

Synthesis and Properties of Di- π -[8]annulene cerium(IV), Cerocene

Andrew Streitwieser,* Steven A. Kinsley, Chris Henry Jenson, and John T. Rigsbee

Department of Chemistry, University of California, Berkeley, California 94720-1460

Received April 8, 2004

An efficient synthesis of di- π -([8]annulene)cerium(IV) (cerocene) is reported by the reaction of $K[Ce(C_8H_8)_2]$ with allyl bromide. Cerocenes can also be prepared by oxidation of the corresponding cerates with silver iodide in THF, but this reaction is more variable. Cerocene reacts only slowly with UCl_4 to give uranocene. $K[Ce(C_8H_8)_2]$ and cerocene undergo electron exchange on the NMR time scale. Electrochemical study of cerocene shows redox with the cerate ion, $Ce(C_8H_8)_2^-$, to be reversible with a relatively low reduction potential (-0.6 V vs NHE). The corresponding praseodymium salt, $K[Pr(C_8H_8)_2]$, does not undergo comparable reversible oxidation; its cyclic voltammetry is compared with that of $K_2[Yb(C_8H_8)_2]$. The chemistry of cerocene resembles that of di- π -([8]annulene)actinide(IV) compounds.

Introduction

Di- π -[8]annulene cerium(IV), cerocene, $Ce(C_8H_8)_2$, is an especially interesting metallocene that is formally a lanthanide(IV) analogue of uranocene, $U(C_8H_8)_2$,¹ but combines a strong oxidizing agent, Ce(IV), and a strong reducing agent, cyclooctatetraene (COT) dianion, in the same molecule. The first successful synthesis of cerocene resulted surprisingly from the use of a reducing agent, triethylaluminum, in a reaction using cerium(IV) isopropoxide with neutral cyclooctatetraene as a reactant and solvent.² Subsequent work from this group³ and others⁴ has provided further characterization of cerocene and various ring-substituted analogues. Crystal structures of $Ce(C_8H_7Me)_2$ ⁵ and $Ce[C_8H_5(SiMe_3)_2]$ ⁶ show that cerocenes have a uranocene-type sandwich structure.

Cerocene has received further recent attention from theoretical studies, which suggest that it is better described as a neutral compound of Ce(III) involving two [8]annulene rings with a total charge of -3 .⁷ X-ray absorption near-edge structure measurements (XANES) are consistent with these calculations.⁸ Further calcu-

lational studies suggest the possibility of oxidation of other lanthanide(III) COT salts, $K[Ln(C_8H_8)_2]$, to their neutral counterparts, $Ln(C_8H_8)_2$.⁹

Although we confirmed the reported preparation of cerocene, its use of COT as a solvent does not permit a practical extension to substituted derivatives. In a 1985 communication we described a better approach based on the mild oxidation of potassium di- π -[8]annulene cerate(III) with solid silver iodide in THF.³ In the present paper we describe more details of this procedure, a method that has also now been used by others.⁴ We also discuss problems with this approach and describe a new and simpler method. We have also further studied the electrochemistry of cerocene and report a new value for the Ce(IV)/Ce(III) couple based on more recent information on electrochemical standards in tetrahydrofuran.¹⁰ To study the possibility of the existence of additional neutral compounds of the type $Ln(C_8H_8)_2$, we have also explored the electrochemistry and oxidation of the praseodymium compound $K[Pr(C_8H_8)_2]$.

Results and Discussion

Oxidation of Cerates. The COT derivatives of trivalent lanthanides have long been known and are readily prepared from the reaction of COT dianions with the lanthanide halides.¹¹ The Ce(III) compounds are now conveniently accessible by reaction of $CeI_3(THF)_4$ ¹² with COT dianions. Thus, we considered that a convenient preparation of cerocene would be based on oxidation of potassium di- π -([8]annulene)cerate(III). A number of oxidizing agents were tried including O_2 , $NOBF_4$, Br_2 , $(NH_4)_2Ce(NO_3)_6$, and $K_2S_2O_8$. The first two produced cerocene in yields of about 5%; the rest gave overoxidation to COT and Ce^{3+} . A suspension of silver iodide in THF, however, gave the desired result. The

* To whom correspondence should be addressed. E-mail: astreit@socrates.berkeley.edu.

(1) Streitwieser, A.; Muller-Westerhoff, U. *J. Am. Chem. Soc.* **1968**, *90*, 7364.

(2) Greco, A.; Cesca, S.; Bertolini, G. *J. Organomet. Chem.* **1976**, *113*, 321–330. It is surprising that this method is successful; the analogous reaction was used by Wilke to make $Ti(C_8H_8)_2$, which does not have both COT rings planar. See: Breil, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 898–899.

(3) Streitwieser, A.; Kinsley, S. A.; Rigsbee, J. T.; Fragalà, I. L.; Ciliberto, E.; Rösch, N. *J. Am. Chem. Soc.* **1985**, *107*, 7786–7788.

(4) For a recent review of Ce(IV) [8]annulene complexes see: Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851–1896.

(5) Boussie, T. R.; Eisenberg, D. C.; Rigsbee, J.; Streitwieser, A.; Zalkin, A. *Organometallics* **1991**, *10*, 1922–1928.

(6) Killmann, U.; Herbst-Irmer, R.; Stalke, D.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1618–1621.

(7) (a) Dolg, M.; Fulde, P.; Küchle, W.; Neumann, C. S.; Stoll, H. *J. Chem. Phys.* **1991**, *94*, 3011–3017. (b) Dolg, M.; Fulde, P.; Stoll, H.; Preuss, H.; Pitzer, R. M. Chang, A. *Chem. Phys.* **1995**, *195*, 71–82.

(8) Edelstein, N. M.; Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Sofield, C. D. *J. Am. Chem. Soc.* **1996**, *118*, 13115–13116.

(9) Liu, W.; Dolg, M.; Fulde, P. *Inorg. Chem.* **1998**, *37*, 1067–1072.

(10) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.

(11) Hodgson, K.; Mares, F.; Starks, D.; Streitwieser, A. *J. Am. Chem. Soc.* **1973**, *95*, 8650–8658.

Table 1. Visible Spectra of (RC₈H₇)₂Ce Anion and Neutral in THF

R	K ⁺ (RC ₈ H ₇) ₂ Ce ⁻	(RC ₈ H ₇) ₂ Ce
H	692 ^a	472 (570) ^b
methyl	706	477 (570) ^b
<i>n</i> -butyl	708	478 (~585) ^b
<i>tert</i> -butyl	707	483 (567) ^b
<i>tert</i> -butoxy	724	492

^a Lit.¹³ 691 nm. ^b Shoulder; λ_{max} by Gaussian deconvolution.

use of a 10-fold excess of suspended silver iodide gave up to 78% yields of cerocene. This procedure was also used to prepare several substituted cerocenes: 1,1'-dimethyl (whose crystal structure has been determined),⁵ 1,1'-di-*n*-butyl, 1,1'-di-*tert*-butyl, and 1,1'-di-*tert*-butoxy. These compounds were characterized primarily by spectroscopic measurements (Table 1). Cerocene itself has a pronounced λ_{max} at 469 nm ($\epsilon = 8000$) with a shoulder (Figure S1, Supporting Information). This spectrum was deconvoluted using two Gaussian functions, also shown in Figure S1 (Supporting Information), to give a least-squares fit.

The method has also been applied by others; for example, the Ce³⁺ salts of 1,4-bis(trimethylsilyl)cyclooctatetraene and 1,3,6-tris(trimethylsilyl)cyclooctatetraene dianions were oxidized with AgI to the corresponding cerocenes. The latter cerocene, Ce(1,3,6-TMS₃-C₈H₅)₂, was characterized by its X-ray crystal structure.⁶

Nevertheless, we have found the AgI oxidation to be inconsistent. Yields were frequently variable, and some samples gave overoxidation. We therefore considered approaches involving one-electron oxidation by alkyl halides based on the work of Kagan et al.¹⁴ in the oxidation of Sm(II) to Sm(III). We also note that we have previously used benzyl bromide to oxidize the Yb(II) salt of a COT to the Yb(III) salt.¹⁵ Benzyl chloride did not react with K[Ce(C₈H₈)₂] over several days. Benzyl bromide did give cerocene plus some decomposition products. 1,2-Diphenylethane (bibenzyl) was identified in the reaction mixture by NMR. This is the expected byproduct of a one-electron transfer process between the cerium(III) salt and benzyl bromide to form benzyl radicals that couple in solution. The solubility of both cerocene and bibenzyl in hydrocarbon solvents makes the separation and purification of cerocene difficult. It was desirable, therefore, to find a reagent that would provide byproducts that would be more easily removed.

Ethyl iodide produced low yields of cerocene with considerable decomposition. Allyl bromide gave by far the best results, producing cerocene in 80% yields after isolation, with no apparent decomposition products. These are the highest consistent yields seen using any of the previous oxidizing agents. The byproduct formed was determined by NMR to be 1,5-hexadiene. Again, this is undoubtedly formed via the free radical process discussed earlier. This byproduct has a low boiling point of 60 °C and is easily removed along with any unreacted allyl bromide under vacuum at the end of the reaction.

(12) Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1987**, *6*, 23–27.

(13) Mares, F.; Hodgson, K. O.; Streitwieser, A., Jr. *J. Organomet. Chem.* **1971**, *28*, C24–C26.

(14) Kagan, H. B.; Namy, J. L.; Girard, P. *Tetrahedron Supp.* **1981**, *9*, 175.

(15) Eisenberg, D. C.; Kinsley, S. A.; Streitwieser, A. *J. Am. Chem. Soc.* **1989**, *111*, 5769–5772.

In an NMR tube, allyl bromide showed reaction with cerates within 2 min and no decomposition reactions even after several days. A typical and general procedure consists of dissolving completely a sample of K[Ce(C₈H₈)₂] or other substituted COT derivative in THF, then adding a 3-fold excess of allyl bromide and allowing the solution to stir for 12 h. The product is recovered by removing solvent, organic reaction byproducts, and unreacted allyl bromide under vacuum and extracting the remaining material with the appropriate hydrocarbon solvent. The method was applied to the synthesis of cerocene, 1,1'-di-*tert*-butylcerocene, and 1,1',4,4'-tetrakis(trimethylsilyl)cerocene. The last compound was not obtained analytically pure but was characterized by MS and NMR and appears to be identical to the product prepared using AgI by Kilimann et al.⁶

Some Properties and Reactions. Although Ln(C₈H₈)₂⁻ salts behave as ionic salts of COT²⁻, cerocene does not. For example, K[Ce(C₈H₈)₂] reacts rapidly with UCl₄ to give uranocene in high yield,¹¹ whereas a THF solution of cerocene with UCl₄ in an NMR tube shows a small peak for uranocene at -36 ppm only after several days. In this respect, cerocene behaves much like a thorocene, which also reacts slowly with UCl₄ to give the corresponding uranocene.¹⁶ Similarly, cerocene does not react with trimethylchlorosilane.

Electron exchange has been shown to occur on the NMR time scale (second-order rate constants on the order of 10⁷ M⁻¹ s⁻¹) between potassium bis(*tert*-butyl[8]annulene)ytterbate(II) and potassium bis(*tert*-butyl[8]annulene)ytterbate(III).¹⁵ Similar rapid electron exchange on the NMR time scale has been shown between the III and IV oxidation states of actinocenes of uranium, neptunium, and plutonium.¹⁷ The corresponding behavior has now been found for cerium. The ¹H NMR spectrum of a nearly saturated solution of the diamagnetic bis(*tert*-butyl[8]annulene)cerium(IV) in THF-*d*₈ is shown in Figure 1A. It shows a clean singlet at δ 2.2 ppm for the *tert*-butyl protons. The ring protons show up as a multiplet around δ 6 ppm but will not be relevant in this study. Other peaks are due to solvent (δ 1.73 and 3.58 ppm) and residual stopcock grease (δ 0.05 ppm). The ¹H NMR spectrum of the paramagnetic potassium bis(*tert*-butyl[8]annulene)cerate(III) at 20 °C is shown in Figure 1B. The ring protons are now too broad to be seen and the *tert*-butyl protons occur as a broad resonance at δ 4.4 ppm. The position of this peak is temperature dependent, as is usual for such paramagnetic species. An approximately 50:50 mixture of these two compounds is shown in Figure 1C. Resonances corresponding to the solvent and grease are unchanged, but the metallocene resonances are gone. Close examination shows a small broad peak in the baseline overlapping with the downfield solvent peak. If this is the exchanging peak, it should be affected by changes in temperature.

The NMR spectrum at several temperatures is shown in Figure 2. As the temperature is raised, the broad peak sharpens with the high-temperature fast exchange limit about 65 °C. At this temperature the shift of the

(16) LeVanda, C.; Streitwieser, A., Jr. *Inorg. Chem.* **1981**, *20*, 656–659.

(17) Eisenberg, D. C.; Streitwieser, A.; Kot, W. K. *Inorg. Chem.* **1990**, *29*, 10–14.

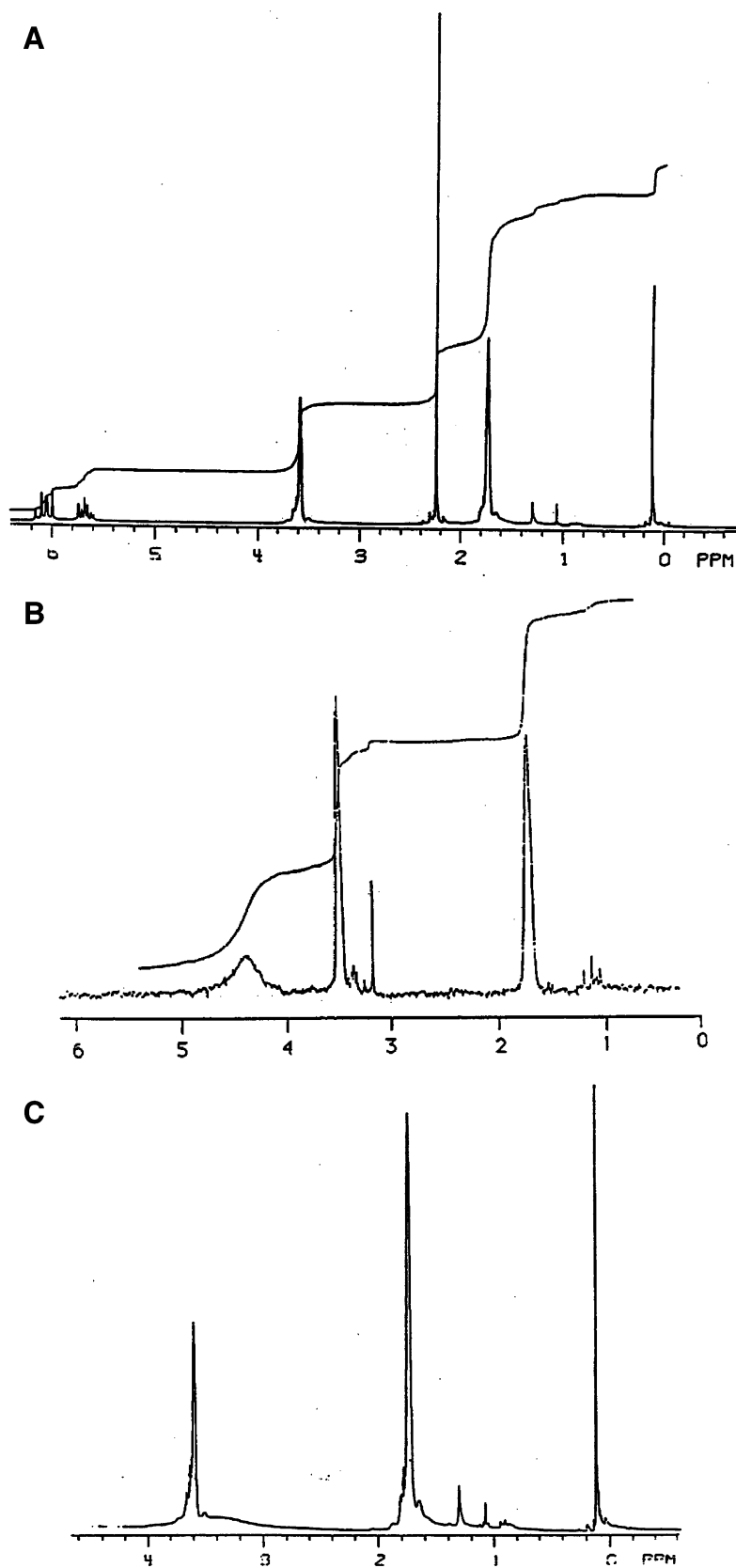


Figure 1. (A) ¹H NMR of Ce(*tert*-butylC₈H₇)₂ in THF-*d*₈ at 20 °C. (B) ¹H NMR of K[Ce(*tert*-butylC₈H₇)₂] in THF-*d*₈ at 20 °C. (C) ¹H NMR of a 50:50 mixture of Ce(*tert*-butylC₈H₇)₂ and K[Ce(*tert*-butylC₈H₇)₂] in THF-*d*₈ at 20 °C.

exchange peak is about 3 ppm, about that expected for the average of the two species. The coalescence temperature is about room temperature, and the difference in chemical shifts is too small to freeze out the exchange.

The phenomenon is clearly an electron exchange process analogous to that observed with other actinide and lanthanide metallocenes. In particular, the similarity of temperature ranges indicates that the cerocene-

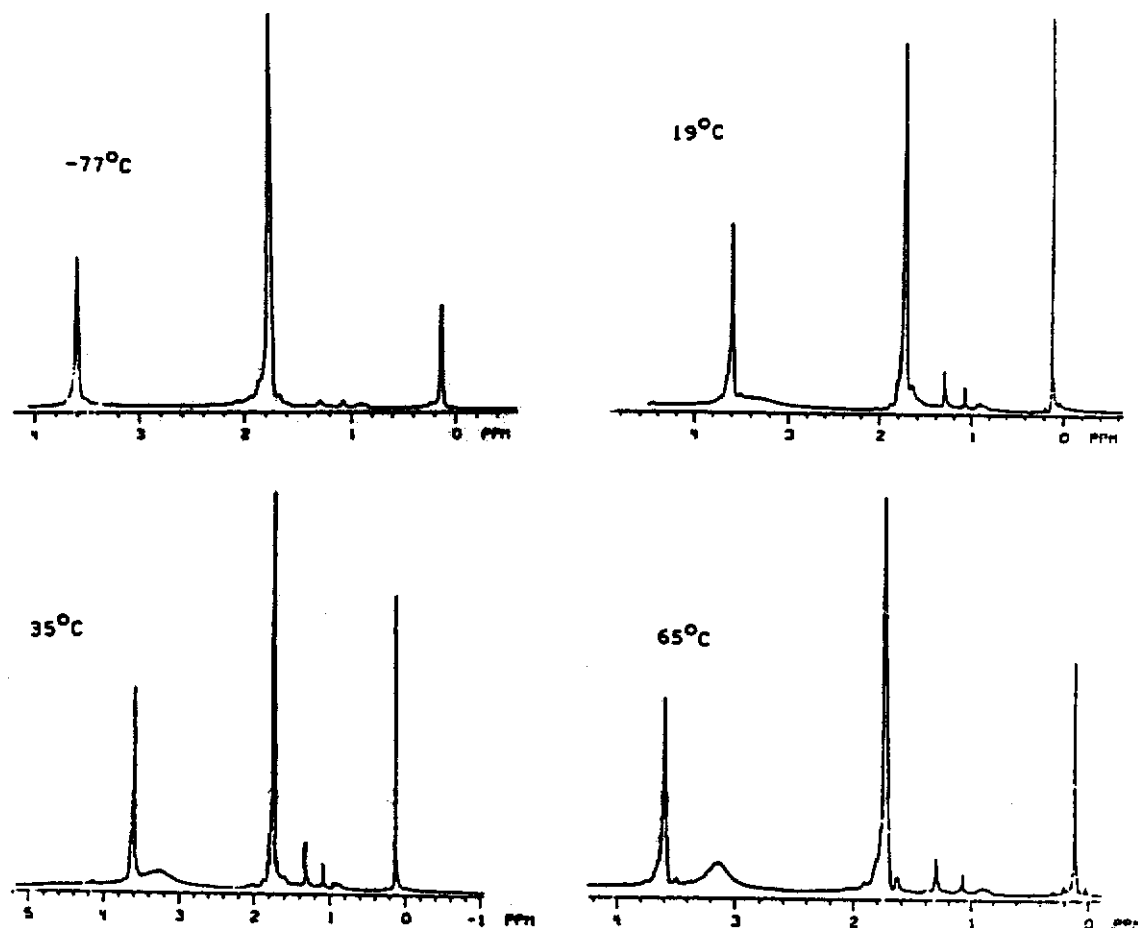


Figure 2. Effect of temperature on the ^1H NMR of a 50:50 mixture of $\text{Ce}(\text{tert-butylC}_8\text{H}_7)_2$ and $\text{K}[\text{Ce}(\text{tert-butylC}_8\text{H}_7)_2]$ in THF-d_8 .

cerate exchange, like that of the actinocenes, has rate constants of comparable orders of magnitude to the $\text{Yb(II)}-\text{Yb(III)}$ exchange cited above.

Electrochemistry of $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$, $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$, and $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$. The bis-[8]annulene)cerate anion exhibits a fully reversible oxidation–reduction wave at -1.4 V relative to either internal or external ferrocene. Using a value of the ferrocene $^{+1/0}$ couple of 0.56 V vs SCE (in THF with $[\text{Bu}_4\text{N}][\text{PF}_6]$),¹⁰ the cerocene $^{0/-1}$ couple is -0.8 V vs SCE or -0.6 V vs NHE. This value is less negative than originally reported from this group,³ but the major difference is the more accurate value for the ferrocene $^{+1/0}$ couple in the exact media.¹⁸ The less negative value of the cerocene $^{0/-1}$ couple is more consistent with the -0.4 V vs NHE value for the cerium-(IV/III) catecholate couple found by Sofen et al.¹⁹ Although not as negative, a value of -0.6 V vs NHE is still abnormally low for a Ce(IV/III) couple. Figure 3 shows the one-electron oxidation–reduction wave for cerocene $^{0/-1}$.

One of the difficulties in obtaining the value of E° for the cerocene $^{0/-1}$ couple is due to an apparent reaction of one of the cerocene species with ferrocene or ferrocenium ion. Shown in Figure S3 (Supporting Information) is the cyclic voltammogram of cerocene with an internal standard of ferrocene. Although not completely

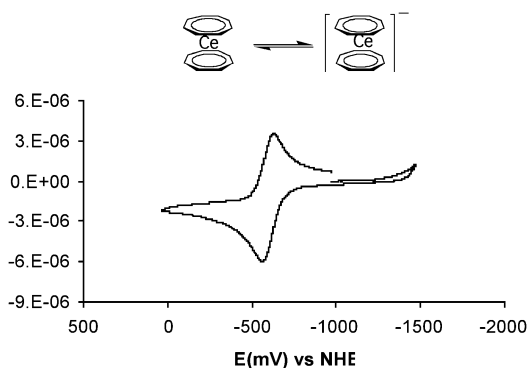


Figure 3. Cyclic voltammogram of $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$, ~ 1 mM in THF. The electrochemically interrelated sandwich complexes are shown as $\text{Ce}(\text{C}_8\text{H}_8)_2$ and $[\text{Ce}(\text{C}_8\text{H}_8)_2]^-$. The scan rate is 0.100 V/s and referenced to external ferrocene.

reversible, the peak-to-peak separation of the cerocene and ferrocene is identical, indicating a one-electron process, and the same value of E_0 is obtained from measurement of the difference between the oxidation waves or the reduction waves.

The ability to reversibly remove an electron from the bis([8]annulene)cerate anion does not prove the existence of Ce(IV) in the neutral sandwich compound. If the electron comes from the central metal, then the oxidation state of cerium would be formally Ce(IV) ($4f^0\pi^4$); if the electron comes from the π -system of the rings, then the oxidation state of cerium would be Ce(III) ($4f^1\pi^3$). But an analogous situation is that of the oxidation of

(18) At the time of the original study, a value of 0.4 V vs NHE was used for ferrocene. See ref 10.

(19) Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 1611–1616.

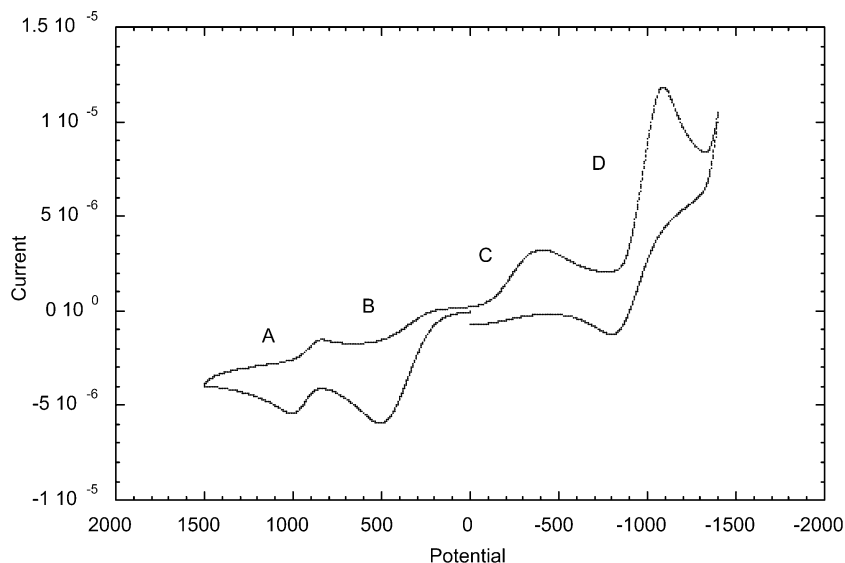


Figure 4. Cyclic voltammogram of $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$, ~ 1 mM in THF. The scan rate is 0.100 V/s.

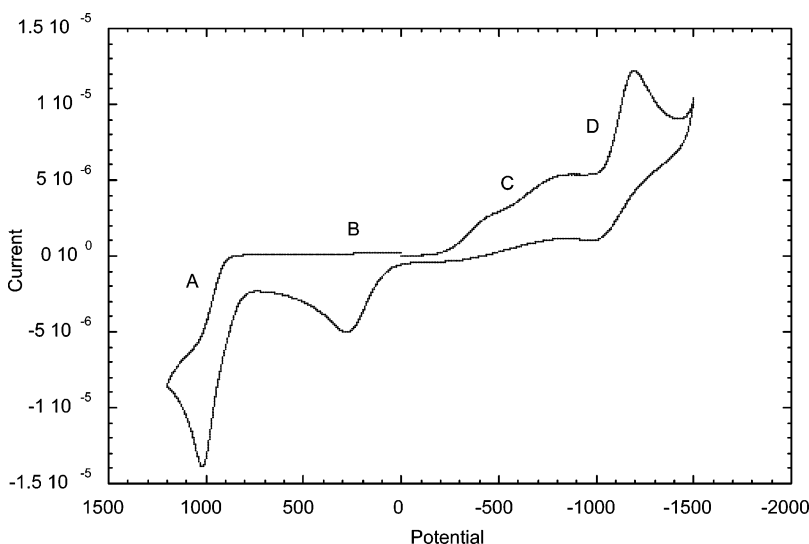


Figure 5. Cyclic voltammogram of $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$, ~ 1 mM in THF. The scan rate is 0.100 V/s.

$\text{K}_2\text{Yb}(\text{C}_8\text{H}_8)_2$ to $\text{KYb}(\text{C}_8\text{H}_8)_2$. The kinetics of this process was cited above,¹⁵ and there is little doubt that the oxidation state of the central metal changes from Yb(II) to Yb(III). The cyclic voltammogram is shown in Figure 4. Wave A is the reversible redox of $\text{Yb}(\text{C}_8\text{H}_8)_2^{2-}/\text{Yb}(\text{C}_8\text{H}_8)_2^-$ (at -0.3 V vs NHE); wave B is some further irreversible oxidation. Waves C and D resemble closely the successive one-electron oxidations of $\text{C}_8\text{H}_8^{2-}$ to C_8H_8^- and to C_8H_8 observed for COT in THF by Lehmkuhl et al.²⁰ The Yb compounds behave essentially as ionic salts of COT dianion, and such oxidations to COT are to be expected. Moreover, any inadvertent oxidation during preparation of the sample will result in COT; thus, detection of COT is not meaningful.

The electrochemistry of bis-[8]annulenepraseodymate ion differs significantly from its two analogues. The voltammogram in Figure 5 shows two nonreversible oxidations. The oxidation wave at $E = -0.8$ V is sometimes present in the oxidation of sandwich complexes in THF; however, this wave is not present in all voltammograms and probably is not that of a C_8H_8

sandwich complex. It frequently disappeared on repeat scans, which suggests an electrochemical event followed by a chemical reaction or rearrangement into something else having a different potential. A possible candidate is the peroxide initially formed when oxygen reacts with COT. Assuming that the first, lower oxidation (-0.22 V vs NHE) is the removal of one electron from $[\text{Pr}(\text{C}_8\text{H}_8)_2]^-$ to give neutral $\text{Pr}(\text{C}_8\text{H}_8)_2$, then Figures S4–S7 (Supporting Information) show that this oxidation is not reversible. When ferrocene is added, the solution becomes unstable, and the waves for both the ferrocene and $[\text{Pr}(\text{C}_8\text{H}_8)_2]^-$ become irreversible and unstable. To overcome this difficulty, cerocene was used as an internal standard (Figure S8, Supporting Information). In this system, both the reversible cerocene standard and the irreversible $[\text{Pr}(\text{C}_8\text{H}_8)_2]^-$ are observed, the oxidation of $[\text{Pr}(\text{C}_8\text{H}_8)_2]^-$ occurring 0.38 V higher than that of $[\text{Ce}(\text{C}_8\text{H}_8)_2]^-$. Waves C and D again show the normal oxidation of $\text{C}_8\text{H}_8^{2-}$ to C_8H_8^- and to C_8H_8 .

The initial oxidation reaction that does occur is suggested by the results of chemical oxidation. On treatment of $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$ with allyl bromide, most of the $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$ was recovered unchanged. A small

(20) Lehmkuhl, H.; Kintoff, S.; Janssen, E. *J. Organomet. Chem.* **1973**, *556*, 41–52.

yield was obtained, however, of the known triple-sandwich compound $\text{Pr}_2(\text{C}_8\text{H}_8)_3$,²¹ which was identified by the molecular ion in its mass spectrum. We suggest that removal of one electron from the $\text{Pr}(\text{C}_8\text{H}_8)_2^-$ gives a praeseodymium complex that disproportionates to $\text{Pr}_2(\text{C}_8\text{H}_8)_3$ plus cyclooctatetraene. The chemical reaction suggests that the initial voltammetric oxidation of $\text{Pr}(\text{C}_8\text{H}_8)_2^-$ is coupled to the disproportionation that results only in the net oxidation of one $\text{C}_8\text{H}_8^{2-}$ to COT. The product $\text{Pr}_2(\text{C}_8\text{H}_8)_3$ is still a salt of $\text{C}_8\text{H}_8^{2-}$ that can undergo additional further oxidation to COT in waves C and D.

It is interesting to note that the class of compounds $\text{Ln}_2(\text{C}_8\text{H}_8)_3$ is the only product observed from the reaction of cyclooctatetraene with lanthanide metal vapor, even for cerium. The reductive elimination of neutral cyclooctatetraene is observed upon the heating of any lanthanide sandwich complex where the central metal atom is in the higher of two available oxidation states. The trivalent complex $\text{K}[\text{Yb}(\text{C}_8\text{H}_8)_2]$ is converted to the divalent $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ by reductive elimination of neutral cyclooctatetraene when heated in vacuo at 200 °C.²² We note further that the reaction of $\text{Ce}_2(\text{C}_8\text{H}_8)_3$ with cyclooctatetraene is apparently reversible. When $\text{Ce}(\text{C}_8\text{H}_8)_2$ is heated in vacuo, the brown $\text{Ce}(\text{C}_8\text{H}_8)_2$ initially sublimates, but upon continued heating, the green compound $\text{Ce}_2(\text{C}_8\text{H}_8)_3$ sublimates and neutral cyclooctatetraene is observed.² The reverse reaction is in the original report of cerocene;² reaction of $\text{Ce}_2(\text{C}_8\text{H}_8)_3$ with neutral cyclooctatetraene in the presence of a catalytic amount of triethylaluminum gave $\text{Ce}(\text{C}_8\text{H}_8)_2$. At room temperature, the equilibrium favors cerocene; at higher temperatures, in vacuo, the equilibrium shifts to the right.

On the basis of NMR studies of the electron exchange between $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ and $\text{K}[\text{Yb}(\text{C}_8\text{H}_8)_2]$,¹⁵ and between $\text{K}[\text{U}(\text{C}_8\text{H}_8)_2]$ and $\text{U}(\text{C}_8\text{H}_8)_2$,¹⁷ the first step of oxidation is probably an outer sphere mechanism, removing an electron from the ring. This is followed by a rapid transfer of an electron from the central metal in the case of ytterbium and cerium, but not for praeseodymium. Whether viewed as a true tetravalent central metal sandwich compound or as a trivalent central metal in a Kondo type ion,⁹ the energy required is simply too high for praeseodymium, and other pathways result.

Conclusions

In its chemistry, cerocene behaves remarkably like actinide(IV) metallocenes with [8]annulene ligands. Like thorocene and uranocene, in particular, it does not behave as an ionic salt of $\text{C}_8\text{H}_8^{2-}$. Like the higher $\text{An}(\text{C}_8\text{H}_8)_2$ metallocenes it undergoes facile electron exchange with the corresponding $\text{An}(\text{C}_8\text{H}_8)_2^-$ ions on the NMR time scale. The conventional MO picture of the actinide sandwiches is given schematically in Figure 6. Instead of a simple electron transfer redox reaction between an electron-rich ligand orbital and a lower-lying empty metal orbital, orbital overlap gives a doubly occupied bonding orbital that provides ring–metal bonding. Since this bonding MO has a contribution from

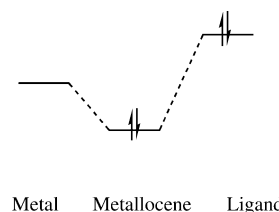


Figure 6. Schematic diagram of ring–metal bonding in metallocenes.

the metal, the result is transfer of electron density from ligand to metal. If the metal was originally +4, some measures of the effective oxidation state of the metal would be expected to give values less than 4. In the case of cerocene this transfer of electron density is apparently substantial, but it is still chemically reasonable and consistent to regard the central metal in this case as formally +4. Accordingly, the simple model in Figure 6 is an effective model at the one-electron MO level that rationalizes the observed chemistry.

Experimental Section

General Procedures. All air-sensitive materials were handled under argon either in a Vacuum Atmospheres Model HE-243 glovebox with a Model HE-93A MOD drytrain or using standard Schlenk line techniques. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. ¹H NMR spectra were obtained on UC Berkeley 200 and 250 MHz superconducting FT spectrometers equipped with Cryomagnets Inc. magnets and Nicolet Model 1280 data collection systems, a Bruker 500 MHz AM 500 superconducting FT spectrometer with an Aspect 3000 computer system, and a 90 MHz JEOL FX90Q FT spectrometer. Temperatures were measured with a thermocouple mounted next to the NMR tube. Cyclooctatetraene (COT) (obtained from BASF) was vacuum distilled or vacuum transferred prior to use and stored over 3 Å molecular sieves. Allyl bromide was washed two times with a saturated aqueous NaHCO_3 solution and then with distilled water. MgSO_4 was added and the mixture was fractionally distilled. The highest boiling fraction was degassed using three freeze–pump–thaw cycles, taken into the glovebox, and stored over 4 Å Linde molecular sieves. All other reagents, unless otherwise noted, were obtained from commercial suppliers and used without further purification. Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California at Berkeley.

Potassium Bis- π -(8-annulene)cerate(III).¹³ The earlier preparation was improved by the use of $\text{CeI}_3(\text{THF})_4$.¹² To a stirring mixture solution of 2.00 g (19.2 mmol) of freshly distilled cyclooctatetraene (BASF) in 40 mL of THF was added 1.62 g (41.4 mmol) of freshly cut potassium metal. After stirring for 4 h, most of the potassium had reacted. The mixture was filtered and added slowly to a stirring mixture of 4.09 g (5.10 mmol) of $\text{CeI}_3(\text{THF})_4$ and 80 mL of THF. The resulting green solution was allowed to stand for several hours without stirring to allow the precipitate to settle to the bottom. The mixture was filtered, and the volume of the green filtrate was reduced to 25 mL. The green precipitate was removed from the mother liquor and washed three times with 5 mL of THF to yield after drying in vacuo 1.56 g (79%) of product. This product can be crystallized from diglyme to give $[\text{K}(\text{diglyme})][\text{Ce}(\text{C}_8\text{H}_8)_2]$. Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_3\text{KCe}$: C, 50.7; H, 5.8; K, 7.5. Found: C, 48.0; H 6.0; K, 9.2.

Preparation of $\text{Ce}(\text{C}_8\text{H}_8)_2$. From AgI. To 0.200 g (0.52 mmol) of $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$ in an argon atmosphere glovebox was added 30 mL of THF, with stirring until all dissolved. To this pale green solution under red light was then added 1.21 g (5.2

(21) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625–631.

(22) Kinsley, S. A.; Streitwieser, A.; Zalkin, A. *Organometallics* **1985**, *4*, 52–57.

mmol) of AgI, which had been freshly ground in a mortar. The deep brown mixture was stirred for 2 min and filtered with fine filter paper to give a clear dark brown solution. The filter paper was rinsed several times with small portions of THF, leaving a fine black material in the filter paper. The solvent was removed from the filtrate in vacuo, to leave a brown-black powder, which was rinsed several times with small portions of hexane, yielding 0.142 g (0.41 mmol, 78%) of $\text{Ce}(\text{C}_8\text{H}_8)_2$. ^1H NMR (THF- d_6): δ 5.9 (s); (toluene- d_6): δ 5.75 (s).

From Allyl Bromide. To a 500 mL round-bottom flask equipped with a magnetic stirbar was added 0.65 g (1.8 mmol) of potassium bis-(8-annulene)cerate(III) and 200 mL of dry THF. To this light green solution was added 0.70 g (5.9 mmol) of allyl bromide. This solution was allowed to stir overnight, the solvent was removed in vacuo, and the remaining solid was extracted with 3×250 mL portions of toluene. The extracts were filtered and combined, and the toluene was removed in vacuo. The resulting finely crystalline black powder was washed three times with hexane and dried in vacuo, giving 0.56 g (89% yield); $m/z = 348$, $\lambda_{\text{max}} = 470$ nm; ^1H NMR (THF- d_6) δ 5.90 (s). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{Ce}$: C, 55.1; H, 4.6. Found: C, 54.4, H, 4.5. The UV-vis spectrum and mass spectrum are shown in Figures S1 and S2 (Supporting Information). The molecular ion is correct for $\text{Ce}(\text{C}_8\text{H}_8)_2^+$, and important fragment peaks occur for $\text{Ce}(\text{C}_8\text{H}_8)^+$ and C_8H_8^+ .

Bis- π -[bis(1,4-trimethylsilyl)-8-annulene]cerium(IV).⁶ The preparation differs from that of Kilmann et al.,⁶ by the use of NaH, CeI_3 , and allyl bromide. To a solution of 5.0 g (20 mmol) of 1,4-bis(trimethylsilyl)cyclooctatriene²³ in 100 mL of THF was added with stirring a large excess (4.79 g, 200 mmol) of freshly ground NaH over 4 h. The dark green mixture was allowed to stir overnight and filtered, and the THF was removed in vacuo from the filtrate. The resulting material was washed with hexane to remove unreacted cyclooctatriene, leaving 0.84 g (2.9 mmol) of a cream-colored disodium 5,8-bis-(trimethylsilyl)cyclooctatetraenediide. To this material dissolved in 100 mL of THF was added 1.17 g (1.4 mmole) of $\text{CeI}_3(\text{THF})_4$ in 50 mL of THF. The dark green mixture was filtered, and the THF was removed from the filtrate in vacuo, leaving a dark green solid. This solid was washed with pentane, dried under vacuum, and dissolved in THF. To the green solution was added 0.73 g (6.0 mmol) of allyl bromide. This solution became dark brown over several minutes and was allowed to stir overnight. The THF, excess allyl bromide, and reaction byproducts were removed under vacuum. The product was extracted from the remaining material with pentane. Pentane was removed from the combined washes in vacuo, leaving 0.96 g of a dark brown semisolid material. ^1H NMR (250 MHz, toluene- d_6): δ 0.06 (s, 3H), 5.6–6.2 (m, 1H); m/z 636; $\lambda_{\text{max}} = 470$ nm.

Oxidation of $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$ with Allyl Bromide. In an argon atmosphere glovebox, 0.16 g (0.41 mmol) of $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$ was added to a 100 mL flask equipped with a stir bar. Addition of 20 mL of degassed, anhydrous THF dissolved the bright yellow powder to give a golden yellow solution. Allyl bromide (0.06 g, 0.5 mmol), degassed by four freeze-pump-thaw cycles on a Schlenk line, was added to the flask, via syringe. After 24 h, removal of the THF in vacuo from the now pale yellow solution left a yellow powder. The powder was extracted two times with 30 mL of toluene. The toluene-insoluble powder was redissolved in THF; removal of the THF in vacuo left 0.095 g of a bright yellow powder, $\lambda_{\text{max}} = 504$ nm (lit.¹³ for $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$, $\lambda_{\text{max}} = 502$ nm.). The toluene was removed from the faint yellow extract, leaving a small amount (<20 mg) of pale yellow powder. UV-vis: (in THF) $\lambda_{\text{max}} = 426, 400, 376, 254$ nm. MS: m/z 594 ($\text{Pr}_2(\text{C}_8\text{H}_8)_3 = 594$).

Ligand Exchange Reaction. A sample of $\text{Ce}(\text{C}_8\text{H}_8)_2$ was placed in an NMR tube equipped with a stopcock joint. THF-

d_6 was added, and the cerocene was allowed to dissolve into a brown solution. To this tube was added an approximately comparable amount of UCl_4 , and the tube was removed from the box and sealed under vacuum. After several days, a small peak in the ^1H NMR appeared at -36 ppm corresponding to uranocene.

Electrochemistry. General. Electrochemical measurements were conducted with a Bioanalytical Systems CV-50 potentiostat with platinum disk working, platinum wire auxiliary, and silver wire reference electrode. Samples were measured with 0.1 M Bu_4NBF_4 as the supporting electrolyte, and ferrocene was added as either an internal or external reference after measurements involving cerocene. Due to an apparent reaction with ferrocene, cerocene was used as an internal standard for electrochemical measurements of $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$. The lanthanide complexes $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$, $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$, and $\text{K}[\text{Pr}(\text{C}_8\text{H}_8)_2]$ for the electrochemical measurements were prepared from previously reported methods^{11,22} and purified by crystallization.

Tetrahydrofuran (THF) for the electrochemical measurements was distilled from sodium benzophenone, stirred with lithium aluminum hydride, vacuum transferred and degassed via freeze-pump-thaw, and stored over activated 3 Å molecular sieves. Tetra-*n*-butylammonium tetrafluoroborate was obtained from Fluka (puriss) and recrystallized from either ethyl acetate/hexane or acetone/ether and dried in vacuo or prepared as given below. Tetra-*n*-butylammonium hexafluorophosphate was obtained from Fluka (puriss) and dried in vacuo prior to use. Ferrocene was obtained commercially (Aldrich) and sublimed prior to use.

Cyclic Voltammetry Methods. Approximately 10 mL of a stock solution of the electrolyte in THF (in the range of 0.1 M) was added to the electrochemical cell in an argon glovebox. The electrodes were then set up, and the background voltammogram was recorded. If this was clear, the sample was added (in the general range of 1×10^{-3} M, although this is not critical and was usually not weighed out), and the appropriate sweeps were carried out. Scan rates were in the range 100–400 mV/s, with the majority of the measurements being made at 100 mV/s. A small amount of ferrocene was added until the ferrocene peaks were clearly visible. Electrodes were wiped with Kimwipes and rinsed with THF between samples, unless they were dirty enough to require repolishing or cleaning, in which case they had to be removed from the glovebox. The bis[8]annulene lanthanates are extremely air-sensitive. Noticeable color changes in solutions were apparent after 30 min exposure to the glovebox atmosphere, even though standard tests (e.g., lack of fuming from diethylzinc) indicated an oxygen “free” atmosphere.

Acknowledgment. This research was supported in part by the Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, and by grants from the National Science Foundation. Special thanks to Profs. R. A. Anderson for his donation of anhydrous PrCl_3 and J. R. Long for use of electrochemical equipment and glovebox. S.K. also thanks Laurance Beauvais, Miriam Bennett, and Matthew Shore for their assistance in obtaining the cyclic voltammograms.

Supporting Information Available: Eight figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(23) Bellema, J. M.; Davison, J. B. *J. Organomet. Chem.* **1975**, *86*, 69–74.