The Synthesis and Characterization of the First Trimethylhydrazido(1–) Complex of Titanium [$CpTiCl_2(NMeNMe_2)$] ($Cp = \eta^5\text{-}C_5H_5$, $Me = CH_3$)

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Although [$CpTiCl_2(N_2Ph)$] and [$Cp_2TiCl(N_2Ph)$] complexes have recently been synthesized, no titanium complexes containing N_2R_2 or N_2R_3 type of ligands have been reported [1]. A considerable number of molybdenum and tungsten complexes containing N_2R or N_2R_2 (R = H, alkyl or aryl) ligands are now well known [2, 3]. So far the only complexes containing N_2R_3 ligand that have been synthesized are [$Cp_2W(NRNH_2)$][BF_4] (R = *p*-XC_6H_4; X = H, F, Me, or OMe) [4], [$Mo(NNMePh)(NHNMePH)(S_2CNMe_2)_2$][$BPh_4$] [5], [$CpMo(NO)I(NRNR'R'')$] (R = H or alkyl; R′ = H, alkyl or aryl; R″ = alkyl or aryl) [6] and the more recent ones [$Mo\{HB(Me_2Pz)_3\}(NO)I(NHNRR')$] ($Me_2Pz$ = 3,5-dimethylpyrazolyl; R = R′ = H or Me; R = H, R′ = Me or Ph; R = Me, R′ = Ph) and [$W\{HB(Me_2Pz)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)\}(NO)Br(NHNRR')$] (R = R′ = H or Me; R = H, R′ = Ph) [7]. The study of N_2R, N_2R_2 and N_2R_3 complexes is of great importance towards understanding the mechanism of nitrogen fixation in nitrogenase enzyme systems and designing a catalytic system capable of fixing nitrogen. We now report the synthesis and characterization of the first trimethylhydrazido(1–) complex of titanium [$CpTiCl_2(NMeNMe_2)$] from the reaction of [$CpTiCl_3$] with $LiNMeNMe_2$ and $Me_3SiNMeNMe_2$ derivatives.

Experimental

The following compounds were prepared according to normal procedures: [$CpTiCl_3$] [8] and Me_2NNHMe [9]. Butyl lithium LiBu in hexane was obtained commercially. Microanalysis and ^1H NMR were carried out at the University of Sussex. All experiments were performed in conventional schlenk glassware under dry deoxygenated nitrogen using solvents dried by the usual procedures.

Preparation of Trimethylhydrazido Derivatives; $LiNMeNMe_2$ and $Me_2SiNMeNMe_2$

The trimethylhydrazido(1–) ligand $NMeNMe_2$ was obtained from $LiNMeNMe_2$ or $Me_3SiNMeNMe_2$ compounds. The new compounds were also made using trimethylhydrazine as the starting material according to the reaction equation:

$$\begin{tikzcd}[column sep=small] Me_2NNHMe + LiBu \arrow[r] & nBuH + LiNMeNMe_2 \arrow[d, "Me_3SiCl"] \\ & Me_3SiNMeNMe_2 + LiCl \end{tikzcd}$$

$Bu = CH_3CH_2CH_2CH_2$, $nBuH = CH_3CH_2CH_2CH_3$.

To prepare $LiNMeNMe_2$ derivative a known amount of trimethylhydrazine was added to 100 cm^3 of THF (tetrahydrofuran) in a schlenk tube. Then an equimolar solution of LiBu in hexane was added in drops to a well stirred solution using a syringe degased several times with nitrogen. The silicon derivative was made by reacting an equimolar amount of Me_3SiCl with the mixture of LiBu and Me_2NNHMe and then distilling. The redistilled product had ^1H NMR that agreed with the $Me_3SiNMeNMe_2$ formulation. The $Me_3SiNMeNMe_2$ derivative thus obtained was used in the subsequent reaction (*vide infra*).

Synthesis of [$CpTiCl_2(NMeNMe_2)$] from [$CpTiCl_3$] using $LiNMeNMe_2$

[$CpTiCl_3$] (0.30 g, 1.37×10^{-3} mol) was dissolved in THF (6 cm^3) to give a yellow solution. An equimolar solution of $LiNMeNMe_2$ in THF was added in drops to a well stirred solution of [$CpTiCl_3$]. A blue colouration formed at the point of addition. The solution became purple and finally bluish green. Within a few minutes a crystalline yellow precipitate was produced. This was filtered off and dried *in vacuo*. The yield of the product was 0.20 g (57%). The precipitate is soluble in $CHCl_3$, CH_2Cl_2 and acetone but sparingly soluble in THF. The product was characterized by analysis and ^1H NMR (Table I).

Synthesis of [$CpTiCl_2(NMeNMe_2)$] using $Me_3SiNMeNMe_2$

[$CpTiCl_3$] (1.20 g, 5.47×10^{-3} mol) was dissolved in THF (13 cm^3) to give a clear yellow solution. $Me_3SiNMeNMe_2$ reagent (1 cm^3, 0.80 g, 5.47×10^{-3} mol) was added dropwise to the stirred

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TABLE I. Analytical and ^{1}H NMR Data for [$CpTiCl_2(NMeNMe_2)$].

Compound Prepared from	Found (%)			Calculated (%)			^{1}H NMR (δ)		
	C	H	N	C	H	N	Cp	Me	Me_2
$LiNMeNMe_2$	37.12	5.57	10.78	37.35	5.45	10.89	6.51	3.54	2.89
$Me_3SiNMeNMe_2$	37.16	5.77	10.79				6.51	3.54	2.89

[$CpTiCl_3$] solution at room temperature. There was an immediate precipitation of a yellow product in 57% yield (0.80 g). The precipitate was filtered off and dried on a vacuum line. The product was characterized by analysis and ^{1}H NMR (Table).

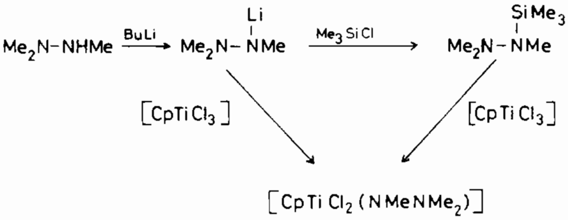
Results and Discussion

The synthesis of the lithium derivative $LiNMeNMe_2$ from LiBu and trimethylhydrazine was carried out using THF as the most suitable solvent in which a clear solution could be formed. Although the lithium derivative was not isolated and characterized, it is presumed that the most reasonable reaction between LiBu and Me_2NNHMe gives rise to the $LiNMeNMe_2$ derivative.

Other solvents such as ether and dimethoxyethane were tried but the lithium product $LiNMeNMe_2$ was insoluble in the solvents and simply precipitated out. An attempt to make the lithium derivative by direct reaction of LiBu in hexane and Me_2NNHMe was found unsuitable as the reaction proved quite explosive. Hence THF was adopted as the appropriate solvent for the subsequent reactions since the reactants were soluble in it.

$LiNMeNMe_2$ is extremely reactive and highly air sensitive. A cursory investigation of the reaction between the lithium reagent and [Cp_2TiCl]$_2$ or [Cp_2TiCl_2] or [$ReOCl_3(PPh_3)$] indicated that the reactions were quite complex, as mixed products appeared to be forming from each reaction as evidenced by various colour changes and differences in solubility of products. The only reaction from which an analytically pure product was obtained was that between $LiNMeNMe_2$ and [$CpTiCl_3$] complex. Even then, the solution initially turned blue and finally bluish-green before a yellow precipitate could be obtained. Hence it became necessary to find a less reactive derivative of $NMeNMe_2$. This was achieved by reacting a solution of $LiNMeNMe_2$ in THF with Me_3SiCl to give the silicon derivative $Me_3SiNMeNMe_2$. The trimethylhydrazido silicon derivative was found to undergo a clean reaction with [$CpTiCl_3$] forming a clear yellow solution from which a yellow product precipitated out. The yield was 57% and the analysis of the sample of the product conformed with the complex being formulated as [$CpTiCl_2(NMeNMe_2)$] (Table I). The analytical data and ^{1}H NMR indicated that the products from the reaction between $LiNMeNMe_2$ and [$CpTiCl_3$] on one hand and that between $Me_3SiNMeNMe_2$ and [$CpTiCl_3$] on the other were identical. The product is fairly air stable when dry at room temperature but gradually decomposes when moist.

The reaction between the new ligand trimethylhydrazido(1−) and [$CpTiCl_3$] to produce the new complex [$CpTiCl_2(NMeNMe_2)$] can be represented in the diagram:

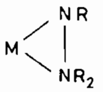


The structures of $M{-}N_2R$ [3, 10], $M{-}N_2R_2$ [11] and the $M{-}N_2R_3$ [4–7] type of complexes are well known. Most of the $M{-}N_2R$ complexes are linear (A) and the rest are bent (B):

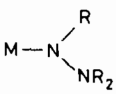
(A) (B)

R = H, alkyl or aryl group

The molybdenum complex [$MoBr(N_2Et)(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) is of type (A) whereas the rhodium complex [$RhCl_2(N_2Ph)(PPh_3)_2$] [10] is type (B). The $M{-}N_2R_2$ complexes known so far, of which [$WCl(N_2H_2)(dppe)_2$][BPh_4] [12] and [$Mo(N_2Ph_2)_2(S_2CNMe_2)_2$] [11] are typical examples, are linear $M{-}N{=}NR_2$. Of the $M{-}N_2R_3$ molybdenum and tungsten complexes now known, two types of bonding modes (I) and (II) have been identified:

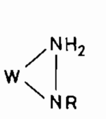


(I)

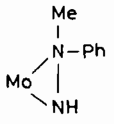


(II)

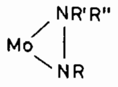
The complexes $[Cp_2W(NRNH_2)]^+$ [4], $[Mo(NNMePh)(NHMePh)(S_2CNMe_2)_2]^+$ [5] and $[CpMo(NO)I(NRNR'R'')]$ [6] exhibit the bonding mode (II) whereas $[Mo\{HB(Me_2Pz)_3\}(NO)I(NHNRR')]$ and $[W\{HB(Me_2Pz)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)\}(NO)Br(NHNRR')]$ [7] complexes have type (II) bonding mode. The respective linkage structures (E), (F), (G) and (H) of the hydrazido(1−) ligand group in these complexes are as shown below:



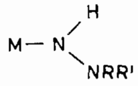
(E)



(F)



(G)

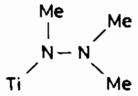


(H)

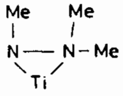
M = Mo or W

It has been suggested [7] that the hydrazido(1−) ligand N_2R_3 tends to adopt the bonding mode (I) as illustrated by structures (E) to (G) except in cases where steric factors are operative such as those imposed by the tridentate ligands $[HB(Me_2Pz)_3]^-$ and $[HB(Me_2Pz)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)]^-$ in the complexes discussed above. In such cases, bonding mode (II) is assumed as exhibited in the linkage structure (H).

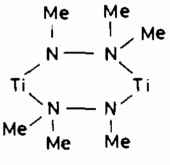
The ^1H NMR of $[CpTiCl_2(NMeNMe_2)]$ shows peaks at 6.51, 3.54 and 2.89 (δ) in the ratio 5:3:6. These are assigned to Cp, Me and Me_2 protons respectively. From ^1H NMR alone it is not possible to distinguish between the possible bonding modes (X), (Y) and (Z) of the trimethylhydrazido(1−) $NMeNMe_2$ ligand.



(X)



(Y)



(Z)

It will be interesting to find out if the ligand takes up bonding modes (X) and (Y) exhibited by the molybdenum and tungsten hydrazido(1−) complexes so far known, or bonding mode (Z). Crystals of $[CpTiCl_2(NMeNMe_2)]$ were sent for an XOray structural determination but unfortunately decomposed on the way. However, attempts are under way to get suitable crystals for an X-ray crystal structural analysis to elucidate the nature of bonding of the trimethylhydrazido(1−) ligand.

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