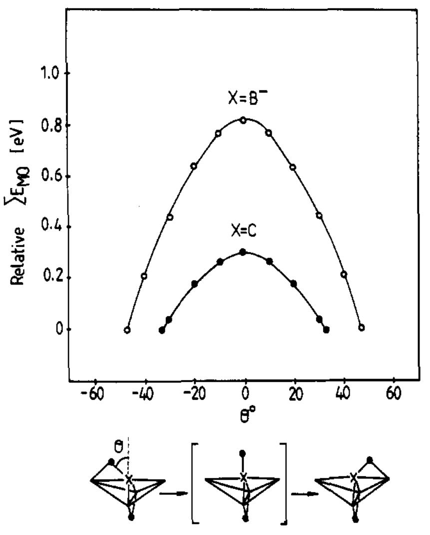

**Figure 2.** A possible mechanism for Fe–H–X exchange between the two FeX "wing-tip" sites and calculated barriers for X = C and B using the extended Hückel method. Zero energies are taken for the experimental geometries in each case.

The $^{13}$C NMR of HFe$_4$(CO)$_{12}$CH in the carbonyl region shows only four types of CO even at −80 °C, thereby showing that a low barrier path for FeHC proton exchange between the two carbon "wing-tip" sites (Figure 2) exists.[7] On the other hand, the $^{13}$C NMR of I in the carbonyl region at −80 °C exhibits six types of CO (seven expected for the static structure), thereby demonstrating that no such low barrier path for the exchange of the FeHB proton between the two boron "wing-tip" sites exists. The process occurring in the former may be envisioned as a simple proton flip between the two carbon "wing-tip" sites as shown in Figure 2.[19] Modeling this process with extended Hückel calculations shows that the barrier associated with this mechanism in I is significantly larger than that in HFe$_4$(CO)$_{12}$CH (Figure 2). This is attributed to a stronger FeH interaction in the FeHX unit when X is boron. Thus, as one goes from HFe$_4$(CO)$_{12}$CH to I, processes in which the XH bond is retained and FeH broken are inhibited by stronger FeH interactions while processes whereby the hydrogen wanders over the cluster framework are enhanced by both stronger FeH and weaker XH interactions.

These observations constitute a basis for understanding some thermodynamic and kinetic factors responsible for moving a hydrogen atom to and away from a main-group atom bound to a multinuclear transition-metal cluster site. If the hydrogen is viewed as a proton, one factor revealed by the calculations and corroborated by the experiments seems rather elementary—the proton seeks maximum charge[20,21] and the greater the difference in availability of charge at potential sites, the greater the barrier to mobility. Phosphine substitution on iron increases the available electron density at adjacent sites, thereby attracting protons from elsewhere in the cluster into deeper potential wells. Carbon "substitution" for boron pulls in electron density and the proton with it. A more subtle point made by this work is the importance of viewing the C (or B) atom as a participant in the cluster framework bonding. Thus, because C(B)–Fe bonding exists, the endo hydrogens can be considered as protons chasing available charge and hydrogenation/dehydrogenation of the C(B)–H moiety can be rapid and easily reversed by relatively small perturbations. This exactly fulfils the requirements for an effective catalytic site.

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**Registry No.** I, 99582-34-0; II, 102132-76-3; III, 102132-77-4.

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[19] There are obviously other mechanisms possible but this is a simple one that makes the point.

[20] This correlation has been suggested to account for the hydrogen locations in simpler systems. DeKock, R. L.; Jasperse, C. P. *Inorg. Chem.* **1983**, *22*, 3839.

[21] Not all possible edge-bridging sites have been calculationally explored. Because energy differences between different hydrogen arrangements are intrinsically small, other factors, e.g., steric, may be important also.

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# Synthetic, X-ray Structural, and Photoluminescence Studies on Pentamethylcyclopentadienyl Derivatives of Lanthanum, Cerium, and Praseodymium

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*Summary:* Reactions of anhydrous lanthanum, cerium, or praseodymium chlorides with 2 equiv of (pentamethylcyclopentadienyl)lithium in THF solution followed by solvent removal and crystallization from diethyl ether afford the crystalline complexes $(\eta^5\text{-}C_5Me_5)_2LnCl_2Li(OEt_2)_2$ (**1**, Ln = La; **2**, Ln = Ce; **3**, Ln = Pr) in good yields. Crystals of **2** belong to the tetragonal space group $P\bar{4}2_1m$ with $a$ = 11.313 (4) Å, $c$ = 12.959 (3) Å, and $D_{calcd}$ = 1.27 g cm$^{-3}$ for $Z$ = 2. Least-squares refinement based on 760 observed reflections led to a final $R$ value of 0.074. The Ce–Cl distance is 2.812 (1) Å. The photoluminescence spectrum of **2** is discussed and interpreted.

Although research concerning the organometallic chemistry of the lanthanides is currently expanding at a rapid rate, comparatively little is known about organic derivatives of the earliest lanthanides La (f$^0$), Ce (f$^1$) and Pr (f$^2$).[1] In particular, lanthanocene chloride complexes of the type (Cp$_2$LnCl)$_x$ are not available for these metals,[2,3] a feature

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[1] (a) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (b) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (c) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, p 173. (d) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.

[2] Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672.

[3] The synthesis and molecular structure of the related neodymium analogue [Cp$_2$NdCl(THF)]$_2$ has been recently described: (a) Chen, W. *Yingyang Huaxue* **1983**, *1*, 55 [*Chem. Abstr.* **1984**, *101*, 192119u]; (b) Chen, W.; Jin, W.; Jin, Z.; Liu, Y., Poster at the NATO-ASI "Fundamental and Technological Aspects of Organo-f-Element Chemistry", Acquafredda di Maratea, Sept 1984.

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that has severely limited the development of their further chemistry. Recently, this problem has been partially overcome by utilizing cyclopentadienyl ligands that contain two bulky trimethylsilyl substituents[4] and by bridging the two cyclopentadienyl ligands.[5,6]

The utility of the pentamethylcyclopentadienyl ligand in the stabilization of $[(C_5Me_5)_2LnCl]_x$ derivatives of other lanthanides[1,7-10] and yttrium[11] suggested to us that pentamethylcyclopentadienyl derivatives of the three earliest lanthanides might be stabilized in a similar manner. In this communication, we report on the synthesis and spectroscopic properties of the first pentamethylcyclopentadienyl complexes of lanthanum, cerium, and praseodymium, as well as the results of the first X-ray crystallographic investigation and photoluminescence study of a cyclopentadienylcerium compound.[12]

Reactions of anhydrous lanthanum, cerium, or praseodymium trichlorides with 2 equiv of (pentamethylcyclopentadienyl)lithium in tetrahydrofuran (THF) solution, followed by removal of the solvent and crystallization of the products from diethyl ether, afford crystalline complexes of the composition $(\eta^5\text{-}C_5Me_5)_2LnCl_2Li(OEt_2)_2$ (**1**, Ln = La; **2**, Ln = Ce; **3**, Ln = Pr) in 60–70% yields.[13] All operations must be carried out under an atmosphere of prepurified argon, since **1**–**3** are extremely air-sensitive. The pale yellow lanthanum complex **1** is diamagnetic, and its $^1H$ NMR spectrum ($CDCl_3$) exhibits a sharp singlet resonance at $\delta$ 1.92 for the equivalent methyl protons. The praseodymium complex **3** is pale green, whereas the cerium analogue **2** is bright yellow. Vacuum sublimation (300–320 °C ($10^{-4}$ torr)) of the residue from the cerium trichloride/(pentamethylcyclopentadienyl)lithium reaction over a period of 3 days likewise produces a bright yellow sublimate which on the basis of analytical and spectral data is postulated to be the neutral complex $[(C_5Me_5)_2CeCl]_2$ (**4**, 83% yield).[14]

The structure of **2** is shown in Figure 1.[15] The overall geometry is quite similar to that of the related early lanthanide complex $[\eta^5\text{-}C_5H_3(SiMe_3)_2]_2Nd(\mu\text{-}Cl)_2Li(THF)_2$,[4] but the cerium derivative is in fact isostructural with $(\eta^5\text{-}C_5Me_5)_2Yb(\mu\text{-}I)_2Li(OEt_2)_2$.[16] Apparently, the combination of the larger cerium ion and the smaller chloride just balance the smaller ytterbium ion and the larger iodide. The Ce–Cl distance of 2.812 Å is larger by 0.03 Å than that predicted[17] from either the Nd–Cl length of 2.744 Å or the Y–Cl length of 2.595 (1) Å.[16] It is, however, shorter than the 2.855 (2) and 2.935 (2) Å values found in $[Ce(C_8H_8)Cl{\cdot}2OC_4H_8]_2$.[18]

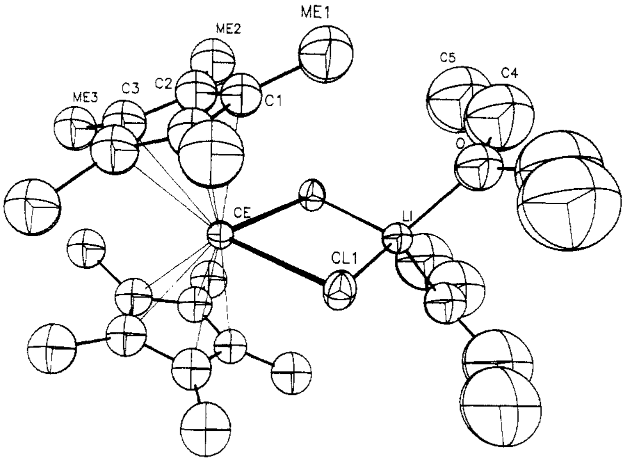

**Figure 1.** The molecular structure of **2**, which lies on a crystallographic mm site.

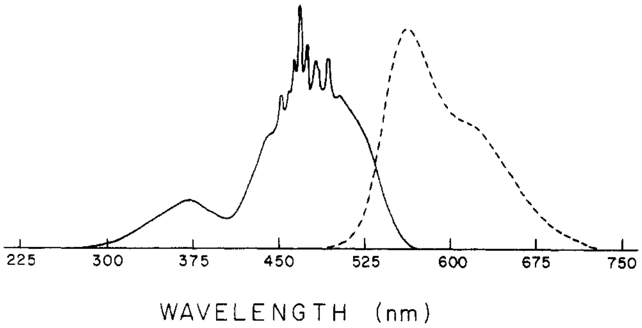

**Figure 2.** Room-temperature excitation (solid trace) of **2** obtained while monitoring the emission spectrum at 560 nm. The emission spectrum (dashed trace) was obtained by using an excitation wavelength of 480 nm.

Photoluminescence spectra obtained upon excitation of **2** and **4** were found to be identical and extremely intense. The room-temperature excitation and emission spectra for **2** as obtained in the solid state are shown in Figure 2. The luminescence spectrum consists of two overlapping bands split by approximately 1530 $cm^{-1}$, and this separation corresponds to the spin–orbit splitting of the $^2F$ ground state.[20] The excitation spectrum consists of two well-resolved band systems, one of which was found to exhibit fine structure on top of a broad background. Each band represents a transition from the $^2F_{5/2}$ ground level to ex-

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(8) Tilley, T. D.; Anderson, R. A. *Inorg. Chem.* **1981**, *20*, 3267.

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(10) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.

(11) Evans, W. J.; Peterson, T. J.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554.

(12) After this study had been completed, the synthesis of the lanthanum analogue **1** was independently described: Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(13) In a typical preparation, 2.0 g (8.1 mmol) of $PrCl_3$ was slurried in dry THF and solid $C_5Me_5Li$ (2.3 g, 16.2 mmol) was added at room temperature. The mixture was heated to reflux for 12 h, the solvent was removed under vacuum, and the residue was extracted with diethyl ether. The extracts were filtered through a plug of Celite, and the filtrate was concentrated until crystals began to form. The solution was cooled to −20 °C, and the pale-green crystals were collected and dried (3.2 g, 62%). Anal. Calcd for $C_{28}H_{50}Cl_2LiO_2Pr$: C, 52.75; H, 7.91. Found: C, 52.55; H, 7.71.

(14) Anal. Calcd for $C_{20}H_{30}ClCe$: C, 53.85; H, 6.78. Found: C, 53.40; H, 6.61. $^1H$ NMR (THF-$d_8$); $\delta$ 2.95 (very br). Complex **4** is also extremely air-sensitive.

(15) Single crystals of **2** were obtained by crystallization from diethyl ether. The compound crystallizes in the tetragonal space group $P\bar{4}2_1m$; cell constants $a$ = 11.313 (4) Å, $c$ = 12.959 (3) Å, and $D_{calcd}$ = 1.27 g $cm^{-3}$ for $Z$ = 2. Least-squares refinement based on 760 observed reflections ($I \geq 3\sigma(I)$) led to a final $R$ value of 0.074 ($R_w$ = 0.086). An empirical absorption correction was performed. The data-to-parameter ratio was 16, and the GOF was 1.4. All atoms were corrected for anomalous dispersion effects. The terminal carbons atoms of the diethyl ether groups suffered from such extensive disorder that they only appeared as a smear of electron density on the final difference Fourier map. Nevertheless, it was possible to refine the positional and isotropic thermal parameters of this atom. Expectedly, the latter was exceptionally large. Only the cerium and chlorine atoms were treated with anisotropic thermal parameters. The details of data collection and refinement are as given by Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

(16) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.

(17) Based on a comparison of ionic radii: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Interscience: New York, 1980; p 982.

(18) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 171.

(19) Luminescence spectra were obtained on a 2:2:2 Spex Fluorolog-II instrument, with a 1-nm band-pass being used for all data collections.

cited states derived from the $5d^1$ configuration. The splitting of the 5d excited states is a consequence of crystal field interactions.[20]

Ce(III) photoluminescence in both 2 and 4 was observed at significantly lower energies than is normally found for Ce(III)-activated oxidic phosphors,[21,22] indicating the presence of sizable nephelauxetic effects in the metal-ligand bonding. These observations are consistent with the existence of significant covalency in the Ce(III) bonding. Comparable effects have been noted in examinations of the photoluminescence associated with Tb(III) cyclopentadienyl compounds.[23]

**Acknowledgment.** We are grateful to the National Science Foundation for grants in support of this research program.

**Supplementary Material Available:** Tables of bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(20) Blasse, G.; Bril, A. *Philips Tech. Rev.* **1970**, *31*, 1970.

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# *Additions and Corrections*

A. Dale Harley, Robert R. Whittle, and Gregory L. Geoffroy*: Crystal and Molecular Structures of Bent and Planar Forms of Binuclear $Co_2(\mu\text{-}PPh_2)_2(CO)_6$ (1). Comments on the Relative Energies of the Two Forms of 1 and Related Molecules. **1983**, *2*, 383.

The crystal structure of 1 was incorrectly solved in the space group *Ia* (No. 9, nonstandard setting of *Cc*) but using the symmetry-equivalent positions of *Cc*. The structure has been completely resolved by using the original data and correct symmetry-equivalent positions for *Ia* to final residuals of $R = 0.034$ and $R_w = 0.043$. There were no significant changes in the structures of the two independent molecules of 1 with only minor modifications in bond lengths and angles. We sincerely thank W. C. Fultz (present address J. C. Huber Co.) for assistance in the final structure solution.

**Supplementary Material Available**: Complete tables of atomic positional parameters, bond lengths and angles, symmetry operations, and structure factors and Figure 1, ORTEP drawing of molecule 1, Figure 2, ORTEP drawing of molecule II, Figure 3, ORTEP drawing of molecule I viewed down the Co–Co axis, and Figure 4, ORTEP drawing of molecule II viewed down the Co–Co axis (26 pages). Ordering information is given on any current masthead page (also available from the authors upon request).

Charles Kutal,* Michael Weber, Guillermo Ferraudi,* and David Geiger: A Mechanistic Investigation of the Photoinduced Reduction of Carbon Dioxide Mediated by Tricarbonylbromo(2,2′-bipyridine)rhenium(I). **1985**, *4*, 2161–2166.

On p 2164, in section d under Results and Discussion, the fifth sentence should read "...bands arising from $\pi$–$\pi^*$ and $\pi^*$–$\pi^*$ transitions have been identified at 386 and 530–560 nm, respectively, ...".