

10-25-2001

# The Tetramethylpiperidiny-1-Oxide Anion (TMPO<sup>-</sup>) as a Ligand in Lanthanide Chemistry: Synthesis of the Per(TMPO<sup>-</sup>) Complex $[(\text{ONC}_5\text{H}_6\text{Me}_4)_2\text{Sm}(\mu\text{-ONC}_5\text{H}_6\text{Me}_4)]_2$

William J. Evans

*University of California, Irvine*

Jeremy M. Perotti

*University of California, Irvine, [perotti@nova.edu](mailto:perotti@nova.edu)*

Robert J. Doedens

*University of California, Irvine*

Joseph W. Ziller

*University of California, Irvine*Follow this and additional works at: [https://nsuworks.nova.edu/cnso\\_chemphys\\_facarticles](https://nsuworks.nova.edu/cnso_chemphys_facarticles) Part of the [Chemistry Commons](#)

## NSUWorks Citation

Evans, W. J., Perotti, J. M., Doedens, R. J., & Ziller, J. W. (2001). The Tetramethylpiperidiny-1-Oxide Anion (TMPO<sup>-</sup>) as a Ligand in Lanthanide Chemistry: Synthesis of the Per(TMPO<sup>-</sup>) Complex  $[(\text{ONC}_5\text{H}_6\text{Me}_4)_2\text{Sm}(\mu\text{-ONC}_5\text{H}_6\text{Me}_4)]_2$ . *Chemical Communications*, 2001, (22), 2326 - 2327. <https://doi.org/10.1039/B106869P>. Retrieved from [https://nsuworks.nova.edu/cnso\\_chemphys\\_facarticles/136](https://nsuworks.nova.edu/cnso_chemphys_facarticles/136)

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# The tetramethylpiperidiny-1-oxide anion (TMPO<sup>-</sup>) as a ligand in lanthanide chemistry: synthesis of the per(TMPO<sup>-</sup>) complex [( $\eta^1$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>Sm( $\mu$ - $\eta^1$ : $\eta^2$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>]

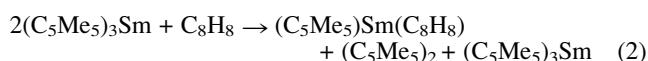
William J. Evans,\* Jeremy M. Perotti, Robert J. Doedens and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA.  
E-mail: wevans@uci.edu

Received (in Purdue, IN USA) 28th July 2001, Accepted 14th September 2001  
First published as an Advance Article on the web 25th October 2001

(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm reacts with the free radical 2,2,6,6-tetramethylpiperidiny-1-oxyl (TMPO) to form (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm and the per nitroxide [( $\eta^1$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>Sm( $\mu$ - $\eta^1$ : $\eta^2$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>]

Recent studies of the chemistry of (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>M complexes<sup>1</sup> have shown that these sterically crowded molecules can function as reducing agents, even though the metal is not redox active. This sterically induced reduction<sup>2</sup> is likely to occur *via* a half reaction like that shown in equation (1). For example, (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm reduces C<sub>8</sub>H<sub>8</sub> according to equation (2).<sup>3</sup>



To probe the mechanism of the Sm(III) reduction reaction and to explore the possibility that radical intermediates are involved, the reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm with the commonly-used free radical trapping agent 2,2,6,6-tetramethylpiperidiny-1-oxyl (TMPO)<sup>4–10</sup> was studied. We report here the unexpected result that TMPO can replace all of the C<sub>5</sub>Me<sub>5</sub> groups in (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm to form an unusual per(TMPO<sup>-</sup>) metal complex.

Reaction of ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub> with (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm in toluene gave crystals of a yellow complex, **1**.<sup>†</sup> Examination of the mother-liquor by <sup>1</sup>H NMR spectroscopy revealed the formation of the reduction byproduct expected from equations (1) and (2), namely, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>, but no signals were observed which could be attributed to products such as (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>) or (C<sub>5</sub>Me<sub>5</sub>)ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>. Instead, X-ray crystallography<sup>†</sup> revealed that ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub> had been reduced with formation of a bimetallic homoleptic samarium complex, [( $\eta^1$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>Sm( $\mu$ - $\eta^1$ : $\eta^2$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>], **1**, Fig. 1, in which TMPO<sup>-</sup> anions were the sole ligands, equation (3). Although several metal complexes of TMPO and TMPO<sup>-</sup> have been reported in

the literature,<sup>5–11</sup> to our knowledge this is the first example

$$2(C_5Me_5)_3Sm + 6 ONC_5H_6Me_4 \rightarrow Sm_2(ONC_5H_6Me_4)_6 + 3(C_5Me_5)_2 \quad (3)$$

of a per(TMPO<sup>-</sup>) metal complex and the first example in which TMPO is a ligand for the large electropositive lanthanide elements. The only homoleptic TMPO system we could find in the literature is the boron system, B(ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>3</sub>.<sup>9</sup>

Complex **1**, which has a center of inversion, has four terminal TMPO<sup>-</sup> ligands bound only through oxygen. Two bridging TMPO<sup>-</sup> units connect the two samarium centers *via* bridging oxygen atoms and each also coordinates to one samarium with its nitrogen atom. This gives each samarium a formal coordination number of 5. Both of these coordination modes are preceded in ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub> metal chemistry.<sup>5–10</sup> The overall structure of **1** is reminiscent of bimetallic alkoxide-bridged lanthanide and yttrium structures such as [(Ph<sub>3</sub>CO)<sub>2</sub>Ln( $\mu$ -OCPh<sub>3</sub>)<sub>2</sub>], and [(Ph<sub>3</sub>SiO)<sub>2</sub>Ln( $\mu$ -OSiPh<sub>3</sub>)<sub>2</sub>].<sup>11</sup> This comparison indicates that the TMPO<sup>-</sup> anion is comparable in steric bulk to large alkoxide ligands. The 2.110(5) and 2.124(5) Å terminal Sm–O (ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>) bond lengths are shorter than the 2.295(4) and 2.354(4) Å bridging Sm–O distances as expected. The 2.537(6) Å Sm–N bond length is significantly longer than the Sm–O bonds in **1** as expected for a Sm ← NR<sub>3</sub> donor bond. The Sm–N bond is shorter than typical bonds of this type in samarium metallocenes,<sup>12</sup> which is consistent with the fact that the formal coordination number of samarium in Sm<sub>2</sub>(ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>6</sub> is much less than in the metallocenes. The difference in length between the Sm–N bond and the bridging Sm–O distances is similar to that observed in several high valent transition metal complexes in which TMPO<sup>-</sup> is bound side-on.<sup>7,8,10</sup> The three N–O bond lengths in **1** (1.434(7), 1.433(8), and 1.427(8) Å) are similar and are nearly 0.15 Å longer than the corresponding 1.283(9) Å bond length in the structure of the isolated free radical,<sup>4</sup> which is consistent with the formation of TMPO<sup>-</sup> anions.<sup>7,8</sup>

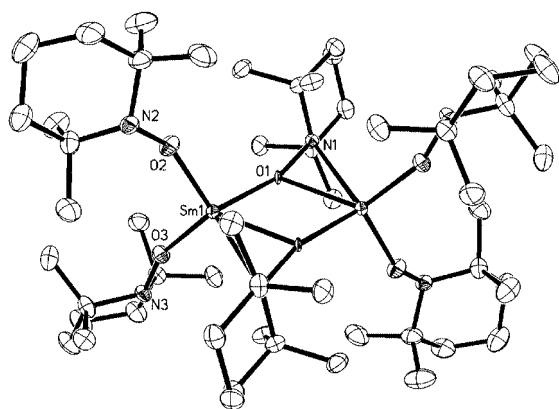
The isolation of **1** shows that ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub> readily replaces C<sub>5</sub>Me<sub>5</sub> in organolanthanide complexes and the reduced nitroxyl can function as the sole ligand in lanthanide compounds.

We thank the National Science Foundation for funding.

## Notes and references

<sup>†</sup> *Synthesis of 1*: under a N<sub>2</sub> atmosphere, an H-shaped reaction vessel was charged in one side-arm with (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm (42 mg, 0.075 mmol), dissolved in 12 mL of toluene and with neat ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub> (71 mg, 0.45 mmol) in the other. The H-tube was evacuated to the vapor pressure of the solvent and the ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub> containing side-arm was placed in an 80 °C bath. (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>Sm reacted with the ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub> vapor over several days to form yellow crystals (32 mg, 68% yield) and (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> (21 mg, 99%). Anal. Calcd. for C<sub>27</sub>H<sub>54</sub>N<sub>3</sub>O<sub>3</sub>Sm: Sm, 24.29. Found: Sm, 25.10%. IR (thin film from toluene, cm<sup>-1</sup>): 2964m, 2930w, 2876w, 1544s, 1455m, 1413s, 1297w, 1262s, 1089s br, 1019s br, 803s, 741w, 699s.

*Crystallographic data for 1*: C<sub>27</sub>H<sub>54</sub>N<sub>3</sub>O<sub>3</sub>Sm, *M* = 619.08, triclinic, *a* = 10.3838(11), *b* = 11.9579(13), *c* = 12.8023(14) Å,  $\alpha$  = 85.934(2),  $\beta$  = 83.450(2),  $\gamma$  = 66.8500(10)°, *V* = 1451.5(3) Å<sup>3</sup>, *T* = 163(2) K, space group *P*1, *Z* = 2,  $\mu$ (Mo-K $\alpha$ ) = 2.053 mm<sup>-1</sup>, 15 802 reflections measured on a



**Fig. 1** Thermal ellipsoid plot for [( $\eta^1$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>Sm( $\mu$ - $\eta^1$ : $\eta^2$ -ONC<sub>5</sub>H<sub>6</sub>Me<sub>4</sub>)<sub>2</sub>], **1**, with ellipsoids drawn at the 50% probability level (all hydrogen atoms have been omitted for clarity).

Siemens CCD diffractometer, 6872 unique ( $R_{\text{int}} = 0.0366$ ) which were used in all calculations. The final  $R1$  was 0.0591 ( $I > 2.0\sigma(I)$ ) and  $wR2$  (all data) was 0.1655. The SMART program package was used to determine the unit-cell parameters and for data collection (30 s per frame counting time for a sphere of diffraction data). The raw frame data were processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. CCDC reference numbers 170799 and 170800. See <http://www.rsc.org/suppdata/cc/b1/b106869p/> for crystallographic data in CIF or other electronic format.

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