

as the degree of oligomerization will require an x-ray crystallographic determination. It is clear, however, that these lanthanide-butadiene complexes represent a new class of organolanthanide compounds.

These results suggest to us that a variety of organic species previously thought to be of little use as ligands for lanthanide metals will interact with these elements to form isolable complexes. Moreover, we expect the ligand chemistry to be observed will be distinct from that found for other organometallic systems. We are actively pursuing these ideas.

**Acknowledgment.** Support of this research by the Louis Block Fund for Basic Research and Advanced Study, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the Division of Basic Energy Sciences of the Department of Energy is gratefully acknowledged.

## References and Notes

- Presented in part at the Second Joint Conference of the Canadian Institute of Chemistry and the American Chemical Society, Montreal, June 1, 1977.
- Only a few examples fall outside the following four classes: halides, oxygen donor ligands, nitrogen donor ligands, anionic organic ligands.<sup>3</sup>
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- P. L. Timms, *Angew. Chem., Int. Ed. Engl.*, **14**, 273 (1975); E. A. Koerner Von Gustorf, O. Jaenicke, O. Wolfbeis, and C. R. Eady, *ibid.*, **14**, 278 (1975); P. S. Skell and M. J. McGlinchey, *ibid.*, **14**, 195 (1975); K. J. Klabunde, *ibid.*, **14**, 287 (1975).
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- Lanthanide metals also have been used in nonpreparative metal vaporization experiments. Low temperature matrices of the lanthanide metals with CO and argon<sup>10</sup> and with lanthanide trihalides<sup>11</sup> have been described. The formation of lanthanide propene matrices has been cited in a review<sup>12</sup> and a referee has pointed out that the formation of a dysprosium butadiene matrix was mentioned at a 1971 I.U.P.A.C. conference.<sup>13</sup>
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- Unpublished results, cited by P. S. Skell and M. J. McGlinchey in ref 5.
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- P. L. Timms, *J. Chem. Educ.*, **49**, 782 (1972). Typically 2–3 g of lanthanide metal were vaporized from a GTE Sylvania tungsten basket (BC-1004) coated with aluminum cement into a cylindrical reaction tube 70 mm in diameter and 300 mm long.
- Incomplete carbon and hydrogen combustion is commonly observed in previously reported classes of organolanthanides: (a) F. A. Hart, A. G. Massey, and M. S. Saran, *J. Organomet. Chem.*, **21**, 147 (1970); (b) M. Tsutsui and N. Ely, *J. Am. Chem. Soc.*, **97**, 1280, 3551 (1975); (c) K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwieser, Jr., *ibid.*, **95**, 8650 (1973).
- Analytical data were obtained from A. Bernhardt Microanalytical Laboratory, D-5250 Engelskirchen, West Germany, and Pascher Microanalytical Laboratory, D-Buschstrasse 54, 5300 Bonn, West Germany.
- Approximately 10% conversion at room temperature; cf. 16% conversion for transition metal-butadiene complexes.<sup>19</sup> Hydrolytic decomposition product mixtures vary depending on the decomposition temperature, e.g., at 0 °C a higher proportion of 1-butene is observed.
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- Decomposition of other lanthanide-diene complexes is initially observed at the following temperatures: Nd(C<sub>4</sub>H<sub>6</sub>)<sub>3</sub>, 175 °C; Nd[(CH<sub>3</sub>)<sub>2</sub>C<sub>4</sub>H<sub>4</sub>]<sub>2</sub>, 190 °C; Er(C<sub>4</sub>H<sub>6</sub>)<sub>3</sub>, 100 °C; Sm(C<sub>4</sub>H<sub>6</sub>)<sub>3</sub>, 130 °C; La[(CH<sub>3</sub>)<sub>2</sub>C<sub>4</sub>H<sub>4</sub>]<sub>2</sub>, 80 °C.
- Hydrogenation of Er[(CH<sub>3</sub>)<sub>2</sub>C<sub>4</sub>H<sub>4</sub>]<sub>2</sub> in THF solution with 10% palladium on charcoal for 16 h at 3.5 atm H<sub>2</sub> decomposes only 20% of the compound producing ~60% C<sub>6</sub> species and 30% higher molecular weight products. Hydrogenation of 2,3-dimethyl-1,3-butadiene in THF solution under the same conditions produces complete conversion to 2,3-dimethylbutane within 3 h.
- Er[(CH<sub>3</sub>)<sub>2</sub>C<sub>4</sub>H<sub>4</sub>]<sub>2</sub> (II): 800 nm (ε60), 600 (200), 400 (1300), no maxima. For several of these complexes, some small broad bands are observed in the visible and near-infrared regions superimposed on the intense band. These small bands are displaced from 10–30 nm from the position of 4f–4f transitions observed for the corresponding Ln(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>, LnCl<sub>3</sub>, etc., and are considerably broader. Sharp trivalent absorptions are observed upon partial decomposition/reaction of the complexes with appropriate reagents. Broad absorption spectra have previously been described for organolanthanides but only in the visible region of the spectrum.<sup>16c</sup>
- NMR spectroscopy is usually useful for the characterization of organolanthanide complexes of diamagnetic La<sup>3+</sup> and paramagnetic Nd<sup>3+</sup> and Sm<sup>3+</sup> (R. G. Hayes and J. L. Thomas, *Organomet. Chem. Rev., Sect. A.*, **7**, 1 (1971)). For the diene complexes of these metals, however, we have not observed any comparably sharp, assignable resonances over a 300-ppm range by FTNMR spectroscopy. This result is consistent with the other unusual physical properties displayed by these complexes and is not due to limited solubility.
- These complexes are insufficiently volatile for mass spectral analysis.
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- P. S. Skell, E. M. Van Dam, and M. P. Silvon, *J. Am. Chem. Soc.*, **96**, 626 (1974).
- P. S. Skell and L. R. Wolf, *J. Am. Chem. Soc.*, **94**, 7919 (1972).
- Structures in which the metal is trivalent can be envisioned if the butadiene ligands oligomerize. Such structures require very low coordination numbers for the metal centers, which is inconsistent with the thermal stabilities of I–V.

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Received July 15, 1977

## Nonaqueous Reductive Lanthanide Chemistry. 2. Conversion of *cis,cis*-1,5-Cyclooctadiene to Cyclooctatetraenyl Dianion by Reduced Praseodymium and Potassium

Sir:

We recently have described the synthesis of a new class of organolanthanide complexes obtained from 1,3-butadienes and vaporized lanthanide metal atoms as part of a general investigation of the nonaqueous reductive chemistry of the lanthanide elements.<sup>1</sup> Concurrently with the metal vaporization studies we have endeavored to develop solution syntheses of lanthanide complexes in which a reduced oxidation state of the metal is involved. Since our previous results suggested that a variety of unsaturated organic molecules would be useful in organolanthanide chemistry, we have continued with such reactants in our solution studies. We report here preliminary results of an investigation of the reductive chemistry of PrCl<sub>3</sub> which has led to a facile laboratory-scale synthesis of the cyclooctatetraenyl dianion, C<sub>8</sub>H<sub>8</sub><sup>2-</sup>, from the readily available *cis,cis*-1,5-cyclooctadiene (1,5-C<sub>8</sub>H<sub>12</sub>).

Anhydrous PrCl<sub>3</sub><sup>2,3</sup> (2.5 g, 10 mmol) is reduced by potassium (1.2 g, 30 mmol) in tetrahydrofuran (THF) at reflux in ~4.5 h to form a black slurry. Removal of THF from this slurry by filtration<sup>4</sup> gives a gray powder which reacts with 1,5-C<sub>8</sub>H<sub>12</sub><sup>5</sup> (45 mL, 366 mmol) over a period of several days at room temperature. After removal of excess 1,5-C<sub>8</sub>H<sub>12</sub>, the reaction residue is extracted with THF to give an intensely colored red-brown solution from which ~1.0 g<sup>6</sup> of a red-brown solid, I, is isolable. I is not particularly stable, decomposing slowly in an inert atmosphere at room temperature. Spectral, magnetic, and analytical data on I were not definitive owing to this decomposition; hence simple chemical decomposition was examined to minimally identify carbon fragments present. Oxidative decomposition of I in benzene-*d*<sub>6</sub> gave almost exclusively 1,3,5,7-cyclooctatetraene, C<sub>8</sub>H<sub>8</sub><sup>7</sup>! Soxhlet extraction with diethyl ether of samples of I which are partially decomposed gives yellow solids which have infrared and NMR spectra<sup>8</sup> which match those reported for K<sub>2</sub>C<sub>8</sub>H<sub>8</sub>,<sup>9</sup> but which by elemental analysis<sup>10</sup> contain praseodymium, possibly as K[Pr(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>].<sup>11,12</sup> In further confirmation of the presence of C<sub>8</sub>H<sub>8</sub><sup>2-</sup>, I is observed to slowly react with UCl<sub>4</sub> at room temperature to form uranocene, U(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>.<sup>13,14</sup> Although the mechanisms of formation of I and its subsequent decomposition

