Facile Dinitrogen Reduction via Organometallic Tm(II) Chemistry

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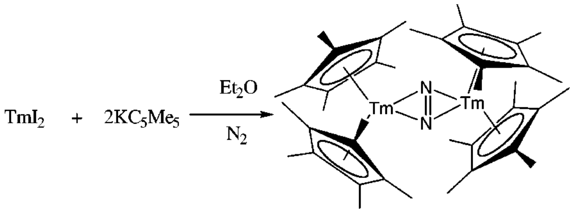
The reduction of dinitrogen has been studied for many decades with a variety of metal ligand systems in efforts to understand the facile conversion to ammonia accomplished by natural systems.[1−3] The recent isolation of the first molecular complex of thulium(II), namely $TmI_2(DME)_3$,[4] provides an opportunity to approach dinitrogen reduction chemistry with a new metal oxidation state system, a situation that is unusual since most of the oxidation states thermodynamically accessible in molecular complexes have already been discovered. Although preliminary studies[5] suggested that Tm(II) might be too reactive to be as readily utilized as samarium(II), e.g. no organometallic Tm(II) derivatives have been isolable so far, it has recently been shown that TmI_2 can function in organic synthesis as a much more powerful replacement for SmI_2/HMPA[6] (reduction potentials vs NHE: Tm(II) −2.3 V; Sm(II) −1.5 V).[7]

We now report that Tm(II) can be used in situ to accomplish dinitrogen reduction chemistry via organometallic intermediates. This provides a new option in dinitrogen reduction chemistry and demonstrates that organometallic Tm(II) chemistry is accessible. It is also noteworthy that with this new oxidation state, formation of organometallic dinitrogen complexes is facile, even in the *absence* of the common ancillary ligand, C_5Me_5.

TmI_2, prepared directly from Tm and I_2,[8] reacts with KC_5Me_5 in Et_2O under nitrogen to form a white precipitate and a reddish orange solution from which $[(C_5Me_5)_2Tm]_2N_2$, **1**, can be crystallized in 55% yield.[9] The complex was characterized by infrared spectroscopy and X-ray crystallography,[10] eq 1.

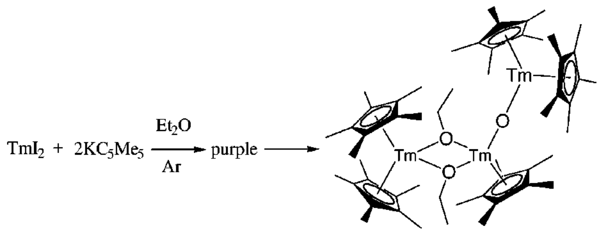


(1)

1

Complex **1** is not isomorphous with the analogous Sm(II) dinitrogen reduction product $[(C_5Me_5)_2Sm]_2N_2$, **2**,[11] but it has a similar structure with a coplanar Tm_2N_2 subunit. This unusual mode of dinitrogen coordination, first observed with solvent-free $(C_5Me_5)_2Sm$,[8] has not subsequently been found in other metallocene systems to our knowledge, although it has been observed in nitrogen−donor ligand systems.[12−19] Unfortunately, the structural data were poor and a detailed analysis of the bonding in **1** was not possible.

The control reaction of TmI_2 with KC_5Me_5 in Et_2O under argon proceeds differently. It forms a purple solution[20] that changes color to orange when dinitrogen is added. In the absence of nitrogen, the purple solution slowly changes to yellow-orange over a period of hours. Isolated from this solution were yellow crystals of a complex which indicated that diethyl ether cleavage had occurred: $[(C_5Me_5)_2Tm]_2(\mu\text{-OEt})_2[(C_5Me_5)Tm](\mu\text{-O})[Tm(C_5Me_5)_2]$, **3**, eq 2.[21]



(2)

3

Although the crystallographic data obtained on **1** and **3** did not provide structural details, they did show the strong reducing power of Tm(II) in the presence of the $C_5Me_5^-$ ligand. One way to modify the reduction potential of this system and to possibly obtain better structural data was to use trimethylsilyl-substituted cyclopentadienyl ligands. Lappert has shown that $C_5H_3(SiMe_3)_2$ can be effective for this purpose.[22]

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(8) This reaction was conducted according to the experimental methods used to produce DyI_2, see: Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11749−11750.

(9) $\mathbf{[(C_5Me_5)_2Tm]_2N_2}$, **1**. A suspension of solvent-free KC_5Me_5 (150 mg, 0.86 mmol) in 10 mL of Et_2O was added to a suspension of solvent-free TmI_2 (180 mg, 0.43 mmol) in 10 mL of Et_2O. Within 5 min, an orange color developed and after 30 min the reaction was centrifuged to yield a red-orange solution. Cooling to −30 °C led to the formation of crystals suitable for crystallography (90 mg, 47%). IR (cm^{-1}): 3694w, 2922s, 2856s, 2725w, 1552w, 1455m, 1262m, 1092m, 1019m, 799m, 690m. **1** crystallizes in the space group $P\bar{1}$ with $a = 10.729(2)$ Å, $b = 11.031(3)$ Å, $c = 16.677(4)$ Å, $\alpha = 78.063(4)°$, $\beta = 78.276(4)°$, $\gamma = 83.708(4)°$, $V = 1886.0(7)$ Å, and $\rho_{calcd} = 1.597$ Mg/m^3 for $Z = 2$ at 163 K. It was necessary to refine all light atoms with isotropic temperature factors. After the final least-squares cycle, $wR2 = 0.3662$ and GOF = 1.059 for 190 variables refined against 8802 data. As a comparison for refinement on F, $R1 = 0.1235$ for those 6395 data with $I > 2.0\sigma(I)$.

(10) Due to the large paramagnetism of Tm(III) ($\mu_{eff} = 7.4\ \mu_B$), NMR spectroscopy was not useful.

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(20) The ^1H NMR spectrum of this complex, which is under investigation, gives a broad singlet at δ −1.90 in $(CD_3CD_2)_2O$.

(21) $\mathbf{[(C_5Me_5)_2Tm](\boldsymbol{\mu}\text{-OEt})_2[(C_5Me_5)Tm](\boldsymbol{\mu}\text{-O})[Tm(C_5Me_5)_2]}$, **3**. A suspension of solvent-free KC_5Me_5 (150 mg, 0.86 mmol) in 10 mL of Et_2O was added to a suspension of solvent-free TmI_2 (180 mg, 0.43 mmol) in 10 mL of Et_2O under an argon atmosphere. The mixture became purple after 2 h and then slowly changed to yellow-orange. Addition of hexanes and cooling to −30 °C led to the formation of yellow crystals of **3** suitable for crystallography. The structural data provided only atomic connectivity due to disorder in the ethoxy ligands and detailed metrical parameters will not be presented.

(22) Cassani, M. C.; Duncalf, D. J.; Lappert, M. F. *J. Am. Chem. Soc.* **1998**, *120*, 12958−12959 and the references therein.

10.1021/ja011282l CCC: $20.00

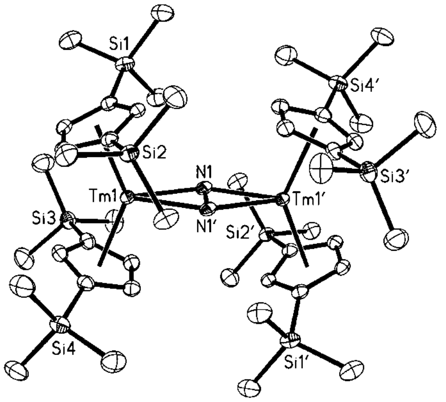

Figure 1. Structure of **4** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)−N(1′), 1.259(4); Tm(1)−N(1), 2.273(2); Tm(1)−N(1′), 2.272(2); Tm(1)−Ring Centroid, 2.328; Tm(1)−Ring Centroid, 2.323; Ring Centroid−Tm−Ring Centroid, 138.8; Tm(1)−N(1)−Tm(1′), 147.84(10); N(1)−Tm(1)−N(1′), 32.16(10).

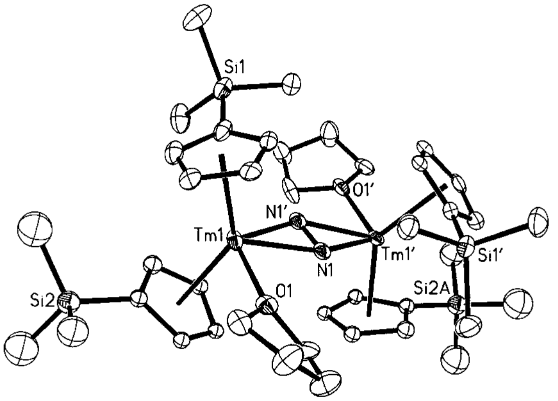

Figure 2. Structure of **5** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): N(1)−N(1′), 1.236(8); Tm(1)−N(1), 2.302(4); Tm(1)−N(1′), 2.274(4); Tm(1)−Ring Centroid, 2.355; Tm(1)−Ring Centroid, 2.371; Ring Centroid−Tm(1)−Ring Centroid, 132.2; Tm(1)−N(1)−Tm(1′), 148.22(19); N(1)−Tm(1)−N(1′), 31.34(18).

The reaction of $KC_5H_3(SiMe_3)_2$ with TmI_2 in Et_2O under nitrogen[23] forms a dark yellow solution from which dark yellow crystals of $\{[C_5H_3(SiMe_3)_2]_2Tm\}_2N_2$, **4**, Figure 1, can be isolated in 85% yield.[24] Excellent crystallographic data were obtained which provided details on the structure, which is similar to those of **1** and **2.** The two bent metallocene units complex the dinitrogen such that the two Tm centers and the two nitrogen atoms are coplanar. The 1.259(4) Å NN distance in **4** is much longer than the 1.088 Å distance in **2**[8] and the 1.097 Å distance in free N_2.[25] This is consistent with the much stronger reduction potential of Tm(II) vs Sm(II).

Although there are numerous systems in which the $C_5H_3(SiMe_3)_2$ ligand can effect chemistry similar to C_5Me_5,[26] the monosubstituted trimethylsilylcyclopentadienyl ligand, $C_5H_4(SiMe_3)$, is used much less frequently. However, we find that this ligand is also useful in isolating a thulium dinitrogen complex. Moreover the reaction can be done in THF, a solvent that decomposes the samarium dinitrogen complex, $[(C_5Me_5)_2Sm]_2N_2$, **2**,[11] to form $(C_5Me_5)_2Sm(THF)_2$ and N_2. Reaction of TmI_2 with $KC_5H_4(SiMe_3)$ in Et_2O under nitrogen or argon fails to give an observable reaction. However, reaction in THF under nitrogen forms an olive green complex from which the THF adduct $\{[C_5H_4(SiMe_3)]_2Tm(THF)\}_2N_2$, **5**, can be isolated in 87% yield.[27] As shown in Figure 2, even in the presence of coordinated THF, the two metallocene units complex the dinitrogen side on in the same plane. The 1.236(8) Å NN distance in **5** is equivalent within experimental error to that in **4**, which shows that even this $C_5H_4(SiMe_3)$-complexed Tm(II) can be a strong reductant.

These results show that Tm(II) can be used to effect reduction chemistry in an organometallic environment even though the large reduction potential limits the stability of Tm(II) organometallic compounds. Not only reduction of dinitrogen but also cleavage of diethyl ether is observed, and this suggests extensive organometallic chemistry is possible under the proper conditions. These results also show that the planar M_2N_2 geometry in $[(C_5Me_5)_2Sm]_2N_2$ is not a rare anomaly, but may be common to the lanthanide metallocenes, even in the presence of THF. Access to such complexes with the smaller, more reducing thulium and with a variety of cyclopentadienyl ligands including $Me_3SiC_5H_4$ opens new options to study this dinitrogen chemistry. The extent of this high Tm(II) reactivity is being explored.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters for **4** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Reactions conducted under argon in ether give a purple solution with ^1H NMR (500 MHz, d^{10}-diethyl ether): ∂ 38.4 (s, 36 H), −4.4 (s, 4H), −7.5 (s, 2H) ppm.

[24] $\{[C_5H_3(SiMe_3)_2]_2Tm\}_2N_2$, **4**. Under a dinitrogen atmosphere, solvent-free TmI_2 (220 mg, 0.50 mmol) was added to a solution of $KC_5H_3(SiMe_3)_2$ (260 mg, 1.05 mmol) in 10 mL of Et_2O. After being stirred 5 h, the solution was centrifuged to remove a white precipitate (KI) leaving a dark yellow solution. Removal of the solvent under vacuum yielded a yellow-brown solid (270 mg, 85%). Redissolving in Et_2O/hexane and cooling to −30 °C gave crystals of **4** suitable for analysis. IR (cm^{-1}): 3686w, 3053w, 3030w, 2949m, 2891w, 1552w, 1436m, 1401w, 1312w, 1247s, 1077m, 923m, 8389m, 776m, 753m, 687m. Anal. Calcd for $C_{44}H_{84}N_2Si_8Tm_2$: C, 43.90; H, 7.03; N, 2.33; Si, 17.40. Found: C, 43.44; H, 7.05; N, 2.18; Si, 17.35. **4** crystallizes in the space group $P\bar{1}$ with $a = 11.2674(4)$ Å, $b = 12.4255(5)$ Å, $c = 13.4634(5)$ Å, $\alpha = 112.9470(10)°$, $\beta = 93.3990(10)°$, $\gamma = 102.8430(10)°$. $V = 1669.82(11)$ Å^3, and $\rho_{calcd} = 1.344$ Mg/m^3 for $Z = 1$ at 168(2) K. Two molecules of diethyl ether were present per dimeric formula unit. Hydrogen atoms were located from a difference Fourier map and refined (x, y, z, and U_{iso}). At convergence, $wR2 = 0.0527$ and GOF = 1.064 for 506 variables refined against 7905 data. As a comparison for refinement on F, $R1 = 0.0221$ for those 7218 data with $I > 2.0\sigma(I)$.

[25] Tables of Interatomic Distances and Configurations in Molecules and Ions. *Chemical Society Special Publications*; Sutton, L. E., Ed.; The Chemical Society: London, 1958; Vol. 11.

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[27] $\{[C_5H_4(SiMe_3)]_2Tm(THF)\}_2N_2$, **5**. A solution of $KC_5H_4(SiMe_3)$ (230 mg, 1.3 mmol) in 5 mL of THF was added to an emerald green solution of TmI_2 (275 mg, 0.65 mmol) in 10 mL of THF. The color immediately changed to olive green. Concentration to half the volume and addition of 5 mL of ether/hexanes, followed by cooling to −30 °C led to olive green crystals of **5** (300 mg, 87%) suitable for crystallography. IR (cm^{-1}): 3686w, 3057w, 2953vs, 2926vs, 2856vs, 1567w, 1459s, 1378w, 1247m, 1181w, 1077w, 1038m, 1015m, 907w, 834s, 799m, 752w, 687w. Anal. Calcd for $C_{40}H_{68}N_2O_2Si_4Tm_2$: C, 45.36; H, 6.47; N, 2.64. Found: C, 45.10; H, 6.44; N, 2.39. **5** crystallizes in the orthorhombic space group $Fdd2$ with $a = 18.7713(8)$ Å, $b = 23.0503(10)$ Å, $c = 23.3755(10)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$. $V = 10114.2(8)$ Å^3, and $\rho_{calcd} = 1.391$ Mg/m^3 for $Z = 8$ at 168 K. At convergence, $wR2 = 0.0754$ and GOF = 1.082 for 217 variables refined against 6139 data (as a comparison for refinement on F, $R1 = 0.0290$ for those 5483 data with $I > 2.0\sigma(I)$).