Side-on Dihapto-bonding of Hydrazide(1−) and Diazenide(1−) to Titanium

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The complexes $[Ti(\pi\text{-}C_5H_5)Cl_2L]$ (L = N=NPh or $NPhNH_2$) have been shown by *X*-ray crystallography to contain side-on dinitrogen moieties, the former being the first example of this kind of co-ordination of a diazenido-ligand.

The only clearly defined intermediate in the protonation of co-ordinated dinitrogen to ammonia is hydrazide(2−). Our recent theoretical discussion[1] of other possible intermediates, hydrazide(1−) and diazenide(1−) in their lithium salts, suggested that these should contain side-on dinitrogen moieties. We now report the structures of two titanium complexes which are consistent with these predictions.

The complex $[Ti(C_5H_5)Cl_3]$ reacts with the silyl hydrazines,[2] $Me_3SiNMeNMe_2$, $Me_3SiNHNMe_2$, or $Me_3SiNHNHPh$ to yield titanium hydrazides $[Ti(C_5H_5)Cl_2(N_2R^1R^2R^3)]$ ($N_2R^1R^2R^3$ = $NMeNMe_2$, $NHNMe_2$, or $NPhNH_2$) (**1**) as yellow dioxygen-stable crystalline solids. The compounds react with an excess of hydrogen chloride to regenerate $[Ti(C_5H_5)Cl_3]$ and the parent hydrazine hydrochloride. They form 1 : 1 adducts with MeCN, and, where there is a hydrogen atom on the α-nitrogen atom, they react with bases to yield dinuclear species, $\{Ti(C_5H_5)ClNNR^2R^3\}_2$. These presumably contain a double hydrazido(2−)-bridge, similar to that formed by the deprotonation of the analogous amido-complexes.[3] Because hydrazines are bases which can also deprotonate the hydrazido(1−)-ligands, they are less satisfying than the silylhydrazines in the original preparative reaction. We determined the structure of the product (**1**) of the reaction of $[Ti(C_5H_5)Cl_3]$ with $Me_3SiNHNHPh$.

The reaction of $Me_3SiN{=}NPh$[4] with $[Ti(C_5H_5)Cl_3]$ to give the diazenido-complex $[Ti(C_5H_5)Cl_2(N_2Ph)]$ (**2**) has already been reported.[5] This orange dioxygen-stable solid has ν(N=N) anomalously low at 1593 and 1632 cm^{-1}, and it

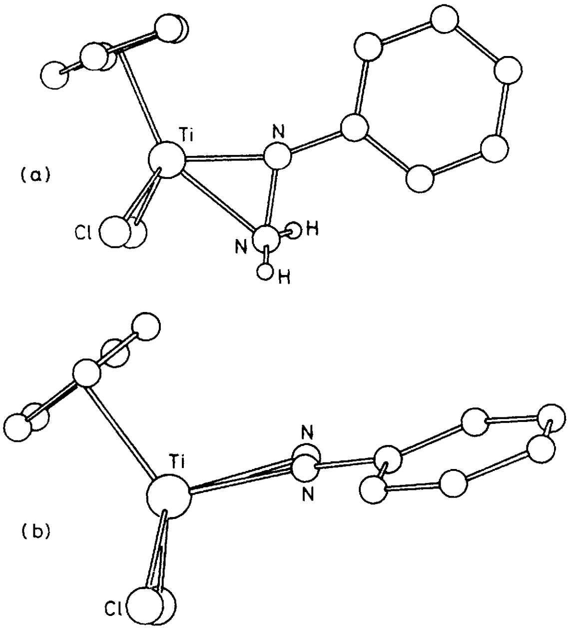

Figure 1. Molecular structures of $[Ti(C_5H_5)Cl_2(NH_2NPh)]$ (**1**) (a) and $[Ti(C_5H_5)Cl_2(NNPh)]$ (**2**) (b).

reacts with an excess of HCl to yield $PhNHNH_2{\cdot}HCl$. We have also determined its structure.

Crystal data: for $[Ti(C_5H_5)Cl_2(NH_2NPh)]$ (**1**), $C_{11}H_{12}Cl_2N_2Ti$, $M = 291.04$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 7.664(8)$, $b = 9.322(8)$, $c = 9.85(1)$ Å, $\alpha = 95.27(8)$, $\beta = 105.8(8)$, $\gamma = 112.59(7)°$, $U = 610$ Å^3, $D_c = 1.59$ g cm^{-3}. From 1313 reflections measured at −42 °C (Mo-K_α radiation, $\lambda = 0.71069$ Å), 1200 with $I > 2\sigma(I_0)$ were used for refinement to achieve final reliability factors covering all hydrogen atoms of $R = 7.00$ and $R_w = 8.36\%$ (SHELXTL program). The essential structure is shown in Figure 1, and important dimensions in Figure 2. For $[Ti(C_5H_5)Cl_2(NNPh)]$ (**2**), $C_{11}H_{10}Cl_2N_2Ti$, $M = 289.02$, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 13.73(1)$, $b = 12.854(5)$, $c = 14.567(7)$ Å, $\beta = 109.85(5)°$, $U = 2419$ Å^3, $D_c = 1.59$ g cm^{-3}. From 2592 reflections measured at −35 °C (Mo-K_α radiation, $\lambda = 0.71069$ Å), 2058 with $I > 2\sigma(I_0)$ were used to achieve final reliability factors covering all hydrogen atoms of $R = 4.43$ and $R_w = 4.40\%$ (SHELXTL program). The structure and dimensions are also shown in Figures 1 and 2.†

The side-on structure for the hydrazido(1 −)-derivative (**1**) is similar to that predicted[1] and is not without precedent. Indeed $[W(C_5H_5)_2(NH_2NPh)]^+$ has a very similar structure.[6] The nitrogen–nitrogen distance in (**1**) corresponds to a single-bond length, and the metal atom, nitrogen atoms and phenyl carbon atoms are all in the same plane. During the formation of (**1**), one hydrogen atom moves to the adjacent nitrogen atom producing an NH_2 group. The individual molecules are bound together by strong hydrogen-bonds to give a centrosymmetric arrangement of pairs of molecules (Figure 3). This hydrogen-bonding may provide the driving force for the hydrogen migration.

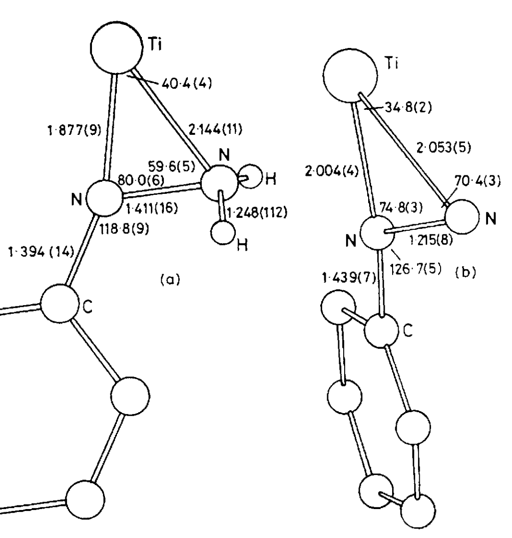

Figure 2. Important bond lengths (Å), and angles (degrees) in (**1**) (a) and (**2**) (b).

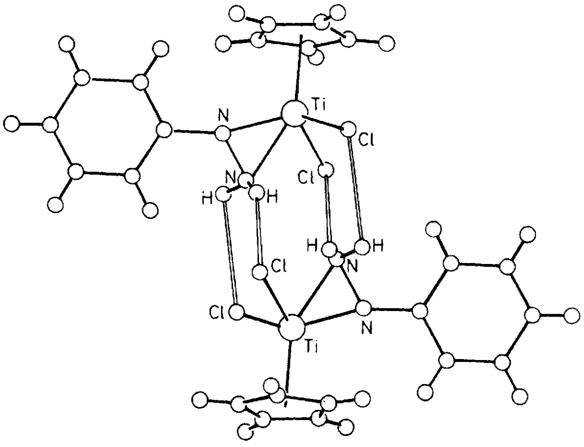

Figure 3. Dinuclear unit of $[Ti(C_5H_5)Cl_2(NH_2NPh)]$ (**1**) formed by hydrogen bonding.

There are many reports in the literature of end-on singly bent and doubly bent diazenido(1 −)-complexes.[7] The phenyldiazenido-complex (**2**) is unique because no other diazenido-complex has this side-on configuration. The nearest analogues are $[Ni(CNBu^t)_2(diazofluorene)]$ and $[Ru(CO)_2(N_2C_5Cl_4)(PPh_3)_2]{\cdot}CH_2Cl_2$ obtained by direct reaction of the appropriate diazoalkane with a metal(0) complex.[8] They are geometrically similar although the charge distributions are different from that in (**2**). The nitrogen–nitrogen bond in (**2**) has the length of a double bond, with the TiNN triangle more nearly isosceles than in (**1**). The phenyl ring is coplanar with the TiNN triangle in both compounds [deviations 11.3° in (**1**) and 9.8° in (**2**)], but there is a striking difference between the orientations of the N_2 fragments relative to the $Ti(C_5H_5)Cl_2$ moiety.

$[Ti(C_5H_5)Cl_2(NH_2NPh)]$	$[Ti(C_5H_5)Cl_2(NNPh)]$
(**1**)	(**2**)

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

In (**1**), the two nitrogen atoms lie within the idealized symmetry plane of the $Ti(C_5H_5)Cl_2$ fragment, whereas in (**2**) they are in a plane vertical to this symmetry plane (Figure 1). This difference may be rationalised by considering the interaction of the π-type orbitals of the ligands with the orbitals of a generalised $M(C_5H_5)L_2$ fragment.[9] For this purpose, we consider the dinitrogen fragments to be $RNNH_2^+$ (aminonitrene) and RN_2^+,[10] and consequently the $M(C_5H_5)L_2$ counterpart is the d^2-system $Ti(C_5H_5)Cl_2^-$. If we assume‡ that the dominant π-type interaction involves the nitrene-type p-orbital in the ligand of (**1**) and one of the two-centre π^*-orbitals in the ligand of (**2**), then the orientations of these orbitals give the relative orientation of the dinitrogen fragments with respect to $M(C_5H_5)L_2$. The important π-type orbital of $Ti(C_5H_5)Cl_2^-$ is the a″-orbital, oriented in a plane vertical to the $Ti(C_5H_5)Cl_2$ mirror plane.[9] Since the N–N axis is perpendicular to the nitrene-type p-orbital in (**1**), but parallel to the π^*-orbital in (**2**), the observed orientation follows naturally.

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