

intermediate is involved in the trimer to tetramer reaction.

The synthesis of $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ from the trimer isocyanates and $\text{Ru}_3(\text{CO})_{12}$ clearly occurs in two steps. After the mixture is refluxed for 1 h, the only isocyanate cluster remaining is $[\text{Ru}_4(\text{NCO})(\text{CO})_{13}]^-$ and the only other clusters present in solution are $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ and some $\text{Ru}_3(\text{CO})_{12}$. Approximately 22% of $[\text{Ru}_3(\text{NCO})(\text{CO})_{11}]^-$ is converted into $[\text{Ru}_4(\text{NCO})(\text{CO})_{13}]^-$ at this stage. The conversion of this remaining isocyanate into $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ occurs gradually over a period of 12 h, similar to the rate of conversion of $[\text{Ru}_4(\text{NCO})(\text{CO})_{13}]^-$ to $[\text{Ru}_4\text{N}(\text{CO})_{12}]^-$. As suggested in Scheme I, we believe there is both a direct path (faster) from $[\text{Ru}_3(\text{NCO})(\text{CO})_{10}]^-$ and $\text{Ru}_3(\text{CO})_{12}$ to $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ as well as an indirect route (slower) that proceeds through $[\text{Ru}_4(\text{NCO})(\text{CO})_{13}]^-$. It is possible that the direct condensation of $[\text{Ru}_3(\text{NCO})(\text{CO})_{10}]^-$ with $\text{Ru}_3(\text{CO})_{12}$ is promoted by the isocyanate group that is capable of acting as a bridging ligand, and thereby stitching together the two trimers.

The reversion of the nitrido ligand back to the isocyanato ligand requires both elevated temperatures and high pressures of CO. Regardless of which nitrido cluster was initially charged in the reaction, it appears that $[\text{Ru}_4\text{N}(\text{CO})_{12}]^-$ is the last detectable nitrido cluster present prior to isocyanate formation. While it is reasonable to suggest that the isocyanates are formed via a reverse of the mechanism shown in Scheme II, further fragmentation of $[\text{Ru}_4\text{N}(\text{CO})_{12}]^-$ under high CO pressure cannot be ruled out.

The migration of CO to and from the nitrogen atom is related to several reactions discovered with carbido clusters,⁴⁶⁻⁵³ and it seems probable that these are mechanis-

tically similar. This reaction offers one of the most interesting and promising means of activating the usually reluctant nitride or carbide ligand in metal clusters. Further, in the case of nitrogen we have a reaction that is directly analogous to the surface reaction of nitrogen atoms with carbon monoxide.^{7,8} By further study of these and related clusters we hope to be able to elucidate more on the mechanism of the CO migration.

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Registry No. I-PPN, 92845-78-8; II-PPN, 83312-28-1; II-(PhCH₂Et₃N), 84809-77-8; III-PPN, 84809-76-7; PPN[$[\text{Ru}_4(\text{NCO})(\text{CO})_{13}]^-$], 92845-79-9; PPN[$[\text{Ru}_4(\text{N}^{13}\text{CO})(\text{CO})_{13}]^-$], 92845-75-5; PPN[$[\text{Ru}_3(\text{NCO})(\text{CO})_{11}]^-$], 92900-63-5; $[\text{Ru}_3(\text{N}^{13}\text{CO})(\text{CO})_{11}]^-$, 92845-76-6; $[\text{Ru}_3(\text{NCO})(\text{CO})_{10}]^-$, 92900-64-6; $[\text{Ru}_3(\text{N}^{13}\text{CO})(\text{CO})_{10}]^-$, 92900-61-3; PPN[$[\text{Ru}(\text{CO})_3(\text{NO})]$], 92845-81-3; (PPN)₂[$[\text{Ru}_6(\text{CO})_{18}]$], 62501-17-1; $[\text{HRu}_3(\text{CO})_{11}]^-$, 60496-59-5; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{Ru}(\text{CO})_6$, 16406-48-7; NOPF₆, 16921-91-8; NCO⁻, 661-20-1.

Supplementary Material Available: Lists of calculated and observed structure factors, isotropic and anisotropic thermal parameters, and complete bond angles (16 pages). Ordering information is given on any current masthead page.

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Dipotassium Bis([8]annulene)ytterbate(II) and -calcate(II)[†]

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The title compounds were prepared by stoichiometric reaction of cyclooctatetraene, potassium, and either ytterbium or calcium, in liquid ammonia solution. The dimethoxyethane adducts of $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ and $\text{K}_2[\text{Ca}(\text{C}_8\text{H}_8)_2]$ are crystalline and have similar X-ray powder patterns; $\text{K}_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ and $\text{K}_2[\text{Ca}(\text{C}_8\text{H}_8)_2]$ have identical infrared spectra. X-ray structure analysis of $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ shows planar parallel eclipsed [8]annulene rings sandwiching a centrosymmetric ytterbium. A potassium coordinated with dimethoxyethane is at the opposite side of each ring. Crystals of $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ crystallize in the triclinic system of space group $P\bar{1}$ with $a = 9.346$ (4) Å, $b = 9.775$ (4) Å, $c = 7.740$ (4) Å, $\alpha = 91.72$ (4)°, $\beta = 109.16$ (4)°, and $\gamma = 86.22$ (4)° at $T = 23$ °C.

Introduction

The organolanthanide complexes involving lanthanide(III) ions and the [8]annulene dianion¹ include complexes of the type $\text{K}[\text{Ln}(\text{C}_8\text{H}_8)_2]$,² $\text{Ce}_2(\text{C}_8\text{H}_8)_3$,³ $[\text{Ln}(\text{C}_8\text{H}_8)(\text{OC}_4\text{H}_9)][\text{Ln}(\text{C}_8\text{H}_8)_2]$,⁴ $[\text{Ln}(\text{C}_8\text{H}_8)\text{Cl}(\text{OC}_4\text{H}_9)_2]$,⁵ (C_8H_8) -

$\text{LnR}(\text{C}_4\text{H}_8\text{O})_2$,⁶ $(\text{C}_8\text{H}_8)\text{Ce}(\text{O}-i\text{-C}_3\text{H}_7)_2\text{Al}(\text{C}_2\text{H}_5)_2$,⁷ and $\text{Ln}(\text{C}_8\text{H}_8)(\text{C}_5\text{H}_5)$.⁸ The determination of the structures of

(1) Controversy exists in naming sandwich organometallic actinide and lanthanide compounds of cyclooctatetraene dianion; [8]annulene dianion is chosen here because this name properly describes the delocalization of charge in the ligand and also emphasizes the formal oxidation state of the metal. See: Zalkin, A.; Templeton, D. H.; Luke, W. D.; Streitwieser, A., Jr. *Organometallics* **1982**, *1*, 618.

[†]Dedicated to the memory of the late Professor Earl L. Muettterties, who shared the same birthdate as one of us.

$[\text{Ce}(\text{C}_8\text{H}_8)\text{Cl}(\text{OC}_4\text{H}_9)_2]_2$,⁹ $[\text{K}(\text{C}_6\text{H}_{14}\text{O}_3)]_2[\text{Ce}(\text{C}_8\text{H}_8)_2]$,¹⁰ and $[\text{Nd}(\text{C}_8\text{H}_8)(\text{OC}_4\text{H}_9)]_2[\text{Nd}(\text{C}_8\text{H}_8)_2]$ ⁴ have shown that the [8]annulene rings of the complexes are planar with equivalent carbon-carbon bond lengths and that the lanthanide ions in the complexes containing $[\text{Ln}(\text{C}_8\text{H}_8)_2]^-$ are sandwiched by two [8]annulene rings. In contrast to the number of classes of complexes reported involving lanthanide(III) ions, there are reports of only two classes of [8]annulene complexes involving lanthanide(II) ions. The structures of these classes have not been elucidated.

The first lanthanide [8]annulene complexes reported $\text{Ln}(\text{C}_8\text{H}_8)$ ($\text{Ln} = \text{Eu}, \text{Yb}$)¹¹ are the only [8]annulene complexes that have been shown to contain a divalent lanthanide. The characterization of the lanthanide(II) [8]annulene complexes is limited. The infrared spectrum of $\text{Yb}(\text{C}_8\text{H}_8)$ ¹² suggests a highly symmetric complex (the only bands present between 1000 and 600 cm^{-1} occur at 888 and 678 cm^{-1}), and the low solubility of the complexes in hydrocarbons, ethers, and liquid ammonia suggests that the class $\text{Ln}(\text{C}_8\text{H}_8)$ is polymeric. No reactions of the divalent lanthanide complexes have been reported, except for their violent reaction with oxygen.

The report of synthesis of $K_2[\text{Ce}(\text{C}_8\text{H}_8)_2]$ from the reduction of $\text{Ce}(\text{C}_8\text{H}_8)_2$ by 2 equiv of potassium in 1,2-dimethoxyethane¹³ is the only example of a bis([8]annulene) compound with a central metal atom in a formal 2+ oxidation state. The cerium complex as its bis(1,2-dimethoxyethane) adduct was characterized by elemental analysis and infrared spectrum. The structure of $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Ce}(\text{C}_8\text{H}_8)_2]$ is not known, but the infrared spectrum of the cerium complex does contain bands (887 and 682 cm^{-1}) that are consistent with the presence of an [8]annulene dianion.¹⁴ Although there are reports of Ce(II) from the reduction of Ce(III) in other systems,¹⁵ the presence of the cerium(II) ion in $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Ce}(\text{C}_8\text{H}_8)_2]$ has not been shown by chemical or spectroscopic methods.

In order to study a bis([8]annulene) compound with a divalent central metal atom, we have now synthesized and characterized the divalent ytterbium complex $K_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$, **1**, and its calcium analogue, $K_2[\text{Ca}(\text{C}_8\text{H}_8)_2]$, **2**. The determination of the structure of the bis(1,2-dimethoxyethane) adduct of **1** by single-crystal X-ray diffraction is the first structure solved for a complex of [8]annulene dianion with a divalent lanthanide. In prior work on the bis(cyclopentadienyl)lanthanide(II) complexes,¹⁶ a comparison of the infrared spectra of $\text{Yb}(\text{C}_5\text{H}_5)_2$ and $\text{Ca}(\text{C}_5\text{H}_5)_2$

had suggested that the ytterbium complex is isostructural with the calcium complex and, therefore, that the ring-metal bonding in the ytterbium complex is highly ionic. In this work the infrared spectra and X-ray powder patterns of **1** and **2** are used to show that **1** and **2** are isostructural.

Experimental Section

General Data. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Ytterbium metal turnings were purchased from Alfa/Ventron. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. 1,2-Dimethoxyethane (DME) was distilled from Na/K alloy. Cyclooctatetraene (COT) (BASF) was vacuum distilled and stored over molecular sieves (3 Å). Liquid ammonia was vacuum transferred into the reaction vessels from a solution of sodium in liquid ammonia. All air-sensitive compounds were handled in a helium or argon atmosphere glovebox or by standard Schlenk techniques. Infrared spectra were determined with a Perkin-Elmer Model 283 infrared recording spectrophotometer. Samples for infrared determination were prepared in a glovebox as Nujol mulls. Visible spectra of THF solutions of the organometallic compounds were determined with a Cary Model 118 spectrophotometer; results are expressed as λ_{max} in nanometers ($\log \epsilon$). ¹H NMR of the organometallic compounds were determined in sealed tubes of THF-*d*₆ solutions on a JEOL FX-90Q. The chemical shifts of the proton resonances are referenced to the low-field residual proton resonance of THF-*d*₆ (set as 3.58 ppm). Samples for X-ray powder pattern determination were prepared by grinding the crystalline sample to a fine powder and sealing the powder into a quartz capillary under argon. X-ray powder pattern data were taken with a Debye-Scherrer camera using nickel-filtered copper $K\alpha$ X-rays. Elemental analyses were performed by the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley.

Reactions in Liquid Ammonia. The reaction vessel used for the syntheses in liquid ammonia was a two-necked 100-mL round-bottom flask with side arm. During the reactions, the flask was connected through one neck to a Schlenk line and cooled in a dry ice/2-propanol bath. While the liquid ammonia was transferred into the reaction vessel during the course of the reaction, the vacuum manifold was isolated from the vacuum pump. The vacuum manifold was protected from developing high ammonia pressure by a mercury bubbler. After the metals were added to the ammonia, a septum was placed on the free neck of the flask (under argon purge) and cyclooctatetraene was added to the blue solution via syringe. Since cyclooctatetraene freezes on contact with liquid ammonia at that low temperature, the dry ice bath was removed to facilitate reaction. When the reaction was complete, the ammonia was allowed to evaporate through the mercury bubbler, leaving the pyrophoric material behind.

X-ray Analysis. With the exception of the ORTEP program, all computer programs used were written by A.Z. for a CDC 7600 computer.

An irregular, orange-red single crystal fragment of 1,2-DME with maximum dimensions of 0.2 mm was sealed inside a quartz capillary in an argon atmosphere and examined with a modified Picker FACS-I automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube. Least-squares refinement of the setting angles of 24 centered reflections ($27^\circ > 2\theta > 20^\circ$) using Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation gave $a = 9.346$ (4) Å, $b = 9.775$ (4) Å, $c = 7.740$ (4) Å, $\alpha = 91.72$ (4)°, $\beta = 109.16$ (4)°, $\gamma = 86.22$ (4)°, and $V = 666.5$ Å³ at 23 °C. The space group of the crystal is triclinic $P\bar{1}$ with one formula unit in the unit cell. The calculated density of the crystal (molecular weight of $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ is 639.80) is 1.59 g cm^{-3} .

Intensities were collected to a maximum 2θ value of 50° using a θ - 2θ scan technique. Three standard reflections were measured at every 250th measurement; the three standards showed an isotropic decay of about 5%, and the data were adjusted accordingly. A total of 4729 intensities were measured and averaged to give 2361 unique data of which 2312 were used in the least squares with $F^2 > 1\sigma(F^2)$. The data were not corrected for absorption because of the difficulty of seeing the faces and measuring the crystal's irregular dimensions. The absorption coefficient

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(12) The infrared spectrum of $\text{Yb}(\text{C}_8\text{H}_8)$ is reported in ref 4.

(13) The synthesis of $\text{Ce}(\text{C}_8\text{H}_8)_2$ and its reduction is reported in ref 3.

(14) The dipotassium salt of [8]annulene has absorbances in the 1000-600 cm^{-1} region at 880 and 684 cm^{-1} as reported in: Fritz, H. P.; Keller, H. *Chem. Ber.* 1962, 95, 158. The infrared spectra of all of the f-block [8]annulene complexes reported include strong absorbances at 890 \pm 20 and 690 \pm 20 cm^{-1} .

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(16) Fischer, E. O.; Fischer, H. *Angew. Chem.* 1964, 76, 52.

calculates to 38 cm^{-1} , and an error of approximately 5% in the intensities is estimated.

Trial positions for the ytterbium and potassium atoms were obtained from a three-dimensional Patterson function and were refined by least squares. An electron density map revealed all of the non-hydrogen atoms. All of the non-hydrogen atoms were refined with anisotropic temperature factors, and the hydrogen atoms were included at their estimated positions, but not refined. The F magnitude was used in the full-matrix refinement.

The final weighted R factor¹⁷ was 0.034 for 2312 data with $F^2 > \sigma(F^2)$, and the goodness of fit was 1.33. The assigned weights $w = (\sigma(F))^{-1}$ were derived from $\sigma(F^2) = [c + (pF^2)^2]^{1/2}$, where c is the variance due to counting statistics and $p = 0.05$. An empirical extinction correction of the form $F_c = F_0(1 + kI)$, where $k = 2.13 \times 10^{-7}$, was applied to the data. Scattering factors were taken from literature sources,¹⁸ and anomalous scattering terms were applied.¹⁹

Preparation of 1 and 2. The procedure for the synthesis of the divalent ytterbium complex follows with differences for the procedure for the calcium complex noted. Cyclooctatetraene (1.79 g, 17 mmol) was added to a dry ice/2-propanol cooled liquid ammonia solution of 0.67 g (17 mmol) of potassium metal and 1.49 g (8.6 mmol) of ytterbium metal. The dry ice/2-propanol bath was removed from the reaction vessel at this time to allow the ammonia solution to warm. As the reaction began, the solution turned green as a bright orange precipitate appeared (the solution and precipitate were bright yellow for the calcium reaction). The ammonia was allowed to evaporate, and a bright orange solid was left in the reaction vessel (bright yellow for calcium). When the reaction vessel was warmed with a heat gun, the solid turned bright pink (pale green for calcium). The yield of the solid was 3.57 g (90%). Yields from the liquid ammonia reactions were typically about 90%. Crystals of the THF adducts of 1 and 2 were obtained by the slow cooling of a saturated solution of 1 or 2 in the ether. The THF adducts of 1 and 2 rapidly lost THF of solvation (ca. 1 hour in an argon atmosphere or ca. 5 min, in vacuo) and decomposed to unsolvated powders. Analysis of 2 as a THF complex was not satisfactory, but the analysis does suggest that there are two THF molecules per potassium atom. Anal. Calcd for 2·4THF ($\text{C}_{32}\text{H}_{48}\text{O}_4\text{K}_2\text{Ca}$): C, 62.49; H, 7.87; K, 12.71. Found: C, 61.73; H, 7.40; K, 11.8.

The unsolvated powders were heated at 200°C , in vacuo, for 1 to ensure the complete removal of solvated THF. The yield of powder was 57% for 1 (67% for 2) from the first crop of crystals. The infrared spectra of 1 and 2 are shown in Figure 2. $^1\text{H NMR}$: 1, δ 5.47 \pm 0.03 (s); 2, δ 5.47 \pm 0.03 (s). Visible spectrum: 1, 504 nm (850). Satisfactory analyses of the powders were difficult to obtain, especially in the case of the ytterbium complex. Anal. Calcd for 1 ($\text{C}_{16}\text{H}_{16}\text{K}_2\text{Yb}$): C, 41.82; H, 3.51; K, 17.01. Found: C, 39.66; H, 3.64; K, 19.2. Anal. Calcd for 2 ($\text{C}_{16}\text{H}_{16}\text{K}_2\text{Ca}$): C, 58.85; H, 4.94; K, 23.94. Found: C, 58.47; H, 5.22; K, 23.4.

The slow cooling of a saturated solution of 1 or 2 in DME gave crystals of the complexes as DME adducts. The DME adducts of 1 and 2 were stable and gave satisfactory analyses for one DME molecule per potassium. Anal. Calcd for 1·2DME ($\text{C}_{24}\text{H}_{36}\text{O}_4\text{K}_2\text{Yb}$): C, 45.06; H, 5.67; K, 12.22. Found: C, 44.79; H, 5.59; K, 12.4. Anal. Calcd for 2·2DME ($\text{C}_{24}\text{H}_{36}\text{O}_4\text{K}_2\text{Ca}$): C, 56.88; H, 7.16; K, 15.43. Found: C, 57.11; H, 7.07; K, 16.07.

Preparation of $\text{K}[\text{Yb}(\text{C}_8\text{H}_8)_2]$, 3. In a procedure that is analogous to the procedure used to synthesis 1 and 2, the potassium salt of bis([8]annulene)ytterbium(III) was prepared by the addition of 0.88 g (8.4 mmol) of cyclooctatetraene to a dry ice/2-propanol cooled liquid ammonia solution of 0.73 g (4.2 mmol) of ytterbium metal and 0.16 g (4.2 mmol) of potassium metal. When the reaction was complete and the solvent had evaporated, a bright orange powder was left in the reaction vessel. This powder turned bright blue when the reaction vessel was warmed with a heat gun and exposed to a vacuum. The crude yield of this powder was 1.50 g (86%). Satisfactory analysis could not be obtained

Table I. Positional Parameters for $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ ^a

atom	x	y	z
Yb	0	0	0
K	0.35199 (13)	-0.34073 (12)	0.09645 (17)
O(1)	0.5266 (4)	-0.5865 (4)	0.2003 (5)
O(2)	0.6346 (4)	-0.3377 (4)	0.3517 (6)
C(1)	0.2982 (6)	-0.0479 (6)	0.1970 (8)
C(2)	0.2208 (7)	-0.1188 (6)	0.2916 (7)
C(3)	0.1084 (7)	-0.2140 (6)	0.2420 (8)
C(4)	0.0252 (7)	-0.2787 (6)	0.0758 (10)
C(5)	0.0200 (6)	-0.2717 (6)	-0.1077 (9)
C(6)	0.0944 (7)	-0.1982 (6)	-0.2010 (7)
C(7)	0.2084 (6)	-0.1027 (6)	-0.1517 (8)
C(8)	0.2936 (6)	-0.0416 (6)	0.0138 (9)
C(9)	0.4371 (9)	-0.7001 (7)	0.1946 (12)
C(10)	0.6448 (7)	-0.5787 (6)	0.3691 (8)
C(11)	0.7322 (7)	-0.4573 (7)	0.3771 (9)
C(12)	0.7098 (8)	-0.2143 (7)	0.3748 (10)

^a In this table and in Table II, the number in parentheses is the estimated standard deviation in the least significant digits.

Table II. Selected Interatomic Distances (Å)

atom 1- atom 2	dist	atom 1- atom 2	dist
Yb-C(1)	2.719 (5)	K-C(1)	2.998 (6)
-C(2)	2.736 (5)	-C(2)	3.026 (6)
-C(3)	2.760 (5)	-C(3)	3.036 (6)
-C(4)	2.783 (5)	-C(4)	3.027 (6)
-C(5)	2.773 (5)	-C(5)	3.025 (6)
-C(6)	2.729 (5)	-C(6)	3.025 (6)
-C(7)	2.711 (5)	-C(7)	3.012 (6)
-C(8)	2.715 (5)	-C(8)	2.989 (6)
O(1)-C(9)	1.425 (8)	K-O(1)	2.796 (4)
-C(10)	1.411 (7)	-O(2)	2.731 (4)
O(2)-C(11)	1.415 (7)	K-O(1) ^a	2.928 (4)
-C(12)	1.414 (8)		
C(11)-C(10)	1.481 (10)		

^a Atom at position 1 - x, -1 - y, -z.

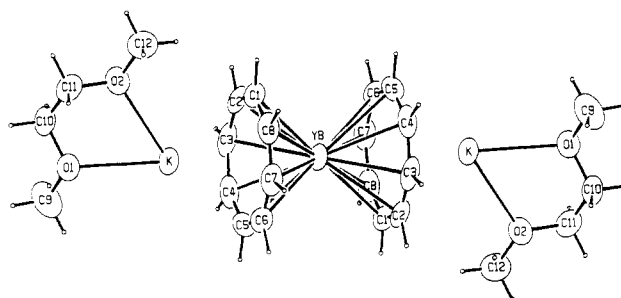


Figure 1. ORTEP drawing of $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$ showing atomic numbering scheme.

for 3, but the infrared spectrum of 3 (the major absorbances in the $600\text{--}1000 \text{ cm}^{-1}$ region are given in Table III) is similar to the infrared spectra of the other bis([8]annulene)lanthanide salts.^{2b} λ_{max} of 3 in THF is 574 nm (1400). A portion of this powder was crystallized from DME to give 3·DME. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{YbK}$: C, 47.05; H, 5.13; K, 7.66. Found: C, 46.51; H, 4.91; K, 8.27; N, 0.28.

Results and Discussion

Structure of $[\text{K}(\text{C}_4\text{H}_{10}\text{O}_2)]_2[\text{Yb}(\text{C}_8\text{H}_8)_2]$. The atomic parameters and distances are listed in Tables I and II. Figure 1 shows an ORTEP view of a formula unit with the numbering scheme used for the atoms in Table II. Additional atomic distances are available as supplementary material.

The [8]annulene rings of 1·2DME are planar with all the carbon-carbon bond lengths equivalent. The maximum

(17) $R = \sum |F_o| - |F_c| / \sum |F_o|$.

(18) For Yb, K, O, and C atoms: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV. For H atoms: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175.

(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* 1970, 53, 1891.

Table III. Comparison of Infrared Spectra^{a, b}

U(C ₈ H ₈) ₂ ^c	K[La(C ₈ H ₈) ₂] ^d	K[Yb(C ₈ H ₈) ₂] ^e (3)	K ₂ [Yb(C ₈ H ₈) ₂] ^{e, f} (1)	assign ^f
698 vs	680 vs	690 vs	683 vs	ρ(CH), A _{2u}
746 s	740 m	741 s	740 m	ν(CC), A _{2u}
777 m	771 w	770 w		ρ(CH), E _{1u}
792 m				
900 s	892 s	899 s	879 s 888 s	β(CH), E _{1u}

^a Abbreviations: vs, very strong; s, strong; m, medium; w, weak. ^b Nujol mulls. ^c Reference 29. ^d Reference 28. ^e This work. ^f Infrared of 1 and 2 are identical.

deviation from the least-squares plane of the ring for any carbon atom is 0.01 Å. The carbon-carbon distances within the ring range from 1.40 to 1.42 Å with an average of 1.41 ± 0.01 Å. The bond angles within the ring are all within their standard deviations of 135°.

The ytterbium atom is on the center of symmetry and is sandwiched by two planar [8]annulene ligands; the potassium atoms are each coordinated to one dimethoxyethane ligand and a [Yb(C₈H₈)₂] dianion. The average ytterbium-to-carbon distance is 2.74 ± 0.03 Å; the distance of the ytterbium atom to the least-squares plane of the [8]annulene is 2.03 Å. The two sandwiching [8]annulene rings are parallel-planar and are exactly eclipsed (being related to each other through the center of symmetry), making the symmetry of the [Yb(C₈H₈)₂] dianion D_{8h}. 1 is the only bis([8]annulene) complex of a lanthanide that exhibits eclipsed rings. In K(C₆H₁₄O₃)[Ce(C₈H₈)₂]¹⁰ the [8]annulene rings are in a staggered conformation (i.e., the symmetry of the [Ce(C₈H₈)₂] anion is D_{8d}) and in [Nd(THF)₂(C₈H₈)] [Nd(C₈H₈)₂]¹⁴ the [8]annulene rings are nearly eclipsed, but not parallel-planar. The eclipsed vs. staggered arrangement of bis([8]annulene) rings is not considered to be indicative of the type of ring-metal bond for these complexes. Wide-line NMR studies on crystals of U(C₈H₈)₂ indicate that the barrier to ring rotation is essentially 0 kcal mol⁻¹.²⁰ Any conformational preference for the rings in the bis([8]annulene) complexes is more than likely due to crystal packing forces and not due to orbital interactions between the metal and ligands.

The average potassium-to-carbon distance is 3.02 ± 0.02 Å; the distance of the potassium atom to the least-squares plane of the [8]annulene ring is 2.39 Å. The potassium atom is also coordinated to two oxygen atoms of a DME ligand at 2.796 (4) and 2.731 (4) Å and to an oxygen atom of an adjacent DME ligand at a distance of 2.928 (4) Å.

The average Yb-C distance (2.74 ± 0.03 Å) in 1·2DME is the same as the average Ce-C distance (2.74 ± 0.02 Å) in [K(C₆H₁₄O₃)[Ce(C₈H₈)₂].¹⁰ These equal distances are consistent with Raymond's arguments on the ionic nature of the metal-carbon bond in ([8]annulene)lanthanide complexes,²¹ since the ionic radii of Ce(III) and Yb(II) are the same.²² Note that the addition of the calculated ionic radius of carbon in [8]annulene dianion, 1.49 Å,²³ to the extrapolated ionic radius for a 10-coordinate divalent ytterbium cation, 1.25 Å,²⁴ gives a Yb-C distance of 2.74 Å.

Physical Properties. The physical properties for 1 and 2 are similar to the properties reported for the trivalent lanthanide complexes K[Ln(C₈H₈)₂].² The most noticeable similarity is the air sensitivity of the compounds K₂[M-

(C₈H₈)₂]; 1 and 2 enflame in contact with air.

Compounds 1 and 2 are thermally stable, showing no sign of decomposition when heated to 360 °C sealed under 1 atm of argon or to 200 °C in vacuo. In THF solution, 1 is oxidized to K[Yb(C₈H₈)₂], 3, by O₂, CCl₄, COT, and U(C₈H₈)₂; the presence of the bright blue ytterbium(III) complex was indicated by its visible spectrum. Compound 3 is thermally unstable and is converted to 1 (by the loss of COT) when heated at 310 °C sealed under 1 atm of argon or to 200 °C in vacuo. A mass spectrum of 1 shows no *m/z* that can be attributed to the ionization of the sandwich compound.

Compounds 1 and 2 have the same solubility properties; they are insoluble in hydrocarbon solvents such as hexane, toluene, and benzene but soluble in ethers such as diethyl ether, THF, and DME. The slow cooling of a saturated solution of 1 or 2 in an ether gives crystals of the ether adduct. The THF adducts of 1 and 2 rapidly lose THF in vacuo or in an argon atmosphere (ca. 1 h), but the DME adducts are stable at ambient temperatures. As with all of the lanthanide [8]annulene complexes, 1 and 2 exist as powders in the absence of coordinated ether molecules.

¹H NMR Spectra. The ¹H NMR of 1 and 2 were determined in THF-*d*₆ solutions. The eight equivalent protons of 2 occur as a singlet at δ 5.47. This resonance is observed upfield from the resonances reported for K-[Y(C₈H₈)₂] and K[La(C₈H₈)₂] that occur at 5.75 and 5.90 ppm, respectively, relative to external Me₄Si.^{2b} The ring proton resonance of 1 is observed at δ 5.47. In its ground state, the ytterbium(II) ion has no unpaired electrons²⁵ and is diamagnetic; the lack of a shift in the observed ring proton resonance of 1 relative to 2 shows that 1 contains the diamagnetic lanthanide(II) ion.

Visible Spectra. The bright orange 1 in THF solution has an intense, broad absorbance in the visible region at 504 nm. In THF solution, 2 has no absorbance in the visible region. The pale green color of 2 is due to trace impurities; repeated recrystallization of 2 from THF gives a pure white powder.

The visible spectrum of 1 in THF can be readily interpreted. Earlier studies on the class K[Ln(C₈H₈)₂] led to the conclusion that the broad absorption bands in the visible region of these complexes are due to ligand-to-metal charge transfer.² The visible absorbance of 1 can also be assigned to a ligand-to-metal charge-transfer band. Preliminary studies on the di-*tert*-butyl derivative of 1, K₂[Yb(C₈H₇(C₄H₉)₂)₂], show the visible absorbance red-shifted to 520 nm.²⁶ Alkyl substituents on the [8]annulene dianion make the ligand more reducing and would shift a ligand-to-metal charge-transfer band to lower energy. Since the Yb(II) ion in 1 has completely filled 4f orbitals, π-f charge transfer can be ruled out and the visible absorbance of 1 can be assigned as a ligand π-to-metal d charge transfer.

(20) Anderson, S. E. *J. Organomet. Chem.* 1974, 71, 263.

(21) Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* 1980, 13, 276. Baker, E. C.; Halstead, G. W.; Raymond, K. N. *Struct. Bonding (Berlin)* 1976, 25, 23.

(22) Shannon, R. D. *Acta Crystallogr., Sect. A* 1976, A32, 751.

(23) In this type of [8]annulene complex, Raymond employs a radius of 1.49 Å for a ring carbon atom; see ref 21.

(24) See ref 22. Each [8]annulene dianion is considered to be a ten-electron donor so that each ring formally donates five electron pairs.

(25) Ytterbium(II) has a ground-state configuration of [Xe]4f¹⁴.

(26) The report of K₂[Yb(*t*-BuC₈H₇)₂] and the crystal structure of its diglyme adduct is in preparation.

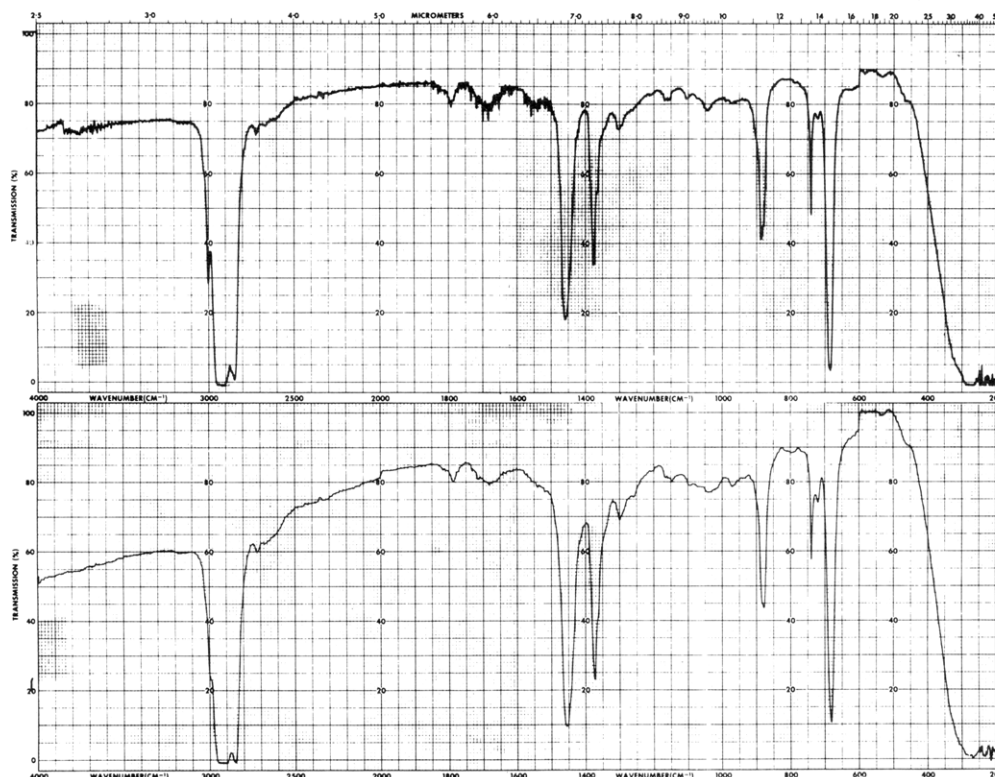


Figure 2. Infrared spectra (Nujol mull) of $K_2[Ca(C_8H_8)_2]$ (top) and $K_2[Yb(C_8H_8)_2]$ (bottom).

Infrared Spectra. The infrared spectra of **1** and **2** as Nujol mulls are shown in Figure 2. The infrared spectra of 1-2DME and 2-2DME are available as supplementary material.

The infrared spectra of **1** and **2** are identical; the infrared spectra of 1-2DME and 2-2DME are also identical. This similarity of infrared spectra was anticipated, since ytterbium(II) and calcium(II) have almost identical ionic radii²² and previous work had shown that the infrared spectra of $CaCp_2$ and $YbCp_2$ are similar,¹⁶ even though the sample of $YbCp_2$ may have been contaminated with $YbCp_3$.²⁷

Infrared spectra for the 600–1000 cm^{-1} region of some bis([8]annulene) complexes are compared in Table III. It has been noted previously that the infrared spectra of all of the bis([8]annulene) sandwich complexes of the f transition metals are similar as a result of their similar structures.² The assignment of the infrared absorbances of these complexes is still in question; a recent assignment²⁸ (shown in Table II) is additionally consistent with the fact that **1** and **2** have the same infrared spectra. An earlier assignment attributed the strong band at 698 cm^{-1} to a ring-metal-ring tilt.²⁹ Such an assignment could not give identical spectra for **1** and **2**, since the difference in mass of ytterbium and calcium would cause a difference in energy for any absorbances which involve the central metal. Since the infrared spectra of **1** and **2** are identical in the 400–4000 cm^{-1} region, then any absorbance involving the central metal must occur outside of this range.

Powder Pattern. The measured powder patterns of 1-2DME, 2-2DME, and the powder pattern calculated from the single-crystal X-ray data of 1-2DME are available as

(27) Calderazzo, F.; Pappalardo, R.; Losi, S. *J. Inorg. Nucl. Chem.* **1966**, *28*, 987.

(28) Aleksanyan, V. T.; Garbusova, I. A. Chernyshova, T. M.; Todres, Z. V. *J. Organomet. Chem.* **1981**, *217*, 169.

(29) Hocks, L.; Goffart, J.; Duyckaerts, G.; Teysse, P. *Spectrochim. Acta, Part A* **1974**, *30A*, 907. These authors comment that the band at 698 cm^{-1} in $U(C_8H_8)_2$ is unusually high for ring-metal-ring tilt.

supplementary material. The powder pattern of 1-2DME was calculated by using the cell dimensions and the structure factor of the single crystal structure determinations. Only two weak lines out of 21 lines calculated for 1-DME are not observed in the pattern of 2-2DME.³⁰ Since the ytterbium(II) complex contains 50 more electrons than the calcium complex, one expects and finds intensity differences in the measured powder patterns of 1-2DME and 2-2DME. Nevertheless, the X-ray powder pattern are sufficiently similar that 1-2DME and 2-2DME are clearly isostructural.

Conclusion

Except for the differences that can be attributed to either the difference in the number of electrons between ytterbium and calcium or to the availability of a trivalent state for the ytterbium complex, **1** and **2** behave as identical complexes. Since it is highly unlikely that the 4f and 5d orbitals are involved in the ring-metal interaction of **2**, these orbitals also play no major role in the ring-metal interaction of **1**. The agreement of the ring-metal distance in 1-2DME with the sum of the ionic radius of carbon in the [8]annulene dianion and the ionic radius of 10-coordinate ytterbium(II) also suggests the lack of significant covalent interaction between the ring and metal in **1**. The results reported in this paper further emphasize the unimportance of the 4f and 5d orbitals in ytterbium(II) chemistry; e.g., the ring-metal interaction in **1** is essentially ionic.

Acknowledgment. This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

(30) The powder patterns are compared for lines with a *d* spacing between 9.75 and 3.10 Å.

Registry No. 1, 92670-61-6; 1-2DME, 92670-63-8; 2, 92670-66-1; 3, 92670-64-9; Yb, 7440-64-4; Ca, 7440-70-2.

Supplementary Material Available: Infrared spectra (1-2DME, 2-2DME), calculated (1-2DME) and measured (1-2DME

and 2-2DME) powder patterns, least-squares plane ([8]annulene), listing of anisotropic thermal parameters, calculated hydrogen positions, C-C distances, selected angles and observed structure factors for 1-2DME (17 pages). Ordering information is given on any current masthead.

Silacyclopropenes. 3. Palladium-Catalyzed Insertion Reactions[†]

Dietmar Seyferth,* Mark L. Shannon, Steven C. Vick, and Thomas F. O. Lim

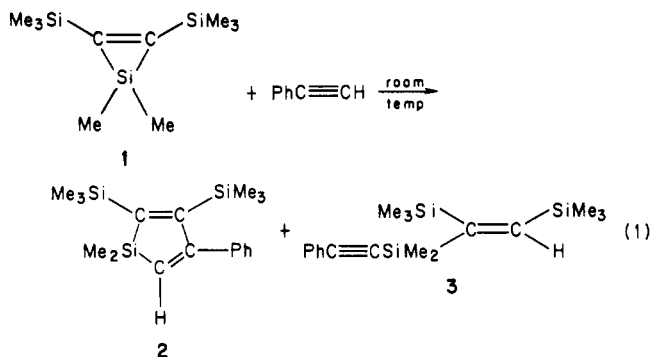
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received June 19, 1984

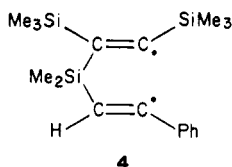
Bis(triphenylphosphine)palladium dichloride was found to catalyze two types of processes with 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene: (1) *formal* dimethylsilylene extrusion followed by trapping of this species by unsaturated organic species that are present; (2) insertion of unsaturated substrates into the silirene ring. Such catalyzed reactions with terminal acetylenes, allenenes, and some terminal 1,3-dienes are described.

Introduction

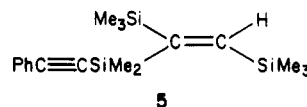
In part 2¹ we reported thermal and UV-induced "two-atom" insertions of various unsaturated compounds (aldehydes, ketones, styrenes, conjugated terminal acetylenes, terminal 1,3-dienes, a conjugated imine) into the SiC₂ ring of 1,1-dimethyl-2,3-bis(trimethylsilyl)silirene, 1. For instance, in the case of phenylacetylene this reaction gave the silacyclopentadiene 2 in 30% yield. In addition, an acyclic product, 3, also was produced in 70% yield (eq 1).



The available evidence suggested that a free radical process with a 1,5-diradical intermediate (4 in the case of the



phenylacetylene reaction) was involved. When the silirene 1/phenylacetylene reaction was carried out with UV irradiation, no cyclic product was obtained. The products were the acyclic product 3 and its trans isomer 5. We have also examined reactions with silirene 1 with acetylenes and other unsaturated compounds in the presence of catalytic quantities of (Ph₃P)₂PdCl₂.



Transition-metal complex catalyzed cleavages of and insertions into Si-C and Si-Si bonds have received attention in recent years.² We do not intend an exhaustive review of this topic and mention only a few representative examples in eq 2-6.

In view of this fairly broad applicability of transition-metal complexes as catalysts in organosilicon reactions, we felt that a study of such catalyzed reactions of the strained, highly reactive silirene ring^{1,4} might be fruitful. We report here our results of this investigation.

Results and Discussion

In view of the already demonstrated thermal and photochemical reactions of 1,1-dimethyl-2,3-bis(trimethyl-

(1) Part 2: Seyferth, D.; Vick, S. C.; Shannon, M. L. *Organometallics* 1984, 3, 0000.

(2) (a) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* 1970, 23, C7. (b) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* 1971, 27, C31. (c) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* 1972, 94, 9263. (d) Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* 1972, 35, 297. (e) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* 1975, 97, 931. (f) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* 1975, 887. (g) Sakurai, H.; Imai, T. *Chem. Lett.* 1975, 891. (h) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* 1976, 114, C19. (i) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* 1977, 131, 147. (j) Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* 1978, 146, 87. (k) Matsumoto, H.; Nagashima, S.; Kato, T.; Nagai, Y. *Angew. Chem.* 1978, 90, 288. (l) Matsumoto, H.; Yako, T.; Nagashima, S.; Motegi, T.; Nagai, Y. *J. Organomet. Chem.* 1978, 148, 97. (m) Matsumoto, H.; Motegi, T.; Hasegawa, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* 1978, 51, 1913. (n) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* 1980, 186, 51. (o) Matsumoto, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* 1980, 199, 43. (p) Matsumoto, H.; Shono, K.; Wada, A.; Matsubara, I.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* 1980, 199, 185. (q) Watanabe, H.; Saito, M.; Sutou, N.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* 1981, 617. (r) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* 1981, 215, 149. (s) Watanabe, H.; Saito, M.; Sutou, N.; Kishimoto, K.; Inose, J.; Nagai, Y. *J. Organomet. Chem.* 1982, 225, 343.

(3) Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* 1967, 32, 885.

(4) Seyferth, D.; Annarelli, D.; Vick, S. C. *J. Organomet. Chem.*, 1984, 272, 123.

[†]Dedicated to the memory of Earl L. Muetterties, an outstanding and original scientist and an old friend from graduate school days.