

Reaction of cyclopentadienyltitanium tribromide with o-*phenylenebis(dimethylarsine).* To cyclopentadienyltitanium tribromide (0.8 g, 2.2 mmol) in 40 cm^3 of toluene, was added *o*-phenylenebis(dimethylarsine)(pdma) with constant stirring, and the solution was kept at room temperature for 30 min. The colour changed from orange to red. Removal of the solvent under reduced pressure left a red solid which was purified by vacuum sublimation at 140 °C (10^{-1} Torr), m.p. 181—183 °C (Found: C, 29.5; H, 3.65; Br, 39.1. $C_{15}H_{21}As_2Br_3Ti$ requires C, 28.2; H, 3.30; Br, 37.5%).

Reaction of trimethylsilylcyclopentadienyltitanium trichloride with o-*phenylenebis(dimethylarsine).* To trimethylsilylcyclopentadienyltitanium trichloride (0.43 g, 1.4 mmol) in 10 cm^3 of benzene was added pdma. The colour of the solution changed to orange. After stirring for 15 min, the solvent was removed under reduced pressure, leaving an orange solid which was purified by sublimation at 130 °C (10^{-1} Torr), m.p. 90—93 °C (Found: C, 37.8; H, 5.10; Cl, 18.4. $C_{18}H_{29}As_2Cl_3SiTi$ requires C, 37.45; H, 5.05; Cl, 18.4%).

Apparatus.—Melting points (uncorrected) were determined by mounting the sample in a sealed capillary tube, and using a Gallenkamp hot-stage apparatus.

Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer.

N.m.r. spectra were recorded on a Perkin-Elmer R12 or HA100 spectrometer. Spectra were calibrated with respect to tetramethylsilane at τ 10.

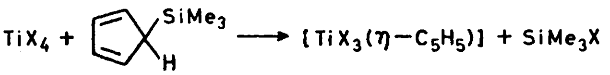
Mass spectra were recorded with a MS12 spectrometer.

RESULTS AND DISCUSSION

η-Cyclopentadienyl Titanium Trihalides.—A number of routes are currently available (many in the patent literature) for the synthesis of the monocyclopentadienyl derivatives $[TiX_3(\eta-C_5H_5)]$ (X = Cl, Br, or I), but none is entirely satisfactory. The known routes use either the action of a metal cyclopentadienide [12-16] or cyclopentadiene [14] on a titanium halide, or conversion of a cyclopentadienyl titanium derivative to the appropriate halide.[11,15,17-24] It is also possible to prepare a variety of ring-substituted species by treatment of substituted cyclopentadienes with metal halides.

The method for the preparation of η-cyclopentadienyltitanium trihalides which, until now, has been most satisfactory, has been the one which involves the preliminary formation of $[TiCl_2(\eta-C_5H_5)_2]$ and subsequent treatment of this product with titanium tetrachloride; although this is not a difficult preparation, it is rather time consuming, and the final product is only obtained in low yield.

We have found that the desired compounds can be obtained in a single step by reaction (1). The reaction is normally carried out in benzene or dichloromethane. The advantages of this route are as follows: (*a*) the silicon reagents are easily obtained and manipulated, since they are air-stable and liquid, (*b*) the reaction is essentially quantitative, with yields of up to 95%, after 30 min reaction time (sometimes under reflux), (*c*) the reaction is not markedly exothermic except in the case of titanium tetrachloride, (*d*) the colour changes which are observed can be used as indicators of the course of the reaction, (*e*) the products are easily separated by filtration or sublimation, and (*f*) no matter how long the reaction is allowed to proceed, there is no evidence for any formation of $[TiX_2(\eta\text{-}C_5H_5)_2]$.



(1)

The advantages of trimethylsilylcyclopentadiene as a cyclopentadienyl donor, compared with sodium cyclopentadienide, are: (*a*) it gives much the higher yields in its reactions with metal halides, (*b*) it is much less of a reducing agent than sodium cyclopentadienyl, which can cause reduction of $Ta^{V} \longrightarrow Ta^{IV}$ and $Ti^{IV} \longrightarrow Ti^{III}$, and (*c*) it gives much cleaner products than does sodium cyclopentadienyl and, moreover, it reacts quickly with metal halides.

The major metal-containing fragments in the mass spectra of the compounds are given in Table 1, *cf.* data on chloride and bromide only by Nesmeyanov *et al.*[12] These fragments are simply due to loss of cyclopentadienyl radicals and halogen atoms. In all cases, the species observed with the highest *m*/*e* is the monomeric parent molecular ion.

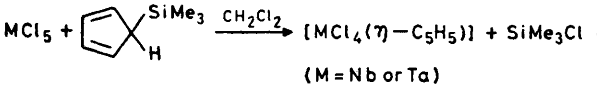
TABLE 1

Major metal-containing fragments in the mass spectra of $[TiX_3(cp)]$ (X = Cl, Br, or I)

Ion	X = Cl	X = Br	X = I
		m/*e*(*I*) *	
$TiX_3(cp)^+$	218 (100)	350 (47)	494 (64)
$TiX_2(cp)^+$	183 (56)	271 (100)	367 (100)
$TiX(cp)^+$	148 (29)	192 (36)	240 (96)
$Ti(cp)^+$		113 (10)	113 (96)
TiX_3^+	153 (14)	285 (28)	429 (9)
TiX_2^+	118 (68)	206 (66)	302 (55)
TiX^+	83 (63)	127 (89)	175 (82)
Ti^+	48 (10)	48 (32)	48 (—)

* *I* is expressed as the relative abundance given by the percentage intensity of a peak relative to that of the most intense ion in the spectrum.

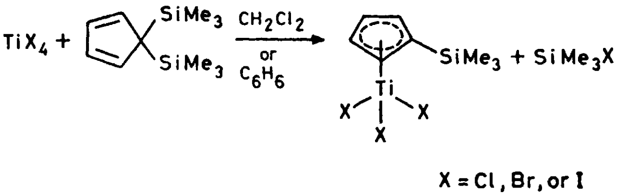
η-Cyclopentadienylniobium Tetrachloride and η-Cyclopentadienyltantalum Tetrachloride.—These two complexes were unknown at the start of this work but, during the course thereof, preliminary reports of their preparation appeared.[8,9] The present syntheses, which lead to the formation of η-cyclopentadienylmetal tetrachlorides in extremely high yield (93—95%), are as shown in equation (2). The deeply coloured complexes are insoluble in most of the solvents for which ^1H n.m.r. spectroscopy would be feasible; hexamethylphosphortriamide does dissolve them, but with some decomposition. Hence satisfactory structural data on the complexes could not be obtained. The mass spectra of the complexes do not show a peak corresponding to the parent molecular ion, undoubtedly because at the high temperatures (200—250 °C) necessary in order to obtain the spectra some decomposition had taken place. The niobium complex is much the more sensitive to oxygen, as evidenced by the fact that it could not be prevented from forming oxygenated species in the mass spectrometer probe.



(2)

Bis(trimethylsilyl)cyclopentadiene Reactions.—Bis(trimethylsilyl)cyclopentadiene, a by-product in the preparation of trimethylsilylcyclopentadiene, has also been found to react with titanium tetrahalides to yield new complexes, reaction (3). In this elimination reaction only one trimethylsilyl group is cleaved by the metal halide, since allylic C–SiMe₃ is readily cleaved by electrophilic reagents. Thus the reactions proceed in a manner very similar to those involving trimethylsilylcyclopentadiene. The resulting complexes in the two series have similar properties although the substituted species have the greater solubilities, as expected, and the lower melting points.

Care must be taken in the reactions involving titanium tetraiodide. Previous and careful sublimation is necessary in order to eliminate any traces of iodine, which would react preferentially with the trimethylsilyl reagents.



(3)

The mass spectra of the complexes (Table 2) contain, in all cases, a peak corresponding to the parent molecular ion, the major metal-containing fragments being due to the loss of methyl groups from the Me_3Si– groups, or of cyclopentadienyl radicals and halogen atoms. Amongst the non-transition metal fragments the appearance of peaks due to the ions $SiMe_3X^+$, $SiMe_2X^+$, $SiMeX^+$, and $SiMe_3^+$ is noteworthy.

The n.m.r. spectra of the complexes show certain characteristic features (Table 3); these are a sharp singlet at τ 9.2—9.7 for the Me_3Si– group and the splitting of the cyclopentadienyl peak into two triplets.

Attempts to prepare bis(cyclopentadienyl) derivatives, both substituted as well as unsubstituted, by use of stoicheiometric amounts of the metal halide and the silicon reagent were unsuccessful. The reactions were monitored by ^1H n.m.r. spectroscopy. The resulting spectra showed two sets of peaks, one corresponding to the presence of (trimethylsilylcyclopentadienyl)titanium trichloride and the other to bis(trimethylsilylcyclopentadienyl)titanium dichloride. The reaction mixture was held under reflux for one month, but successive n.m.r. spectra taken at regular intervals did not show any alteration in the relative intensities of the peaks; this indicated that the reaction had reached equilibrium. The use of more forcing conditions *e.g.* a solvent of higher boiling point (xylene) did not lead to further reaction. Possibly the use of trialkyl(cyclopentadienyl)tin compounds would be more effective in this respect, owing to the lower metal–carbon bond strength where M = Sn than for M = Si.

TABLE 2

Major fragments in the mass spectra of $[TiX_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$

Ion	X = Cl	X = Br	X = I
	m/e(*I*)		
$TiX_3(Me_3Si\text{-}\eta\text{-}C_5H_4)^+$	290 (2)	422 (—)	566 (63)
$TiX_3(Me_2Si\text{-}\eta\text{-}C_5H_4)^+$	275 (100)	407 (—)	551 (12)
$TiX_3(MeSi\text{-}\eta\text{-}C_5H_4)^+$	260 (24)	392 (—)	
$TiX_3(Si\text{-}\eta\text{-}C_5H_4)^+$		377 (—)	
$TiX_3(\eta\text{-}C_5H_4)^+$		349 (1)	
$TiX_2(Me_3Si\text{-}\eta\text{-}C_5H_4)^+$			439 (91)
$TiX_2(Me_2Si\text{-}\eta\text{-}C_5H_4)^+$	240 (13)	328 (1)	424 (89)
$TiX_2(MeSi\text{-}\eta\text{-}C_5H_4)^+$	225 (1)		
$TiX_2(Si\text{-}\eta\text{-}C_5H_4)^+$	210 (3)	298 (—)	
$TiX_2(\eta\text{-}C_5H_4)^+$		270 (2)	
$TiX(Me_3Si\text{-}\eta\text{-}C_5H_4)^+$			
$Ti(Me_3Si\text{-}\eta\text{-}C_5H_4)^+$			185 (11)
$TiX_3(\eta\text{-}C_5H_5)^+$	218 (4)		494 (86)
$TiX_2(\eta\text{-}C_5H_5)^+$	183 (2)		367 (89)
$TiX(\eta\text{-}C_5H_5)^+$	148 (4)		240 (69)
$Ti(\eta\text{-}C_5H_5)^+$			113 (100)
TiX_3^+	153 (2)	285 (100)	429 (40)
TiX_2^+	118 (5)	206 (87)	302 (87)
TiX^+		127 (48)	175 (89)
Ti^+	48 (—)	48 (4)	48 (51)
$(Me_3Si\text{-}\eta\text{-}C_5H_4)^+$	137 (3)		
$(Me_2Si\text{-}\eta\text{-}C_5H_4)^+$	122 (13)	122 (32)	122 (22)
$(MeSi\text{-}\eta\text{-}C_5H_4)^+$	107 (8)	107 (21)	107 (40)
$SiMe_3^+$	73 (8)	73 (16)	73 (89)
$SiMe_3X^+$	108 (2)		200 (11)
$SiMe_2X^+$		137 (11)	
$SiMeX^+$	78 (2)		

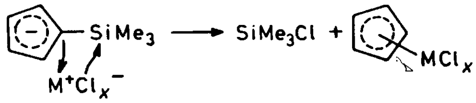
TABLE 3

Hydrogen-1 n.m.r. data on cyclopentadienyl and silylcyclopentadienyl metal halide complexes

Complex	Solvent	τ C_5H_5	τ $SiMe_3$	τ C_5H_4
$[TiCl_3(\eta\text{-}C_5H_5)]$	CH_3CN	2.75 (s)		
$[TiBr_3(\eta\text{-}C_5H_5)]$	CH_3CN	2.71 (s)		
$[TiI_3(\eta\text{-}C_5H_5)]$	CH_2Cl_2	2.89 (s)		
$[TiCl_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$	CH_3CN		9.64 (s)	2.70 (t); 2.47 (t)
$[TiBr_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$	CH_3CN		9.68 (s)	2.69 (t); 2.43 (t)
$[TiI_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$	$CDCl_3$		9.20 (s)	2.88 (t); 2.53 (t)

s = Singlet, t = triplet.

The reactions described in this section can be understood in terms of an electrophilic attack on the cyclopentadienyl group with cleavage of the silicon–carbon bond, see (4). The cleavage of cyclopentadienyl–, indenyl–, and fluorenyl–silicon bonds can be brought about easier than that of any other silicon–hydrocarbon bonds. Thus the cyclopentadienyl–silicon bond can be cleaved with manganese pentacarbonyl halides and even with dimanganese decarbonyl itself.[25]



(4)

Lewis Acid Character of $[TiCl_3(cp)]$ *and* $[TiBr_3(cp)]$.—The reduced Lewis acid character of $[TiCl_3(cp)]$ with respect to that of the titanium tetrachloride is evident from the apparent lack of reaction between $[TiCl_3(cp)]$ and pyridine, PPh_3, SMe_2, or $AsMe_3$. Indeed, the only established adducts of these Lewis acids are $[TiCl_3(cp)(pdma)]$, where pdma = *o*-phenylenebisdimethylarsine, and $[TiCl_3(cp)](bipy)]$, where bipy = 2,2′-bipyridyl.[10] In the present investigation, the reactions between $[TiCl_3(cp)]$, $[TiBr_3(cp)]$, and $[TiCl_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$ with a variety of potentially chelating ligands have been investigated in order to provide more information on the acceptor properties of these Lewis acids and on the steric restrictions on the titanium atoms therein.

Treatment of $[TiCl_3(cp)]$ in toluene with *o*-phenanthroline (phen) at room temperature led to the formation and precipitation of $[TiCl_3(cp)(phen)]$ as a deep pink crystalline solid. From the wavenumbers of the group of intense bands (at *ca.* 330 cm^{-1}) in the i.r. spectrum of this complex, attributable to Ti–Cl stretching modes, it is evident that the co-ordination number of titanium in this complex is at least six,[26] and thus that the ligand is, as usual, functioning in a bidentate fashion. The complex is insoluble in common organic solvents, and so no further structural information thereon could be obtained.

By contrast to its reaction with pdma, phen, and bipy, $[TiCl_3(cp)]$ was found not to react with 1,2-dimethoxyethane, 2,5-dithiahexane, or 1,2-bisdiphenylphosphinoethane. No n.m.r. peaks are shifted for solutions of $[TiCl_3(cp)]$ in these solvents, indicating no co-ordination in solution, and only the starting products could be recovered on removal of the ligand from a solution of $[TiCl_3(cp)]$ in each ligand. In the case of $[TiCl_3(cp)]$ in *NNN′N′*-tetramethylethylenediamine (tmen), an extra n.m.r. peak was observed at τ 3.05, suggesting the formation of $[TiCl_3(cp)(tmen)]$ in solution, but the brown solid isolated from these solutions did not analyse correctly for this complex.

Similar problems arise on treatment of $[TiBr_3(cp)]$ with these ligands. No reaction took place in the case of tmen in toluene, but in that of pdma in toluene a red product could be isolated from the reaction mixture. Although the analytical figures on this material were unsatisfactory, it should probably be formulated as $[TiBr_3(cp)(pdma)]$ since its n.m.r. spectrum (Table 4) indicates co-ordination by the ligand and the MeAs resonance occurs as a doublet, well separated from that of free diarsine and similarly placed to that of $[TiCl_3(cp)(pdma)]$.[10] Attempts at purification of this complex,

TABLE 4

Hydrogen-1 n.m.r. on relevant diarsine complexes

Complex	Solvent	τ or τ C_5H_5 C_5H_4	τ $SiMe_3$	τ $AsMe_2$	τ C_6H_4
$[TiCl_3(cp)(pdma)]$[10]	$CDCl_3$	3.13 (s)		8.25 (s) 8.30 (s)	2.38 (m)
$[TiBr_3(cp)(pdma)]$	CH_2Cl_2	3.07 (s)		8.11 (s) 8.39 (s)	2.41 (m)
$[TiCl_3(Me_3Si\text{-}\eta\text{-}C_5H_4)(pdma)]$	$CDCl_3$	3.02 (t) 2.85 (t)	9.54 (s)	8.67 (s)	2.54 (m)

s = Singlet, t = triplet, m = multiplet.

e.g. by sublimation, were not successful owing to partial loss of the ligand during this process. Similar reactions with bipy and phen afforded green products which are undoubtedly indicative of reduction of Ti^{IV} to Ti^{III}.[27]

The present results seem, therefore, to confirm the very poor acceptor ability of both $[TiCl_3(cp)]$ and $[TiBr_3(cp)]$ for a wide range of potentially bidentate ligands.

Only one reaction of $[TiCl_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$ with a bidentate ligand was attempted, *viz.* that with pdma, and this led (in benzene at room temperature) clearly to the isolation of an orange 1 : 1 adduct. The MeAs resonance is in this case a singlet, and the two triplets characteristic of the C_5H_4 resonance (τ 3.02, 2.85) are shifted upfield from that of $[TiCl_3(Me_3Si\text{-}\eta\text{-}C_5H_4)]$ (τ 2.70, 2.47).

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