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# *Communications to the Editor*

## Low-Valent Chemistry of Titanium Benzamidinates Leading to New Ti $\mu$-N$_2$, $\mu$-O, Alkyl Derivatives, and the Cyclometalation of TMEDA

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In efforts to develop alternative ligand arrays to the ubiquitous $\mathrm{Cp_2}$ fragment, whose transition metal chemistry has been widely explored[1−3] and has provided a host of important discoveries over the years, a number of research groups have turned their attention to nitrogen-based donors.[4−7] For comparison to our work on early transition metal porphyrin derivatives,[8−10] we recently began a study of the $\mathrm{N_4}$-donor environment provided by bis-amidinate ligand systems. In particular, we were attracted to the *N,N′*-bis(trimethylsilyl)benzamidinate ligand system, as this has shown considerable promise for the stabilization of a wide variety of early transition metal complexes in a variety of oxidation states.[11−13]

Following our recent report[14] on the reaction chemistry of $[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{ZrCl_2}$, we now report related results on the corresponding Ti system developed earlier by Roesky[15] and Gambarotta.[16] Our studies have yielded a range of new Ti(III) species with some unusual reactivity, including the cyclometalation of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and the cleavage of an amidinate ligand.

As shown is Scheme 1, reduction of $[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{TiCl_2}$ with 1% Na/Hg in toluene under $\mathrm{N_2}$, followed by crystallization from hexanes, yielded blue-black crystals of the diamagnetic complex $\{[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{Ti}\}_2(\mu\text{-}\mathrm{N_2})$ in 18% yield. The X-ray structure[17] reveals five-coordinate titanium and the end-on bonding mode of the bridging $\mathrm{N_2}$.[18] The benzamidinates are bonded in a typical manner, with the metal atom essentially in the NCN plane. The extremely short Ti−($\mu$-N$_2$) bond distances (1.771(5) and 1.759(5) Å) and the long N−N bond length (1.275(6) Å) are similar to values reported[19,20] for the diamagnetic species $\{[\mathrm{(Me_3Si)_2N}]\mathrm{TiCl(C_6H_5N)_2}\}_2(\mu\text{-}\mathrm{N_2})$ (1.759 and 1.263 Å) and $\{[\mathrm{(Me_3Si)_2N}]\mathrm{TiCl(TMEDA)}\}_2(\mu\text{-}\mathrm{N_2})$ (1.762 and 1.289 Å) and are suggestive of extensive delocalization of the $\mathrm{Ti_2}(\mu\text{-}\mathrm{N_2})$ core compared to metallocene systems. For comparison, the paramagnetic metallocene complexes $(\mathrm{Cp^*{}_2Ti})_2(\mu\text{-}\mathrm{N_2})$,[21] $[\mathrm{Cp_2Ti(PMe_3)}]_2(\mu\text{-}\mathrm{N_2})$,[22] and $[\mathrm{Cp_2Ti(p\text{-}CH_3C_6H_4)}]_2\mathrm{Ti}(\mu\text{-}\mathrm{N_2})$[23] show Ti−($\mu$-N$_2$) bonds of 2.017, 1.921, and 1.962 Å and N−N bond lengths of 1.160, 1.191, and 1.162 Å, respectively. In spite of the long N−N bond in $\{[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{Ti}\}_2(\mu\text{-}\mathrm{N_2})$, the compound is thermally robust and is unreactive toward $\mathrm{H_2}$, CO, or alkynes, even after heating to 70 °C for several days.

Carrying out the above reduction under an atmosphere of CO resulted in the formation of highly $\mathrm{O_2}$-sensitive $\{[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{Ti}\}_2(\mu\text{-O})$, which was isolated as red crystals from hexanes in 18% yield. No other products were isolated from the reaction mixture, and the fate of the carbon atom remains to be determined. Repeating the reduction in the absence of CO yielded only intractable oils. Related reactions involving low-valent tantalum are known to form oxo and dicarbide species;[24] nonetheless, in general, C−O bond cleavage remains rare.[25] Due to the scarcity of structurally characterized ($\mu$-oxo)dititanium(III) species, we carried out single-crystal X-ray analysis,[17] which confirmed the five-coordinate, bridging oxo structure. The molecule has a nearly linear Ti−O−Ti linkage of 177.2(2)° which is intermediate to values reported for $(\mathrm{Cp_2Ti})_2(\mu\text{-O})$[26] and $(\mathrm{Me_3tacn})_2\mathrm{Ti_2(NCO)_4}(\mu\text{-O})$[27] (170.9 and 180.0° respectively). The short Ti−O bond (1.821(4) Å) suggests partial double bond character and is similar to those of $(\mathrm{Cp_2Ti})_2(\mu\text{-O})$[26] and $(\mathrm{Me_3tacn})_2\mathrm{Ti_2(NCO)_4}(\mu\text{-O})$[27] (tacn = triazacyclononane), which both have bond lengths of 1.838 Å. The compound is paramagnetic, with a $\mu_{\mathrm{eff}} = 2.4\ \mu_{\mathrm{B}}$, consistent with two essentially uncoupled d$^1$-Ti centers. This value is similar to those for $(\mathrm{Me_3tacn})_2\mathrm{Ti_2\text{-}(NCO)_4}(\mu\text{-O})$ and $(\mathrm{Me_3tacn})_2\mathrm{Ti_2(NCS)_4}(\mu\text{-O})$, which display only weakly antiferromagnetic coupling ($J = 7$ cm$^{-1}$ av).[27]

A rare example of a Ti(III) alkyl, $[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{TiMe}$, was prepared in 69% yield via the Na/Hg reduction of $[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{TiMe(Cl)}$ in THF. The paramagnetic product was isolated as red crystals from hexamethyldisiloxane and is stable for weeks at room temperature in a fluorescent-lit drybox. Attempts to carry out the reduction in benzene resulted in the

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(17) Crystal data for $\{[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{Ti}\}_2(\mu\text{-}\mathrm{N_2})$: *Pna*2$_1$, $a = 25.2377(14)$ Å, $b = 14.1803(8)$ Å, $c = 19.4904(11)$ Å, $V = 6975(1)$ Å, $Z = 4$, $d_{\mathrm{calc}} = 1.122$ cm$^{-1}$, $\mu = 4.04$ cm$^{-1}$, $T = -110$ °C, no. of observations = 4166, no. of parameters = 647, $R = 4.48$, $R_{\mathrm{w}} = 4.86$. For $\{[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{Ti}\}_2(\mu\text{-O})$: $P2_1/n$, $a = 15.753(1)$ Å, $b = 27.0170(3)$ Å, $c = 18.9861(3)$ Å, $\beta = 90.388(1)°$, $V = 8080(1)$ Å, $Z = 4$, $d_{\mathrm{calc}} = 1.100$ cm$^{-1}$, $\mu = 3.56$ cm$^{-1}$, $T = -100$ °C, no. of observations = 7344, no. of parameters = 974, $R = 6.83$, $R_{\mathrm{w}} = 8.06\%$. For $[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{TiMe}$: $P2_1/n$, $a = 10.4828(2)$ Å, $b = 32.0722(4)$ Å, $c = 11.5537(2)$ Å, $\beta = 116.0329(1)°$, $V = 3490(1)$ Å, $Z = 4$, $d_{\mathrm{calc}} = 1.123$ cm$^{-1}$, $\mu = 4.03$ cm$^{-1}$, $T = -124$ °C, no. of observations = 3222, no. of parameters = 521, $R = 3.99$, $R_{\mathrm{w}} = 4.37$. For $[\mathrm{PhC(NSiMe_3)_2}]\mathrm{Ti}[\eta^2\text{-}\mathrm{Me_3SiNC(H)Ph}][\eta^3\text{-}\mathrm{CH_2N(Me)CH_2CH_2N(Me)_2}]$: $P2_1$, $a = 10.1066(4)$ Å, $b = 16.5269(7)$ Å, $c = 11.4930(3)$ Å, $\beta = 115.628(1)°$, $V = 1730(1)$ Å, $Z = 4$, $d_{\mathrm{calc}} = 1.159$ cm$^{-1}$, $\mu = 3.76$ cm$^{-1}$, $T = -133$ °C, no. of observations = 2074, no. of parameters = 351, $R = 4.06$, $R_{\mathrm{w}} = 4.21$. Details of the structure determination are provided as supporting information.

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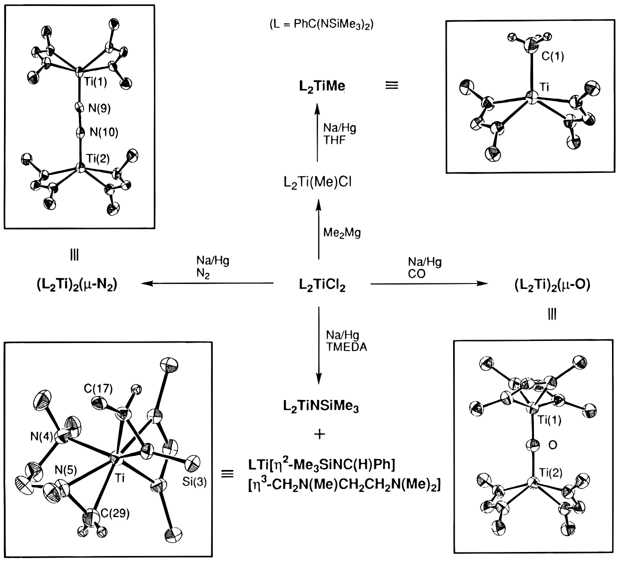
**Scheme 1**[a]



[a] Phenyl groups (except for the ipso carbon on the $\eta^2$-imine ligand) and methyl groups on Si are omitted from the ORTEP diagrams for clarity.

isolation of low yields of $[PhC(NSiMe_3)_2]_2TiMe_2$, possibly due to disproportionation. X-ray structure analysis[17] revealed a monomeric, five-coordinate titanium, as shown in Scheme 1. The Ti−$CH_3$ bond length (2.120(5) Å) is considerably shorter than related parameters in $(\eta^7\text{-}C_7H_7)(DMPE)TiEt$[28] and $Cp^*_2TiCH_2C(CH_3)_3$[29] (2.211 and 2.231 Å, respectively), presumably due to a lower coordination number in the former. The methyl hydrogens were located and refined isotropically, revealing a close contact between Ti and H(3) at a distance of 2.51(5) Å. In addition, the acute Ti−C(1)−H(3) angle (104(3)°), compared to the other Ti−C−H angles (113(3) and 112(3)°), lends additional support to the existence of an agostic interaction with the unsaturated metal center.[30]

Unprecedented reactivity leading to the formation of two products was discovered when $[PhC(NSiMe_3)_2]_2TiCl_2$ was reduced by 1% Na/Hg in the presence of TMEDA in toluene. Following extraction into hexanes and cooling to −40 °C, yellow crystals of $[PhC(NSiMe_3)_2]_2TiNSiMe_3$ were isolated in 24% yield. The identity of the imido species follows from a combination of analytical data (MS, combustion analysis) and NMR spectroscopy.[31] Further concentration of the mother liquor and cooling yielded red-black crystals of a second product, $[PhC(NSiMe_3)_2]Ti[\eta^2\text{-}Me_3SiNC(H)Ph][\eta^3\text{-}CH_2N(Me)CH_2CH_2N(Me)_2]$, in 42% yield. As illustrated in Scheme 1, the X-ray crystal structure shows a seven-coordinate Ti bonded to an amidinate ligand, an $\eta^2$-imine, and a tridentate metalated TMEDA ligand. The long C−N (imine) bond (1.446(8) Å) implies[32] substantial metallaaziridine character and formulation of the product as Ti(IV) as opposed to Ti(II). The Ti−C(29) bond (2.130(8) Å) of the $\eta^3$-TMEDA ligand is typical for Ti(IV) alkyls; this interaction is no doubt responsible for the shortness of the Ti−N(5) bond (2.220(5) Å), which is considerably shorter than the 2.351(5) Å found between Ti and N(4).

The room temperature $^1$H-NMR spectrum is complex, showing a multitude of broad resonances, apparently due to hindered rotation and/or the presence of diastereomers. On warming to 90 °C, however, the spectrum sharpens to give a pattern consistent with the solid-state structure, with three singlets for the inequivalent−$SiMe_3$ groups and a singlet for the imine hydrogen at 5.49 ppm.[33] The complexity of the room temperature spectrum is independent of concentration or the addition of TMEDA, consistent with an intramolecular rearrangement.[34]

C−N oxidative cleavage of an amidinate is precedented[14] by our recent discovery of a similar reaction in the reduction of $[PhC(NSiMe_3)_2]_2ZrCl_2$; however, the Ti case differs in that it apparently involves bimolecular reactivity (perhaps via a bridging amidinate), in which a $N(SiMe_3)$ moiety is transferred[35] from one Ti center to another. We speculate that the coordinatively unsaturated $\eta^2$-iminoacyl complex thus formed reacts with TMEDA, resulting in cyclometalation and reduction of the iminoacyl to the imine final product.[36] Although we are unaware of other cases involving TMEDA, this unusual cyclometalation bears an analogy to the Ru-mediated metalation of DMPE first reported in 1965 by Chatt.[37−39] Further synthetic and mechanistic studies are currently in progress.

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**Supporting Information Available:** Full experimental details and characterization data for all new compounds; details of structure determinations, including tables of crystal and data collection parameters, temperature factor expressions, ORTEP representations, and positional parameters (48 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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