# Insertion and Related Reactions of Bis(η-cyclopentadienyl)dimethyltitanium, η-Cyclopentadienyltrimethyltitanium, and Trichloro(η-cyclopentadienyl)titanium and Other Titanium Compounds

By **Robin J. H. Clark,* James A. Stockwell,** and **John D. Wilkins,** Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

The reaction of $[(cp)_2TiMe_2]$ with cyclohexyl isocyanide ($C_6H_{11}NC$) yields the complex $[(cp)_2TiMe\{C(Me){:}NC_6H_{11}\}]$, which further reacts with iodine to give the complex $[(cp)_2TiI\{C(Me){:}NC_6H_{11}\}]$. The reactions of $[(cp)TiMe_3]$ with NO, $SO_2$, RNC (R = $C_6H_{11}$ or *p*-tolyl), MeNCO and PhNCS have been studied and the complexes $[(cp)TiMe\{ON(Me)NO\}_2]$ and $[(cp)TiMe_2(SO_2Me)]$ have been isolated and characterised. The reactions of $[(cp)TiCl_3]$ and $[(cp)TiMe_3]$ with Lewis bases have been studied and the complexes $[(cp)TiCl_3(diars)]$ and $[(cp)TiCl_3(bipy)]$ isolated [diars = *o*-phenylenebis(dimethylarsine), bipy = 2,2′-bipyridyl]. The complexes $[(cp)_2TiBr(OCH_2CH_2CH{:}CH_2)]$ and $[(cp)TiMe_2(OCH_2CH_2CH{:}CH_2)]$ have been prepared and it has been shown that the olefinic group is not co-ordinated to the titanium atom in either case. Attempts to co-ordinate the olefinic grouping of the ligand $Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}N(Me){\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$ to titanium tetrachloride and titanium trichloride are also described.

THERE is currently considerable interest in so-called insertion reactions involving the metal–carbon bonds of compounds of the early transition elements.[1-9] In particular those reactions involving unsaturated reagents are of interest because the mechanism of Ziegler catalysis is thought to involve insertion of an olefin into a titanium–carbon σ-bond.[10] Reactions of σ-bonded alkyls of several early transition-metals with reagents such as NO,[2,3,6] $O_2$,[11-13] $SO_2$,[2,8,9,14] CO,[1,15] RNC,[5] RNCO,[5] and RNCS [4] have been studied. In many cases insertion of the unsaturated reagent into the metal–carbon bond is observed. We have now studied the reactions of $[(cp)_2TiMe_2]$ and $[(cp)TiMe_3]$ (cp = η-cyclopentadienyl) with some potential insertion reagents together with some related reactions of $[(cp)TiCl_3]$ and other organotitanium compounds.

## EXPERIMENTAL

*Starting Materials.*—Solvents were dried and degassed by standard methods before use. $[(cp)_2TiMe_2]$ Was prepared from $[(cp)_2TiCl_2]$ (Alfa Inorganics) by the method of Wailes *et al.*[8] $[(cp)TiMe_3]$ Was prepared from $[(cp)TiCl_3]$ by the literature method,[16] a fresh sample being prepared immediately before each reaction. $[(cp)_2Ti(CH_2Ph)_2]$ Was prepared from $[(cp)_2TiCl_2]$ and a freshly prepared and standardised solution of $PhCH_2MgBr$. $TiCl_4$ Was supplied by B.D.H. Cyclohexyl isocyanide and *p*-tolyl isocyanide were prepared by literature methods; [17] methyl isocyanate and phenyl isothiocyanate were obtained from Eastman-Kodak and Koch-Light respectively. *o*-Phenylenebis(dimethylarsine) (diars) was prepared in the Departmental synthetic laboratory, and $Me_3As$ was prepared from $AsCl_3$ and

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MeMgI in $\mathrm{Bu^n{}_2O}$. The above liquid ligands were dried with molecular sieves (4A) and freshly distilled before use. Solid ligands [2,2′-bipyridyl, triphenylphosphine (B.D.H.)] were dissolved in the appropriate solvent and dried over $\mathrm{LiAlH_4}$. Iodine was sublimed prior to use. $\mathrm{SO_2}$ (B.D.H.) and $\mathrm{H_2}$ (B.O.C.) were used as supplied. NO (Matheson) was dried by passage through a trap at −78 °C while CO (Air Products) was purified by passage through a solution of alkaline pyrogallol and dried over phosphoric oxide.

*N*-But-3-enyl-*NN′N′*-trimethylethanediamine (bte) was prepared by the following route. *NNN′*-Trimethylethanediamine (50 cm$^3$) and 1-bromobut-3-ene (10 g) were stirred at room temperature for 3 h. Fractionation of the mixture yielded a final fraction (b.p >100 °C at 15 mmHg) which was shown (g.l.c.) to contain 90% of the product and 10% of unchanged secondary amine. The secondary amine was removed as follows. The sample was dissolved in water, acidified with perchloric acid, cooled to 3—4 °C, and sufficient of an ice-cold solution of $\mathrm{NaNO_2}$ was added to react with the secondary amine. The solution was set aside at room temperature for *ca.* 1 h and then extracted with $\mathrm{CHCl_3}$ (2 × 50 cm$^3$). The aqueous layer was made alkaline (NaOH solution) and extracted with ether (2 × 50 cm$^3$). After the drying ($\mathrm{Na_2SO_4}$) of the ether extract and its fractional distillation, bte (98% pure by g.l.c.) was obtained as the final fraction (b.p. 80—85 °C at 15 mmHg).

*Preparation of* $\mathrm{[(cp)TiMe\{ON(Me)NO\}_2]}$. NO Was passed into a solution of $\mathrm{[(cp)TiMe_3]}$ (*ca.* 1 g) in pentane (100 cm$^3$) at −78 °C. The mixture was stirred at −78 °C for 1.5 h after which the excess of NO was pumped off; the yellow solid complex was filtered off, washed with pentane (2 × 10 cm$^3$), dried *in vacuo*, and stored in a vacuum manifold.

*Preparation of* $\mathrm{[(cp)TiMe_2(SO_2Me)]}$. Sulphur dioxide was carefully admitted to a solution of $\mathrm{[(cp)TiMe_3]}$ (1 g) in pentane (30 cm$^3$) at −78 °C. The solvent was decanted from the red solid which had formed after 5 min reaction time, and the red solid was then washed with pentane at −30 °C to remove any unchanged $\mathrm{[(cp)TiMe_3]}$. The product was dried *in vacuo* and stored in a vacuum manifold.

*Preparation of* $\mathrm{[(cp)TiCl_3(diars)]}$. A solution of diars (0.0014 mol) in toluene (20 cm$^3$) was slowly added to a solution of $\mathrm{[(cp)TiCl_3]}$ (0.0014 mol) in toluene (30 cm$^3$). The volume of the solution was reduced to *ca.* 20 cm$^3$ and cyclohexane (20 cm$^3$) was added. A pale yellow solid slowly precipitated from the solution on cooling. The solid was filtered off, washed with cyclohexane (2 × 10 cm$^3$), and dried *in vacuo*. A *ca.* $10^{-3}$ M-solution in MeCN gave $\Lambda_m = 2.9\ \mathrm{cm^2\ \Omega^{-1}\ mol^{-1}}$.

*Preparation of* $\mathrm{[(cp)TiCl_3(bipy)]}$. The procedure was the same as for $\mathrm{[(cp)TiCl_3(diars)]}$ except that the pale pink solid precipitated immediately the solutions of $\mathrm{[(cp)TiCl_3]}$ and 2,2′-bipyridyl were mixed.

TABLE 1

Analytical data for the complexes prepared

| Complex[a] | Colour | Found (%) C | H | N | Ti | Cl or Br | Calculated (%) C | H | N | Ti | Cl or Br |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\mathrm{[(cp)_2TiMe(CMe{:}NC_6H_{11})]}$ | Pale yellow | 72.1 | 8.6 | 4.2 | 14.7 | | 72.0 | 8.6 | 4.4 | 15.1 | |
| $\mathrm{[(cp)_2TiI(CMe{:}NC_6H_{11})]}$ | Yellow | 49.9 | 6.3 | 3.3 | 10.2 | | 50.4 | 5.6 | 3.3 | 11.2 | |
| $\mathrm{[(cp)TiMe\{ON(Me)NO\}_2]}$ | Yellow | 33.6 | 4.9 | 20.2 | 17.4 | | 34.6 | 5.1 | 20.2 | 17.2 | |
| $\mathrm{[(cp)TiMe_2(SO_2Me)]}$[b] | Red | 42.6 | 6.2 | | 21.5 | | 43.2 | 6.3 | | 21.6 | |
| $\mathrm{[(cp)TiCl_3(diars)]}$ | Pale yellow | 36.6 | 4.4 | | 9.6 | 20.3 | 35.6 | 4.4 | | 9.5 | 21.1 |
| $\mathrm{[(cp)TiCl_3(bipy)]}$ | Pale pink | 46.2 | 3.7 | 7.4 | 12.5 | | 48.0 | 3.5 | 7.5 | 12.8 | |
| $\mathrm{[TiCl_4(bte)]}$[c] | Yellow | 29.3 | 6.0 | 7.4 | | | 31.2 | 5.8 | 8.1 | | |
| $\mathrm{[(cp)_2TiBr(bea)]}$ | Pale orange | 50.1 | 5.0 | | | 24.7 | 51.2 | 5.2 | | | 24.3 |
| $\mathrm{[(cp)TiMe_2(bea)]}$ | Yellow-orange[d] | 60.7 | 8.3 | | 21.1 | | 61.7 | 8.5 | | 22.4 | |

[a] cp = η-cyclopentadienyl group, diars = *o*-phenylenebisdimethylarsine, bipy = 2,2′-bipyridyl. [b] Found S, 13.7, required S, 14.4. [c] Could not be obtained pure. [d] Liquid.

But-3-enyldimethylarsine (bda) was prepared by the literature method.[18] But-3-enol (Hbea) was obtained from Fluka and dried as previously reported.[19]

*Preparation of Complexes.*—All manipulations were carried out *in vacuo* or in an atmosphere of dry oxygen-free nitrogen.[11] Analyses and spectral measurements were performed as previously described.[19] Analytical data for the complexes prepared are listed in Table 1.

*Preparation of* $\mathrm{[(cp)_2TiMe\{C(Me){:}NC_6H_{11}\}]}$. $\mathrm{[(cp)_2TiMe_2]}$ (1.1 g, 0.005 mol) in pentane (50 cm$^3$) was treated with a solution of cyclohexyl isocyanide (1.2 g, 0.011 mol) in pentane (10 cm$^3$) at *ca.* −30 °C. The mixture was stirred for 1 h at −30 °C and then warmed to room temperature; the volume of solution was reduced until an off-white solid could be obtained on cooling of the solution to −78 °C. The solid was recrystallised from pentane to yield a pale-yellow solid which was dried *in vacuo* and stored in a vacuum manifold.

$\mathrm{[(cp)_2TiI\{C(Me){:}NC_6H_{11}\}]}$ was prepared by mixing equimolar quantities of iodine and $\mathrm{[(cp)_2TiMe\{C(Me){:}NC_6H_{11}\}]}$ in $\mathrm{CH_2Cl_2}$ at 0 °C and removing the solvent *in vacuo*.

*Reaction of* $\mathrm{TiCl_4}$ with bte. A solution of bte (1.1 g, 0.006 mol) in hexane (10 cm$^3$) was slowly added to a solution of $\mathrm{TiCl_4}$ (1.1 g, 0.006 mol) in hexane (50 cm$^3$) at room temperature. The yellow solid which precipitated from solution was filtered off, washed with hexane (2 × 10 cm$^3$), dried *in vacuo*, and stored in a vacuum manifold. Although the analytical data for this complex are not wholly satisfactory, there seems to be little doubt as to its correct formulation.

*Preparation of* $\mathrm{[(cp)_2TiBr(bea)]}$. But-3-enol (Hbea) (0.11 g, 0.0015 mol) in hexane (5 cm$^3$) was added to a suspension of $\mathrm{[(cp)_2TiBr_2]}$ (prepared by the method of Lappert *et al.*)[20] in $\mathrm{Et_3N}$ (0.17 g, 0.0017 mol) and benzene (50 cm$^3$). After the mixture had been stirred for six days at room temperature, the white solid formed was extracted with diethyl ether. The complex was precipitated by adding hexane to the resulting solution, and then allowing a slow evaporation of the solvent. The resulting pale orange crystals were filtered off and dried *in vacuo*. A *ca.* $10^{-3}$M-solution in MeCN gave $\Lambda_m = 28.4\ \mathrm{cm^2\ \Omega^{-1}\ mol^{-1}}$.

*Preparation of* $\mathrm{[(cp)TiMe_2(bea)]}$. A solution of Hbea

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(0.13 g, 0.0018 mol) in pentane (40 cm$^3$) was slowly added during 30 min to a stirred solution of $[(cp)TiMe_3]$ (0.29 g, 0.0018 mol) in pentane (50 cm$^3$) at $-78$ °C. The mixture was slowly warmed to room temperature, filtered, and the solvent removed to yield a pale orange oil. The oil was sublimed (50 °C, $10^{-1}$ mmHg) onto a cold probe ($-78$ °C). A solid was thereby obtained, which melted to a pale yellow liquid at *ca.* 0 °C.

## RESULTS AND DISCUSSION

*Reactions with Isocyanides.*—Bis($\eta$-cyclopentadienyl)-dimethyltitanium reacts readily with cyclohexyl isocyanide to yield $[(cp)_2TiMe\{C(Me){:}NC_6H_{11}\}]$ (I). No further insertion ensues even if an excess of $C_6H_{11}NC$ is present. It may be deduced from the $^1$H n.m.r. spectrum of this complex (Table 2) that insertion into one of the Ti–Me bonds has taken place; two distinct methyl resonances are present and the cyclopentadienyl resonances are shifted only slightly from their values for the dimethyl complex. The i.r. spectrum of the insertion product shows a band at 1 680 cm$^{-1}$ attributable to $\nu$(C=N) while there is no band at *ca.* 2 200 cm$^{-1}$ attributable to either a free or a co-ordinated isocyanide group. The mass spectrum (60 °C input) of the insertion product showed the parent ion ($m/e$ = 317) and no ions of higher mass. It thus seems likely that the complex is monomeric but, unfortunately, this could not be established for certain because it decomposed very quickly in solvents suitable for molecular-weight measurements. Similar modes of insertion have been noted with other early transition-metal alkyls.[5] Attempts to prepare a complex analogous to (I) using *p*-tolyl isocyanide yielded only sticky brown solids at room temperature, but reaction at $-50$ °C yielded a material which appeared to be a mixture of $[(cp)_2TiMe_2]$ and an insertion product. The complex $[(cp)_2Ti(CH_2Ph)_2]$ did not react with $C_6H_{11}NC$ even after several hours' reaction time at room temperature.

TABLE 2

Proton n.m.r. spectral data [a]

| Complex | | Solvent | cp | X-Me | Ti-Me | Other resonances |
|---|---|---|---|---|---|---|
| $[(cp)_2TiMe_2]$ | | $C_6D_6$ | 5.69(10.0) | | 0.05(5.9) | |
| $[(cp)TiMe_3]$ | | $C_6D_6$ | 5.90(5.0) | | 1.18(9.4) | |
| $[(cp)_2TiMe\{C(Me){:}NC_6H_{11}\}]$ | [I] | $C_6D_6$ | 5.14(10.0) | 2.02(3.1) [c] | 0.69(3.1) | 3.5 [b] (1.1) CH group, 0.8—1.9 [b] (11) $CH_2$ groups |
| $[(cp)TiMe_2(SO_2Me)]$ | [III] | $CDCl_3$ | 6.37(5.0) | 2.55(3.3) [d] | 0.88(5.8) | |
| $[(cp)TiMe\{ON(Me)NO\}_2]$ | [II] | $CDCl_3$ | 6.22(4.7) | 3.90(6.1) [e] | 0.82(3.0) | |
| $[(cp)TiCl_3]$ | | $CDCl_3$ | 7.11 | | | |
| diars | | $CDCl_3$ | | 1.23(12.0) | | 7.45 [b] (4.4) aromatic protons |
| $[(cp)TiCl_3(diars)]$ | | $CDCl_3$ | 6.87(5.0) | $^{1.70}_{1.75}$(12.0) | | 7.62 [b] (3.8) aromatic protons |

[a] P.p.m. downfield from $Me_4Si$; figures in parentheses indicate relative integrated intensities. [b] Complex multiplet. [c] X = C. [d] X = S. [e] X = N. [f] X = As.

In view of the lack of reactivity of (I) towards an excess of $C_6H_{11}NC$ it was of interest to investigate the reactivity of the remaining Ti–Me group. The complex (I) was found to react at 0 °C with iodine to yield, in moderate purity, $[(cp)_2TiI\{C(Me){:}NC_6H_{11}\}]$. Cleavage reactions with iodine are typical of early transition-metal alkyls.[21] The Ti–Me group of complex (I) also reacted rapidly with $SO_2$ to yield a product whose i.r. spectrum showed bands attributable to S=O and Ti–O–Ti groups. This suggests that, after an initial insertion into the TiMe group, decomposition takes place.

Attempts to isolate pure products from the reactions between $[(cp)TiMe_3]$ and cyclohexyl and *p*-tolyl isocyanides have yielded only impure products even at reaction teperatures of $-30$ °C. Insertion apparently takes place but this is followed by further reactions, possibly involving insertion of further isocyanide molecules into the $Ti(CMe){:}NR$ moiety formed in the initial reaction. Multiple insertion of cyanides into metal–carbon bonds has been observed elsewhere.[22]

*Reactions with Nitric Oxide* (*Scheme*).—The reaction between NO and $[(cp)TiMe_3]$ at $-78$ °C yielded the complex $[(cp)TiMe\{ON(Me)NO\}_2]$, (II), in which two molecules of NO have inserted into each of two Ti–Me groups. The $^1$H n.m.r. spectrum of (II) (Table 2) shows two methyl resonances, one attributable to a Ti–Me group and the other at a position close to that of all complexes containing the *N*-methyl-*N*-nitrosohydroxylamino-group.[3,9] The i.r. spectrum of (I) is very similar (excluding bands associated with the cyclopentadienyl groups) to the spectra of the complexes $[Me_4W\{ON(Me)NO\}_2]$ and $[MeTaCl_2\{ON(Me)NO\}_2]$, which have each been shown by *X*-ray crystallographic studies to contain an *N*-methyl-*N*-nitrosohydroxylamino-group acting as a chelating ligand.[6,23] The similarity of the i.r. spectra of the complexes above with those of the complexes $[(cp)_2MMe\{ON(Me)NO\}]$ (M = Ti or Zr) [9] suggests that both NO groups are co-ordinated to the metal atoms.

The complex (II) was stable *in vacuo* or under nitrogen but it detonated quite readily and decomposed in air.

*Reaction with Sulphur Dioxide.*—Under carefully controlled conditions the reaction of $[(cp)TiMe_3]$ with $SO_2$ yields $[(cp)TiMe_2(SO_2Me)]$ (III). The complex (III) reacts with further quantities of $SO_2$ yielding non-stoichiometric products. The mass spectrum of (III) did not show a peak corresponding to the parent ion, but a peak at $m/e$ = 207 corresponding to the loss of one methyl group therefrom. The n.m.r. spectrum clearly showed that only one Ti–Me group had reacted with $SO_2$ and that reaction had not taken place with a cyclopenta-

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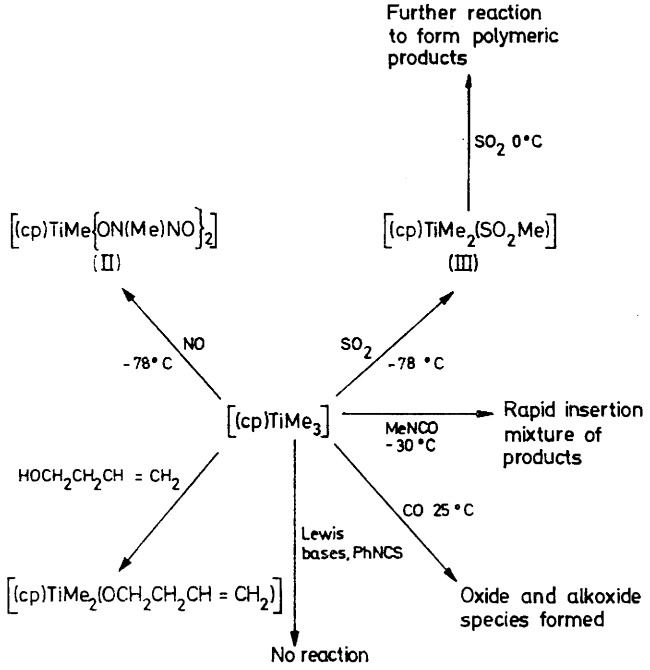
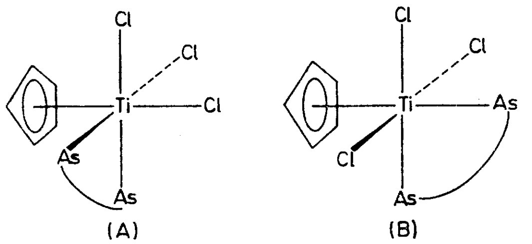
dienyl group. (The reaction of [(cp)$_2$ZrMeCl] with SO$_2$ yields a product in which SO$_2$ has reacted with one of the cyclopentadienyl groups.)[8] The i.r. spectrum of the complex shows bands typical of η-cyclopentadienyl groups and bands at 980 and 935 cm$^{-1}$ attributable to $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ respectively. The small frequency separation of these bands suggests that the complex is an *OO'*-sulphinate containing the $\overline{\mathrm{OTiOS}}\mathrm{Me}$ grouping.[24] Similar insertion reactions have been observed with other organotitanium compounds.[8,14]



SCHEME Reactions of [(cp)TiMe$_3$]



Structures proposed for the complex [(cp)TiCl$_3$(diars)]

*Reactions with* CO *and* H$_2$.—[(cp)TiMe$_3$] Was found to react rapidly with CO at temperatures between 0 and 25 °C but only a variety of non-stoicheiometric products could be obtained. None of the products showed bands in the 1 600—2 100 cm$^{-1}$ region attributable to metal–carbonyl or metal–acyl systems; rather, the products showed bands in the 1 050—1 150 cm$^{-1}$ region associated with MOC groups of alkoxides [25] or at *ca.* 860 cm$^{-1}$ typical of groups of the type Ti=O · · · Ti.[26] The failure to isolate stoicheiometric products from these reactions contrasts with the ease with which reactions of [(cp)$_2$-TiRCl] (R = Me or CH$_2$Ph) take place with CO (yielding acyl complexes) and of [(cp)$_2$Ti(CH$_2$Ph)$_2$] with CO {yielding [(cp)$_2$Ti(CO)$_2$]}.[1,27]

The reaction between [(cp)TiMe$_3$] and hydrogen is slower than the reaction with CO, and at room temperature it yields a black insoluble pyrophoric solid which could not be characterised.

*Reactions with Heterocummulenes*.—[(cp)$_2$TiMe$_2$] Reacted only very slowly with MeNCO at room temperature, and after several days only a trace of solid product had formed. The complex [(cp)TiMe$_3$] was much more reactive towards MeNCO, reaction taking place at −30 °C to yield a red oil from which a red solid could be sublimed; this also could not be characterised. [(cp)TiMe$_3$] was found not to react with PhNCS even after 2 h at 60 °C.

*Reactions of* [(cp)TiCl$_3$] *and* [(cp)TiMe$_3$] *with Lewis Bases*.—The reactions of [(cp)TiCl$_3$] and [(cp)TiMe$_3$] (Scheme) with Lewis bases have been carried out to provide information about the acceptor properties and steric requirements of the titanium atoms therein. Anagnostopoulos and Nicholls [28] reported that [(cp)-TiCl$_3$] formed a complex with pyridine but not with Ph$_3$P or Me$_2$S. We have reinvestigated the reaction between [(cp)TiCl$_3$] and pyridine and have been unable to isolate a pyridine complex therefrom. A concentrated solution of [(cp)TiCl$_3$] in pyridine deposited orange crystals which, on being pumped at room temperature, yielded the unchanged [(cp)TiCl$_3$]. There was also no evidence for complex formation between [(cp)TiCl$_3$] and Me$_3$As or Ph$_3$P. However, reaction with the chelating ligands *o*-phenylenebis(dimethylarsine) (diars) and 2,2'-bipyridyl (bipy) yielded 1 : 1 complexes. The 2,2'-bipyridyl complex was insoluble in common organic solvents but the diarsine complex gave an essentially non-conducting solution in acetonitrile.

The i.r. spectrum of [(cp)TiCl$_3$] shows a group of bands centred at 405 cm$^{-1}$ [25] attributable mainly to TiCl stretching fundamentals; in the complexes [(cp)TiCl$_3$-(diars)] and [(cp)TiCl$_3$(bipy)] the corresponding group of bands is shifted to *ca.* 243 and *ca.* 240 cm$^{-1}$ respectively; this shift is consistent with an increase in the co-ordination number of the metal atom.[29] The MeAs resonances are well separated from those of the free diarsine and the cyclopentadienyl resonance is a singlet suggesting that the complex is not dissociating in solution. It is very unlikely that the diarsine would act as a unidentate ligand and in consequence only two structures seem possible for this complex (Figure). Each of these contains two pairs of virtually identical methyl groups, consistent with the appearance of the n.m.r. spectrum. There was no change in the n.m.r. spectrum on cooling the compound to −60 °C and therefore the compound could have

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one of the structures A or B, or further it could consist of a mixture of these isomers which rapidly interconvert even at −60 °C.

The steric crowding would be little different from that in the complex [(cp)TiCl(ox)$_2$] (ox = the quinolin-8-olato group) which has been shown to be non-ionic and to have two bidentate ligands.[30]

No reaction was observed between [(cp)TiMe$_3$] and the ligands pyridine, 2,2′-bipyridyl, and diarsine at room temperature. A reduction in acceptor properties of a metal atom when chlorine is replaced by a methyl group is well known.[31-34]

*Attempted Preparations of Complexes containing Co-ordinated Olefinic Groups.*—These reactions were carried out in an attempt to prepare a complex in which an olefinic group is co-ordinated to the metal atom. Earlier work with these systems has been reported.[19]

TABLE 3

Proton n.m.r. and i.r. spectral data for complexes derived from Hbea [a]

$H_2C{=}CH{-}CH_2{-}CH_2{-}O{-}$
A B C D

| Complex | Solvent | $\delta_A$ | $\delta_B$ | $\delta_C$ | $\delta_D$ | ν(C=C)/cm$^{-1}$ [e] |
|---|---|---|---|---|---|---|
| Mebea [d] | Neat liquid | 4.97 m | 5.77 m | 2.23 m | 3.29 t | 1 641 s |
| [(cp)$_2$TiCl(bea)] [b,d] | CHCl$_3$ | 5.05 | 5.74 | 2.17 | 4.43 | 1 639 s |
| [(cp)$_2$TiBr(bea)] | CCl$_4$ | 5.06 m | Too weak | 2.16 m | 4.31 t | 1 639 m |
| [(cp)$_2$TiMe(bea)] [d] | CHCl$_3$ | 5.12 | *c* | 2.04 | 4.06 | 1 636 s |
| [(cp)TiMe$_2$(bea)] | C$_6$D$_6$ | 5.05 m | *c* | 2.38 m | 4.26 t | 1 641 m |

[a] N.m.r. shifts downfield from internal Me$_4$Si, except where stated otherwise. m = multiplet t = triplet. [b] N.m.r. shift relative to solvent CHCl$_3$. [c] Obscured by solvent. [d] Data taken from ref. 19. [e] I.r. intensity designations: s = strong, m = medium.

The ligand Me$_2$NCH$_2$CH$_2$N(Me)CH$_2$CH$_2$CH=CH$_2$ (bte) has been treated with titanium tetrachloride to yield the somewhat impure complex [TiCl$_4$(bte)]. There was no evidence for co-ordination of the olefinic group; ν(C=C) is not altered significantly in the complex {ν(C=C) for the free ligand at 1 647 cm$^{-1}$, ν(C=C) for the complex [TiCl$_4$(bte)] at 1 640 cm$^{-1}$} and the low-frequency i.r. spectrum resembled that of the six-co-ordinate complex [TiCl$_4$(Me$_2$NCH$_2$CH$_2$NMe$_2$)].[35] Attempts to prepare the complex [TiCl$_3$(bte)], either by direct reaction of the ligand with TiCl$_3$ or *via* the complex TiCl$_3$·3L (L = tetrahydrofuran or MeCN), yielded impure products.

We have extended the range of complexes containing the M–O–CH$_2$CH$_2$CH=CH$_2$ M(bea) group, originally studied by Clark and Coles.[19] The complex [(cp)TiMe$_2$(bea)] has been prepared by treating the alcohol HOCH$_2$CH$_2$CH=CH$_2$ (Hbea) with [(cp)TiMe$_3$] (Scheme). The mass spectrum of the product showed an ion at $m/e$ = 214, corresponding to the molecular ion. The complex [(cp)$_2$TiBr(bea)] has also been prepared for the first time, the route being the same as that employed in the preparation of [(cp)$_2$TiCl(bea)].[19]

The proton n.m.r. and i.r. spectra (Table 3) of the bea complexes are very similar to those previously reported for related complexes. There is no evidence in any case for co-ordination of the olefinic group to the metal atom. The complex [(cp)TiMe$_2$(bea)] was heated at 60 °C for 3 h in [$^2H_6$]benzene in an attempt to promote an insertion reaction of the olefinic group but there was no change in the $^1$H n.m.r. spectrum by such treatment. This observation is taken as further evidence for the weakness of the interaction between the titanium atom and olefins.

Attempts to prepare zirconium and hafnium complexes of the type [(cp)$_2$MX(bea)] (X = halogen) yielded products contaminated with [{(cp)$_2$MX}$_2$O].

## DISCUSSION

The insertion reactions discussed above follow similar patterns to those observed for other early transition-metal alkyls. Thus the most reactive reagents are those which can be regarded as having some free radical or carbene character *e.g.* CO, NO, O$_2$, and RNC. It seems likely that the reactions with NO and O$_2$ proceed *via* homolytic routes. Shortland and Wilkinson [3] have suggested that the reaction between WMe$_6$ and NO proceeds *via* the intermediate [Me$_5$WONMe], which then reacts with another molecule of NO. It seems likely that a similar mechanism operates in the reaction of [(cp)TiMe$_3$] with NO.

The insertion reactions observed with RNC, SO$_2$, and MeNCO seem likely to proceed *via* the formation of a weak donor–acceptor complex with [(cp)TiMe$_3$] followed by transfer of the methyl group. Although we have been unable to prepare any complexes of [(cp)TiMe$_3$] with Lewis bases, the preparation of complexes of [(cp)TiCl$_3$] with such bases suggests that the molcule [(cp)TiMe$_3$] would not be too sterically crowded to form at least a weak complex prior to the insertion reaction taking place.

A feature of insertion reactions is that where more than one metal–carbon σ-bonded group is present, not all of the groups react with the inserting reagent. Thus in the reaction between [(cp)$_2$TiMe$_2$] and C$_6$H$_{11}$NC only one Ti–Me group reacts, the remaining Ti–Me group being only

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reactive towards reagents such as $I_2$ and $SO_2$. It seems likely that the rather bulky nature of the Ti–C(Me)$:$NC$_6$H$_{11}$ moiety prevents further reaction. Steric effects are probably responsible for the inertness of $[(cp)_2Ti(CH_2Ph)_2]$ towards $C_6H_{11}NC$. (It is not likely to be an electronic effect of the benzyl group, because $[Zr(CH_2Ph)_4]$ has been found to undergo insertion reactions with a number of reagents.[2]) $[(cp)TiMe_3]$ Has been found to be more reactive than $[(cp)_2TiMe_2]$. Thus for example $[(cp)TiMe_3]$ reacts with NO at −78 °C whereas $[(cp)_2TiMe_2]$ only reacts with NO at room temperature.[9] This suggests that the greater steric crowding around the titanium atom in $[(cp)_2TiMe_2]$ is responsible for its lesser reactivity as compared with $[(cp)TiMe_3]$. Steric effects around the metal atom and the bulk of the inserting reagent have also been found to be important in influencing insertion reactions of $[Me_xMCl_{5-x}]$ (M = Nb or Ta; $x = 1, 2,$ or 3).[4,5,7]

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