Photocycloadditions of 1,2-dihydroxy-3,5-cyclohexadiene derivatives **3** and **4** to arenes and subsequent elimination of oxy substituents provide us with a convenient route to a variety of cyclodimers of benzene, energy-rich molecules expected to exhibit novel properties. The extension of this route to the synthesis of other cyclodimers, and the chemistry of these compounds, will be investigated.

Acknowledgment. We thank the National Science Foundation and the Louis Bloch Fund of the University of Chicago for the support of this work, Professor David Evans for a valuable suggestion in the syntheses of these compounds, and the National Cancer Institute for a grant to the University of Chicago Cancer Research Center to purchase the NMR spectrometer used in this work.

Heptamethylindenyl Lanthanide(III) Complexes of Lanthanum, Neodymium, and Erbium

Minoru Tsutsui,[1] Li-Ban Chen, and David E. Bergbreiter*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

T. Ken Miyamoto*

Department of Chemistry, Faculty of Science
The University of Tokyo, Tokyo 113, Japan

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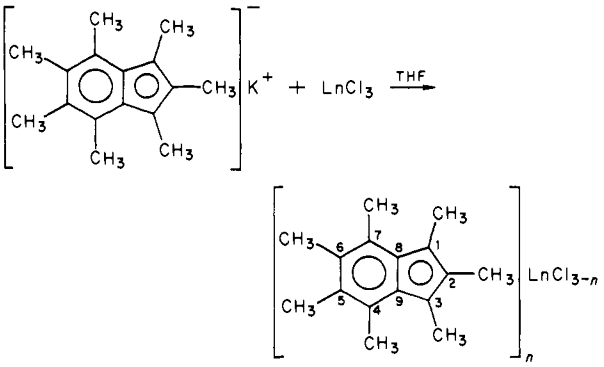
The π-complex chemistry of the lanthanides has been relatively undeveloped compared to that of the d-block elements.[2] For example, synthesis of all three types of organometallic compounds, LnL_3, LnL_2Cl, and $LnLCl_2$ (Ln = La–Lu, L = a π ligand such as cyclopentadienyl (Cp), methylcyclopentadienyl, or indenyl), poses a challenging problem for the design of potentially active homogeneous catalysts from lanthanide elements.[3] While compounds like $LnCp_3$ are known for a whole series of lanthanides,[4-6] the other two types of synthetic precursors, $LnCp_2Cl$ and $LnCpCl_2$ are available solely for the late members of the series (Sm–Lu).[7] It has often been claimed that this trend is due to the large ionic radii and poor ligand field–metal interaction of the early lanthanides.

One approach to circumventing this synthetic problem is to use the chelate effect to achieve enforced metal–ligand coordination. Indeed, a chelate ligand, 1,3-dicyclopentadienylpropane, has been prepared and has allowed the successful isolation of $(Cp(CH_2)_3Cp)LnR$ where Ln = La or Ce and R = Cl, C_6H_5, or $C_2C_6H_5$.[8] Unfortunately, the low solubilities of these compounds in common organic solvents limited their applications as homogeneous catalysts.

Another approach which we have used is to use bulky ligands to protect the metal–ligand bonds in the expected organolanthanides. In this connection, Wayda and Evans have reported the reaction of pentamethylcyclopentadienyllithium with $NdCl_3$.[9] However, in this case, the expected $[(C_5Me_5)_2NdCl]_2$ was not formed and a lithium salt, $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$, was isolated instead. Here we report our work with a new ligand, heptamethylindenyl (Hmi), which has recently been prepared in these laboratories.[10] Both the steric bulk and the electronic character of this ligand resulting from the seven methyl groups favor stabilization of lanthanide–carbon bonds. With the aid of this ligand, the π-complexes, $(Hmi)LnCl_2$ (**1**) and $(Hmi)_3Ln$ (**3**) have been synthesized for both early and late lanthanide elements according to reaction 1. In addition, $(Hmi)_2LnCl$ (**2**) can be prepared although in the case of **2a** this complex has been shown to be a mixture of **1a**, **2a**, and **3a** by ^{13}C NMR spectroscopy.



(1)

a, Ln = La; b, Ln = Er; c, Ln = Nd

Alkali metal salts of heptamethylindenide were used as precursors of the lanthanide complexes. The alkali metal salts of Hmi can be prepared by using either lithium, sodium, or potassium. The potassium salt was most useful because of its higher reactivity toward lanthanide halides. The potassium salt was obtained by reaction of heptamethylindene with a dispersion of potassium metal in refluxing THF and could be isolated as a crystalline solid when solutions which were >0.5 M were cooled to room temperature. The lanthanide salts themselves are obtained by addition of a stoichiometric amount of KHmi (**4**) to the desired amount of $LnCl_3$ and allowing the resulting suspension to stir at 25 °C for ca. 2 days. When the ratio of KHmi to $LnCl_3$ was 3:1 (equiv/equiv), the product $Ln(Hmi)_3$ was purified by crystallization by slowly evaporating the THF solution which remained after removing by centrifugation any solids which were left after the reaction was complete. The lanthanide complexes **1** and **2** were obtained by using 1:1.05 and 2:1 ratios of KHmi to $LnCl_3$, respectively. Complexes **1** and **2** were purified by removing the initial precipitate by centrifugation, evaporating the resulting THF solution, adding a second portion of THF, again removing any insoluble material by centrifugation, and then removing the remaining THF in vacuo. Satisfactory elemental analyses were obtained for **1a**, **1b**, **2b**, **1c**, **2c**, **3c**, and **4**.[11] Complexes **3a** and **3b** analyzed correctly for lanthanide metal and hydrogen but had low values for carbon. All of the complexes **3** contained THF since no effort was made to dry them. However, the THF could easily be removed under vacuo (such dried complexes **3** seemed qualitatively less stable). Analytical samples of **3a**, **3b**, and **3c**

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[11] Anal. Calcd for $C_{32}H_{53}KO_4$ (**4**, KHmi·4THF): C, 71.06; H, 9.88; K, 7.23. Found: C, 70.54; H, 9.26; K, 8.12. Calcd for $C_{20}H_{29}Cl_2LaO$ [**1a**, $La(Hmi)Cl_2 \cdot THF$]: C, 48.50; H, 5.90; Cl, 14.32; La, 28.05. Found: C, 47.74; H, 5.64; Cl, 13.63; La, 28.19. Calcd for $C_{18}H_{25}Cl_2ErO_{0.5}$ [**1b**, $Er(Hmi)Cl_2 \cdot 0.5THF$]: C, 44.34; H, 5.17; Cl, 14.54; Er, 34.31. Found: C, 43.52; H, 5.62; Cl, 14.41; Er, 34.74. Calcd for $C_{32}H_{42}ClEr$ [**2b**, $Er(HMi)_2Cl$]: C, 61.07; H, 6.73; Cl, 5.63; Er, 26.57. Found: C, 59.98; H, 7.10; Cl, 5.43; Er, 26.96. Calcd for $C_{60}H_{87}ErO_3$ [**3b**, $Er(Hmi)_3 \cdot 3THF$]: C, 70.40; H, 8.57; Er, 16.34. Found: C, 65.98; H, 7.67; Er, 16.30. Calcd for $C_{16}H_{21}Cl_2Nd$ [**1c**, $Nd(Hmi)Cl_2$]: C, 44.85; H, 4.94; Cl, 16.55; Nd, 33.66. Found: C, 43.98; H, 5.44; Cl, 16.71; Nd, 33.60. Calcd for $C_{36}H_{50}ClNdO$ (**2c**, $Nd(Hmi)_2Cl \cdot THF$): C, 63.73; H, 7.43; Cl, 5.23; Nd, 21.26. Found: C, 62.73; H, 7.24; Cl, 5.26; Nd, 21.93. Calcd for $C_{68}H_{103}NdO_5$ (**3c**, $Nd(Hmi)_3 \cdot 5THF$): C, 71.34; H, 9.07; Nd, 12.60. Found: C, 70.84; H, 9.07; Nd, 12.69.

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Table I. ^{13}C NMR Spectral Data for Heptamethylindenyl Complexes of Lanthanum Chloride and Related Derivatives of Heptamethylindene[a]

compd	C(9), C(8)	C(2)	C(7), C(4), C(5), C(6)	C(1), C(3)	$CH_3(4)$, $CH_3(7)$, $CH_3(5)$, $CH_3(6)$	$CH_3(3)$, $CH_3(1)$	$CH_3(2)$
Hmi-H	144.5, 141.6	140.3	131.9, 129.9, 127.3, 125.5	46.0, 132.6	15.7, 15.4, 15.2	14.4, 11.2	15.1
KHmi	123.8	122.9	121.0, 116.8	95.8	16.7, 15.6	13.9	10.7
La(Hmi)$_3$[b]	129.5	124.5	124.4, 124.1	106.3	16.8, 15.6	13.3	10.1
La(Hmi)$_2$Cl[b]	131.0	127.0	124.9, 124.6	107.4	16.9, 15.6	13.8	11.2
La(Hmi)Cl$_2$[b,c]	131.5	127.9	125.7, 125.6	109.0	16.8, 15.6	14.3	11.3

[a] Spectra recorded using THF as solvent and C_6D_6 as internal lock. Chemical shifts referenced to THF (β) = 25.3. Peak assignments are based on the numbering scheme shown in reaction 1. [b] The spectrum of this compound containing a CD_3 group at C(3) was virtually identical with the nondeuterated species ($\Delta\delta$ < 0.4) except for the relative intensity of the $CH_3(1)$, $CH_3(3)$ resonance. [c] This spectrum contained peaks due to 1a and 3a.

all contained <0.5 % chlorine, indicating that KCl was not an impurity in these samples. No significant amount of K was found in **1**, **2**, or **3** using a flame test. In the case of **2a** ^{13}C NMR spectroscopy showed the presence of **1a**, **2a**, and **3a**. Although giving correct analyses, **2b** and **2c** may be similarly contaminated. These complexes are stable as solutions in THF containing 10% benzene-d_6 for up to 1 month at 25 °C as judged by NMR studies of **1a**, **2a**, and **3a**. These complexes were all soluble to the extent of ca. 0.3 M in THF, ether, and hexamethylphosphoramide but were only sparingly soluble in benzene, cyclohexane, and other hydrocarbon solvents. These complexes were unstable in CS_2, alcohols, ketones, and Me_2SO and are very sensitive to oxygen and moisture. Heptamethylindene was typically seen as a minor component of spectroscopic samples and may have resulted either from adventitious hydrolysis or may have been formed as a byproduct (e.g., by reduction of $LnCl_3$ by KHmi) in reaction 1.

NMR characterization of these complexes were confined to **1a**–**3a** because of the paramagnetic nature of **1b**–**3b** and **1c**–**3c**. ^{13}C NMR spectroscopy proved most useful. Each complex could clearly be distinguished from the starting material **4** (Table I). In addition most complexes could be distinguished from each other. The pattern and multiplicity of absorptions seen was consistent with a pentahapto structure for **1a**–**3a** although a trihapto structure was not rigorously excluded. A rapidly equilibrating monohapto structure which would have been in accord with these spectral data was excluded by the absence of any significant shift on substitution of a CD_3 group for a CH_3 group.[12,13] Solutions of **1a** did not disproportionate over the period of a month at room temperature although **1a** and **3a** did disproportionate to form a mixture of **1a**, **2a**, and **3a**.

Complexes **1**–**3** were also characterized by IR and UV–visible spectroscopy.[14] UV–visible spectra of **1**–**3** had maximum absorptions in the UV region at longer wavelength relative to heptamethylindenyl and were very similar to KHmi in THF.[15] The visible spectra of the Nd and Er complexes exhibited the f–f transitions characteristic of the trivalent state of these lanthanide ions.

Taken together these results show that the heptamethylindenyl ligand does indeed allow the isolation of some previously unavailable types of organolanthanide complexes. Further studies of synthesis of other lanthanide complexes of this ligand and applications of the resulting complexes are continuing.

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Registry No. 1a, 80434-36-2; **1b**, 80422-17-9; **1c**, 80422-18-0; **2a**, 80422-19-1; **2b**, 80422-20-4; **2c**, 80422-21-5; **3a**, 80422-22-6; **3b**, 80422-23-7; **3c**, 80434-37-3; **4**, 80422-16-8.

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(12) This deuterated ligand, Hmi-d_3 was prepared by a route similar to that previous described[11] by using CD_3Li instead of CH_3Li.

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(14) HMI and all of its derivatives show similar infrared absorptions. IR (Nujol mull) 1640 (w) and 1580 (w) (C=C and ring skeletal vibration), 1300 (w or m), 1280 (w), 1160 (m), 1100 (m), 1080 (w), 1050 (w), 1020 (s), and 1000 (s) (ring-methyl in-plane deformation), 970 (w), 920 (w), 840 (w), 770 (w), and 660 (w) (ring–methyl out-of-plane deformation) cm^{-1}. The absorption intensities of the complexes are stronger at 1300 cm^{-1} and weaker at 1640 cm^{-1} than those of Hmi–H, respectively. Some complexes show THF absorptions at 1050 and 900 cm^{-1}.

(15) UV spectra in THF: heptamethylindene, 226 and 267 nm; metal complexes, ca. 230 and 270 nm. Visible spectra (nm) in THF: **3c**, 810, 751, 588*, 530, 515; **2c**, 815, 805, 748, 599*, 535, 520; **1c**, 807, 750, 587*, 530; 3b, 980, 657, 558, 525*, 492, 442; **2b**, 978, 655, 557, 523*, 490, 452; **1b**, 986, 660, 552, 530*, 493, 455. Asterisks indicate hypersensitive transitions.

The Laser vs. the Lamp. A Novel Laser-Induced Adiabatic Reaction and Luminescence of Benzophenone

Nicholas J. Turro,* Masayuki Aikawa, and Ian R. Gould

Chemistry Department, Columbia University
New York, New York 10027

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The molecular photophysics and photochemistry of benzophenone and its derivatives in fluid organic solvents represent a keystone in the development and history of mechanistic organic photochemistry.[1] Pulsed laser flash spectroscopy[2] has been an important and powerful method for the determination of the dynamics of quenching and reactions of benzophenone triplets. It is generally assumed that the nature and behavior of the photochemistry and photophysics of a system are qualitatively the same whether laser excitation or conventional steady-state lamp excitation is employed. We report here evidence that a laser, but not a conventional lamp, can induce a novel, unprecedented emission from benzophenone and substituted benzophenones.[3]

Excimer laser excitation (15-ns pulse; 249, 308, or 351 nm) of benzophenone in Freon-113 (5×10^{-5}–10^{-2} M) produces the emission spectra[4] shown in Figure 1. At relatively low laser power (curve c, 18 mJ) the observed spectrum is very similar to the phosphorescence produced by conventional lamp excitation of benzophenone. Increasing the laser power (curves a and b) or using a focused beam results in the observation of a new emission whose maximum (after subtraction of the conventional benzophenone phosphorescence)[5] occurs at 520 nm. This novel emission

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