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Preparation of Complexes Containing $\mathrm{Ti{=}E}$, $\mathrm{Ti_2(\mu\text{-}E)_2}$, and $\mathrm{Ti(\eta^2\text{-}E_2)}$ (E = O, S) Functionalities from a Reactive Titanium Dinitrogen Complex

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Compounds containing multiple bonds between early transition metals and the lighter group 16 elements (O and S) have recently attracted considerable attention.[1,2] This interest has focused on group 4 metallocene derivatives where a variety of chalcogenide species have been isolated and characterized, although terminal oxo and sulfido derivatives of titanium have been reported for compounds utilizing aryloxide[3] and N_4-macrocycle[4−10] ligands. Group 4 metallocene examples include Bergman's $Cp^*_2Zr{=}E$ species (E = O, S),[11,12] Andersen's trapping of $Cp^*_2Ti{=}O$ using pyridine,[13] and Parkin's use of $Cp^*_2Zr(CO)_2$ in a series of reactions leading to terminal chalcogenides.[14] More recently, Piers reported related studies on the heavier chalcogenide (Se, Te) derivatives of decamethyltitanocene.[15]

We recently reported[16] some low-valent titanium amidinates prepared by the Na/Hg amalgam reduction of the Ti(IV) amidinate, L_2TiCl_2 (L = $PhC(NSiMe_3)_2$).[17] The putative Ti(II) intermediate was trapped using N_2 to give the dark blue dinitrogen complex, $(L_2Ti)_2(\mu\text{-}N_2)$,[16] in moderate yield. Here we report reactivity studies of this compound.

Unlike the labile N_2 ligand of $(Cp^*_2Ti)_2(\mu\text{-}N_2)$,[18] which is rapidly lost in solution at room temperature, the Ti_2N_2 linkage is much more robust remaining unchanged in refluxing toluene.[19] Initial attempts to displace the N_2 ligand with alkynes, ethylene, PMe_3, and CO gave no reaction at 70 °C in C_6D_6 solution. It was observed, however, that the addition of a large excess of THF to a toluene solution of the compound changed the color from dark blue to green. Attempts to isolate a THF-containing product by crystallization from THF/hexanes were unsuccessful, and removal of the THF afforded pure starting material. In contrast, addition of pyridine (Py) immediately gave a red solution, from which dark-red diamagnetic crystals were isolated from hexanes −30 °C. ^{1}H-NMR data showed a Py:amidinate ratio of 1:2, and X-ray crystallography confirmed the product to be $[L_2Ti(Py)]_2(\mu\text{-}N_2)$ (Scheme 1) with an intact Ti_2N_2 core.[20] Addition of 2 equiv of RNC (R = 2,6 dimethylphenyl) to $(L_2Ti)_2(\mu\text{-}N_2)$ in toluene afforded the related isocyanide adduct, $[L_2Ti(CNR)]_2(\mu\text{-}N_2)$. Interestingly, the IR spectrum of this complex shows a ν_{CN} at higher energy (2143 cm^{-1}) than that in the free ligand (2115 cm^{-1}). This result, combined with crystallographic data and the lack of reactivity toward CO, suggests extreme reduction of the μ-N_2 ligand.[21]

Exposure of $[L_2Ti(Py)]_2(\mu\text{-}N_2)$ in hexanes to dry O_2 formed an orange solution, from which the peroxo derivative, $L_2Ti(\eta^2\text{-}O_2)Py$ precipitated within minutes. The crystal structure (Scheme 1) shows a 7-coordinate Ti with two bidentate amidinate ligands, an η^2-O_2 ligand, and a coordinated Py.[22] The peroxide ligand displays a rather long O−O bond (1.465(3) Å) and typical Ti−O bonds (1.856(3), 1.850(2)) compared to $(Me_3\text{-}tacn)Ti(O_2)(NCO)_2$[4] (1.348(5), 1.821(5), 1.815(4) Å) and $Ti(O_2)(C_6H_4NO_2)_2(HMPA)$[23] (1.419(6), 1.842(4), 1.853(4) Å).

Reaction of $[L_2Ti(Py)]_2(\mu\text{-}N_2)$ with excess elemental sulfur in toluene took a slightly different course, displacing both the N_2 and Py to give the base-free disulfide complex $L_2Ti(\eta^2\text{-}S_2)$, characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography.[20]

Toluene solutions of $L_2Ti(\eta^2\text{-}S_2)$ react with Hg metal to give an orange-red solution along with black precipitate after 12 h. Following workup and extraction with Et_2O, orange-red crystals were obtained in moderate yield by cooling to −30 °C. Room-temperature ^{1}H-NMR data taken in $CDCl_3$ showed a relatively complex spectrum that is very similar to that of an orange compound prepared cleanly by the addition of dry O_2 to powdered $(L_2Ti)_2(\mu\text{-}N_2)$. X-ray crystallography confirmed them to be the homologous compounds $L_2Ti(\mu\text{-}E)_2TiL[\eta^1\text{-}NC(Ph)N(SiMe_3)_2]$. Results for the O_2-derived product (Scheme 1[22]) show that one of the amidinate ligands has undergone a 1,3-

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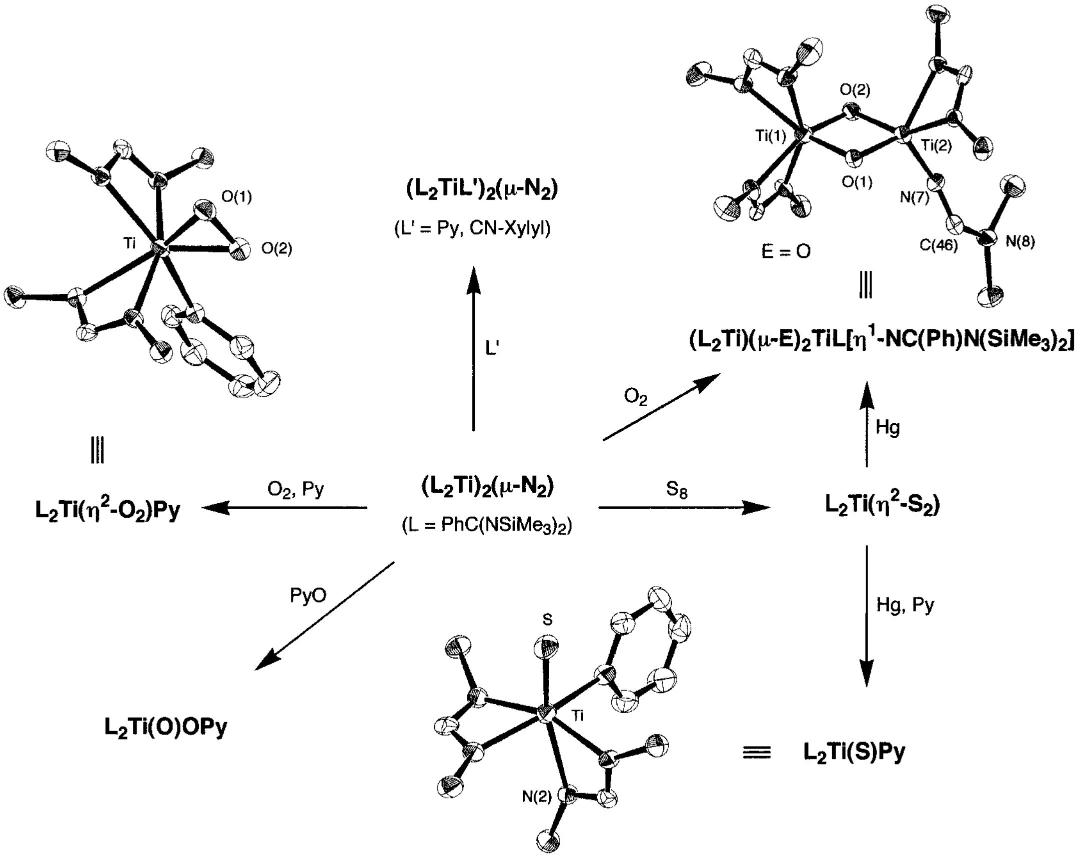
Scheme 1



ORTEP representations drawn with 50% elipsiods; methyl and phenyl groups omitted for clarity

silyl migration to form an unusual η^1-NC(Ph)N(SiMe$_3$)$_2$ ligand. We know of only one other structurally characterized transition metal complex featuring this ligand, [TaCl$_4$(NC(Ph)N(SiMe$_3$)$_2$]$_2$,[24] which was prepared by reaction of TaCl$_5$ with PhC(NSiMe$_3$)-N(SiMe$_3$)$_2$ in CH$_2$Cl$_2$. The Ti$_2$O$_2$ core of L$_2$Ti(μ-O)$_2$TiL[η^1-NC(Ph)N(SiMe$_3$)$_2$] is essentially planar with a Ti−O−Ti−O torsion angle of 1.3(2)°. The two Ti atoms are separated by only 2.75 Å, and the Ti−O bonds are unsymmetrical; they alternate in length with values of 1.863(6), 1.817(4), 1.883(6), and 1.790(4) for Ti(1)−O(1), Ti(2)−O(1), Ti(2)−O(2), and Ti(1)−O(2), respectively. Coordination of the amidinates at Ti(1) is typical; in contrast, Ti(2) features 5-coordinate pseudo square-pyramidal geometry. The η^1-imido ligand has a short Ti-N(7) bond (1.835(7) Å) and what appears to be localized N(7)−C(46) (1.28(1) Å) and C(46)−N(8) (1.41(1) Å) bonds. The sulfur analogue is isostructural, in spite of the longer Ti−Ti distance (3.27 Å).[20]

Formation of the bridging sulfido by S-atom abstraction with Hg suggested the intermediacy of a terminal sulfido species, which was subsequently isolated by trapping as a pyridine adduct (Scheme 1). ^{1}H-NMR spectroscopy showed it to contain 1 equiv of pyridine per 2 amidinate ligands, a result that was confirmed by X-ray structural analysis. The 6-coordinate pseudo-octahedral Ti has a Ti−S bond of 2.139(1) Å which is shorter than that in Cp*$_2$Ti(S)Py[25] (2.217(1) Å) and Na$_2$[CpTi(μ-S)(S)]$_2$ (2.187(1), 2.202(1) Å)[26] but is slightly longer than the related parameter in (NEt$_2$)$_2$[TiSCl$_4$][27] (2.111(2) Å). IR spectroscopy shows an absorption at 520 cm^{-1} for the Ti−S bond which is comparable to those reported for (NEt$_2$)$_2$-[TiSCl$_4$][27] (530 cm^{-1}) and TiS(C$_{22}$H$_{22}$N$_4$)[28] (545 cm^{-1}). Heating solutions to 70 °C resulted in clean formation of the bridging sulfido dimer, L$_2$Ti(μ-S)$_2$TiL[η^1-NC(Ph)N(SiMe$_3$)$_2$]. The closely related terminal oxo derivative, L$_2$Ti(O)OPy, has also been prepared from the reaction of (L$_2$Ti)$_2$(μ-N$_2$) with 2 equiv of Py−O in toluene.[20] Although it is isomeric with the peroxo complex, L$_2$Ti(O$_2$)Py, we have as yet seen no evidence for interconversion between the two. Further reactivity studies are in progress.

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Supporting Information Available: Text giving selected spectroscopic data and elemental analyses for new compounds and full details of crystal structure determinations including tables of crystal and data collection parameters, temperature factor expressions, positional parameters, and bond lengths, and angles and ORTEP representations (30 pages). Ordering information is given on any current masthead page.

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