### Communications to the Editor

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.

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### **References and Notes**

- (1) Presented in part at the Second Joint Conference of the Canadian Institute of Chemistry and the American Chemical Society, Montreal, June 1, 1977.
- (2) Only a few examples fall outside the following four classes: halides, oxygen donor ligands, nitrogen donor ligands, anionic organic ligands.<sup>3</sup> (3) T. Moeller in "Comprehensive Inorganic Chemistry", J. C. Bailar, Jr., et
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  (8) S. C. Engerer and W. J. Evans, unpublished observations.
- (9) 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
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- (17) Analytical data were obtained from A. Bernhardt Microanalytical Laboratory, D-5250 Engelskirchen, West Germany, and Pascher Microanalytical Lab-
- oratory, D-Buschstrasse 54, 5300 Bonn, West Germany.
   (18) 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. (19) P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Am. Chem. Soc.*, 95, 3337 (1973).
- (20) 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.
  (21) 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 atmH<sub>2</sub> decomposes only 20% of the compound that an advantage of 20% of the compound that the compound the transfer of 20% of the compound that the composite of 20% of the compound that the composite of 20% of the composite o
- producing  $\sim$ 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
- (22) 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(C5H5)3, LnCl3, 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.16

- (23) NMR spectroscopy is usually useful for the characterization of organo-lanthanide 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.
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- (30) 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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# 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.1 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  $\sim$ 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  $1,5-C_8H_{12}$ (45 mL, 366 mmol) over a period of several days at room temperature. After removal of excess  $1,5-C_8H_{12}$ , the reaction residue is extracted with THF to give an intensely colored red-brown solution from which  $\sim 1.0 \text{ g}^6$  of a red-brown solid, l, 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- $d_6$  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  $K[Pr(C_8H_8)_2]^{.11,12}$  In further confirmation of the presence of  $C_8H_8^{2-}$ , I is observed to slowly react with UCl<sub>4</sub> at room temperature to form uranocene,  $U(C_8H_8)_2$ .<sup>13,14</sup> Although the mechanisms of formation of I and its subsequent decomposition

remain to be determined, it is clear that  $C_8H_8^{2-}$  is generated from  $1,5-C_8H_{12}$  in this reaction.

Several control reactions were conducted to define the role of praseodymium in this remarkable conversion. The reaction of  $1,5-C_8H_{12}$  with K alone at room temperature does not lead to formation of  $K_2C_8H_8$ . Such a reaction is not necessarily a valid control, however, since it is possible that the PrCl<sub>3</sub> is incompletely reduced by potassium, forming, instead, a potassium-praseodymium-chloride matrix which contains active potassium with a large effective surface area. Reduced metal matrices of this type are postulated in the K-KI-metal halide preparations of activated metals by the Rieke method.<sup>15</sup> To examine the effects of larger potassium surface area and more severe conditions, <sup>16</sup> we reacted potassium with 1.5-C<sub>8</sub>H<sub>12</sub> at 97 °C over a 5-day period. The volatile products of this reaction are cis-bicyclo[3.3.0]oct-2-ene and a trace of 1,3-cyclooctadiene, as previously reported.<sup>17</sup> The solid residue which remains following the removal in vacuo of volatiles can be extracted with THF to give an intense purple solution.<sup>18</sup> Removal of the THF gives a gray-purple solid which by IR, NMR, and elemental analysis contains C<sub>8</sub>H<sub>8</sub><sup>2-.19</sup> Air oxidation gives 1,3,5,7-C<sub>8</sub>H<sub>8</sub>, identified by NMR and GC-mass spectroscopy. In a higher temperature, large-scale reaction,  $1.5-C_8H_{12}$  (108) g, 1 mol) at reflux reacted with K (4.5 g, 0.12 mol) in 10 h to form, following THF extraction and solvent removal, 14.2 g of gray-green solids which either could be used directly in syntheses requiring  $C_8H_8^{2-}$  or could be converted to 1,3,5,7- $C_8H_8$  in 30% yield.<sup>21</sup> Although the yield based on  $1,5-C_8H_{12}$  is not large, the reaction does provide a method of obtaining quantities of  $C_8H_8^{2-}$  and 1,3,5,7- $C_8H_8$  for laboratory synthesis directly from potassium and 1,5-C<sub>8</sub>H<sub>12</sub>, and is more efficient than the praseodymium-based synthesis.

To determine if PrCl<sub>3</sub> acts only as a partially reducible matrix which generates a large surface area for the remaining potassium in the room temperature conversion of 1.5-C<sub>8</sub>H<sub>12</sub> to  $C_8H_8^{2-}$ , a reaction analogous to the PrCl<sub>3</sub>-K reaction was investigated using MgCl<sub>2</sub> as the reducible halide. The reaction itself is similar to the praseodymium reaction and a red-brown product is also obtained. This product, however, does not react with UCl<sub>4</sub> to form  $U(C_8H_8)_2$ , does not give IR or NMR spectra consistent with  $K_2C_8H_8$ , and cannot be air oxidized to 1,3,5,7-C<sub>8</sub>H<sub>8</sub>.

Although the above result does not exclude the possibility that PrCl<sub>3</sub> acts as a dispersing agent for K, it does suggest that there are specific metal requirements for the room temperature reaction. Initial studies with other lanthanide trichlorides show that not all lanthanides are as effective as praseodymium; i.e., there appears to be a differentiation in the chemistry of the lanthanides in these reduction reactions. These above results and the possibility that lower valent lanthanide complexes of  $1,5-C_8H_{12}$  or  $C_8H_8$  are involved in the  $1,5-C_8H_{12}$  to  $C_8H_8^{2-1}$ conversion are under further investigation.

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. We also thank Bell Laboratories for a special fellowship (to A.L.W.).

#### **References and Notes**

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- Brown-colored filtrates were sometimes observed but did not appear to affect subsequent reactions. This brown product is under investigation.
- (5) Purified by passing through a column of neutral alumina, Brockmann activity

- grade I, followed by degassing. Yields vary depending on reaction times. For a 2-day reaction, 0.2 to 0.3 (6) g are usually obtained. For reaction times of 5 days, 0.8 to 1.0 g are commonly isolated
- Identified by NMR and GC-mass spectrum. The oxidative decomposition was accomplished by bubbling air through an NMR sample of I. Yields are variable depending on the age of the sample. IR (Nujol,  $cm^{-1}$ ): 680 (s), 800 (s), 880 (m), 975 (s), 1020 (s), 1260 (s). <sup>1</sup>H
- NMR (THF): δ 5.77 (s).
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- (11) K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitweiser, Jr., J. Am. Chem. Soc., 95, 8650 (1973). (12) After I is extracted with diethyl ether, a brown THF-soluble product, II, re-
- mains as well as a considerable amount of a THF-insoluble material, III, both of which contain praseodymium by elemental analysis. Found for II: C, 48.81; H, 4.40; K, 9.76; Pr, 35.20; Cl, 0.29. Cf. calcd for KPrC<sub>16</sub>H<sub>18</sub>: C, 49.33; H, 4.73; K, 10.04; Pr, 35.97. Found for III: C, 20.18; H, 1.95; K, 7.98; Pr, 57.90; Cl, 0.34.
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- (18) The colors of the THF extract are variable. Blue, green, and brown have been observed, but purple is the most common. In previous reactions, the residual solids were destroyed hydrolytically
- (19) IR (Nujol, cm<sup>-1</sup>): 660 (w, sh), 680 (s), 720 (w), 800 (m), 880 (s), 1020 (m), in (Nujo), cm<sup>-1</sup>): beb (w, sh), 580 (s), 720 (w), 600 (m), 600 (s), 720 (m), 1060 (w), 1425 (w, sh), 1530 (s), 1670 (w), 1795 (w). NMR (THF):  $\delta$  5.76. Anal. Calcd for K<sub>2</sub>C<sub>8</sub>H<sub>8</sub>: C, 52.69; H, 4.42; K, 42.88. Found: C, 52.00; H, 5.27; K, 41.83. A previous elemental analysis was similarly low in K.<sup>9</sup> K<sub>2</sub>C<sub>8</sub>H<sub>8</sub>:THF is variably described as white or yellow.<sup>20</sup>
- (20) H. P. Fritz and H. Keller, Z. Naturforsch., B, 16, 231 (1961).
- 0.2 to 0.3 mL C<sub>6</sub>H<sub>8</sub> can be obtained per gram of crude solid by dry air oxidation in tetrahydrofuran at 0 °C. *CAUTION*: This solid is pyrophoric. Undergraduate participants in the University of Chicago, Department of (22)
- Chemistry Laboratory Option Program for sophomores

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### **Resonance Raman Spectra of Copper(III) Peptide** Complexes

Sir:

Interest in the possible role of copper(III) in biochemistry has been heightened by the evidence presented by Hamilton and coworkers<sup>1,2</sup> for its involvement in galactose oxidase, and by the demonstration by Margerum and coworkers<sup>3,4</sup> that deprotonated oligopeptide complexes of copper(III) are reasonably stable in neutral aqueous solution. Such complexes display intense absorption at 365 nm ( $\epsilon \sim 7100 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>3</sup> attributable to N (amide)  $\rightarrow$  Cu<sup>III</sup> charge transfer, shifted to lower energy from the position (230-280 nm) of the corresponding copper(II) peptide bands<sup>5</sup> and are therefore good

coo<sup>(-)</sup> Ι II

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