Ligation Studies of Titanium–Phenoxide and –Dimethylamide Derivatives with Covalent Metal Halides: a Route to Binuclear Transition-metal Complexes

By **Steven R. Wade, Malcolm G. H. Wallbridge,** and **Gerald R. Willey,*** Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

Convenient and high-yield syntheses for [Ti(cp)(OPh)$_3$] and [Ti(cp)Cl(OPh)$_2$] (cp = η-C$_5$H$_5$) are described. The donor characteristics of the mixed phenoxides [Ti(cp)$_n$(OPh)$_{4-n}$], n = 0, 1, or 2, [{TiCl$_2$(OPh)$_2$}$_2$], [Ti(cp)Cl(OPh)$_2$], and of Ti(NMe$_2$)$_4$ have been investigated. Reactions with MCl$_3$ (M = Ti, V, or Cr), VOCl$_3$, MX$_4$ (M = Ti, Zr, Hf, or Sn; X = Cl or Br), and MCl$_5$ (M = Nb, Ta, or Mo) generally feature exchange of OPh and NMe$_2$ groups with halide rather than complexation. In several instances, using appropriate reaction conditions, the solid adducts MX$_4$·Ti(NMe$_2$)$_4$ (M = Sn, X = Cl or Br; M = Zr or Hf, X = Cl), SnCl$_4$·[Ti(cp)$_2$(OPh)$_2$], and ZrCl$_4$·Ti(OPh)$_4$ have been isolated and fully characterised by analytical and spectral data.

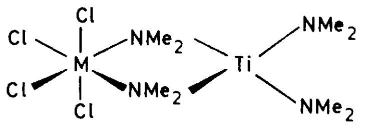
THE ability of titanium amides and thiolates to act as bridging ligands in the formation of heterobinuclear transition-metal complexes has been recognised, *viz.* *N*-bridged [Ti(cp)(NMe$_2$)$_3$·M(CO)$_3$], M = Cr, Mo, or W, and Ti(NMe$_2$)$_4$·SnCl$_4$;[2] *S*-bridged [Ti(cp)$_2$(SR)$_2$·M(CO)$_4$], M = Cr, Mo, or W, R = Me or Ph,[3-5,*] and [{Ti(cp)$_2$(SR)$_2$·CuX}$_n$], R = Me or Ph, X = Cl or Br.[6] For phenoxides, reaction of [Ti(cp)$_2$(OPh)$_2$] with Mo(CO)$_6$ gives the trinuclear *O*-bridged [Ti(cp)$_2$(OPh)$_2$·Mo(CO)$_2$·Ti(cp)$_2$(OPh)$_2$].[5] More recently, a variety of phenoxo-bridged titanium compounds, such as [{Ti(OPh)$_2$}$_3$H] and [{TiCl(OPh)$_2$(thf)$_2$}$_2$H] (thf = tetrahydrofuran), have been prepared by treating [TiCl$_2$(OPh)$_2$] with reducing agents.[7] Perhaps the main point of interest of these mixed-metal complexes concerns the presence or otherwise of a direct metal–metal bond across the MX$_2$M′ ring,[8] and the presence of different oxidation states for the metal atoms.

As an alternative to complexation, facile cleavage of Ti–N bonds can lead to scrambling reactions as demonstrated by the [Ti(cp)(NMe$_2$)$_3$]– and [Zr(cp)$_2$(NMe$_2$)$_2$]–MCl$_4$ (M = Si or Ge) systems where NMe$_2$–halide exchange is predominant.[9]

In this study the donor behaviour of the potential chelating ligands Ti(NMe$_2$)$_4$, [{TiCl$_2$(OPh)$_2$}$_2$], [Ti(cp)$_n$(OPh)$_{4-n}$] (n = 0, 1, or 2), and [Ti(cp)Cl(OPh)$_2$] towards suitable covalent metal halides has been studied to examine in more detail the factors which influence the ability of different groups to act as donors as opposed to undergoing exchange reactions.

RESULTS AND DISCUSSION

Reactions with Ti(NMe$_2$)$_4$.—Direct interaction of Ti(NMe$_2$)$_4$ and SnX$_4$ (X = Cl or Br) in n-pentane resulted in the precipitation of pale brown 1 : 1 adducts. Similar reactions with solid ZrCl$_4$ or HfCl$_4$ gave pale yellow solids, which proved to be non-stoicheiometric, possibly due to incomplete solvolysis of the metal halide lattice. As an alternative approach, ligand displacement of trimethylamine from MCl$_4$·2NMe$_3$ (M = Zr or Hf)[10,11] gave authentic 1 : 1 complexes. The possibility of complexation and/or reduction of Ti(NMe$_2$)$_4$ with the released NMe$_3$ was eliminated on the evidence of a separate study in which the tetra-amide remained unchanged in the presence of an excess of amine. The complexes MX$_4$·Ti(NMe$_2$)$_4$ (M = Sn, X = Cl or Br; M = Zr, X = Cl; M = Hf, X = Cl) are all highly air and moisture sensitive, and decompose in both co-ordinating (*e.g.* C$_5$H$_5$N, MeCN, or thf) and non-co-ordinating (CHCl$_3$, CH$_2$Cl$_2$, or C$_6$H$_6$) solvents. The proposed binuclear structure assumes the titanium in a pseudo-tetrahedral environment linked by two bridging amide groups to the heterometal which adopts a six-co-ordinate *cis* configuration (see below).



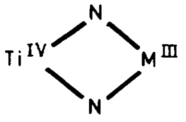
M = Sn, Zr, or Hf

Evidence for bidentate chelation comes from i.r. data, where intense broad bands at **325** [ν(Sn–Cl)], **221** [ν(Sn–Br)], **351**, **310** [ν(Zr–Cl)], and **301** cm^{-1} [ν(Hf–Cl)] respectively are typical of six-co-ordinate metal(IV) species. The intense ν_{asym}(TiN$_4$) stretching mode observed at 591 cm^{-1} for free Ti(NMe$_2$)$_4$[12] is seen to split in the complexes, *viz.* 724, 498 cm^{-1} [SnCl$_4$·L, L = Ti(NMe$_2$)$_4$], 723, 487 cm^{-1} (SnBr$_4$·L), 722, 509 cm^{-1} (ZrCl$_4$·L), and 723, 493 cm^{-1} (HfCl$_4$·L), in keeping with a reduction of Ti–N (d_π–p_π) bond order on co-ordination. Additional bands in the spectra of SnBr$_4$·L (466 cm^{-1}) and ZrCl$_4$·L (480 cm^{-1}) are tentatively assigned as ν(Sn–N) and ν(Zr–N) modes respectively.[13] Splitting of the N–CH$_3$ modes also occurs, *e.g.* the intense ν_{sym}(NC$_2$) mode at 945 cm^{-1} of Ti(NMe$_3$)$_4$[12] is found as a multiplet at 892, 878, and 861 cm^{-1} in SnCl$_4$·Ti(NMe$_2$)$_4$. The choice of solvent for these reactions is of paramount importance as complexation is observed *only* when n-pentane is used. Thus, reaction between Ti(NMe$_2$)$_4$ and SnCl$_4$ in benzene results in a dark brown solid from which

---

[*] Similar complexes involving [M(cp)$_2$(SR)$_2$] (M = Cr, Mo, or W; cp = η-C$_5$H$_5$) as a bidentate *S*-donor have been described, see *e.g.* A. R. Dias and M. L. H. Green, *J. Chem. Soc. A*, 1971, 1951; W. E. Douglas and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1972, 1796.

$[TiCl_3(NMe_2)]$ and $[TiCl_2(NMe_2)_2]$ were isolated by fractional sublimation. Equally, NMe_2–halide exchange was found for the $Ti(NMe_2)_4$–$MCl_4 \cdot 2NMe_3$ (M = Ti or Zr) systems in benzene and other halogenocarbon solvents; $[TiCl_2(NMe_2)_2]$ is the sole identifiable product in each case.



(1)

Reactions with $VCl_3 \cdot 3thf$, $MCl_3 \cdot 2NMe_3$ (M = Ti, V, or Cr), and $VOCl_3$ were studied in various solvents with the expectation of mixed metal–mixed valence rings of the type (1). Although *N*-chelation to these tervalent metal ions seemed feasible in view of the rapacious ' hard ' nature of the latter, the only products obtained from obviously complex mixtures were $[TiCl_3(NMe_2)]$ and $[TiCl_2(NMe_2)_2]$ following NMe_2–halide exchange.* These products were isolated by fractional sublimation as deep green $[TiCl_3(NMe_2)]$ and brown $[TiCl_2(NMe_2)_2]$ solids and identified by spectral (i.r. and ^1H n.m.r.) and volumetric (chloride) analyses.

Reactions with $[Ti(cp)_2(OPh)_2]$, $[Ti(cp)(OPh)_3]$, *and* $[Ti(cp)Cl(OPh)_2]$.—The complex $[Ti(cp)(OPh)_3]$ was obtained as bright yellow crystals from the reaction of $[Ti(cp)Cl_3]$ with three mole equivalents of PhOH in benzene solution using NEt_3 as a suitable scavenger for released HCl. Attempts to prepare $[Ti(cp)Cl(OPh)_2]$ following a similar route were unsuccessful; the required amount of amine hydrochloride was obtained but concentration of the resulting solution resulted in intractable dark brown oils. This mixed chloro–phenoxo-species was obtained, however, *via* disproportionation of $[Ti(cp)Cl_3]$ with two mole equivalents of $[Ti(cp)(OPh)_3]$ (see Experimental section). Both compounds are readily soluble in polar and non-polar solvents and are monomeric in benzene solution. Molecular-weight determinations (cryoscopic in benzene) gave: $[Ti(cp)(OPh)_3]$, 400, calc. 392.3; $[Ti(cp)Cl(OPh)_2]$, 342, calc. 334.6; $[Ti(cp)_2(OPh)_2]$ [19] 368, calc. 364.3, was also confirmed as a monomer.

The ^1H n.m.r. spectra (Table 1) of these phenoxides point to σ-bonded monomeric titanium species as demonstrated by the i.r. and molecular-weight data. There is a sharp singlet (cyclopentadienyl protons) and a complex multiplet (*o*-, *m*-, and *p*-protons of the phenyl ring). Chemical shifts are invariant with temperature (283—353 K, C_6D_6; 223—353 K, $CDCl_3$) but markedly solvent dependent; variations between $\delta_{aromatic}$ (C_6D_6, $C_6D_5CD_3$) and $\delta_{non\text{-}aromatic}$ (CCl_4, $CDCl_3$, CD_3CN) values are viewed as resulting from the aromatic ring–solvent interactions with cp and OPh ligands, as opposed to the variations arising from the change in the polarity of the solvent.

TABLE 1

Proton n.m.r. data for titanium phenoxides *

	$CDCl_3$		C_6D_6	
Compound	Singlet	Complex multiplet	Singlet	Complex multiplet
$[Ti(cp)_2(OPh)_2]$	6.27 (cp)	6.63—6.68 (*ortho*)	5.89 (cp)	6.77—6.93 (*ortho* + *para*)
		6.75—6.85 (*para*)		
		7.18—7.27 (*meta*)		7.22—7.32 (*meta*)
$[Ti(cp)(OPh)_3]$	6.37 (cp)	6.87—6.97 (*ortho* + *para*)	5.97 (cp)	6.25—6.92 (*ortho* + *para*)
		7.21—7.31 (*meta*)		7.07—7.17 (*meta*)
$[Ti(cp)Cl(OPh)_2]$	6.54 (cp)	6.95—7.13 (*ortho* + *para*)	6.06 (cp)	6.83—6.96 (*ortho* + *para*)
		7.30—7.45 (*meta*)		7.05—7.14 (*meta*)

* δ (p.p.m.) values recorded at room temperature (290 K) with $SiMe_4$ as internal standard.

Reactions of $[Ti(cp)_2(OPh)_2]$, $[Ti(cp)(OPh)_3]$, and $[Ti(cp)Cl(OPh)_2]$ with a number of ' hard ' covalent metal halides invariably resulted in phenoxide–halogen exchange leading to complex mixtures. Adduct formation was found only in one case, *viz.* $SnCl_4 \cdot [Ti(cp)_2(OPh)_2]$ precipitated from solution as a pale pink solid when $SnCl_4$ was added dropwise to a chilled n-hexane solution of $[Ti(cp)_2(OPh)_2]$. The band at 1 284 cm^{-1} in the i.r. spectrum of $[Ti(cp)_2(OPh)_2]$ [19] assigned as a ν(C–O) mode appears as a single band at lower energy (1 204 cm^{-1}) in the complex, denoting σ-bonded phenoxide groups. A strong broadened ν(Sn–Cl) mode at 345 cm^{-1} is in accord with a proposed *cis* chelated six-co-ordinate structure. Solution studies were marred by immediate decomposition of the complex in the common solvents even in an inert atmosphere. The choice of n-hexane as reaction solvent proved to be fortuitous as repeat experiments in benzene and halogenocarbon solvents gave red oily solutions from which only $[Ti(cp)_2Cl_2]$ could be extracted as an identifiable product arising from an exchange reaction.

Investigation of the $[Ti(cp)_2(OPh)_2]$–$TiCl_4$ system in benzene solution showed that the reactions yield a series of intractable red oils; on changing to n-hexane as solvent, a clean reaction occurred to give a red solid. A Soxhlet

---

* In view of their proven ability to form stable *S*-bonded chelates with metal halides and carbonyls, the titanium thiolates $[Ti(cp)_2(SR)_2]$ (R = Et or Ph) appear the more likely precursors for such rings. Preliminary results with the $[Ti(cp)_2(SEt)_2]$–$MCl_3 \cdot 3thf$ and $[Ti(cp)_2(SEt)_2]$–$MCl_3 \cdot 2NMe_3$ systems (M = Ti, V, or Cr), however, point conclusively towards halide exchange rather than the formation of the desired mixed-valence ring species. Each reaction provides $[Ti(cp)_2Cl_2]$ and other, as yet unidentified, products. The relative ' hard ' metal(III) acid–' soft ' *S*-donor ligand mismatch and the ease of degradation of alkanethiolatometal chloride species with incipient thermodynamic and kinetic instability [14–17] are seen as obvious deterrents to complex formation.[18]

extraction with light petroleum (b.p. 40—60 °C) gave (soluble) $[\{\mathrm{TiCl_2(OPh)_2}\}_2]$ and (insoluble) $[\mathrm{Ti(cp)_2Cl_2}]$, approximately 1 : 1, as confirmed by spectral (i.r. and n.m.r.) analyses, equation (1). Related behaviour was observed

$$[\mathrm{Ti(cp)_2(OPh)_2}] + \mathrm{TiCl_4} \xrightarrow{\text{n-hexane}} [\mathrm{Ti(cp)_2Cl_2}] + \tfrac{1}{2}[\{\mathrm{TiCl_2(OPh)_2}\}_2] \qquad (1)$$

in reactions with $\mathrm{MCl_4{\cdot}2NMe_3}$ (M = Zr or Hf) and $\mathrm{SnBr_4}$ with appreciable recovery of the bis(cyclopentadienyl)titanium dihalide in each case. Again halide exchange rather than complexation was observed in reactions with the tervalent metals $\mathrm{MCl_3{\cdot}3thf}$ (M = Ti, V, or Cr).

The complex $[\mathrm{Ti(cp)(OPh)_3}]$ reacts directly with $\mathrm{SnX_4}$ (X = Cl or Br), and by ligand displacement with $\mathrm{MCl_3{\cdot}2NMe_3}$ (M = V or Cr), to give a series of complexes which proved non-stoicheiometric. Work-up of the reaction products of $[\mathrm{Ti(cp)(OPh)_3}]$ with $\mathrm{TiCl_4}$ or $\mathrm{TiCl_3{\cdot}2NMe_3}$ gave only trace amounts of the exchange product $[\mathrm{Ti(cp)Cl_3}]$. Electronegativity effects of the chloro-substituent *in* $[\mathrm{Ti(cp)Cl(OPh)_2}]$ would be expected to diminish the basicity of the donor groups with respect to those in $[\mathrm{Ti(cp)_2(OPh)_2}]$, and this is reflected in the observed chemistry whereby reactions in n-pentane with $\mathrm{TiCl_4}$ and $\mathrm{MCl_4{\cdot}2NMe_3}$ (M = Zr or Hf) gave phenoxide–halide exchange throughout, equation (2). No reaction

$$[\mathrm{Ti(cp)Cl(OPh)_2}] + \mathrm{MX_4} \longrightarrow [\mathrm{Ti(cp)Cl_3}] + [\mathrm{MX_2(OPh)_2}] \qquad (2)$$

was observed between $\mathrm{SnX_4}$ (X = Cl or Br) and $[\mathrm{Ti(cp)Cl(OPh)_2}]$.

Reactions with $\mathrm{Ti(OPh)_4}$.—A convenient route to $\mathrm{Ti(OPh)_4}$ utilises the reaction of $\mathrm{Ti(OEt)_4}$ and four mole equivalents of phenyl acetate in refluxing light petroleum (b.p. 100—120 °C). Removal by distillation of the ethyl acetate formed leaves a deep red solution from which orange crystals of the product separate on cooling to 273 K. The compound $\mathrm{Ti(OPh)_4}$ is variously described as monomeric [20] and dimeric.[7] From our results, obtained cryoscopically in benzene, the molecular weight is concentration-dependent approaching the dimeric value only at higher concentrations. Reaction of $\mathrm{Ti(OPh)_4}$ with an equimolar amount of $\mathrm{TiCl_4}$ in either benzene or n-hexane solutions gave $[\{\mathrm{TiCl_2(OPh)_2}\}_2]$ in almost quantitative yield and offers a viable alternative route to this phenoxo-bridged dimeric species.* With $\mathrm{SnX_4}$ (X = Cl or Br), however, the reactants were recovered unchanged. The pentahalides $\mathrm{MCl_5}$ (M = Nb, Ta, or Mo) gave bright red, yellow, and brown solid products respectively. A complex profile of ν(C–O) bands (1 170—1 260 $\mathrm{cm^{-1}}$) implicate both free and co-ordinated σ-bonded phenoxide groups but the analytical data were inconsistent with a 1 : 1 adduct formulation. One complex was isolated as $\mathrm{ZrCl_4{\cdot}Ti(OPh)_4}$ following direct addition using an n-pentane suspension of $\mathrm{ZrCl_4{\cdot}2NMe_3}$. The pale orange product was extremely air and moisture sensitive and insoluble in the common solvents. From the solid-state i.r. spectrum, the ν(C–O) bands at 1 285, 1 270, 1 250 (sh), and 1 225 (sh) $\mathrm{cm^{-1}}$ do not differ appreciably from those of free $\mathrm{Ti(OPh)_4}$ suggesting a similar structural environment for the ligand in both complexed and non-complexed forms. An intense ν(Zr–Cl) band at 300 (br) $\mathrm{cm^{-1}}$ is consistent with a six-co-ordinate zirconium(IV) moiety. Although $\mathrm{Ti(OPh)_4}$ can function as a weak Lewis acid to give 1 : 1 complexes with a number of ligands [22] there is no complication of side reactions with the released $\mathrm{NMe_3}$ in the present instance. We were able to recrystallise $\mathrm{Ti(OPh)_4}$ unchanged from a neat solution in trimethylamine.

Finally, $[\{\mathrm{TiCl_2(OPh)_2}\}_2]$ proved unreactive towards $\mathrm{SnX_4}$ (X = Cl or Br), $\mathrm{MCl_5}$ (Nb, Ta, or Mo), and $\mathrm{MCl_3{\cdot}2NMe_3}$ (M = Ti, V, or Cr). Equimolar addition to $\mathrm{TiCl_4}$ in n-hexane gave $[\mathrm{TiCl_3(OPh)}]$ in almost quantitative yield. Infrared bands at 1 216, 1 207, and 1 175 $\mathrm{cm^{-1}}$ [ν(C–O) bridging] and 465, 424, and 388 $\mathrm{cm^{-1}}$ [ν(Ti–Cl) terminal] indicate a phenoxide-bridged polymeric structure in the solid state.

EXPERIMENTAL

All manipulations of air-sensitive materials were carried out either using an all-glass vacuum line, or in a nitrogen-filled dry-box. Solvents were distilled from either $\mathrm{P_2O_5}$ or $\mathrm{CaH_2}$ under an inert atmosphere prior to use. The compound $\mathrm{Ti(NMe_2)_4}$ was prepared as described,[23] as was $[\mathrm{Ti(cp)_2(OPh)_2}]$ [19] which was recrystallised from n-hexane. The compound $[\mathrm{Ti(cp)Cl_3}]$ was prepared by a redistribution reaction between $[\mathrm{Ti(cp)_2Cl_2}]$ and $\mathrm{TiCl_4}$.[24]

Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer as Nujol or hexachlorobutadiene mulls sandwiched between CsI plates. Hydrogen-1 n.m.r. spectra (220 MHz) were obtained using a Perkin-Elmer R34 instrument, with $\mathrm{SiMe_4}$ as an internal reference. Molecular weights were determined cryoscopically in benzene. Microanalyses were carried out by BMAC, Teddington, and halide was evaluated by the Volhard method. Data are listed in Table 2.

Preparation of Titanium Phenoxides.—$[\mathrm{Ti(cp)(OPh)_3}]$. A mixture of PhOH (15.6 g, 16.6 mmol) and $\mathrm{NEt_3}$ (16.8 g, 16.6 mmol) in benzene (100 $\mathrm{cm^3}$) was added dropwise with stirring to a benzene (300 $\mathrm{cm^3}$) solution of $[\mathrm{Ti(cp)Cl_3}]$ (12.1 g, 5.5 mmol). A white precipitate formed almost immediately. After stirring for 24 h the mixture was filtered to give a deep yellow solution and three mole equivalents of $\mathrm{NEt_3{\cdot}HCl}$. Concentration of the yellow solution resulted in a dark brown solid, which on recrystallisation (n-hexane) gave $[\mathrm{Ti(cp)(OPh)_3}]$ (15.0 g, 69.3%) as bright yellow crystals, m.p. 365—366 K (uncorrected).

$[\mathrm{Ti(cp)Cl(OPh)_2}]$. The complex $[\mathrm{Ti(cp)(OPh)_3}]$ (1.25 g, 3.2 mmol) in n-hexane (5 $\mathrm{cm^3}$) was added to a slurry of $[\mathrm{Ti(cp)Cl_3}]$ (0.35 g, 1.6 mmol) in n-hexane (10 $\mathrm{cm^3}$), and the resultant solution stirred for 2 h. Removal of the solvent *in vacuo* gave a yellow solid, which on recrystallisation (n-hexane) gave bright yellow needles of $[\mathrm{Ti(cp)Cl(OPh)_2}]$ (1.1 g, 68.8%), m.p. 340—341 K (uncorrected).

$\mathrm{Ti(OPh)_4}$. The complex $\mathrm{Ti(OEt)_4}$ (11.1 g, 48.5 mmol) and

---

* The complex $[\{\mathrm{TiCl_2(OPh)_2}\}_2]$ is dimeric with two bridging phenoxo-groups in the solid state.[21] In solution both a monomeric [20] and a dimeric [7] formulation have been proposed. From mass-spectral data, breakdown to the monomer does occur in the vapour phase.[7]

TABLE 2

Microanalytical data for complexes

Complex	Found (%) C	H	N	Halogen	Calc. (%) C	H	N	Halogen
$[Ti(cp)(OPh)_3]$	70.3	5.1			70.4	5.1		
$[Ti(cp)Cl(OPh)_2]$	61.1	6.4		10.7	61.0	4.5		10.6
$Ti(OPh)_4$	68.6	4.9			68.6	4.8		
$SnCl_4\cdot[Ti(cp)_2(OPh)_2]$	42.5	3.3		22.5	42.3	3.2		22.7
$ZrCl_4\cdot Ti(OPh)_4$	44.1	3.2		21.6	44.1	3.1		21.7
$SnCl_4\cdot Ti(NMe_2)_4$	19.6	4.8	11.2	30.0	19.8	5.0	11.5	29.3
$SnBr_4\cdot Ti(NMe_2)_4$	14.2	2.5	8.2	48.1	14.5	3.6	8.5	48.3
$ZrCl_4\cdot Ti(NMe_2)_4$	21.2	5.4	12.4	31.0	21.0	5.3	12.3	31.0
$HfCl_4\cdot Ti(NMe_2)_4$	17.4	4.3	10.0	25.6	17.6	4.4	10.3	26.0

$PhCO_2Me$ (26.4 g, 24.5 mmol) were dissolved in light petroleum (b.p. 100—120 °C), and the solution heated at reflux under N_2 for 1 h. During this time the solution turned from colourless to deep red. Removal of $EtCO_2Me$ (four mole equivalents) by distillation resulted in an orange solution which was cooled to 273 K, whereupon orange crystals deposited. These were collected and recrystallised from n-hexane (yield 16.4 g, 80.4%).

Preparation of Complexes.—The complexes $SnCl_4\cdot[Ti(cp)_2(OPh)_2]$ and $SnX_4\cdot Ti(NMe_2)_4$ ($X = Cl$ or Br) were prepared by direct addition of the appropriate tin(IV) halide to n-hexane solutions of the ligand, thus $SnCl_4$ (0.35 cm^3, 3.0 mmol) in n-hexane (50 cm^3) was added dropwise to a stirred solution of $[Ti(cp)_2(OPh)_2]$ (1.09 g, 3.0 mmol). The pale brown product precipitated immediately from solution, and was washed *in vacuo* with n-hexane (4 × 100 cm^3) before being pumped *in vacuo* for 3 h at room temperature, and finally sealed into glass ampoules (yield 1.21 g, 65.1%).

The complexes $Ti(OPh)_4\cdot ZrCl_4$ and $Ti(NMe_2)_4\cdot MCl_4$ ($M = Zr$ or Hf) were prepared by displacement of NMe_3 from n-pentane suspensions of the bis(amine) adducts, thus $Ti(NMe_2)_4$ (0.30 cm^3, 1.25 mmol) in n-pentane (100 cm^3) was added dropwise to a suspension of $ZrCl_4\cdot 2NMe_3$ (0.44 g, 1.25 mmol) in n-pentane (200 cm^3). The evolved NMe_3 was trapped in a gas cell, and identified by its i.r. spectrum. After stirring the reaction mixture for 24 h, a yellow precipitate separated and this was collected, washed *in vacuo* (n-hexane, 4 × 100 cm^3), and finally dried by pumping *in vacuo* for 3 h at room temperature (yield 0.49 g, 85.7%).

We thank the S.R.C. for financial assistance in support of this project.

[1/992 *Received, 18th June,* 1981]

REFERENCES

[1] D. C. Bradley and A. S. Kasenally, *Chem. Commun.*, 1968, 1430.

[2] M. F. Lappert and G. Srivastava, *Inorg. Nucl. Chem. Lett.*, 1965, **1**, 53.

[3] K. K. Joshi, R. Wardle, and V. A. Wilson, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 49.

[4] P. S. Braterman, V. A. Wilson, and K. K. Joshi, *J. Chem. Soc. A*, 1970, 191.

[5] H. Köpf and K. H. Räthlein, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 980.

[6] P. S. Braterman and V. A. Wilson, *J. Organomet. Chem.*, 1971, **31**, 131.

[7] A. Flamini, D. J. Cole-Hamilton, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 454.

[8] G. R. Davies and B. T. Kilbourn, *J. Chem. Soc. A*, 1971, 87 and refs. therein.

[9] S. R. Wade and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1981, 1264.

[10] J. Hughes and G. R. Willey, *Inorg. Chim. Acta*, 1976, **20**, 137.

[11] G. R. Willey, *Inorg. Chim. Acta*, 1977, **21**, L12.

[12] H. Bürger, H. Stammreich, and Th. Teixeira Sans, *Monatsh. Chem.*, 1966, **97**, 1276.

[13] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1969, 980.

[14] M. Woods, J. Karbwang, J. C. Sullivan, and C. Deutsch, *Inorg. Chem.*, 1976, **15**, 1678.

[15] P. M. Boorman, T. Chivers, K. N. Mahadev, and B. D. O'Dell, *Inorg. Chim. Acta*, 1976, **19**, L35.

[16] L. S. Jenkins and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1979, 1697.

[17] P. M. Boorman and B. D. O'Dell, *J. Chem. Soc., Dalton Trans.*, 1980, 157.

[18] L. S. Jenkins and G. R. Willey, unpublished work.

[19] K. Andrä, *J. Organomet. Chem.*, 1968, **11**, 567.

[20] M. J. Frazer and Z. Goffer, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2410.

[21] K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, 1966, **5**, 1782.

[22] H. Funk and A. Masthoff, *J. Prakt. Chem.*, 1956, **4**, 35.

[23] D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, 3857.

[24] R. D. Gorsich, *J. Am. Chem. Soc.*, 1960, **82**, 4211.