Side-on versus end-on coordination of dinitrogen to titanium(II) and mixed-valence titanium(I)/titanium(II) amido complexes
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attributed to ylide 3. The spectrum of 3 is similar to those of the other known dialkylpyridine ylides but is somewhat shifted to the blue (364 versus 390-410 nm) of the homocubyl and adamantly ylides.

The optical yield of ylide 3 is reduced by the presence of oxygen, a selective trap of triplet carbene. This result from two conclusions are possible. The singlet and triplet states of 2 may be of comparable energy, as per aryl- and arylalkylcarbenes, and are in rapid equilibrium. Alternatively a referee has suggested that the excited state of 1* may undergo intersystem crossing to form 1* which extrudes nitrogen to form the triplet carbene.

The intensity of the ylide signal (δy = Δνmax) produced in a laser pulse increases steadily as the concentration of pyridine increases until [Py] = 1 M, at which point the optical yield is saturated. A double reciprocal plot of the data (Figure 2) is linear with a slope of 0.45 = k/k [Py]K, where k [Py] is the second-order rate constant for reaction of dimethylylcarbene with pyridine, K is the equilibrium constant (K = [2S]/[2T]) = 1, assuming the triplet is the ground state as per methylene and that singlet-triplet equilibrium is rapid, and k is the sum of all first-order and pseudo-first-order rate constants of all processes which consume the carbene in the absence of pyridine. These processes include isomerization (k1) and reaction of the carbene with solvent (k2H and k2H). Assuming that k[Py]K ~ 10^10 s^-1 ppm the lifetime of the carbene at 1-100 ns in pentane in the absence of pyridine. This lifetime must be controlled in part by reaction with solvent because there is a solute deuterium isotope effect of 1.3 on the slope of plots such as that in Figure 2 in CH2CN vs CD2CN and CHCl3 vs CDC13.

The data convincingly demonstrate that dimethylylcarbene is a true reactive intermediate, a species which exists in a potential energy minimum, and has a finite lifetime in solution.

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(8) Sugiyama, M.; Celebi, S.; Platz, M. S. J. Am. Chem. Soc. Submitted for publication. The singlet and triplet states of methylene are not in rapid equilibrium in solution; their energy separation is too large.

(9) Scheme I is a conventional interpretation of singlet-triplet phenomena in carbene chemistry. However, it has been pointed out [Griller, D.; Nazran, A. S.; Scaino, J. J. Am. Chem. Soc. 1984, 106, 198] that the available data for aryl carbene is consistent with the presence of a single reactive intermediate, one that can undergo reactions normally ascribed to either the triplet or the singlet state of the carbene. In this interpretation a triplet carbene can react with pyridine to form a ylide via a single-triplet surface crossing along the reaction coordinate. The surface crossing mechanism resolves inconsistencies in the kinetics of reaction of triplet diphenylylcarbene and methanol. The data of this work is consistent with a pseudequilibrium or surface crossing mechanism. The traditional mechanism is presented in Scheme I because there is no compelling reason to discard it with dimethylylcarbene.


**Side-On versus End-On Coordination of Dinitrogen to Titanium(II) and Mixed-Valence Titanium(I)/Titanium(II) Amido Complexes**

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Dinitrogen coordination and reduction are among the most challenging of the several transformations (dinitrogen activation, reactivity with unsaturated organic substrates, C-H bond activation, CO chemistry, and Ziegler–Natta catalysis) promoted by divalent titanium compounds. Although the great ability of titanocene systems to give dinitrogen fixation with a variety of bonding modes clearly underlines the strength of divalent titanium as a powerful reducing agent; however, the coordination chemistry of the oxidation state +II remains limited to only a few diverse cases. To date there are no clearly demonstrated examples where fixation/reduction of dinitrogen occurs on a nonmetallicenium titanium system.

Here we report the isolation and characterization of two novel dinitrogen Ti(II) and mixed-valence Ti(I)/Ti(II) amido complexes obtained via chlorine replacement at trans-(TMEDA)TiCl.

The reaction of trans-(TMEDA)TiCl with 1 equiv of (Me3Si)2NLi in toluene under nitrogen at ~80 °C formed a purple jelly suspension which turned into a deep-brown solution upon standing overnight at room temperature. Brown crystals of [(Me3Si)2N]TiCl(TMEDA)(μ-η3)1 were obtained after evaporation and crystallization from ether at ~30 °C (Scheme 1). Occasionally, small amounts of colorless crystals of mo-
nomic \([\text{Me}_2\text{Si}]_2\text{N}_2\)TiCl\(_4\)(TMEDA)\(_2\)Li\) (2)\(^6\) were isolated upon concentration of the mother liquor and further freezing. Conversely, reaction with 2.5 equiv of \((\text{Me}_2\text{Si})_2\text{N}_2\)Li in the presence of a small amount of TMEDA led to the same conditions, to the formation of white crystals of \([(\text{Me}_2\text{Si})_2\text{N}_2]_2\text{TiCl}_4(\text{TMEDA})_2\)Li (2) and deep-purple/black crystals of \([(\text{Me}_2\text{Si})_2\text{N}_2]_2\text{TiCl}_4\)(TMEDA)_2Li (3). The two species were isolated in moderate yield and analytically pure form, upon solvent evaporation and fractional crystallization in ether at -30 °C (Scheme I). In both cases a competitive reaction is probably responsible for the formation of 2 since complexes 1 and 3 are thermally robust and did not show any appreciable decomposition in benzene at -76 °C. Furthermore, 2 was the only identifiable product when the two reactions were carried out in THF. Compound 2 could conveniently be prepared on a very large scale by direct reaction of TiCl\(_4\)(THF)\(_2\) with 2 equiv of \(\text{R}_2\)Li and 2 equiv of TMEDA in ether.\(^9\)

The structures of 1 and 3 have been determined by X-ray analysis.\(^1\) Complex I is binuclear and consists of two identical \([(\text{Me}_2\text{Si})_2\text{N}]_2\text{TiCl}(\text{TMEDA})_2\] fragments each bonded to one of the two nitrogen atoms of a bridging dinitrogen moiety (Figure 1). The two titanium fragments are rotated with respect to each other (torsion angle \(\text{Cl}(1)-\text{Ti}(1)-\text{Ti}(1')-\text{Cl}(1') = 48.7 (5)^\circ\) probably as a result of minimization of steric repulsion between the two bulky amido groups. The coordination geometry of the titanium atom is square-pyramidal with the titanium atom quite elevated above the basal plane [distance from the plane 0.463 (6) Å] defined by chlorine and the nitrogen atoms of TMEDA and amido groups \([\text{N}(1)-\text{Ti}(1)-\text{N}(3), 92.0 (2)^\circ; \text{N}(3)-\text{Ti}(1)-\text{N}(2), 76.2 (2)^\circ; \text{N}(2)-\text{Ti}(1)-\text{Cl}(1), 84.0 (2)^\circ; \text{Cl}(1)-\text{Ti}(1)-\text{N}(1), 36.6 (2)^\circ\)] The apical position of the square-pyramid is occupied by one of the two atoms of the bridging dinitrogen molecule. The considerably short Ti-N distance \([\text{Ti}(1)-\text{N}(4), 1.762 (5) Å\) together with the almost linear arrangement of the \(\text{Ti}(\mu-\text{N}_2)-\text{Ti}\) moiety \([\text{Cl}(1)-\text{Ti}(1)-\text{Cl}(1')=84.0 (2)^\circ\)] and the rather long N-N distance \([\text{N}(4)-\text{N}(4'), 1.289 (9) Å\) are in agreement with the presence of considerable electronic delocalization over the \(\text{Ti}(\mu-\text{N}_2)\) moiety. The Ti-N distance with the trigonal-planar amido group \([\text{Ti}(1)-\text{N}(1), 2.023 (5) Å\) is significantly shorter than those formed by the nitrogen atoms of the TMEDA groups \([\text{Ti}(1)-\text{N}(2), 2.352 (6) Å, \text{Ti}(1')-\text{N}(3), 2.351 (6) Å\)] suggesting the presence of some π-bond character with both silicon and titanium atoms.

\(^{9}\) Complex I: \(\text{dodeca-hexagonal, P4}_2\text{2}_2\text{2}, a = 11.500 (5) Å, c = 31.644 (9) Å, V = 4.919 (3) Å\(^3\), Z = 4, \(R = 0.059, T = 296 K\) for 182 parameters and 1672 significant reflections out of 2244. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced at calculated positions but not refined. Complex 3: orthorhombic, \(\text{P2}_1\text{2}_1\text{2}_1\text{2}, a = 13.240 (5) Å, b = 22.381 (3) Å, c = 11.575 (1) Å, V = 3345.0 (13) Å\(^3\), Z = 2, \(R = 0.077, T = 296 K\) for 113 parameters and 1058 significant reflections out of 1447. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced at calculated positions but not refined. One of the two atoms of the dinitrogen molecules was found disordered over two positions. Disorder was modeled by assigning an occupancy of 50% to one of the two nitrogen atoms.
The chemical connectivity of 3 was also demonstrated by X-ray diffraction analysis. The structure consists of two separate 
\( [\text{Li(TMEDA)}]_2 \) and \( [(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ti}([\mu-\text{Cl}]\text{N}_2)\text{Ti}([\mu-\text{N}_2])_2 \) ionic fragments. The Ti-containing unit is dinuclear and is formed by 
two \( ([\text{Me}_3\text{Si})_2\text{N}]_2\text{Ti} \) groups symmetrically and perpendicularly placed on the two sides of the plane defined by two parallel 
molecules of dinitrogen (Figure 2). Four of the six coordination sites of titanium are occupied by the four nitrogen atoms of the 
two coplanar dinitrogen molecules, the two remaining sites being occupied by the two amido groups. The side-on geometry of the 
two coordinated \( N_2 \) molecules is somewhat reminiscent of that of a recently reported zirconium dinitrogen phosphine complex. 
Even in this case, the \( N-N \) distance \( [N(3)-N(4) = 1.379 (21) \text{ Å} \) is rather long, and it is significantly longer than that displayed by 
complex 1. By contrast, the \( N-N \) distances \( [N(1)-N(3) = 2.236 (19) \text{ Å} \) and \( [N(1)-N(4) = 2.290 (13) \text{ Å} \) are definitely longer 
as a probable result of the different bonding fashion of the Ti. It is very difficult to speculate on the extent of dinitrogen reduction on the 
exclusive basis of the \( N-N \) distances, since the structural features of 3 (with no particularly long \( N-N \) and \( Ti-Ti \) distances) are 
somehow in contradiction with those of 1 with comparable \( N-N \) distance and extremely short \( Ti-Ti \) distance. The completely 
different bonding mode of dinitrogen in the two complexes (end-on versus side-on) is intriguing indeed and at the moment can be 
explained only by the different steric bulk of the two complexes. As expected, complex 1 is diamagnetic while 2 and 3 are 
paramagnetic \( [\mu_{eff} = 1.75 \mu_B, \mu_{eff} = 1.37 \mu_B \) respectively. The low value of the magnetic moment of 3 can be ascribed to either antiferromagnetic or superexchange, since the \( Ti-Ti \) nonbonding distance is rather short \( [Ti(1)-Ti(1a) = 3.680 (8) \text{ Å} \) .

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Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for 1 and 3, and an ORTEP plot for \( Li(TMEDA)_2 \) (15 pages); tables of observed and calculated structure factors for 1 and 3 (21 pages). Ordering information is given on any current masthead page.

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Photoluminescence of Antimony(III) and Bismuth(III) Chloride Complexes in Solution

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Metal-centered (MC) excited states play an important role in the photochemistry and photochemistry of coordination compounds. However, the study of MC states has been essentially limited to d and f block elements, while the main group metals were largely ignored. This lack of knowledge is quite surprising since MC excited states of many main group metal complexes can be easily studied by emission spectroscopy under ambient conditions. Although simple halide complexes of \( s^2 \) metals such as \( Ti^+ \), \( Sn^{2+} \), \( Pb^{2+} \), and \( Sb^{1+} \) are known to be luminescent in solution, this observation has been occasionally used only for analytical applications but hardly for the characterization of the emitting excited state. On the contrary, the emission of \( s^2 \) ions which are doped into host lattices has been studied in detail by solid-state physicists. We report here our observations on the photoluminescence of \( \text{SbCl}_4^-, \text{SbCl}_5^-, \text{BiCl}_4^-, \) and \( \text{BiCl}_5^- \) in solution and discuss the nature of the emitting excited state. While an emission of \( \text{SbCl}_5^- \) in \( CHCl_3 \) has been reported before, the other three complex ions are not yet known to show photoluminescence in solution at room temperature.

The compounds \( [\text{NEt}_4]\text{SbCl}_4 \) and \( [\text{NEt}_4]\text{BiCl}_4 \) were prepared according to a published procedure. The complex ions \( \text{SbCl}_5^- \) and \( \text{BiCl}_5^- \) in acetonitrile were formed by the addition of an excess of \( [\text{NEt}_4]Cl \) to the \( \text{MCI}_4^- \) ions. The absorption spectrum of \( \text{SbCl}_4^- \) in acetonitrile (Figure 1) displays three bands (Table 1). Light absorption by \( \text{SbCl}_5^- \) was accompanied by a red emission (Figure 1, Table 1). The excitation spectrum agreed well with the absorption spectrum. Upon addition of chloride \( \text{SbCl}_4^- \) was converted to \( \text{SbCl}_5^- \) which has an absorption spectrum (Figure 1, Table 1) similar to that of \( \text{SbCl}_4^- \). Light absorption by \( \text{SbCl}_5^- \) led to a green emission (Figure 1, Table 1). Again, the excitation spectrum matched the absorption spectrum. If light absorption was complete \( (A > 2) \), the progressive conversion of \( \text{SbCl}_4^- \) to \( \text{SbCl}_5^- \) was accompanied by the appearance of an isoemissive point at \( \lambda = 613 \) nm. The absorption and emission spectra of \( \text{BiCl}_4^- \) and \( \text{BiCl}_5^- \) (Figure 2) showed features (Table 1) which are analogous to those of \( \text{SbCl}_4^- \) and \( \text{SbCl}_5^- \). In contrast to the antimony complexes, the \( B \) band of the bismuth compounds was not observed in accordance with results on \( \text{Cs}_2\text{NaYC}_6 \) doped with \( \text{BiCl}_5^- \).

According to the VSEPR model the structures of complexes of \( s^2 \) metal ions should be determined by the presence of a stereochemically active lone pair. However, s complexes with a coordination number of six are generally octahedral, and thus they are exceptions from the rule. This applies also to the structures.

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**References**


