Journal of Organometallic Chemistry, 302 (1986) 181–191
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

LITHIUM NITRIDE REDUCTION OF Cp_2TiCl_2 AND $CpTiCl_3$: THE SYNTHESIS OF $(Cp_2TiCl)_2$, $(CpTiCl_2)_n$, $Cp_2Ti(CO)_2$ AND CHLOROTETRATITANIUM AND NITRIDOHEXATITANIUM COMPLEXES

MELVYN KILNER* and GERARD PARKIN

Chemistry Department, The University of Durham, South Road, Durham, DH1 3LE (Great Britain)

(Received July 2nd, 1985)

Summary

Stoichiometric reactions of Cp_2TiCl_2 or $CpTiCl_3$ with Li_3N in various molar ratios result in reduction to $(Cp_2TiCl)_2$, $(CpTiCl_2)_n$ and $(CpTiCl)_4$ and provide useful synthetic routes. Further reduction produces hexanuclear nitrido titanium clusters, Cp_8Ti_6N and $Cp_8Ti_6N_3$, characterised from mass spectral evidence. The nitrido clusters react with HCl to form $(Cp_2TiCl)_2$ and Cp_2TiCl_2. Cp_2TiCl_2 is also obtained by reaction with Me_3SiCl. $Cp_2Ti(CO)_2$ is formed by the reaction between Cp_2TiCl_2 and Li_3N in THF in the presence of CO.

Lithium nitride is not normally regarded as a reducing agent. Indeed, except at temperatures close to its melting point it is considered generally unreactive [1] (except to water [2]) because of the poor solubility of the ionic material [3] in suitable solvents. We have found that, though its solubility in polar solvents, particularly THF, dioxane and monoglyme, is low, it reacts with halides of metals in their high oxidation states. We have found also that it acts as a useful reducing agent for synthetic purposes, providing convenient routes to many useful reagents. The unwanted product, dinitrogen, is spontaneously lost and consequently lithium nitride reductions are not complicated by the presence of the oxidised component. Its use in titanium chemistry was reported recently in a short communication [4]. Lithium nitride was found effective for reductions, which proceed according to eq. 1, of both cyclopentadienyl complexes and binary halides.

$$6L_xTi^{IV}Cl + 2Li_3N \xrightarrow{THF} 6L_yTi^{III} + 6LiCl + N_2 \qquad (1)$$

Such reductions are often found to be preferable to other laboratory methods since they work under non-forcing conditions and give products in good yield.

Titanium may be reduced to its lower oxidation states by a variety of reducing agents [5], and the low valent states may be stabilised by many different ligands. Alkali metals are used to produce titanium(0) [6], and (−1), though alkylsodium,

-lithium [7], Grignard reagents [8] and other less electropositive metals (Zn, Al, Mg) [6] usually produce titanium(II) complexes as the limit of reduction. Lithium aluminium hydride is the preferred reducing agent for McMurry coupling reagents, which are considered to involve titanium(0) [10]. Selective reduction of titanium(IV) to titanium(III) is achieved with alkylaluminium compounds [11], hydrogen [12] etc. Preliminary work suggests that lithium nitride under appropriate conditions and molar ratios can effect a whole range of such reductions, but in this report we describe reductions only of Cp_2TiCl_2 and $CpTiCl_3$.

Results and discussion

Convenient syntheses of $[Cp_2TiCl]_2$, $CpTiCl_2(THF)$ and $[CpTiCl_2]_n$

The reaction between Cp_2TiCl_2 (3 mol) and lithium nitride (1 mol) in THF proceeds smoothly at room temperature and affords a high yield route to $[Cp_2TiCl]_2$ [13]. Thus a one-electron reduction may be selectively achieved [14]. The standard literature method [15] for preparing $[Cp_2TiCl]_2$, involving zinc dust reduction, suffers from the disadvantage that the complex $(Cp_2TiCl)_2ZnCl_2$ is often a major product of the reaction, and only low yields of $(Cp_2TiCl)_2$ can be obtained from the zinc product by pyrolysis or decomposition with Et_2O.

Similarly, $CpTiCl_3$ (3 mol) reacts rapidly with Li_3N (1 mol) in THF to produce $CpTiCl_2(THF)$ in good yield, from which the oligomer $(CpTiCl_2)_n$ may be obtained. Thus, lithium nitride reduction provides a convenient and preferred route to these cyclopentadienyltitanium(III) complexes from the corresponding titanium(IV) compounds, and demonstrates synthetic utility of Li_3N as a selective reducing agent.

The synthesis of cyclopentadienyl chloro- and nitrido-titanium clusters

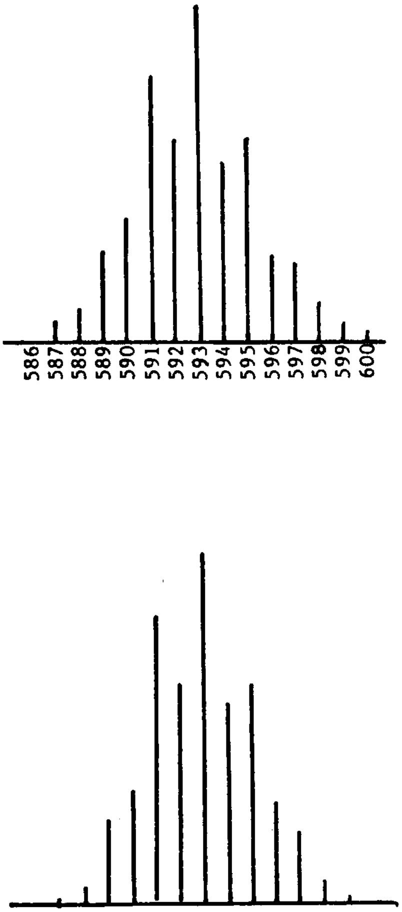
(i) Further reduction of $CpTiCl_2(THF)$ (3 mol) with Li_3N (1 mol) (or reaction of $CpTiCl_3$ (3 mol) with Li_3N (2 mol)) produces a blue-green complex for which mass spectrometry indicates a tetrameric formulation $(CpTiCl)_4$ (**1**). Although a satisfactory elemental analysis could not be obtained for **1**, the results consistently demonstrated the presence of chlorine and absence of nitrogen. The highest observed distribution in the mass spectrum of **1** was at *m/e* 591, corresponding to $C_{20}H_{19}Ti_4Cl_4$ (Ti^{48}, Cl^{35}) (Table 1). The isotope distribution is in accordance with such a molecular formula (Fig. 1) and daughter ions $[Cp_2Ti_4Cl_4]^+$ and $[CpTi_4Cl_4]^+$ support the presence of a Ti_4Cl_4 cluster unit. The ^1H NMR spectrum consists of a singlet (δ 6.5) in C_6D_6 at ambient temperature, which may be the result either of equivalence of the cyclopentadienyl groups or to fluxional changes in the complex at this temperature. In the absence of low temperature studies the latter possibility can not be eliminated.

Related to complex I are several compounds of unidentified constitution which are believed to be [CpTiCl] species [14] e.g. in the polarographic and sodium amalgam reduction of $CpTiCl_3$ and magnesium reduction of Cp_2TiCl_2. Further compounds which may be regarded to be related to **1** are the cycloheptatrienyl [17] and cyclooctatetraene [18] derivatives $[(\eta\text{-}C_7H_7)Ti(THF)]_2(\mu\text{-}Cl)_2$, $[(\eta\text{-}C_8H_8)TiCl]_4$ and $[(\eta\text{-}C_8H_8)Ti(THF)]_2(\mu\text{-}Cl)_2$, but none possess titanium–titanium bonding. In contrast the tetramer $[(\eta\text{-}C_8H_8)TiCl]_4$ is not regarded as a cluster, since the mass spectrum does not show any ions arising from the parent ion but only those for a dimer.

TABLE 1

THE MASS SPECTRUM OF $[C_5H_5TiCl]_4$ (1)

m/e	Assignment (^{48}Ti, ^{35}Cl)
591	$C_{20}H_{19}Ti_4Cl_4{}^+$
462	$C_{10}H_{10}Ti_4Cl_4{}^+$
426	$(Cp_2TiCl)_2{}^+$
397	$CpTi_4Cl_4{}^+$
248	$Cp_2TiCl_2{}^+$
218	$CpTiCl_3{}^+$
118	$TiCl_2{}^+$
148	$CpTiCl^+$
83	$TiCl^+$
48	Ti^+



Calculated distribution for $[C_{20}H_{19}Ti_4Cl_4]$

Fig. 1. Isotopic distribution pattern for $[CpTiCl]_4$ (1) centred at *m/e* 593.

(ii) On the basis of the results described, reduction of Cp_2TiCl_2 (3 mol) with Li_3N (2 mol) would be expected to produce one of the many forms of titanocene [19] such as $\mu(\eta^1:\eta^5\text{-}C_{10}H_8)[(\eta\text{-}C_5H_5)(\mu\text{-}H)Ti]_2$ or $(\eta^1:\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2$-(THF). However, the reaction between Cp_2TiCl_2 (3 mol) and Li_3N (2 mol) in THF under argon produced a deep blue solution from which a very air-sensitive complex **2** was isolated. Characterisation of **2** was difficult owing to unreliable analytical data, but the analysis consistently demonstrated the presence of nitrogen and absence of chlorine. The mass spectrum provide the most useful information as to its identity (see Fig. 2). The highest observed distribution is centred at *m/e* 820, corresponding to $C_{40}H_{38}Ti_6N^+$ (^{48}Ti), but it is not known whether this distribution arises from the parent ion or that with loss of hydrogen, $[P-2H]^+$. Such a loss of hydrogen in the mass spectrum is not without precedent and may be expected where the C–H bond of a cyclopentadienyl ring may undergo an intramolecular oxidative addition to the metal [20]. The most intense titanium-containing distribution is

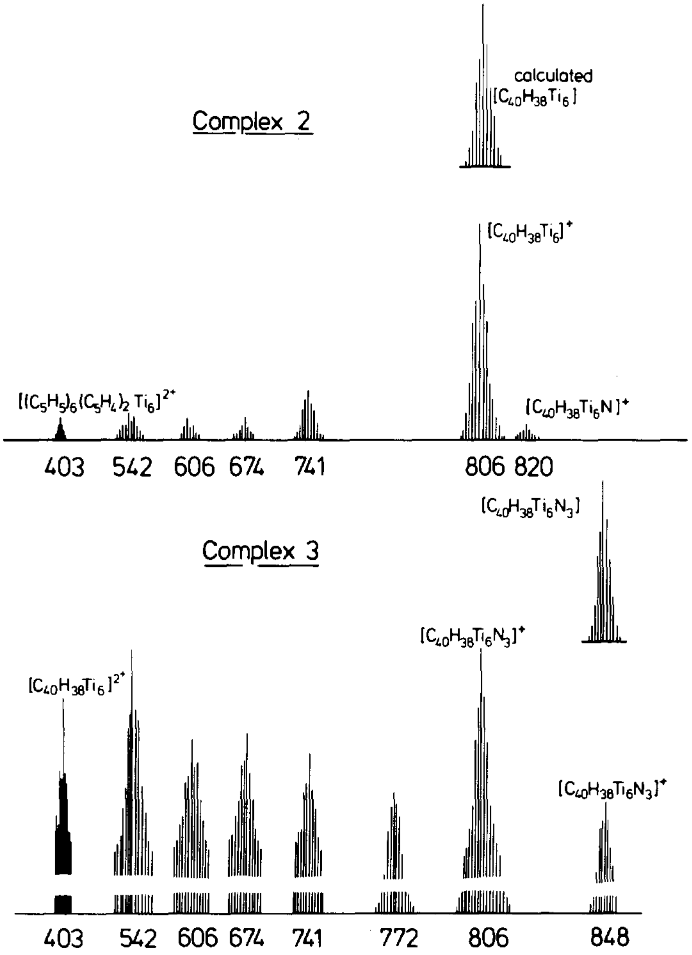


Fig. 2. Mass spectra of complexes **2** and **3**.

centred at *m/e* 806 and corresponds to $C_{40}H_{38}Ti_6^+$. The doubly-charged species, $[C_{40}H_{38}Ti_6]^{2+}$, is also observed at *m/e* 403. Fragmentation resulting in losses of C_5H_5, H and C_5H_4 are observed, as shown in Fig. 2. The absence of a significant peak at *m/e* 128, corresponding to $C_{10}H_8^+$, suggests that the fulvalene moiety is not present in the molecule, and therefore that the cyclopentadienyl groups are either bound in a (η-C_5H_5) mode or in the fulvene ($\eta^1:\eta^5$-C_5H_4)Ti–H mode. The marked intensity of the distribution centred at *m/e* 806, i.e. that corresponding to loss of nitrogen, suggests that the nitrogen atom is not interstitial.

The IR spectrum of **2** (see Fig. 3) supports the presence of an ($\eta^1:\eta^5$-C_5H_4) group in that there is a band at 1265 cm^{-1} which may be assigned to a vibrational mode of a bridging hydride ligand (compare $\mu(\eta^1:\eta^5\text{-}C_{10}H_8)[(\eta\text{-}C_5H_5)(\mu\text{-}H)_2Ti]_2$ [20] 1230 cm^{-1}; $Cp_2Ti(\mu\text{-}H)_2BH_2$ 1350 cm^{-1} [21]; $Cp_2Ti(\mu\text{-}H)_2TiCp_2$ 1450 cm^{-1} [22]. In addition, the IR spectrum provides no indication of the presence of a N–H bond. The ^1H NMR spectrum could not be obtained, and the complex appears to be paramagnetic.

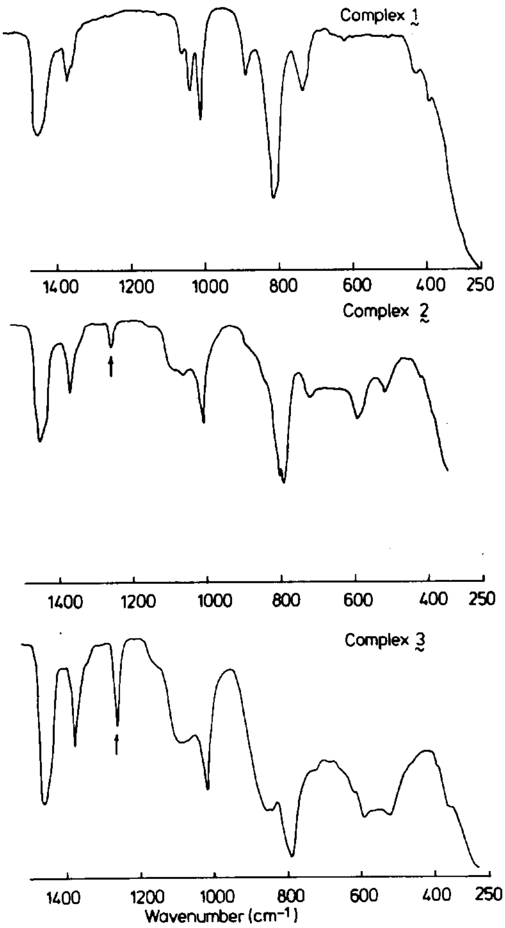


Fig. 3. Infrared spectra of complexes **1**, **2** and **3** (bridging hydride absorption band is marked).

The available evidence suggests that **2** is a hexanuclear titanium cluster containing one non-interstitial nitrogen atom, eight cyclopentadienyl ligands, and bridging hydride ligands. Some of the cyclopentadienyl ligands may be bonded in the ($\eta^1 : \eta^5$-C_5H_4) mode and give rise-to bridging hydride ligands. It is unlikely that the Ti atoms are arranged in an octahedral manner since, on the basis of an extension to the cone angle concept for mononuclear species, a Cp_6M_6 unit is expected to be sterically saturated [23], and so the extra cyclopentadienyl, nitrogen and hydrogen ligands could not be accommodated.

(iii) The reaction between $CpTiCl_3$ (1 mol) and Li_3N (1 mol) in THF under argon produces a blue solid **3**, similar in appearance to **2**. However, there is a noticeable difference in air sensitivity; solid **3** can be handled briefly in air whereas solid **2** decomposes immediately. Complete characterisation of **3** has also proved difficult with similar problems in obtaining elemental analysis and ^1H NMR spectra. However, the mass spectrum provides evidence that **3** is also a hexanuclear titanium cluster. The highest observed distribution is centred at *m/e* 848 and corresponds to $[C_{40}H_{38}Ti_6N_3]^+$ (^{48}Ti), but whether this represents the parent ion or that with loss of 2H is uncertain. The presence of a band in the IR spectrum at 1270 cm^{-1}, assigned to a bridging hydride ligand, suggests that a fulvene moiety may also be present, i.e. $[Cp_6(C_5H_4)_2(\mu\text{-}H)_2Ti_6N_3]$. The mass spectrum also contains $[Cp_6(C_5H_4)_2Ti_6]^+$, corresponding to loss of three nitrogen atoms, as a dominant species, thus suggesting that all the nitrogen atoms are non-interstitial.

Reactions of the nitrido clusters

Attempts to obtain more information on the structures of **2** and **3** were based upon the synthesis of derivatives, the structures of which may be more easily determined. However, **2** and **3** did not react with 2,2′-bipyridine, triphenylphosphine, bis(1,2-diphenylphosphino)ethane (dppe) or CO under normal conditions. Similarly, carrying out the reactions between Cp_2TiCl_2 or $CpTiCl_3$ and Li_3N in the presence of PPh_3 or dppe caused no change in the course of the reaction. However, the reaction between Cp_2TiCl_2 and Li_3N in the presence of CO produced the red dicarbonyl, $Cp_2Ti(CO)_2$. This reaction is of interest in that it demonstrates that the Li_3N reduction of Cp_2TiCl_2 may proceed through a titanocene intermediate, $\{Cp_2Ti\}$, in forming the blue cluster **2**.

The reaction of THF solutions of **2** and **3** with gaseous or aqueous HCl resulted in fragmentation of the hexanuclear clusters and formation of an orange solution containing a mixture of Cp_2TiCl_2, $CpTiCl_3$ and $(Cp_2TiCl)_2O$ as demonstrated by ^1H NMR. When hydrogen chloride was passed over solid **2**, $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ was the only product identified. An attempt to make a chlorinated cluster from **2** and **3** by treatment of their THF solutions with Me_3SiCl resulted in the formation of Cp_2TiCl_2 as the main product, though mass spectral data showed the presence of a higher molecular weight species with *m/e* 258.

No reactions of lithium nitride were observed in toluene, even on heating. However, on addition of a small amount of THF the reactions proceeded as for the reactions in THF alone. The absence of reaction in toluene is possibly attributable to the total insolubility of Li_3N in non-polar solvents. Hence, further investigations involved polar solvents, including dioxane, chlorobenzene, acetonitrile and sulpholane (C_4H_8S), the sulphur analogue of THF. Reactions did proceed in these solvents, but neither **2** or **3** could be isolated. The formation of a green solution in the initial stages of the reaction between Cp_2TiCl_2 (3 mol) or $CpTiCl_3$ (3 mol) and Li_3N (2 mol) suggests that the first stage of the reaction is similar to that in THF, but further reaction with Li_3N resulted in the formation of red-brown solutions which will be the subject of further investigation.

The reactions studied are summarised in Fig. 4. It is clear that the mechanism of the formation of both **2** and **3** is complex. Each reaction involves the transfer of cyclopentadienyl groups; the formation of **2** requires a net loss of cyclopentadienyl groups per titanium whereas the formation of **3** requires the net gain of cyclopentadienyl groups per titanium. Such transfer of cyclopentadienyl groups bound to titanium has been observed before [24–29], e.g.

$$\mathrm{Cp_2TiCl_2 \xrightarrow{Bu^i_2AlCl} (CpTiCl_2)_n}$$

$$\mathrm{Cp_2Ti(CO)_2 \xrightarrow{TiCl_4} Cp_2TiCl_2TiCl_2 \rightarrow (CpTiCl_2)_n}$$

$$\mathrm{Cp_2Ti(CO)_2 \xrightarrow{H_2} Cp_6Ti_6O_8}$$

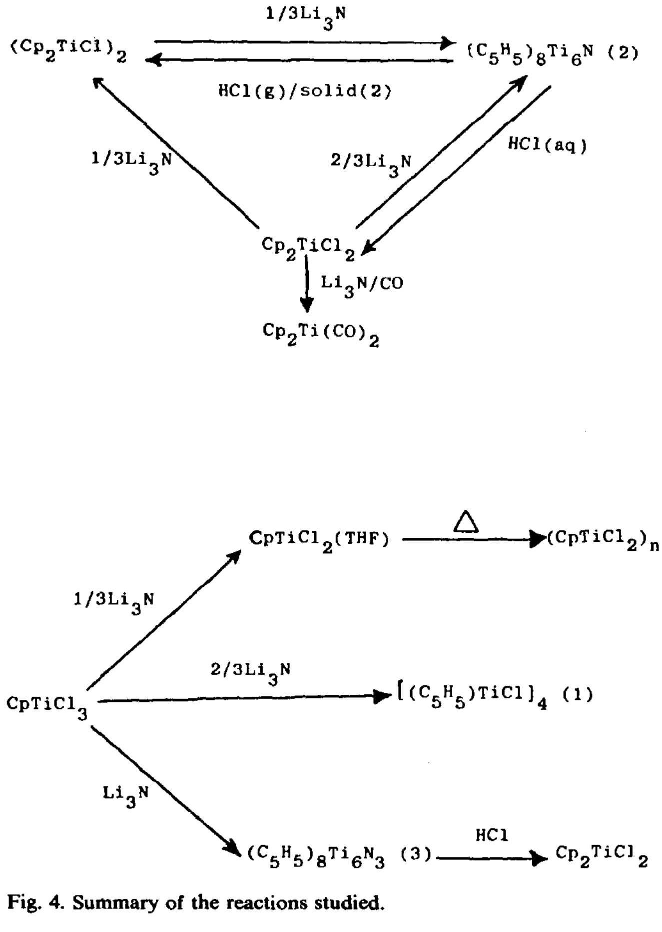


Fig. 4. Summary of the reactions studied.

In general, the early transition metals do not tend to form cluster compounds and very few titanium cluster compounds have been reported. Although infra-red evidence has suggested the presence of a triangular Ti_3 unit in Ti_3Cl_{12} and $[Ti_3(C_6Me_6)_3Cl_6]^+ Cl^-$ [30], the only structurally characterised titanium cluster is $Cp_6Ti_6O_8$ [26]. Previously reported cyclopentadienyl-metal clusters formed from cyclopentadienyl complexes under reducing conditions have invariably been hydride-containing species such as $Cp_4Co_4(\mu_3\text{-H})_4$ [31] and $Cp_5Ni_5H_3$ [29].

The synthesis of nitrido clusters has also only recently been achieved and, to date, clusters with six-coordinate interstitial nitrogen [32] and five [33,34], four [34–36] and three-coordinate [37] nitrogen have been obtained. Their interest is as possible models for nitrogen on a metal surface and comparisons between ammonia synthesis on metal surfaces and the possible stoichiometric or catalytic hydrogenation of dinitrogen with metal clusters has been described [34]. More important in this respect are the nitrido clusters in which the nitrogen atoms are exposed and of low coordination number e.g. $HFe_4N(CO)_{12}$, $HFe_5N(CO)_{14}$ [34] and $[Cp_3M_3(N)(O)(CO)_4]$ ($M_3 = Mo_3$, Mo_2W, MoW_2 and W_3) [37].

It is apparent that Li_3N is a useful reagent for rational synthesis of cyclopentadienylnitrido-metal clusters. It possesses both the qualities favourable for such syntheses in that, it is an effective reducing agent and is able to introduce a bare nitrogen atom into a molecule.

Experimental

Cp_2TiCl_2 and $CpTiCl_3$ were supplied by Alfa or prepared by published procedures [15]. All reactions and manipulations were carried out under argon or nitrogen and solvents were dried by standard methods. ^1H NMR spectra were determined using 60 MHz Varian EM360L and Bruker HX90E spectrometers. IR spectra were recorded as mulls on a Perkin–Elmer 577 machine. Microanalysis was obtained by the microanalytical section of this Department. Mass spectra were obtained on an AEI MS9 spectrometer.

The reaction between Cp_2TiCl_2 (3 mol) and Li_3N (1 mol). The synthesis of $(Cp_2TiCl)_2$

A mixture of Cp_2TiCl_2 (1.0 g, 4.0 mmol) and Li_3N (0.0471 g, 1.35 mmol) (molar ratio 3/1) was placed in a Schlenk tube. THF (25 cm^3) was added and the stirred mixture warmed briefly to initiate the reaction, resulting in the evolution of a gas (presumably N_2). The mixture was filtered after 30 min, to give an olive green filtrate, from which a green solid was obtained by removal of the THF under reduced pressure at room temperature. Toluene (50 cm^3) was added to this solid and the mixture was stirred at room temperature then filtered to remove the LiCl. Removal of the toluene from the filtrate by evaporation under reduced pressure at room temperature gave a microcrystalline green solid, $(Cp_2TiCl)_2$ [yield 0.75 g (88%)], identified by comparison with an authentic sample.

The reaction between $CpTiCl_3$ (3 mol) and Li_3N (1 mol). The synthesis of $CpTiCl_2(THF)$ and $(CpTiCl_2)_n$

A yellow-orange solution of $CpTiCl_3$ (0.535 g, 2.44 mmol) in THF (25 cm^3) was added to a suspension of Li_3N (0.0285 g, 0.81 mmol) in THF (10 cm^3) in a Schlenk tube. A rapid exothermic reaction occurred accompanied by the evolution of a gas (presumably N_2), and the mixture turned green. After ca. 1 h stirring at room temperature, all the Li_3N had reacted, and at this stage the reaction was considered complete. The solution was filtered, and removal of the solvent gave a green solid identified as $CpTiCl_2$ (THF) by comparison with an authentic sample [15].

Alternatively, toluene (15 cm^3) was added to the filtrate and the THF removed under reduced pressure at room temperature. The brown-red solid produced was washed with toluene and dried in vacuo to give red-purple $(CpTiCl_2)_n$ (yield 0.3 g, 67%), identified by comparison with an authentic sample [15].

The reaction between (η-C_5H_5)$TiCl_3$ (3 mol) and Li_3N (2 mol). The synthesis of [(η-C_5H_5)$TiCl$]$_4$ (1)

A mixture of $CpTiCl_3$ (0.515 g, 2.34 mmol) and Li_3N (0.0547 g, 1.56 mmol) was placed in a Schlenk tube. THF (20 cm^3) was added and a green solution was obtained immediately, the reaction being accompanied by evolution of gas and a generation of a little heat. After ca. 2 h all the Li_3N had reacted. Toluene (40 cm^3) was added, and the THF was removed under reduced pressure at room temperature depositing LiCl. The mixture was filtered and the blue-green filtrate taken to dryness to give a blue-green solid **1**. Recrystallisation from toluene gave a high yield of a blue-green powder, characterised as $[CpTiCl]_4$ by mass spectrometry.

The reaction between Cp_2TiCl_2 (3 mol) and Li_3N (2 mol). The synthesis of 2

A mixture of Cp_2TiCl_2 (1.0 g, 4.0 mmol) and Li_3N (0.1 g, 2.85 mmol) [molar ratio 3/2.14] was placed in a Schlenk tube and THF (30 cm^3) was added. The mixture was warmed briefly to initiate the reaction, and a gas was evolved. After ca. 10 min stirring at room temperature the supernatant liquid was green, but continued stirring for 18 h gave a dark-blue solution. The mixture was filtered, and toluene (30 cm^3) was added to the dark-blue filtrate. The THF was removed under reduced pressure at room temperature, and the LiCl filtered off. Complete removal of the toluene from the filtrate under reduced pressure at room temperature gave a blue solid **2**, which on recrystallisation from toluene gave a powder (yield 0.5 g).

The reaction between $(Cp_2TiCl)_2$ and Li_3N. The synthesis of 2

A solution of $(Cp_2TiCl)_2$ in THF was added to Li_3N, and the mixture was warmed slightly to give a blue solution with evolution of a gas. The mixture was filtered and the THF removed from the filtrate under reduced pressure at room temperature to leave a dark-blue residue. Toluene was added to the residue and the mixture stirred at room temperature. After filtration to remove the LiCl, the toluene was removed from the filtrate to produce a blue solid, identified as **2** by comparison of its IR spectrum with that of an authentic sample.

The reaction between $CpTiCl_3$ (1 mol) and Li_3N (1 mol). The synthesis of 3

A yellow-orange solution of $CpTiCl_3$ (0.51 g, 2.3 mmol) in THF (25 cm^3) was added to a suspension of Li_3N (0.082 g, 2.3 mmol) in THF (10 cm^3). The immediate exothermic reaction was accompanied by the evolution of gas. The solution passed through a green to blue-purple colour during ca. 10 min, but stirring was continued for 18 h to ensure complete reaction. Toluene (35 cm^3) was added, and the THF removed under reduced pressure at room temperature. The deposited LiCl was filtered off, and the toluene was removed from the blue filtrate under reduced pressure at room temperature to give a high yield of a blue solid **3**, which was recrystallised from toluene.

The reaction between Cp_2TiCl_2 and Li_3N in the presence of CO. The synthesis of $Cp_2Ti(CO)_2$

A mixture of Cp_2TiCl_2 (2.0 g, 8.0 mmol) and Li_3N (0.2 g, 5.7 mmol) was placed in a Schlenk tube, THF (30 cm^3) was added and CO was bubbled slowly through the stirred mixture for 20 h. The mixture was filtered, and the red-brown filtrate gave a gum upon removal of the THF under reduced pressure at room temperature. Toluene (30 cm^3) was added to this residue, and filtration of the mixture to remove the LiCl gave a red-brown filtrate. The toluene was removed under reduced pressure at room temperature to leave a red-brown solid, $Cp_2Ti(CO)_2$ (yield 0.59 g, 32%), identified by comparison with an authentic sample.

The reaction between 2 and hydrogen chloride

(i) HCl (g) was bubbled through a blue solution of **2** in THF. The solution immediately became orange. The THF was removed under reduced pressure at room temperature to give an orange solid, consisting mainly of Cp_2TiCl_2 according to IR spectroscopy.

(ii) HCl (g) was passed over the powdered blue solid **2** contained in a Schlenk tube. The reaction was slightly exothermic and the blue colour turned to olive-green after 1–2 min. The IR spectrum of the product showed that the major component was $(Cp_2TiCl)_2$.

The reaction between 3 and hydrochloric acid

A solution of **3** in THF was added to concentrated HCl (aq.) to give a red solution. The mixture was filtered and the solvents removed under reduced pressure at room temperature to leave an orange solid. This was extracted into toluene, the mixture filtered, and the toluene removed from the filtrate under reduced pressure at room temperature. The residue was washed with Et_2O and dried in vacuo. The ^1H NMR spectrum demonstrated that it was a mixture of Cp_2TiCl_2, $CpTiCl_3$ and $(Cp_2TiCl)_2O$ in the ratio 1/0.23/0.09.

The reaction between 3 and Me_3SiCl

Me_3SiCl was added to a blue solution of **3** in THF. After 5 min red-brown crystals were deposited. The mixture was filtered and the crystals were washed with THF and dried in vacuo. The product was identified as Cp_2TiCl_2 by comparison of its IR spectrum with that of an authentic sample.

A similar reaction between **2** and Me_3SiCl also gave Cp_2TiCl_2 as the major product.

Acknowledgements

We thank the University of Durham for a research studentship (to G.P.).

References

1 Gmelins Handbuch der Anorganischen Chemie. Lithium, Verlag Chemie, Berlin, 20 (1927) 86; J.C. Bailar (Ed.), Inorganic Syntheses, McGraw-Hill, New York, 4 (1953) 1.

2 W.A. Hart, O.F. Beumel, in J.C. Bailar, H.J. Emeléus, R. Nyholm and A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Pergamon, Oxford, 1 (1973) 357.
3 E. Zintl and G. Brauer, Z. Elektrochem., 41 (1935) 102.
4 M. Kilner, G. Parkin and A.G. Talbot, J. Chem. Soc., Chem. Commun., (1985) 34.
5 M. Bottrill, P.D. Gavens and J. McMeeking, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, Vol. 3, p. 281.
6 P.N. Hawker, P.E. Kuendig and P.L. Timms, J. Chem. Soc., Chem. Commun., (1978) 730; P.N. Hawker and P.L. Timms, J. Chem. Soc., Dalton Trans., (1983) 1123.
7 M.T. Anthony, M.L.H. Green and D. Young, J. Chem. Soc., Dalton Trans., (1975) 1419.
8 H.O. van Oven and H.J. de Liefde Meijer, J. Organomet. Chem., 31 (1971) 71; 23 (1970) 159.
9 S. Pasynkiewicz, R. Giezynski and S. Dzierzgowski, J. Organomet. Chem., 54 (1973) 203.
10 J.E. McMurry, Acc. Chem. Res., 16 (1983) 405; R. Dams, M. Malinowski, I. Westdorp and H.Y. Geise, J. Org. Chem., 47 (1982) 248.
11 S. Dzierzgowski, R. Giezynski, M. Jarosz and S. Pasynkiewicz, J. Organomet. Chem., 152 (1978) 281.
12 R.J.H. Clark, in J.C. Bailar, H.J. Emeléus, R. Nyholm and A.F. Trotman-Dickenson (Eds.), Comprehensive Inorganic Chemistry, Pergamon, Oxford, 1973, Vol. 3, p. 366.
13 G.D. Sekutowski and G.D. Stucky, Inorg. Chem., 14 (1975) 2192.
14 Gmelins Handbuch der Anorganischen Chemie, 1977, Vol. 40, (Part 1); 1980 (Part 2), 1984 (Parts 3 and 4).
15 M.L.H. Green and C.R. Lucas, J. Chem. Soc., Dalton Trans., (1972) 1000.
16 G. Fachinetti, G. Fochi and C. Floriani, J. Chem. Soc., Chem. Commun., (1976) 230.
17 M.L.H. Green, N.J. Hazel, P.D. Grebenik, V.S.B. Mtetwa and K. Prout, J. Chem. Soc., Chem. Commun., (1983) 356.
18 H.R. van der Wal, F. Overzet, H.O. van Oven, J.I. de Boer, H.J. de Liefde Meijer and F. Jellinek, J. Organomet. Chem., 92 (1975) 329.
19 G.P. Pez and J.N. Armour, Adv. Organomet. Chem., 19 (1981) 2, and references therein.
20 H.H. Brintzinger and J.E. Bercaw, J. Amer. Chem. Soc., 92 (1970) 6182.
21 H. Nöth and R. Hartwimmer, Chem. Ber., 93 (1960) 2238.
22 J.E. Bercaw and H.H. Brintzinger, J. Amer. Chem. Soc., 91 (1969) 7301.
23 D.M.P. Mingos, Inorg. Chem., 21 (1982) 464.
24 P.D. Bartlett and B. Seidel, J. Amer. Chem. Soc., 83 (1961) 581.
25 C. Floriani and G. Fachinetti, J. Chem. Soc., Dalton Trans., (1973) 1954.
26 J.C. Huffman, J.G. Stone, W.C. Krusell and K.G. Caulton, J. Amer. Chem. Soc., 99 (1977) 5829.
27 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 94 (1972) 1219.
28 B. Demerseman, G. Bouquet and M. Bigorgne, J. Organomet. Chem., 101 (1975) C24.
29 M.S. Pagnette and L.F. Dahl, J. Amer. Chem. Soc., 102 (1980) 6621.
30 E.O. Fischer and F. Rohrscheid, J. Organomet. Chem., 6 (1966) 53.
31 J. Muller and H. Dorner, Angew. Chem. Int. Ed. Engl., 12 (1973) 843.
32 S. Martinengo, G. Ciani, A. Sironi, B.T. Heaton and J. Mason, J. Amer. Chem. Soc., 101 (1979) 7095.
33 S. Martinengo, G. Ciani and A. Sironi, J. Amer. Chem. Soc., 104 (1982) 328.
34 M. Tachikawa, J. Stein, E.L. Muetterties, R.G. Teller, M.A. Beno, E. Gebert and J.M. Williams, J. Amer. Chem. Soc., 102 (1980) 6648.
35 D.E. Fjare and W.L. Gladfelter, J. Amer. Chem. Soc., 103 (1981) 1572; Inorg. Chem., 20 (1981) 3533.
36 D. Braga, B.F.G. Johnson, J. Lewis, J.M. Mace, M. McPartlin, J. Puga, W.J.H. Nelson, P.R. Raithby and K.H. Whitmire, J. Chem. Soc., Chem. Commun., (1982) 1081.
37 N.D. Feasey and S.A.R. Knox, J. Chem. Soc., Chem. Commun., (1982) 1062; N.D. Feasey, S.A.R. Knox and G.R. Orpen, J. Chem. Soc., Chem. Commun., (1982) 75.