Synthetic Use of Lithium Nitride, an Unusual Reducing Agent. Formation of Ti_4 and Ti_6 Complexes

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Lithium nitride acts as a reducing agent in co-ordinating solvents liberating dinitrogen, reducing $TiCl_4$ to $LiTiCl_4(THF)_4$ (THF = tetrahydrofuran), $(\eta^5\text{-}C_5H_5)_2TiCl_2$ to $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ and $(C_5H_5)_6Ti_6(C_5H_4)_2N$, and $(\eta^5\text{-}C_5H_5)TiCl_3$ to $(\eta^5\text{-}C_5H_5)TiCl_2(THF)$, $[(\eta^5\text{-}C_5H_5)TiCl_2]_n$, and $(C_5H_5)_6(C_5H_4)_2Ti_6N_3$; in the presence of CO, Li_3N reacts with $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (2 : 3 molar ratio) to form $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$.

Except at temperatures close to its melting point (840—845 °C), lithium nitride is regarded as generally unreactive.[1] Water is unusual in that it reacts vigorously at ambient temperature to yield ammonia.[2a] Lithium nitride has a hexagonal ionic structure[3] and its poor solubility contributes much to its limited known chemistry.[4] We have found that its solubility in tetrahydrofuran (THF), though low, is sufficient to enable it to react with halides of metals in their high oxidation states, and we report here a series of reduction reactions involving titanium(IV). Lithium nitride is not normally regarded as a reducing agent. We find it to be a useful synthetic reagent for converting Ti^{IV} into Ti^{III} and lower states in good yield. Lithium nitride reductions, which proceed according to equation (1), are often found to be preferable to other laboratory methods, in requiring non-forcing conditions, and in producing products easily separated from unwanted materials.

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

Titanium(III) chloride is usually prepared by hydrogen reduction of the tetrachloride[2b] at elevated temperatures, though it can also be made using $LiAlH_4$,[5] aluminium alkyls,[2b] *etc.* An active form suitable for McMurry coupling reactions[5] is formed when titanium(IV) chloride (99 mmol) in THF (40 cm^3) is added to Li_3N (33 mmol) at −196 °C, and the mixture stirred at ambient temperature. The adduct $TiCl_4(THF)_2$,[6] formed immediately, is replaced over 12 h by a pale green precipitate of $LiTiCl_4(THF)_4$ [equation (2)], which is recrystallised by Soxhlet extraction to produce pale blue-green microcrystals. The lithium cation may be replaced by tetra-alkylammonium and bis(triphenylphosphino)iminium cations in THF solution, and the corresponding bromides prepared by starting with $TiBr_4$. Authentic samples of the complexes were prepared also by the reaction of commercial titanium(III) halides with lithium halides in THF. Other solvates were prepared using other solvents such as dioxane or monoglyme. Further reactions of Li_3N with the titanium(III) compounds occur to produce grey Ti^{II} compounds, but these have not yet been fully characterised. Preliminary results[7] on coupling of aryl ketones suggest that $LiTiCl_4(THF)_4$ can be used as a convenient and effective substitute for $TiCl_3$ in the conventional McMurry reactions.[5,8]

$$TiCl_4(THF)_2\ (3\,mol) \xrightarrow[THF]{Li_3N\ (1\,mol)} LiTiCl_4(THF)_4 \quad (2)$$

$[(\eta^5\text{-}C_5H_5)_2TiCl]_2$, $(\eta^5\text{-}C_5H_5)TiCl_2(THF)$, and $[(\eta^5\text{-}C_5H_5)TiCl_2]_n$ may all be prepared conveniently using Li_3N as the reducing agent. $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (4 mmol) and Li_3N (1.35 mmol) in THF (25 cm^3) react at ambient temperature over 30 min to produce a green solution from which $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ is isolated in 88% yield [equation (3)]. This preparative method has distinct advantages over the standard method which uses zinc dust as the reductant, in that it avoids the formation of $[(\eta^5\text{-}C_5H_5)_2TiCl]_2ZnCl_2$, which is often a major product. The method has advantages also over the reaction between $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $(\eta^5\text{-}C_5H_5)_2TiBH_4$ since it avoids the prior preparation of the latter complex.

$$(\eta^5\text{-}C_5H_5)_2TiCl_2\ (3\,mol) \xrightarrow[THF]{Li_3N\ (1\,mol)} [(\eta^5\text{-}C_5H_5)_2TiCl]_2 \quad (3)$$

With $(\eta^5\text{-}C_5H_5)TiCl_3$ (2.4 mmol) in THF (35 cm^3), Li_3N (0.81 mmol) reduction produces a green solution from which blue-green crystals of $(\eta^5\text{-}C_5H_5)TiCl_2(THF)$[9] are produced. Alternatively if toluene is added to the reaction mixture, and THF removed under reduced pressure, $[(\eta^5\text{-}C_5H_5)TiCl_2]_n$ is obtained by fractional crystallisation in 67% yield [equation (4)].

$$(\eta^5\text{-}C_5H_5)TiCl_3\ (3\,mol) \xrightarrow[THF]{Li_3N\ (1\,mol)} (\eta^5\text{-}C_5H_5)TiCl_2(THF) \rightarrow [(\eta^5\text{-}C_5H_5)TiCl_2]_n \quad (4)$$

Further reduction of $(\eta^5\text{-}C_5H_5)TiCl_3$ using Li_3N in a higher molar proportion ($3Ti : 2Li_3N$) produces green $(\eta^5\text{-}C_5H_5)_4Ti_4Cl_4$ (*m/z* 591). This diamagnetic complex has a simple ^1H n.m.r. spectrum consisting of a sharp singlet at δ 6.58 at ambient temperature, suggesting only one type of cyclopentadienyl group. Available evidence suggests a tetrahedral cluster with face bridging chloro-ligands as a probable structure {*cf.* [(cyclo-octatetraene)$TiCl]_4$[10]}.

The reactions so far described, which involve $(\eta^5\text{-}C_5H_5)TiCl_3$ and Li_3N in 3 : 1 and 3 : 2 molar ratios, and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and Li_3N in a 3 : 1 molar ratio, have demonstrated clearly that Li_3N acts as a reducing agent without incorporation of nitrogen into the products. Use of the appropriate molar ratio of Li_3N to remove all the chloride from the complexes would therefore be expected to produce the $[C_5H_5Ti]$, or the titanocene $[(C_5H_5)_2Ti]$ moieties and hence lead to known chemistry.[2b] However reaction between $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (4.0 mmol) and Li_3N (2.8 mmol) in THF produced a very air-sensitive blue solid containing nitrogen. Mass spectral studies show the highest titanium-containing ion to be centred at *m/z* 820 corresponding to $[(C_5H_5)_6(C_5H_4)_2Ti_6N]^+$. Fragmentation occurred by loss of nitrogen followed by sequential loss of cyclopentadienyl groups. A different blue complex is formed in the reaction between $(\eta^5\text{-}C_5H_5)TiCl_3$ (2.3 mmol) and Li_3N (2.3 mmol) in THF (25 cm^3). The ion of highest mass number observed in the mass spectrum occurred at *m/z* 848, corresponding to $[(C_5H_5)_6(C_5H_4)_2Ti_6N_3]^+$, the fragmentation pattern being similar to that of the previous blue complex.

Attempts to obtain derivatives of the blue complexes were unsuccessful, the complexes failing to react with 2,2′-bipyridine, triphenylphosphine, 1,2-bisdiphenylphosphinoethane (dppe), and carbon monoxide under a variety of

conditions. Also the reactions between $(\eta^5\text{-}C_5H_5)_2TiCl_2$ or $(\eta^5\text{-}C_5H_5)TiCl_3$ and Li_3N in the presence of PPh_3 or dppe resulted in no change in the course of the reaction. However when the reaction between $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and Li_3N was undertaken in the presence of carbon monoxide, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$[11,12] was obtained.

The synthetic utility of Li_3N as a reducing agent has been well demonstrated and exploratory work indicates that the reagent achieves a wide range of reductions of metals in high oxidation states.

We thank the University of Durham for research studentships (to G. P. and A. G. T.).

Received, 17th February 1984;† Com. 211

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† Received in revised form 9th October 1984.