Reactions of Dichlorodiphenoxotitanium(IV) †

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Spectroscopic data confirm for solution the structure found in the solid state for $\{TiCl_2(OPh)_2\}_2$. The compound has been reduced by alkali metals and a number of compounds which have Ti–H bonds and contain dinitrogen when reductions are carried out under nitrogen have been studied. Examples are $\{Ti(OPh)_2\}_2H(N_2)$ and $\{Ti(OPh)_2\}_3H$. $Ti(OPh)_2Cl_2$ also reacts with $(Me_3SiCH_2)_2Mg$ to give $Ti(OPh)_2(CH_2SiMe_3)_2$.

On the basis of i.r. and n.m.r. spectra and, where paramagnetic, electron paramagnetic resonance spectra of the compounds, very tentative suggestions of structures are made. The lack of crystallinity precludes structural determination.

FOLLOWING our observation [1] that the phenoxide ion can be π-bonded to a metal through the ring carbon atoms rather than through the oxygen atom, it appeared possible that other complexes might have π- rather than σ-phenoxo-groups.

The compound $Ti(OPh)_2Cl_2$ which would be isoelectronic with $(\pi\text{-}C_5H_5)_2TiCl_2$ if the phenoxide ions were π-bonded, is a dimer in the solid state [2] with two bridging phenoxo-moieties. However, it is said [3] to be monomeric in benzene, although the samples were prepared by different synthetic routes.

We have studied various spectra of $Ti(OPh)_2Cl_2$ and conclude that the structure in solution is similar to that in the crystal.

In an unsuccessful attempt to force the phenoxide ion into π-bonding, we have studied its reaction with various

RESULTS AND DISCUSSION

Magnetic and analytical data for the complexes are presented in Tables 1 and 2 respectively.

Spectroscopic Study of $\{Ti(OPh)_2Cl_2\}_2$.—In contrast to a previous report,[3] the molecular weight (572), measured cryoscopically in benzene, of $Ti(OPh)_2Cl_2$ prepared from interaction of 2 mole equivalents of phenol with $TiCl_4$, is close to that required for the dimer (610) and the compound probably has the same structure in solution as in the solid state.[2]

The ^1H n.m.r. spectrum also supports this view. At -60 °C in CD_2Cl_2 the spectrum consists of three broad resonances at δ 7.55, 7.25, and 6.45 of approximate relative intensities $3:5:2$. The high-field resonance presumably arises from the *ortho*-protons of the bridging phenoxo-moieties since they should be more shielded

TABLE 1

E.p.r. data for some paramagnetic titanium compounds in frozen solution at -160 °C

Compound	*g* Values			Solvent	$\dfrac{\mu_{\text{eff.}}{}^{a}}{\text{B.M. (per Ti)}}$
$\{Ti(OPh)_2\}_3H$	1.913	1.941	1.964	thf	0.69
$\{Ti(OPh)_2\}_2(N_2)H$	1.912	1.943	1.982	thf	0.76
$\{Ti(OPh)_2Cl(thf)_2\}_2H$	1.931	1.945	1.979	thf	0.90
$K_{11}Ti_3(OPh)_7$	1.921	1.983	2.018	thf	0.63
$\{Ti(OPh)_2Me\}_n$	1.929	1.950	1.990	Benzene	
$\{Ti(O_2C_6H_4)\}_2(N_2)H\cdot thf$	1.926	1.982	2.037	thf	0.79

a By Evans' method in thf–benzene; invariant from -100 to $+60$ °C.

reducing agents. van Tamelen [4,5] has reported that the reductions of various alkoxide complexes of titanium, including $Ti(OPh)_2Cl_2$, with sodium naphthalide or potassium under nitrogen give appreciable quantities of ammonia *via* an intermediate thought to be of stoicheiometry $Na_{13}Ti_3N_4(OR)_{10}$.

The only other known reactions of $Ti(OPh)_2Cl_2$ are its formation of adducts on interaction with amides [6] or amines [3,6] and its use as a catalyst for the polymerisation of olefins and epoxides.[7]

A new preparation and some reactions of $Ti(O_2C_6H_4)Cl_2$, obtained from interaction of pyrocatechol with $TiCl_4$, are also reported.

† No reprints available.

than the others on account of interaction with the two metal centres. On warming, the three resonances broaden further and coalesce until at room temperature a single resonance is observed at δ 7.1. This behaviour is best interpreted as arising from fast exchange between terminal and bridged phenoxo-groups at higher temperatures.

In the solid-state i.r. spectrum, $\nu(C-O)$ is a broad band at 1 225 cm^{-1} and the peak at 1 600 cm^{-1}, which could be assigned as $\nu(C=O)$ of a π-bonded phenoxo-anion,[1] more probably arises from the out-of-plane deformations of the phenyl ring since it is also present in the i.r. spectrum of free phenol. $\nu(Ti-Cl)$ at 460 and 400 cm^{-1} are suggestive of *cis*-terminal chlorides (*cf.* 495 cm^{-1} for $TiCl_4$).[8]

In the gas phase, however, $\{Ti(OPh)_2Cl_2\}_2$ appears to

[1] D. J. Cole-Hamilton, R. J. Young, and G. Wilkinson, *J.C.S. Dalton,* 1976, 1995.
[2] K. Watenpaugh and C. N. Gaughlan, *Inorg. Chem.,* 1966, **5,** 1782.
[3] M. J. Frazer and Z. Goffer, *J. Inorg. Nuclear Chem.,* 1966, **28,** 2410.
[4] E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Amer. Chem. Soc.,* 1967, **89,** 5707.

[5] E. E. van Tamelen, *Accounts Chem. Res.,* 1970, **3,** 361.
[6] N. Yoshino, K. Dohya, and T. Yoshino, *Kogyo Kagaku Zasshi,* 1971, **74,** 2138 (*Chem. Abs.,* 1972, **76,** 13998a).
[7] F.P. 1,377,130, 1964 (*Chem. Abs.,* 1965, **62,** 6184c).
[8] D. M. Adams, ' Metal–Ligand and Related Vibrations,' E. Arnold, London, 1967.

dissociate to a monomer since the parent ion in the mass spectrum is at m/e 304 a.m.u. Smaller peaks are also detected at m/e 352 and 420 a.m.u. but are assigned to traces of Ti(OPh)₃Cl and Ti(OPh)₄, either present as impurities or, more probably, since TiCl₃(OPh) is also

argon leads to the formation of a black solution from which a very air-sensitive grey powder may be isolated in low yield.* The compound has an analysis and a cryoscopic molecular weight (620) consistent with its formulation as {Ti(OPh)₂}₃H.

TABLE 2

Analytical data for titanium complexes

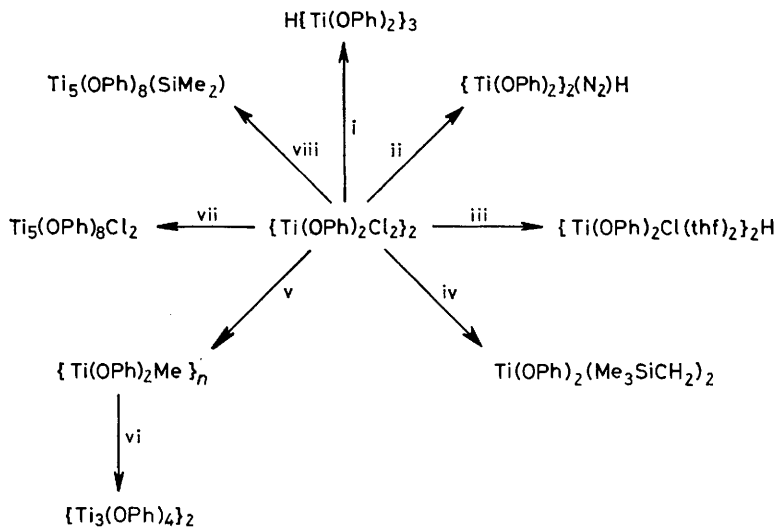| Compound	Colour	Found (%)			Required (%)			M
		C	H	Other	C	H	Other	
{Ti(OPh)₂Cl₂}₂	Deep red	47.1	3.5	Cl, 23.0	47.3	3.3	Cl, 23.3	570 (610)
{Ti(OPh)₂}₃H	Grey	61.9	4.1		61.6	4.3		620 (703)
K₁₁Ti₃(OPh)₇	Grey	41.2	3.5	Ti, 11.9	41.2	2.9	Ti, 11.8	
{Ti(OPh)₂}₂(N₂)H *	Purple	58.9	4.1	N, 4.9	58.1	4.1	N, 5.6	430 (497)
{Ti₃(OPh)₂Cl(thf)₂}₂H	Yellow	59.1	6.9	Cl, 7.9	58.1	6.3	Cl, 8.6	
Ti₅(OPh)₈Cl₂	Orange	53.0	4.0	Cl, 7.7	54.7	3.8	Cl, 6.7	965 (1 055)
Ti₅(OPh)₈(SiMe₂)	Red	59.0	5.1	Si, 2.7	57.6	4.5	Si, 2.7	1 060 (1 042)
{Ti(OPh)₄}₂	Orange	56.3	4.4		55.9	3.9		1 000 (1 032)
Ti(OPh)₂(CH₂SiMe₃)₂	Yellow	58.1	7.7		58.9	7.9		445 (409)
Ti(O₂C₆H₄)Cl₂	Black	32.0	2.0	Cl, 29.7	31.8	1.8	Cl, 31.3	
Ti(O₂C₆H₄)Cl₂·2thf	Brown	44.9	5.2	Cl, 19.5	45.3	5.4	Cl, 19.1	
Ti(O₂C₆H₄)Cl₂·2py	Deep red	50.0	4.3	Cl, 18.1 N, 7.7	49.9	3.7	Cl, 18.4 N, 7.3	
{Ti(O₂C₆H₄)}₂(N₂)H·thf	Brown	46.4	3.8	N, 5.9	46.6	3.9	N, 6.8	

* This compound is sometimes contaminated with a small amount of a sodium-containing species (Na up to 2%).

observed, formed by disproportionation of Ti(OPh)₂Cl₂ in the mass spectrometer.

Reductions of {Ti(OPh)₂Cl₂}₂.—These reductions are summarized in the Scheme.

As in all the complexes reported here, the i.r. spectrum suggests that the compound has σ-bonded phenoxo-groups [$ν$(C–O), 1 258 cm⁻¹].[1] The complex has a magnetic moment in solution of 0.69 B.M. per titanium

H{Ti(OPh)₂}₃

Ti₅(OPh)₈(SiMe₂)   {Ti(OPh)₂}₂(N₂)H

                    viii   i   ii

Ti₅(OPh)₈Cl₂ ◄——vii—— {Ti(OPh)₂Cl₂}₂ ——iii——► {Ti(OPh)₂Cl(thf)₂}₂H

                    v   iv

{Ti(OPh)₂Me}ₙ   Ti(OPh)₂(Me₃SiCH₂)₂

        vi

{Ti₃(OPh)₄}₂

SCHEME Reactions of {Ti(OPh)₂Cl₂}₂ i, 2 g-atom of K under argon, toluene, 25 °C. ii, Excess of Na/Hg under N₂, thf 25 °C. iii, Excess of NaBH₄, thf, 25 °C. iv, (Me₃SiCH₂)₂Mg, diethyl ether, −10 °C. v, Me₂Mg, diethyl ether, −30 °C. vi, Warm to 25 °C. vii, Excess of Zn, toluene, 25 °C. viii, 2 mole equiv. LiN(SiMe₃)₂, petroleum, 25 °C

(a) *Sodium amalgam or potassium metal.* Treatment of a toluene solution of {Ti(OPh)₂Cl₂}₂ with 2 mole equivalents of potassium metal or sodium amalgam under

* The main product from the reductions with K or Na–Hg under argon or nitrogen is a brown phenoxide containing solid, insoluble in all common organic solvents including tetramethyl-ethylenediamine, which is probably {Ti(OPh)₂}ₙ.

† The lack of hyperfine splitting by hydrogen in this and the other hydrido-complexes is unusual but may arise from a small splitting being obscured by the large line width. A similar explanation has been offered for the lack of observable hyperfine splitting by the hydride ligands of TaH₂(cp)₂.[9]

atom at all temperatures from −100 to +60 °C and a broad e.p.r. signal.† This suggests that there is one unpaired electron per three titanium atoms. The presence of at least one hydride is shown by the formation of CHCl₃ on reaction with CCl₄. The compound may have a structure such as (1) or (2). By analogy with {Ti(OPh)₂}₂(N₂)H (see later) we suggest that structure (1) is more probable.

⁹ I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, 1974, **96**, 7374.

The black compound, thought to be $Ti(OCH_2Ph)_2$,[10] isolated in an impure state from the reaction of $TiCl_3$ with benzyl alcohol and methyl-lithium may also be similar to $\{Ti(OPh)_2\}_3H$.

PhO, OPh / PhO, Ti, OPh / Ti Ti / PhO H OPh

(1)

PhO OPh / Ti / PhO H OPh / Ti——Ti / PhO OPh

(2)
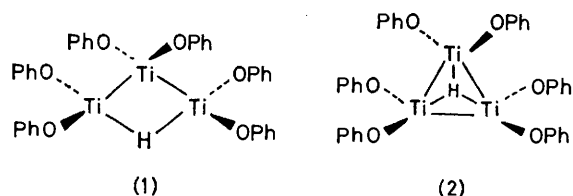
If an excess of potassium is used in the reduction the product, which is insoluble in toluene, is again grey but contains potassium and is probably of stoicheiometry $K_{11}Ti_3(OPh)_7$. The magnetic moment of this material (0.63 B.M. per Ti) and the broad featureless e.p.r. signal are consistent with there being one unpaired electron delocalised over three titanium atoms, thus giving the titanium atoms a formal charge of -1.

Although reduction with 2 mole equivalents of potassium under nitrogen again yields $\{Ti(OPh)_2\}_3H$, action of sodium amalgam in tetrahydrofuran gives low yields * of a purple, nitrogen-containing complex whose analysis is close to that for $\{Ti(OPh)_2\}_2(N_2)H$. The i.r. spectrum of this compound shows no bands readily assignable to $\nu(N{\equiv}N)$ or $\nu(Ti-H)$ which suggests that both the hydride and the nitrogen molecule are bridging and that $\nu(Ti-H-Ti)$ is obscured by one of the intense vibrations of the phenoxide ion [cf. $\nu(Ti-H-Ti)$ in $\{cp_2TiH\}_2$ is at 1 450 cm^{-1}].[11] The Raman spectrum of this compound in tetrahydrofuran is also featureless in the region 1 700—2 500 cm^{-1} suggesting that $\nu(N{\equiv}N)$ is probably obscured by the broad phenoxide vibration near 1 600 cm^{-1}. A similar lowering of $\nu(N{\equiv}N)$ has also been suggested for $\{[(PhLi)_3Ni]_2N_2{\cdot}2Et_2O\}_2$ in which the nitrogen molecule is 'sideways bound'[12] to the nickel atoms. The dimeric formulation for $\{Ti(OPh)_2\}_2(N_2)H$ is confirmed by molecular-weight measurements (430).

The purple colour of this complex suggests that it might possibly be similar to the blue $\{cp_2Ti\}_2N_2$ [13,14] or the purple $\{(Me_5C_5)_2Ti\}N_2$; the latter has been shown to contain an 'end on' bridging N_2 molecule.[15] However, the lack of reversibility of N_2 uptake in our complex together with the observation that it does not readily form adducts with donor molecules [as would be expected for a three-co-ordinate complex of titanium(II)] suggest that this is not so and the presence of the hydride is confirmed by the immediate reaction of the complex with carbon tetrachloride to give chloroform. The magnetic moment (0.76 B.M. per titanium) which is temperature invariant from -100 to $+60$ °C and the

broad featureless e.p.r. signal suggest that the complex contains one unpaired electron per dimer.

This evidence suggests one of the structures (3) or (4), with the N_2 group bridging as a 'sideways bound' ligand with a single Ti–Ti bond or as an imine-like group with no Ti–Ti bond. In either case, $\nu(N{\equiv}N)$ would be expected to be low.

Analogues of these complexes with the N_2 group replaced by an acetylene molecule should exist but, in contrast to the smooth displacement of the sideways bridging N_2 group in $\{[(PhLi)_3Ni]_2N_2{\cdot}2Et_2O\}_2$ by ethylene,[12a] $\{Ti(OPh)_2\}_2(N_2)H$ does not react with diphenylacetylene and attempts to produce the diphenylacetylene analogue by reduction of $\{Ti(OPh)_2Cl_2\}_2$ with

N ||| N / PhO, Ti——Ti OPh / PhO H OPh

(3)

N=N / PhO, Ti Ti OPh / PhO H OPh

(4)
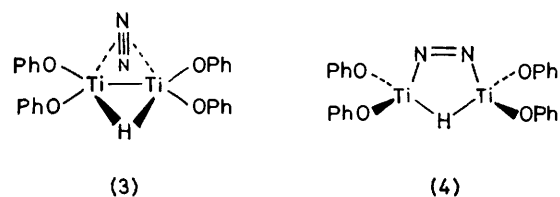
sodium amalgam in the presence of diphenylacetylene under argon give $\{Ti(OPh)_2\}_3H$ as the only characterisable product.

We thus favour structure (4) and attribute the lack of formation of the diphenylacetylene analogue to the apparent difficulty with which acetylenes form bridged systems to give a cis-disubstituted alkene-type compound.†

The reaction of the pyrocatecholate $\{Ti(O_2C_6H_4)Cl_2\}_2$ with sodium amalgam in tetrahydrofuran under nitrogen also gives a purple solid but this time in high yield. Apart from its lower solubility in aromatic solvents, this complex appears to be very similar to $\{Ti(OPh)_2\}_2(N_2)H$ although it crystallises from tetrahydrofuran as a solvate. Thus, the compound gives $CHCl_3$ on interaction with CCl_4, is paramagnetic with a magnetic moment of 0.79 B.M. per titanium, and has a broad e.p.r. signal very similar in shape to that of $\{Ti(OPh)_2\}_2(N_2)H$. Once again, no absorptions arising from $\nu(N{\equiv}N)$ or $\nu(Ti-H-Ti)$ are observed in the i.r. spectrum and, although the complex is insufficiently soluble in benzene for molecular weight measurements, we assign it a structure similar to that shown in (4) but with the two phenoxide ions on each titanium replaced by the pyrocatecholate dianion.

(b) Sodium borohydride. On treating a red tetrahydrofuran solution of $\{Ti(OPh)_2Cl_2\}_2$ with $NaBH_4$, the colour gradually fades to pale yellow as NaCl is precipitated and, after filtration, a yellow crystalline solid of

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* The yield is very sensitive to the rate of stirring of the solution, being higher the greater the amount of agitation, as well as to the N_2 pressure which must be kept above atmospheric.

† Note added in proof. A chromium compound containing a similar bridging N_2 moiety has been reported (P. Sobota and B. Jezowska-Trzebiatowska, J. Organometallic Chem., 1977, 131, 341).

[10] E. E. van Tamelen, B. Åkermark, and K. B. Sharpless, J. Amer. Chem. Soc., 1969, 91, 1553.

[11] J. E. Bercaw and H. H. Brintzinger, J. Amer. Chem. Soc., 1969, 9, 7301.

[12] (a) K. Jonas, Angew. Chem. Internat. Edn., 1973, 12, 997; (b) C. Kruger and Yi-Hung Tsay, Angew. Chem. Internat. Edn., 1973, 12, 998.

[13] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, J. Amer. Chem. Soc., 1972, 94, 1219.

[14] E. E. van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, J.C.S. Chem. Comm., 1972, 481.

[15] R. D. Sanner, D. M. Duggan, T. C. McKenzie, R. E. Marsh, and J. E. Bercaw, J. Amer. Chem. Soc., 1976, 98, 8358.

stoicheiometry $\{Ti(OPh)_2Cl(thf)_2\}_2H$ can be isolated. This is stable only in tetrahydrofuran so that molecular-weight measurements have not been possible but the temperature-independent magnetic moment (0.90 B.M. per titanium) and the single e.p.r. signal suggest a dimeric formulation with one unpaired electron per dimer. Once again the lack of any i.r. peaks in the region expected for terminal $\nu(Ti-H)$ or for BH_4^- suggests a bridging hydride ligand, whose presence is confirmed by reaction of $\{Ti(OPh)_2Cl(thf)_2\}_2H$ with carbon tetrachloride to give chloroform. The i.r. band at 440 cm^{-1} suggests that the chloride is Ti–Cl terminal. We suggest the structure (5) since the alternative (6)

(5)   (6)
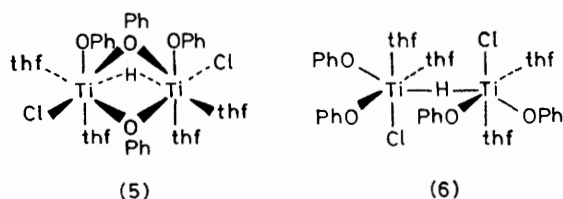
would require a linear Ti–H–Ti bridge which although known, e.g. in $[\{Cr(CO)_5\}_2H]^-$,[16] is unusual.

(c) *Action of alkylating agents* R_2Mg (R = Me_3SiCH_2 or Me) *and* MeMgCl. Like $(\pi\text{-}C_5H_5)_2TiCl_2$,[17] $\{Ti(OPh)_2Cl_2\}_2$ reacts with $(Me_3SiCH_2)_2Mg$ to give a yellow crystalline solid, $Ti(CH_2SiMe_3)_2(OPh)_2$ in which reduction of the metal has not occurred. This diamagnetic compound is monomeric in benzene and stable in solution to 100 °C. Peaks in the i.r. spectrum at 1 205 and 850 cm^{-1} confirm the presence of the Me_3SiCH_2 unit whilst sharp singlets at δ 2.30 (CH_2) and 0.10 (CH_3) indicate that the alkyl groups are equivalent as in (7).

(7)
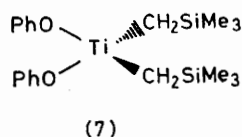
With Me_2Mg or MeMgCl, however, the orange compound formed initially is unstable in solution at room temperature but from the integration of the broad peaks in the n.m.r. spectrum appears to be $\{Ti(OPh)_2Me\}_n$. The i.r. spectrum shows a weak band at 2 950 cm^{-1} arising from the aliphatic $\nu(CH)$. The broad e.p.r. signal from this complex suggests that it is oligomeric with n being an odd number.

The compound formed by decomposition of $\{Ti(OPh)_2Me\}_n$ in petroleum at room temperature has an analysis consistent with its formulation as $Ti_3(OPh)_4$ but it is evidently dimeric, as indicated by its molecular weight (*ca.* 1 000) and its diamagnetism.

(d) *Zinc and* $LiN(SiMe_3)_2$. Zinc powder reacts slowly with $\{Ti(OPh)_2Cl_2\}_2$ in toluene at 25 °C to give an orange

solution from which an orange solid may be isolated. This compound has an analysis and observed molecular weight (965) consistent with its formulation as $Ti_5(OPh)_8Cl_2$; the absence of peaks in the region 500—250 cm^{-1} assignable to $\nu(Ti-Cl)$ in the i.r. spectrum suggests, however, that the chloride ions are bridging since $\nu(Ti-Cl-Ti)$ is known to appear below 250 cm^{-1}.[18] The complex is diamagnetic, suggesting extensive M–M bonding or antiferromagnetic interaction *via* ligand bridges between the unpaired electrons on each titanium atom; a possible structure is shown in formula (8).

A related complex is also formed from the reaction of $\{Ti(OPh)_2Cl_2\}_2$ with $LiN(SiMe_3)_2$, which by comparison with the reaction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with $LiN(SiMe_3)_2$ [19] was expected to give $Ti(OPh)_2\{N(SiMe_3)(SiMe_2CH_2)\}$. The red product contains no nitrogen and has the stoicheiometry $Ti_5(OPh)_8(SiMe_2)$. The presence of the $SiMe_2$ group is confirmed by (*a*) silicon analysis, (*b*) the presence of peaks at 2 956 and 2 920 cm^{-1} [aliphatic $\nu(C-H)$] and 850 cm^{-1} [$\nu(Si-CH_3)$] [20] in the i.r. spectrum, and (*c*) the observation of two peaks at δ 0.5 and 0.48 (*cf.* 0.2 for $LiNSiMe_3$) in the ^1H n.m.r. spectrum; the evidence of

(8)
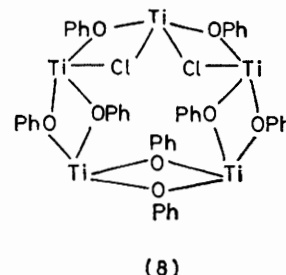
(*c*) suggests that the two methyl groups are non-equivalent. Neither of these diamagnetic complexes reacts with CCl_4 to give chloroform, thus precluding the presence of hydrido-ligands.

Preparation and Reactions of $Ti(O_2C_6H_4)Cl_2$ *with Lewis Bases.*—The reaction between $TiCl_4$ and 1 mol equiv. of pyrocatechol in refluxing toluene gives $Ti(O_2C_6H_4)Cl_2$ [21] as an insoluble black solid in greater than 90% yield. The compound is almost totally insoluble in non-co-ordinating solvents, suggesting that it is associated. Several absorptions in the region 250—500 cm^{-1} confirm that the chloride ions are terminal and suggest either a dimeric structure, (9), similar to that of $\{Ti(OPh)_2Cl_2\}_2$ with the pyrocatecholate bridging, or a polymeric structure with similar bridges. The presence of $\nu(C-O)$ near 1 250 cm^{-1} in this, as in the other pyrocatechol complexes suggests that the pyrocatechol is co-ordinated as a dianion rather than as an *ortho*-benzoquinone type moiety.

$Ti(O_2C_6H_4)Cl_2$ dissolves in tetrahydrofuran (thf) or pyridine from both of which it may be isolated as the 1 : 2 adduct, $Ti(O_2C_6H_4)Cl_2\cdot2S$ (S = thf or pyridine).

[16] L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hauter, *J. Amer. Chem. Soc.*, 1966, **88**, 366.

[17] M. R. Collier, M. F. Lappert, and R. Pearce, *J.C.S. Dalton*, 1973, 445.

[18] R. S. P. Coutts, P. S. Wailes, and R. L. Martin, *J. Organometallic Chem.*, 1973, **47**, 375.

[19] C. R. Bennett and D. C. Bradley, *J.C.S. Chem. Comm.*, 1974, 29.

[20] B. Wozniak, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. (A)*, 1971, 3116.

[21] C. Gopinathan and J. Gupta, *Indian J. Chem.*, 1973, **11**, 948.

The far-i.r. spectrum of the thf adduct is similar to that of Ti(O$_2$C$_6$H$_4$)Cl$_2$,* suggesting that the compound is monomeric with terminal chloride ions. The very
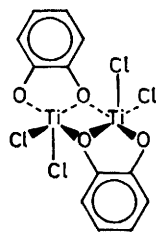
(9)

insoluble pyridine adduct, on the other hand, shows no ν(Ti–Cl) above 250 cm^{-1}, suggesting that the halide ions are bridging and that the compound is polymeric with chloride bridges.

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Limited and Pascher, Bonn. Molecular weights were measured cryoscopically in benzene under nitrogen using an apparatus similar to that described by D. F. Shriver.[22]

I.r. spectra were recorded on a Perkin-Elmer 457 grating spectrometer in Nujol mulls between KBr or CsI plates. ^{1}H N.m.r. spectra were measured on a Perkin-Elmer R12 60 MHz n.m.r. spectrometer, e.p.r. spectra on a Varian Associates E12 at X-band and mass spectra on a AEI MS-9.

Magnetic moments were determined in tetrahydrofuran solution with benzene as an internal reference using the Evans' method.[23]

All the complexes are sensitive to air and/or moisture and were handled by standard Schlenk or suba-seal and catheter tubing techniques under dry oxygen-free nitrogen, unless otherwise stated. Solvents were thoroughly and carefully dried and degassed before use.

The petroleum used had boiling range 40—60 °C unless otherwise stated.

μ-Hydrido-hexakisphenoxotrititanium(II,II,III) (Ti–Ti–Ti).—(a) Ti(OPh)$_2$Cl$_2$ (1.36 g, 4.46 mmol) was dissolved in toluene (30 cm^3) and added from a syringe to a dispersion of potassium (0.35 g, 8.97 mg-atom) in toluene (30 cm^3) under argon or nitrogen. After being stirred for 60 h at room temperature the black solution was filtered to free it from a brown tarry solid. Addition of petroleum (5 cm^3) and cooling of the filtrate afforded a grey air-sensitive powder which was recrystallised from toluene–petroleum; yield ca. 10%.

(b) A similar experiment to that described above was performed but using Na–Hg under argon.

The i.r. spectrum of the product showed the following absorptions: 1 583s, 1 258vs, 1 160m, 1 062w, 1 015w, 995w, 885sh, 850m, 825sh, 750vs, 685m, 620m, and 585m cm^{-1}.

With an excess of potassium and a reaction time of 5 days, a second grey solid, K$_{11}$Ti$_3$(OPh)$_7$ was isolated.

μ-Hydrido-μ-dinitrogen-tetrakisphenoxodititanium(III,IV).

* For this complex ν(Ti–Cl) is assigned to the vibrations at 390 and 460 cm^{-1} since the far-i.r. spectrum of this complex is similar to that obtained by evaporation of an acetone solution of Ti(O$_2$C$_6$H$_4$)Cl$_2$ to dryness, and the peaks at 390 and 460 cm^{-1} disappear on shaking Ti(O$_2$C$_6$H$_4$)Cl$_2$ with KI in acetone.

—Ti(OPh)$_2$Cl$_2$ (0.8 g, 2.62 mmol) in thf (20 cm^3) was added to an excess of sodium amalgam (5 cm^3, 1%) in thf (20 cm^3). The resulting grey suspension was rapidly stirred for 3 h under nitrogen (pressure ca. 5 mmHg above atmospheric). After the mixture had been allowed to settle, the red-brown solution was filtered and evaporated to dryness. The residue was extracted with toluene (20 cm^3) to give a brown tarry solid and a red-brown solution from which the complex was obtained, on addition of petroleum (10 cm^3) and cooling, as purple microcrystals. The complex was recrystallised from toluene–petroleum; yield ca. 10%; $\nu_{max.}$ 1 582s, 1 250sh, 1 223vs, 1 160m, 1 063w, 1 028m, 994m, 885sh, 850s, 750s, 718vw, 687s, 620sh, and 600 m cm^{-1}.

μ-Hydrido-di-μ-phenoxo-bis[chlorophenoxobistetrahydrofurantitanium(III,IV)].—Ti(OPh)$_2$Cl$_2$ (0.55 g, 1.8 mmol) in thf (20 cm^3) was treated with solid NaBH$_4$ (0.158 g, excess). After being stirred for 24 h under argon, the orange solution was filtered and treated with petroleum (5 cm^3). On cooling the mixture a yellow powder separated; this was collected and recrystallised from thf–petroleum to give yellow prisms; yield, ca. 70%; $\nu_{max.}$ 1 580s, 1 260sh, 1 240vs, 1 205vs, 1 158m, 1 062sh, 1 017m, 995w, 885s, 865vs, 818s, 755vs, 718sh, 687s, 640s, 610m, 565sh, 552s, 485m, 440s, 370m, and 350m cm^{-1}. The compound dissolved in toluene but slowly decomposed to give an insoluble brown solid.

Diphenoxobis(trimethylsilylmethyl)titanium(IV).— Ti(OPh)$_2$Cl$_2$ (2.65 g, 6.89 mmol) in diethyl ether (50 cm^3) was treated with Mg(CH$_2$SiMe$_3$)$_2$ (5.79 cm^3, 1.5M in diethyl ether) under argon at -70 °C. The resulting yellow solution was allowed to warm to -10 °C with stirring. After filtration and evaporation to dryness, the yellow tar was extracted with petroleum (50 cm^3) and concentrated, to yield yellow crystals of the complex. These were collected and dried in vacuo; yield ca. 20%; $\nu_{max.}$ 1 587s, 1 260vs, 1 205sh, 1 160m, 1 100sh, 1 068w, 1 022w, 1 000w, 900s, 850vs, 795w, 750vs, 690s, and 660m; δ 7.32, 7.18, 7.10, 7.00, 6.90, and 6.85 (total intensity = 10), 2.30(4), and 0.10(18); CCl$_4$, 36 °C.

Methyldiphenoxotitanium(III)   Oligomer.—Ti(OPh)$_2$Cl$_2$ (1.29 g, 4.23 mmol) in diethyl ether (30 cm^3) was treated with Me$_2$Mg (10.3 cm^3, 0.41M in diethyl ether) at -78 °C under argon. The orange solution was allowed to warm to -30 °C with stirring before being filtered and evaporated to dryness. The residue was dissolved in cold petroleum (50 cm^3) and, after concentration of the yellow solution, the complex was precipitated as thermally sensitive microcrystals. These were collected and dried in vacuo; yield ca. 20%.

When set aside at room temperature for a few hours the complex turned orange and was no longer soluble in petroleum. An analysis of the compound was consistent with its formation as {Ti$_3$(OPh)$_4$}$_2$. This product was also the final one if MeMgX (X = Cl or I) was employed for the reaction; $\nu_{max.}$ 1 585s, 1 257vs, 1 220sh, 1 160m, 1 065w, 1 018m, 998vw, 895s, 845w, 795w, 750vs, 720w, 685s, and 655m cm^{-1}.

1,2;1,5-Di-μ-chloro-1,2;1,5;2,3;2,3;3,4;3,4;4,5;4,5-octakis-μ-phenoxo-pentatitanium(II).—Ti(OPh)$_2$Cl$_2$(1.3 g, 4.26 mmol) and powdered zinc (4 g) were stirred in toluene (40 cm^3) under argon or nitrogen at room temperature for 72 h.

[22] D. F. Shriver, 'The Manipulation of Air-Sensitive Compounds,' McGraw-Hill, 1969.
[23] D. F. Evans, G. V. Fazakerley, and R. F. Phillips, J. Chem. Soc. (A), 1971, 1931.

The red solution was filtered and treated with petroleum (10 cm³). On cooling the complex separated as yellow microcrystals which were recrystallised from toluene–petroleum; yield *ca.* 70%; $\nu_{max.}$ 1 585s, 1 250vw, 1 205sh, 1 160m, 1 067w, 1 020m, 1 000vw, 912s, 842w, 795m, 753vs, 720vw, 687s, and 663w cm⁻¹; $\delta(CCl_4$ at 36 °C) 6.70br.

μ-Dimethylsilyl-octakis-μ-phenoxo-pentatitanium(II).— (a) $LiN(SiMe_3)_2$ (1.78 g, 10.76 mmol) in petroleum (7 cm³) was added to a suspension of $Ti(OPh)_2Cl_2$ (1.64 g, 5.38 mmol) in petroleum (50 cm³) at −70 °C. The suspension was allowed to warm to room temperature with stirring under argon and then stirred for a further 4 h. The orange solution was filtered and concentrated to 10 cm³ to give an orange powder; this was recrystallised from petroleum; yield *ca.* 30%; $\nu_{max.}$ 1 585s, 1 260vs, 1 240sh, 1 160m, 1 065w, 1 020w, 998w, 895s, 845w, 765sh, 750vs, 720vw, 687s, 662m, 620w, 580w, 560w, and 520m cm⁻¹; $\delta(CCl_4$, 36 °C) 6.98 (OPh), 0.51, and 0.48 (SiMe₂).

(b) A similar experiment to that described in (a) was performed in diethyl ether.

Dichloro[pyrocatecholato(2 −)]titanium(IV).—TiCl₄ (5 cm³, 45.5 mmol) was added to a suspension of pyrocatechol (5 g, 45.5 mmol) in toluene (70 ml) at −10 °C. The solution was then refluxed until HCl ceased to be evolved (litmus test on gases, 4 h). After cooling the reaction mixture to room temperature the black crystals that had formed were collected and dried *in vacuo*; yield *ca.* 90%; $\nu_{max.}$ 1 585m, 1 245w, 1 227s, 1 175s, 1 145vw, 1 098m, 1 015m, 975vw, 925w, 875s, 810vs, 742vs, 668vs, 625s, 560m, 550sh, 527s, 450vs, 435s, 408vs, 330vs, and 263m cm⁻¹.

Dichloro[pyrocatecholato(2 −)]titanium(IV)–Tetrahydrofuran-

(1/2).—$Ti(O_2C_6H_4)Cl_2$ (0.5 g) was dissolved in tetrahydrofuran (20 cm³) to give a red-brown solution; the complex was precipitated on addition of petroleum (10 cm³); $\nu_{max.}$ 1 575w, 1 314w, 1 245vs, 1 197m, 1 170sh, 1 100w, 1 040sh, 1 012m, 917w, 880m, 854s, 818vs, 743vs, 650s, 608s, 550w, 465s, 420sh, 400sh, 390s, 335w, and 260w cm⁻¹.

Dichloro[pyrocatecholato(2 −)]titanium(IV)–Pyridine (1/2).— This reaction was carried out as in the preceding experiment, pyridine being used in place of tetrahydrofuran. The complex separated as red crystals; $\nu_{max.}$ 1 630m, 1 600s, 1 580w, 1 528s, 1 505sh, 1 323w, 1 245vs, 1 200m, 1 160w, 1 093w, 1 050w, 1 012m, 1 000m, 910w, 880m, 820sh, 800s, 745vs, 680s, 622sh, 605s, and 485m cm⁻¹.

μ-Hydrido-μ-dinitrogen-bis[pyrocatecholato(2 −)]dititanium-(III,IV)—Tetrahydrofuran (1/1).——$Ti(O_2C_6H_4)Cl_2$ (0.66 g, 2.9 mmol) in thf (40 cm³) was added dropwise at room temperature to sodium amalgam (6 cm³, 1%) in thf (20 cm³). The resulting mixture was stirred under nitrogen at room temperature for 4 h. After being allowed to settle, the dark brown solution was filtered and evaporated to dryness. The residue was extracted with thf–petroleum, and the extract filtered and cooled to give the complex as brown microcrystals; yield >70%; $\nu_{max.}$ 1 575w, 1 318w, 1 250vs, 1 192m, 1 095w, 1 012m, 910sh, 865s, 800vs, 735vs, 620vs, and 500m cm⁻¹.