metal atoms and solvent molecules. The final atomic coordinates are shown in Table VII.

All calculations were performed on a GOULD SEL 32/37 computer, using the GX program package.[29] Neutral-atom scattering factors were taken from ref. 30.

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a listing of observed and calculated structure amplitudes (20 pages). Ordering information is given on any current masthead page.

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Syntheses of Organolanthanum and -cerium Cations and Labile Precursors

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The lanthanide–iodide compounds $Cp''_2Ln(I)(NCMe)_2$ (Ln = La, Ce; $Cp'' = 1,3\text{-}C_5H_3(SiMe_3)_2$) serve as useful precursors for complexes containing the early-lanthanide fragments $[Cp''_2Ln^{III}]^+$. This moiety has been incorporated into compounds in which it binds either neutral or anionic ligands. Among these is the heterobimetallic compound $[Cp''_2Ce(\mu\text{-}\eta^2\text{-}OC)W(CO)(Cp)(\mu\text{-}\eta^2\text{-}CO)]_2$ (**3**), which is unusual in that the cerium(III) center is wholly nonemissive. This observation is explained on the basis of cerium-to-tungsten excited-state energy transfer, since dissolution in polar solvent (acetonitrile) leads to symmetrically solvated ions, loss of close Ce–W contact, and cerium(III) luminescence. Also, the cationic organolanthanide fragments have been seen to bind tetrafluoroborate anion, exhibiting an interesting trend in ligand lability; thus, in $Cp''_2Ln(NCMe)_2(FBF_3)$ (**4**), the nitrile ligands are more labile in THF solution than is the tetrafluoroborate ligand. Finally, the ionic compounds $[Cp''_2Ln(NCMe)(DME)][BPh_4]\cdot 0.5DME$ (**5**) have been prepared and the lanthanum analogue (**5b**) has been structurally characterized.

Introduction

Although the organometallic chemistry of the lanthanide elements has been developing rapidly for several years now,[1] it is apparent that much of this work has focused on the later lanthanides. The chemistry of these metals has proved diverse and interesting, and its development is facilitated by the variety of ligand spheres with which these smaller lanthanides can be stabilized. The earlier, larger lanthanides require a greater degree of steric saturation and have yet to exhibit many of the coordination spheres seen for later lanthanides. In spite of these apparent limitations, there are obvious reasons for pursuing early-lanthanide chemistry. Among the lanthanides, only cerium exhibits a stable +4 oxidation state.[2] While the oxidizing power of Ce(IV) is frequently utilized in organic syntheses,[3] this oxidation state has been observed in the stable organometallic compounds $(C_8H_8)_2Ce$ and $(Cp)_3Ce(O^iPr)$ ($Cp = \eta^5\text{-}C_5H_5$);[4] the former has been shown to be remarkably stable toward hydrolytic decomposition and is reduced to the trivalent anion $[(C_8H_8)_2Ce]^-$ only at very negative potentials.[4b] Also, the chemistries of trivalent lanthanum and cerium have been the subjects of several recent studies, in spite of the difficulties in achieving steric saturation. These efforts are in part spurred by the observation that the early lanthanides are very active catalysts for the polymerization of dienes and highly substituted olefins;[5] the catalysts are derived from mixtures of aluminum alkyls (e.g., $EtAlCl_2$) and either LnX_3 (X = Cl, Br)[5a] or $Ln(acac)_3$,[5b] and the most active catalysts contain Ce, Pr, or Nd. Additionally, $(Cp^*)_2LaCH(SiMe_3)_2$ and related derivatives ($Cp^* = \eta^5\text{-}C_5Me_5$) constitute highly active catalysts or catalyst precursors in olefin hydrogenations, oligomerizations, and hydroamination systems.[6] This is significant since the lanthanides' terrestrial abundance percentages decrease in the order Ce > Nd > La > Gd, etc.[7]

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Recent studies on lanthanum and cerium systems have provided organometallic compounds with a variety of ligand spheres. Rausch,[8] Schumann,[9] and Teuben[10] have prepared Cp* derivatives of the type $[M(L)_x][(Cp^*)_2LnCl_2]$, while Evans has shown that the potassium counterion in $\{[K(THF)][(Cp^*)_2CeCl_2]\}_x$ can support polymerization via triply bridging chlorides.[11] Additionally, the interesting hydride compounds $[Cp^*{}_2LnH]_2$ have been prepared via Ln–alkyl hydrogenolysis.[6a,10] Related compounds utilizing other cyclopentadienyl substitutes include the hydridotripyrazolylborate compound $[HBPz_3]_2Ce(acac)$[12] and the $1,3\text{-}C_5H_3(SiMe_3)_2$ (=Cp″) derivatives $[Cp''{}_2LnCl]_2$ and $[M(L)_2][Cp''{}_2LnCl_2]$.[13] We have shown that the complexed KI can be removed from $[K(THF)_2][(Cp^*)_2CeI_2]$ to give the formally 9-coordinate $(Cp^*)_2Ce(I)(NCMe)_2$,[14] a derivative of which was also prepared by Teuben via an alternate route.[10b] In Cp systems, series of $(Cp)_3Ln(L)$ and $(Cp)_3Ln(L)_2$ are known;[15] also, recent work by Thiele has led to the preparation of $[Na][(Cp)_4Ce]$ and $[(Cp)_2Co][(Cp)Ce(acac)_3]$.[16] The latter is one of few mono-ring derivatives of lanthanum or cerium; $(Cp^*)Ln(I)_2(THF)_3$,[17] $(Cp^*)Ln[CH(SiMe_3)_2]_2$, and $(Cp^*)Ce(OAr)_2$ (OAr = 2,6-di-*tert*-butylphenoxide)[18a–c] are also known. The last compound relieves some of its steric unsaturation by engaging in a weak interaction with a methyl group of one OAr ligand,[18a] while the lanthanum alkyl compound contains an agostic Si–C bond.[18d] Finally, alkyl compounds with lower formal coordination numbers are also known; examples include Schumann's $[Li(tmeda)]_3[LnMe_6]$[19] and Lappert's $La[CH(SiMe_3)_2]_3$ and related $La[CH(SiMe_3)_2]_3X^-$ derivatives.[20]

Another interesting aspect of cerium(III) chemistry is derived from the fact that trivalent cerium exhibits highly efficient luminescence from an excited state that is $4f^0 5d^1$ in nature.[21] This type of process differs considerably from that exhibited by other emissive Ln(III) compounds, in which the transition is contained within the f-orbital manifold; this has been amply demonstrated by the studies of Blasse and co-workers.[21e–h] We have utilized this efficient luminescence as an indicator of the behavior of organocerium(III) species in solution, since the emission is highly sensitive to the nature of the cerium coordination environment.[14,22] In our initial studies we sought an alternative analytical tool with which to veryify the luminescence-derived conclusions. This led us to prepare heterobimetallic derivatives containing ligated carbonylmetalate anions, since infrared spectroscopy is a sensitive probe of their solution structure.[14,23] Further studies allowed us to conclude that polar solvents cause the labilization of these ligands, and we recently communicated our observation of a cationic organocerium(III) species in solution.[23] Cationic compounds of the early transition metals and actinides have only recently been prepared,[24] and in some cases they exhibit useful catalytic activity. Herein we describe the syntheses, structures, and coordination behaviors of compounds containing the $[Cp''{}_2Ln^{III}]^+$ moiety (Ln = La, Ce).

Experimental Section

General Methods. Proton and fluorine NMR spectra were obtained on a Varian XL-400 FT-NMR intrument. Solution infrared spectra were obtained in 0.05 mm path length liquid cells on a Perkin-Elmer M1500 FT-IR spectrophotometer. Luminescence spectra were recorded on a Perkin-Elmer MPF-44A fluorimeter, and luminescence lifetimes were determined with a picosecond laser single-photon-counting system described previously.[14] Solution molecular weight measurements were determined by the Signer isothermal distillation method[25] in a glass apparatus that was constructed locally. Elemental analyses were performed by Oneida Research Serivces, Inc., Whitesboro, NY.

All manipulations were carried out under an atmosphere of either nitrogen or argon. Both gases were dried and deoxygenated by passage through columns of Linde 4A molecular sieves and activated BTS catalyst. Solutions were handled with use of Schlenk techniques in glassware equipped with Solv-seal joints and high-vacuum valves, while solids were transferred in a Vacuum Atmospheres Corp. glovebox under nitrogen. Benzene, tetra-

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hydrofuran, hexane, diethyl ether, and dimethoxyethane were purchased from J. T. Baker, predried over activated molecular sieves, and distilled under nitrogen from sodium benzophenone ketyl. Toluene (Baker) was treated similarly but was distilled from sodium alone. Acetonitrile (Aldrich Gold Label) was distilled from P_2O_5 and then from calcium hydride under nitrogen. NMR solvents C_6D_6, THF-d_8, and toluene-d_8 were freeze–thaw-degassed and vacuum-distilled from sodium–potassium alloy, while CD_3CN and CD_2Cl_2 were freeze–thaw-degassed and vacuum-distilled from P_2O_5. Cerium and lanthanum metal chips, silver tetrafluoroborate, tungsten hexacarbonyl, and sodium tetraphenylborate were purchased from Aldrich Chemical Co. and used as received. The compound 1,3-bis(trimethylsilyl)cyclopentadiene (Cp″H) was prepared according to the literature procedure[26] and metalated with potassium hydride in THF. The compounds $CeI_3(THF)_x$ (x = 3 4),[17] $[K][CpW(CO)_3]$,[27] and $AgBPh_4$[28] were prepared via the literature methods.

$[K(THF)_x][Cp''_2CeI_2]$ (1). Crystalline $CeI_3(THF)_x$ (2.50 g, ca. 3.2 mmol) was suspended in 100 mL of THF. To this solution was slowly added 3.50 g (7.12 mmol) of Cp″K. The solution turned bright yellow and was stirred at 25 °C overnight. The solvent was removed in vacuo, leaving a green residue. This residue was extracted with 70 mL of toluene and the filtrate dried in vacuo. The compound could be crystallized from THF/Et_2O with some difficulty and loss of yield; this gave yellow-green needles, which were analyzed as $[K(THF)_{1.5}][Cp''_2CeI_2]$. Anal. Calcd for $C_{28}H_{54}Si_4CeI_2KO_{1.5}$: C, 35.00; H, 5.63. Found: C, 34.47; H, 5.69. IR (Nujol): 1245 (m), 1079 (m), 920 (m), 837 (s, br), 753 (m) cm^{-1}. NMR (THF-d_8): signals for free THF at 3.56 and 1.78 ppm; 1.29 (br s, Cp″ H) and −0.05 (s, $SiMe_3$) ppm.

$Cp''_2Ce(I)(NCMe)_2$ (2a). The compound $[K(THF)_x]$-$[Cp''_2CeI_2]$ was prepared as above from 2.50 g (3.2 mmol) of $CeI_3(THF)_x$ and 3.50 g (7.12 mmol) of Cp″K. After extraction with toluene, the residue was treated with 25 mL of MeCN. This gave rise to a yellow-green precipitate, which was filtered and dried in vacuo. A second crop was obtained similarly from the filtrate; combined yield 2.13 g, 82%. The compound can be recrystallized by slow cooling of a warm MeCN solution. IR (Nujol): 2304 (w), 2275 (m), 1248 (s), 1081 (s), 921 (m), 832 (vs), 795 (w), 787 (w), 750 (m) cm^{-1}. ^1H NMR (THF-d_8): 1.3 (6 H, CH_3CN), −0.24 (36 H, $SiMe_3$), −1.55 (4 H, H4 and H5 of Cp″), −1.89 (2 H, H2 of Cp″) ppm. The lanthanum analogue $Cp''_2La(I)(NCMe)_2$ (**2b**) was prepared similarly. ^1H NMR (THF-d_8): 6.84 (2 H, H2 of Cp″), 6.65 (4 H, H4, H5 of Cp″), 2.09 (6 H, MeCN), 0.34 (36 H, $SiMe_3$) ppm. Anal. Calcd for $C_{26}H_{48}N_2Si_4ILa$: C, 40.66; H, 6.30; N, 3.94. Found: C, 40.94; H, 6.32; N, 3.64.

$[Cp''_2Ce(\mu\text{-}\eta^2\text{-}OC)W(CO)(Cp)(\mu\text{-}\eta^2\text{-}CO)]_2$ (3). A solution was prepared by adding 2.5 g (3.2 mmol) of $Cp''_2Ce(I)(NCMe)_2$ to 80 mL of THF. To this was added 1.3 g (4.2 mmol) of $[K][CpW(CO)_3]$ and the resulting suspension stirred overnight. The solvent was removed in vacuo and the residue extracted with toluene. The toluene was removed in vacuo and the residue dissolved in 20 mL of diethyl ether. Slow cooling to −78 °C caused the precipitation of large yellow cubes, which were filtered and dried in vacuo (2.3 g, 76%). IR (Nujol): 2026 (w), 1934 (s), 1923 (s), 1770 (m), 1738 (s), 1715 (s), 1646 (s), 1249 (s), 1241 (w), 1081 (m), 1013 (w), 923 (w), 837 (m), 750 (w), 721 (w) cm^{-1}. IR (THF): 2019 (w), 1914 (s), 1824 (s), 1673 (w, sh), 1645 (s) cm^{-1}. IR (CH_3CN): 2020 (w), 1922 (w), 1892 (s), 1773 (s) cm^{-1}. ^1H NMR (THF-d_8): 5.2 (Cp), 0.12 ($SiMe_3$), −0.7 (broad, H2, H4, H5 of Cp″) ppm. Anal. Calcd for $C_{60}H_{94}Si_8O_6W_2Ce_2$: C, 40.39; H, 5.31. Found: C, 40.36; H, 5.23. A molecular weight study in THF (Signer method) indicated a value of ca. 800. A mixed Ce–La analogue was prepared as above with use of 1.0 g (1.31 mmol) of $Cp''_2La(I)(NCMe)_2$, 0.25 g (0.33 mmol) of $Cp''_2Ce(I)(NCMe)_2$, and 0.61 g (1.64 mmol) of $[K]$-$[CpW(CO)_3]$. ^1H NMR (THF-d_8): 6.72 (H4, H5 of La–Cp″), 6.40 (H2 of La–Cp″), 5.31 (W–Cp), 0.39 ($SiMe_3$ of La–Cp″), 0.12 ($SiMe_3$ of Ce–Cp″) ppm. Integration of the last two resonances indicated a 4:1 ratio of La and Ce sites.

$Cp''_2Ce(NCMe)_2(BF_4)\cdot Et_2O$ (4a). In one flask, 1.5 g (1.95 mmol) of $Cp''_2Ce(I)(NCMe)_2$ was suspended in 75 mL of toluene. In a separate flask, 0.462 g (2.2 mmol) of $AgBF_4$ was suspended in 15 mL of toluene. The flasks were connected with use of a vacuum valve adaptor, and the cerium-containing flask was cooled to −78 °C while the $AgBF_4$ suspension was poured in slowly; the resulting suspension was stirred at −78 °C for ca. 1.5 h and at −10 °C for 20 min. The cold reaction mixture was filtered through Celite and the toluene removed in vacuo. Ca. 15 mL of hexane was added, and the resulting pale yellow precipitate was isolated by filtration and dried in vacuo (0.89 g, 66%). It can be recrystallized from CH_3CN/Et_2O at −78 °C to give **4a**. IR (Nujol): 2304 (w), 2270 (m), 1254 (m), 1195 (m), 1087 (s), 923 (m), 839 (vs), 759 (m) cm^{-1}. ^1H NMR (CD_3CN): 35.79 (4 H, H4, H5 of Cp″), −0.21 (36 H, $SiMe_3$), −5.2 (2 H, H2 of Cp″) ppm; as well as resonances for free Et_2O and CH_3CN. The lanthanum analogue $Cp''_2La(NCMe)_2(BF_4)\cdot Et_2O$ (**4b**) was prepared similarly. ^1H NMR (THF-d_8): 6.63 (6 H, H2, H4, H5 of Cp″), 2.04 (6 H, MeCN), 0.22 (36 H, $SiMe_3$) ppm; as well as resonances for Et_2O. Anal. Calcd for $C_{30}H_{58}N_2Si_4OBF_4La$: C, 44.99; H, 7.2; N, 3.49. Found: C, 44.38; H, 6.88; N, 3.21. The ^{19}F NMR data are discussed in the text.

$[Cp''_2Ce(DME)(NCMe)][BPh_4]\cdot 0.5DME$ (5a). In a gas-inlet flask a solution was prepared by dissolving 0.5 g (0.65 mmol) of $Cp''_2Ce(I)(NCMe)_2$ in 30 mL of THF. In a separate flask, 0.311 g (0.73 mmol) of freshly prepared $AgBPh_4$ was suspended in 5 mL of THF. The flasks were connected with use of a vacuum valve adaptor, and the cerium-containing flask was cooled to −78 °C while the $AgBPh_4$ suspension was poured in slowly. The resulting suspension was stirred at −78 °C for 1 h and then warmed to 25 °C and stirred for 10 min. The mixture was filtered through Celite and the filtrate dried in vacuo. The residue was dissolved in DME containing a few drops of CH_3CN, and Et_2O was allowed to diffuse in slowly. This resulted in well-formed yellow-brown cubes (72%). IR(Nujol): 2300 (w), 2264 (m), 1581 (w), 1248 (m), 1079 (s), 1031 (m), 922 (m), 834 (s), 741 (m), 729 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): 37.7 (br s, H4, H5 of Cp″), 6.69, 6.60 (m, B–Ph), −0.135 (br s, $SiMe_3$), −3.45 (br s, DME CH_3 and CH_2), −4.80 (br s, CH_3CN), −6.90 (br s, H2 of Cp″) ppm. The lanthanum analogue $[Cp''_2La(DME)(NCMe)][BPh_4]\cdot 0.5DME$ (**5b**) was prepared similarly and isolated as colorless cubes (75%). ^1H NMR (CD_2Cl_2): 7.45, 7.16, 7.01 (20 H, BPh_4), 6.70 (4 H, H4, H5 of Cp″), 6.60 (2 H, H2 of Cp″), 3.55 (ca. 9 H, $-OCH_3$), 3.51 (ca. 6 H, CH_2O-), 2.11 (3 H, MeCN), 0.34 (36 H, $SiMe_3$) ppm. Satisfactory elemental analyses could not be obtained for these compounds, and the crystallographic study (see below) provided evidence for partial occupancy in the lattice DME sites.

X-ray Crystallography. The structure of **5b** was determined crystallographically with use of a crystal that measured 0.65 × 0.50 × 0.15 mm. The crystal was mounted in a capillary, which was then sealed under nitrogen, and diffraction measurements were made on an Enraf-Nonius CAD4 fully automated diffractometer. Preliminary indications of the unit cell based on 25 randomly selected reflections revealed monoclinic symmetry. The space group, on the basis of the systematic absences, was uniquely assigned as $P2_1$ (No. 4) with one molecule of composition $C_{52}H_{70}LaNO_2Si_4B$ and a half-occupied site of solvent DME forming the asymmetric unit. There were 5745 unique reflections collected, with $2\theta \leq 50°$; of those, 3808 with $I \geq 3\sigma(I)$ were judged observed. The structure was solved by locating the position of the lanthanum atom with use of the Patterson function. Iterative use of the WFOURIER option in DIRDIF revealed the entire non-hydrogen structure. The hydrogens were calculated and input at their idealized positions. The full-matrix refinement of the non-hydrogen atoms and input of hydrogen scattering factors resulted in a convergence of the reliability factor to an unweighted residual of 0.045 and a weighted residual of 0.057. Disorder was observed in the partially occupied lattice DME positions, so these positions were held fixed during subsequent refinement; it proved impossible to distinguish oxygen and carbon atoms, so the system was modeled as a six-carbon fragment. Refinement of both configurations led to indistinguishable residual factors, and the absolute configuration was thus not determined; the set of metrical parameters presented herein is clearly the more reasonable of the two. Crystal data are collected in Table I.

Results and Discussion

Preparation of Cp″-Substituted Precursors. The use of the Cp″ ligand for organolanthanide and organo-

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[26] Fritz, H. P.; Kreiter, C. G. *J. Organomet. Chem.* **1965**, *4*, 313–319.

[27] King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1, pp 161–163.

[28] Popovych, O. *Anal. Chem.* **1966**, *38*, 117–119.

Table I. Crystal Data for 5b

empirical formula	$C_{58}H_{70}Si_4O_2NBLa$
color of cryst	colorless
cryst dimens, mm	0.65 × 0.50 × 0.15
space group	$P2_1$ (No. 4)
unit cell dimens[a]	
a, Å	11.147 (5)
b, Å	15.675 (4)
c, Å	18.168 (7)
α, γ, deg	90
β, deg	96.28 (3)
Z (molecules/cell)	2
V, Å^3	3105 (2)
d(calcd), g/cm^3	1.36
wavelength, Å	0.71069
mol wt	1075.25
abs coeff, cm^{-1}	5.73

[a] 25 °C; 25 reflections.

actinide chemistry has been pioneered by Lappert and co-workers.[13,29] Their studies indicate that this ligand has a steric bulk which is sufficient to stabilize large metal centers to an extent which is comparable to that of Cp*; thus, many of the compounds are similar in the two series. Like Cp*, the Cp″ ligand is known to enhance solubility and crystallinity. However, there are also some significant differences, not the least of which is the fact that a single metal center can accommodate three Cp″ ligands. Thus, the compound Cp''_3Th has been prepared and structurally characterized,[30] while no Cp^*_3M compounds are known. Apparently, while Cp″ has a larger cone angle than Cp*, it is also able to pack more efficiently because of its unsymmetrical nature. In a similar vein, we have concentrated on the use of iodide ligands rather than the more common chlorides. We have found that the iodides are more effective leaving groups in $[Cp^*_2CeX_2]^-$, which is readily converted to the neutral adduct $Cp^*_2Ce(I)(NCMe)_2$ upon dissolution in acetonitrile.[14]

With the above considerations in mind, we attempted the preparation of $[K(ether)_n][Cp''_2CeI_2]$ via the reaction of KCp″ with the known[17] $CeI_3(THF)_x$ (x = 3, 4). This proceeded as indicated in eq 1 to the yellow-green compound 1, which proved very difficult to precipitate.

$$\mathrm{CeI_3(THF)}_x + 2\mathrm{KCp''} \xrightarrow[\mathrm{THF}]{} [\mathrm{K(THF)}_n][\mathrm{Cp''_2CeI_2}] + \mathrm{KI} \quad (1)$$

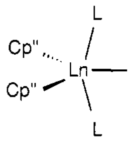
With some effort, the compound could be crystallized from a mixture of THF/diethyl ether, but the yield of this crystallization was low. Elemental analysis was consistent with a value of 1.5 for n. This result seems to preclude a formulation involving loss of coordinated KI (e.g., $Cp''_2CeI(THF)$ or $[Cp''_2CeI]_2$), but it does not allow us to rule out the possibility that the crystallized product adopts a polymeric structure similar to that reported by Evans for $\{[K(THF)][(Cp^*)_2CeCl_2]\}_x$;[11] indeed, it may be that we have crystallized a minor component of a mixture which consists primarily of a more soluble salt-free compound. The Experimental Section contains spectroscopic data for this compound, the formulation of which must be considered tentative. We have not pursued this matter further because of the low yield of crystalline product and the ready availability of the alternative described below. However, it should be noted that the crystalline compound exhibits a luminescence maximum of 536 nm (1 mM THF solution, excitation wavelength 304 nm) and an emission lifetime of 163 ns; these data can be compared to those found for the chloride analogue $[Li(OEt_2)_2][Cp''_2CeCl_2]$, which was found to exhibit an emission wavelength (solid state) of 547 nm and a lifetime of 130 ns.[14]

If the reaction in eq 1 is carried out as described and the crude product instead treated with acetonitrile, the result is precipitation of yellow-green $Cp''_2Ce(I)(NCMe)_2$ (**2a**, eq 2) in 82% overall yield from $CeI_3(THF)_x$. A similar reaction for the lanthanum analogue results in colorless **2b**.

$$[\mathrm{K(THF)}_n][\mathrm{Cp''_2LnI_2}] \xrightarrow{\mathrm{MeCN}} \mathrm{Cp''_2Ln(I)(NCMe)_2} + \mathrm{KI} \quad (2)$$

2a, Ln = Ce
2b, Ln = La

Both compounds exhibit infrared bands at 2304 and 2275 cm^{-1}, consistent with the presence of the nitrile ligands. The crystallographically characterized $Cp^*_2Ce(I)(NCMe)_2$ exhibits a distorted-trigonal-bipyramidal geometry with axial nitrile ligands and an N–Ce–N angle of 150.1 (5)° resulting from the fact that the nitrile ligands bend toward the iodide and away from the Cp* ligands.[14] On the basis of the spectral similarities we propose a related coordination geometry for **2a** and **2b**, although the degree of distortion away from a perfect trigonal bipyramid remains uncertain.



proposed geometry for **2a** *and* **2b** (L = MeCN)

In addition, compound **2a** was found to exhibit a luminescence maximum at 580 nm in 1 mM toluene solution (excitation wavelength 340 nm), but we were unable to determine an emission lifetime. As observed previously, then, acetonitrile is a good ligand in these systems because it readily displaces the complexed salt and gives rise to highly crystalline compounds that are easily precipitated from dry acetonitrile in good yield.

Preparation of a Cerium–Tungsten Metallacycle. Compound **2a** was treated with $[K][CpW(CO)_3]$ so as to replace the iodide ligand with a more labile carbonylmetalate ligand. This reaction gave rise to a yellow solid (**3**, eq 3) that exhibited several terminal CO stretching frequencies and a broad envelope of bands at ca. 1646 cm^{-1}.

$$\mathbf{2a} + [\mathrm{K}][\mathrm{CpW(CO)_3}] \xrightarrow[\mathrm{THF}]{} \tfrac{1}{2}[\mathrm{Cp''_2Ce}(\mu\text{-}\eta^2\text{-OC})\mathrm{W(Cp)(CO)}(\mu\text{-}\eta^2\text{-CO})]_2 + \mathrm{KI} \quad (3)$$

3

In THF solution the spectrum simplified somewhat, containing strong terminal CO bands at 1914 and 1824 cm^{-1}, as well as a strong band at 1645 cm^{-1}. Finally, in MeCN solution the spectrum contained strong bands at 1892 and 1773 cm^{-1}, which can be assigned to the symmetrically solvated anion $[CpW(CO)_3]^-$.[31] If, however, the MeCN was removed in vacuo and the compound redissolved in THF, the original THF spectrum was regenerated. We have communicated the single-crystal X-ray structure of **3** previously.[23] It was found to consist of a centrosymmetric dimer of heterobinuclear adducts, exhibiting a 12-membered-ring structure. As is implied by the representation shown, the 12-membered ring is elongated such that the two cerium centers are closer in space than are the two tungsten centers.

The ability of carbonylmetalates to function as oxygen-centered Lewis bases is well understood.[31] Such a

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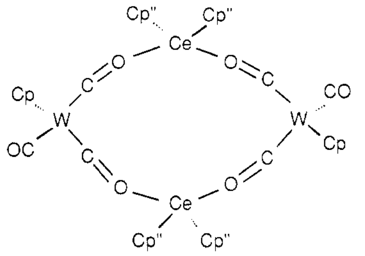
[29] Hitchcock, P. B.; Lappert, M. F.; Michalczyk, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2635–2641.

[30] Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1148–1150.

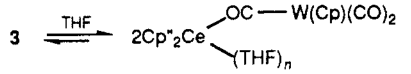
[31] (a) Horowitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219–305. (b) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221–274.



solid-state structure of **3**

process has the effect of drawing electron density into the bridging carbonyl ligand, lowering its stretching frequency substantially. This also has the effect of removing electron density from the terminal carbonyls, as evidenced by the blue shift in their stretching frequencies upon adduct formation. As such, it is unusual for one carbonylmetalate to utilize two carbonyl ligands in bridging, and only two other examples of this phenomenon are known.[32]

Molecular weight studies and infrared studies indicate that in THF solution the 12-membered ring fragments into 2 equiv of the Ce–W dimer. The calculated molecular weight for such a species is 879, and the experimental determination of 800 is in reasonable agreement with this. The presence of a band at 1645 cm^{-1} indicates that the Ce—O═C—W linkage is still present, thus suggesting the process depicted in eq 4. In a more polar solvent such as



$$3 \xrightleftharpoons{\text{THF}} 2\text{Cp}''_2\text{Ce}\begin{matrix}\text{OC—W(Cp)(CO)}_2\\ (\text{THF})_n\end{matrix} \qquad (4)$$

MeCN, the $[\text{CpW(CO)}_3]^-$ moiety is symmetrically solvated. Thus, the cerium center is presumed to exist in MeCN solution as a solvated cationic center, as represented in eq 5. Although the exact number of MeCN ligands is unknown, we suspect that $x = 3$ on the basis of related compounds.

$$3 \xrightleftharpoons[\text{MeCN}]{} 2[\text{Cp}''_2\text{Ce(NCMe)}_x]^+ + 2[\text{CpW(CO)}_3]^- \qquad (5)$$

Luminescence studies on compound **3** provide some interesting information regarding the nature of the Ce–W interactions. Nearly all cerium(III) compounds emit very efficiently out of a ^{2}D state,[21] and we have developed a data base which indicates that a compound with a $\text{Cp}''_2\text{CeLX}$ ligand sphere should emit at ca. 550 nm.[14] In addition, the use of an energy gap law allows us to predict that it should exhibit an emission lifetime of ca. 150 ns. However, **3** is completely nonemissive in THF and toluene and in the solid state, even though the absorption spectrum of **3** appears to be the sum of those for the $\text{Cp}''_2\text{Ce}^{\text{III}}$ and CpW(CO)$_3$ moieties; in other words, adduct formation has not given rise to apparent changes in the ground-state electronic properties of the two fragments. We have considered a number of possible explanations for the nonemissive nature of **3**. Among them are that (1) the unusual 12-membered ring distorts upon excitation, giving rise to a substantial Stokes shift and resulting in quenching via crossing of the excited- and ground-state potential surfaces, (2) the excited state undergoes nonradiative decay by using several quanta of a high-frequency ligand vibrational mode, (3) the tungsten center absorbs all of the incoming radiation, (4) cerium–cerium interactions lead to excited-state energy transfer which is more rapid than emission, and (5) cerium–tungsten interactions operate similarly. We are able to discount a number of these possibilities with the available data. First, we do not think the unusual 12-membered-ring geometry is responsible for quenching, because the compound is also dark in THF solution. Here we have a more "normal" $\text{Cp}''_2\text{Ce(X)(THF)}$ coordination sphere, other examples of which do emit (cf. $\text{Cp}''_2\text{Ce(I)(THF)}$[33]). The possibility of vibrational deactivation is remote, since the energy of the expected emission is high enough that it would require at least 12 quanta of any available vibrational mode to accomplish this. It has been pointed out that such a process becomes increasingly inefficient as the number of required quanta increases, such that a typical limit is ca. 6 quanta.[34] To eliminate the possibility of Ce–Ce interactions (explanation 4 above), we prepared a Ce–La analogue of **3** by running the synthesis (eq 3) with a mixture of 20% **2a** and 80% **2b**. Random statistics would lead to 64% of the La–La compound, 32% of the desired La–Ce compound, and only 4% of the Ce–Ce compound. Since lanthanum(III) has no accessible electronic states, the La–La compound is nonemissive; more importantly, the La–Ce compound could not exhibit Ln–Ln quenching. Although NMR spectroscopy indicated that the 20/80 mixture of **2a** and **2b** was reflected in the final product mixture, no emission was observed. Thus, Ce–Ce interactions do not appear to be the cause of the quenching in **3**. Finally, we note that, when dissolved in MeCN, the compound emits strongly with a luminescence wavelength of 570 nm and a lifetime of 86 ns. We attribute this emission to the cationic $[\text{Cp}''_2\text{Ce(NCMe)}_x]^+$. However, $[\text{CpW(CO)}_3]^-$ is still present in this solution in equimolar quantities. Since it is unable to shut off cerium emission by competitive absorption, we are inclined to eliminate (3) from the list of possible quenching mechanisms.

Mechanism 5 has not been eliminated by any available data, and we currently favor cerium–tungsten interactions as the quenching process. Förster has described excited-state energy transfer operating between two centers whose ground electronic properties remain unchanged by adduct formation (the "weak coupling limit");[35] we noted above that the absorption spectra for the two fragments do not change upon complexation. This type of quenching will arise when there is overlap in the emission spectrum of a luminescent center and the absorption spectrum of a quenching center, *provided* they are located within a critical distance of each other. In this case, one can express the ratio of emission quantum yield in the presence (Φ) and absence (Φ_0) of quencher as shown in eq 6.[36] Here

$$\frac{\Phi}{\Phi_0} = \frac{1}{1 + \left(\frac{R_0}{R}\right)^6} \qquad (6)$$

R is the actual separation between emitter and quencher and R_0 is the critical emitter–quencher separation at which the rate constants for emission and quenching become equal; i.e. the emission quantum yield is halved relative to the case in which the quencher site is absent. The value of R_0 can be determined from eq 7,[36] which equates $R_0{}^6$ to

$$R_0{}^6 = (8.78 \times 10^{-25})\kappa^2 Q n^{-4} \int F(\nu)\ \epsilon(\nu)\ \nu^{-4}\ \mathrm{d}\nu \qquad (7)$$

the product of κ^2, a dipole orientation factor, Q, the

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(32) (a) Conway, A. J.; Gainsford, G. J.; Schrieke, R. R.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2499–2507. (b) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984**, *23*, 432–437.

(33) This results from the dissolution of $\text{Cp}''_2\text{Ce(I)(NCMe)}_2$ (**2a**) in THF solution.[14]

(34) (a) Sveshnikova, E. B.; Serov, A. P.; Kondakova, V. P. *Opt. Spectrosc. (Engl. Transl.)* **1975**, *39*, 162–164. (b) Stein, G.; Wurzberg, E.; *Z. Phys. Chem.* **1976**, *101*, 163–170.

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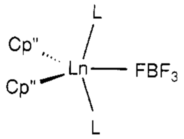
(36) Horrocks, W. D., Jr.; Holmquist, B.; Vallee, B. L. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4765–4768.

quantum yield in the absence of the quencher, n^{-4}, where n is the index of refraction of the solvent, and the integrated area of overlap between absorption and emission spectra for the quencher and emitter, respectively. The last amount was determined to be ca. 2×10^{-17} M^{-1} cm^3 by cut-and-weigh integration of the overlap, which results from crossing of the red edge of the tungsten absorption spectrum and the blue edge of the cerium emission spectrum at ca. 400 nm. It has been pointed out that when one of the communicating states is triply degenerate, one can assume a value of $^2/_3$ for the dipole orientation factor κ^2.[36] Thus, eq 7 indicates that $R_0 = 12 \pm 3$ Å. If we utilize this value in eq 6, while noting that the actual Ce–W separation (from the X-ray structure of 3)[23] is ca. 5 Å, we calculate a quenching efficiency of ca. 99%. Since the THF solution structure (eq 4) would also have the two sites in close proximity, it is also dark. However, when the ions separate in MeCN solution (eq 5), quenching is much less efficient and emission results. It may be worth noting that the 86-ns lifetime observed in 1 mM solution is shorter than might have been expected from the energy gap law.[14] This may reflect some degree of Ce–W quenching occurring across greater distances in the ion pair, but we have not carried out Stern–Vollmer studies to verify this.

Preparation and Studies of Tetrafluoroborate Complexes. The studies described above provided evidence for cationic organocerium(III) species in solution, indicating that the carbonylmetalate functioned as a good leaving group in acetonitrile.[37] To extend these studies and gain more insight on the coordination properties of the Cp''_2Ce^{III} fragment, we sought the complexation of other potentially labile ligands. Initially, we pursued the conversion of 3 to tetrafluoroborate complexes via the reaction of 3 with $AgBF_4$. In toluene solution this resulted in the known[38] polymer $\{Ag([CpW(CO)_3])\}_x$ and a compound of apparent composition $Cp''_2Ce(BF_4)$. We have been unable to crystallize this compound and thus cannot assign a structure. If the same reaction is carried out in acetonitrile, the result is a nitrile adduct of formula $Cp''_2Ce(NCMe)_2(BF_4)$ (**4a**, eq 8). Subsequently we have found

$$3 + 2AgBF_4 \xrightarrow{MeCN} \underset{\mathbf{4a}}{2Cp''_2Ce(NCMe)_2(BF_4)} + 2Ag^0 + [CpW(CO)_3]_2 \quad (8)$$

that the iodide ligand in 2 is sufficiently labile to undergo abstraction with $AgBF_4$, and this reaction constitutes the preferred synthesis for **4a** and the lanthanum analogue **4b**. These compounds crystallize readily from diethyl ether containing a few drops of acetonitrile, giving platelets of formula $Cp''_2Ln(NCMe)_2(BF_4)\cdot Et_2O$. Unfortunately, these crystals failed to diffract, so X-ray data are unavailable. Nonetheless, the spectral data are informative. ^1H NMR spectra are consistent with the proposed formulation, and the infrared spectra exhibited bands at 2304 and 2270 cm^{-1} for the nitrile ligands. Also, the BF_4 ligand was evident from bands at 1195, 1127, 896, and 758 cm^{-1}. Beck has reviewed several aspects of BF_4 coordination (including B–F infrared spectra for the various available binding modes),[39a] and our data best match those seen previously for monodentate coordination. On the basis of these data and on the structures of similar cerium(III) compounds, we propose that 4 adopts a distorted-trigonal-bipyramidal structure with axial nitrile ligands and an equatorial η^1-BF_4 ligand.



proposed structure for 4, L = MeCN

We have also studied the ^{19}F NMR spectra of **4a** and **4b**. In both cases we observe singlets at 20 °C (**4a**, $\delta = -154$ ppm; **4b**, $\delta = -138$ ppm; toluene-d_8 solution, both relative to external $CFCl_3$). The signal for the diamagnetic **4b** is clearly well removed from the signal one observes for free BF_4^- (−153 ppm). The fact that the signal for **4a** is so close to this value is attributed to the paramagnetic shift induced by the Ce(III) center; indeed, the signal also exhibits considerable paramagnetic broadening (fwhm = 800 Hz). Variable-temperature studies failed to provide any evidence for decoalescence of the signals for bridging and terminal fluorides down to −75 °C, although the signal for **4a** did exhibit Curie–Weiss behavior and linear plots of chemical shift (ppm) vs $1/T$ (K) (slope $13\,700 \pm 900$ ppm/K, $r = 0.991$). Even though the high-field signal for the bridging fluoride is sometimes quite broad,[40a] we should have been able to see the large $^2J_{FF}$ coupling (typically 90–160 Hz)[40] in the slow-exchange regime for **4b**; we did not. In THF solution **4a** exhibited a broad signal at −155 ppm; when the solution was cooled, this signal decoalesced into signals at −168 and −150 ppm. The coalescence point was found to be −18 °C, above which added free BF_4^- (as either $NaBF_4$ or $AgBF_4$) fails to undergo rapid exchange with the Ce-bound moiety. As such, we propose that the exchange of THF and MeCN ligands is *more* rapid than is the exchange of BF_4^- moieties under these conditions. The equilibrium is as indicated in eq 9, and we have been

$$Cp''_2Ce(THF)(BF_4) + 2MeCN \rightleftharpoons Cp''_2Ce(NCMe)_2(BF_4) + THF \quad (9)$$

able to shift it by adding measured volumes of acetonitrile to the THF solution; the volume ratio of THF:MeCN was kept at ≥10 to avoid substantial changes in the bulk dielectric constant relative to that of pure THF. This allows us to calculate an equilibrium constant of ca. 500 M^{-1} at −78 °C, indicating the degree to which the $Cp''_2Ce(BF_4)$ moiety favors the nitrile ligand. The coalescence temperature is consistent with an activation free energy of 10.4 kcal/mol, which is similar to the barrier for exchange of free and coordinated THF in $Cp^*_2Lu(THF)(Cl)$ in toluene solution (12.9 kcal/mol).[41]

If **4a** is dissolved in acetonitrile, ^{19}F NMR spectroscopy indicates the presence of only one species whose resonance frequency is temperature-independent between −30 and +35 °C. We conclude that **4a** is fully dissociated in acetonitrile, and the luminescence spectrum is consistent with the presence of the $[Cp''_2Ce(NCMe)_x]^+$ moiety generated from 3 in acetonitrile. Again, if the acetonitrile is removed in vacuo and the residue dissolved in toluene or THF, the

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(37) See also: Evans, W. J.; Bloom, I.; Grate, J. W.; Hughes, L. A.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1985**, *24*, 4620–4623.

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(41) Gong, L.; Streitwieser, A. S., Jr.; Zalkin, A. *J. Chem. Soc., Chem. Commun.* **1987**, 460–461.

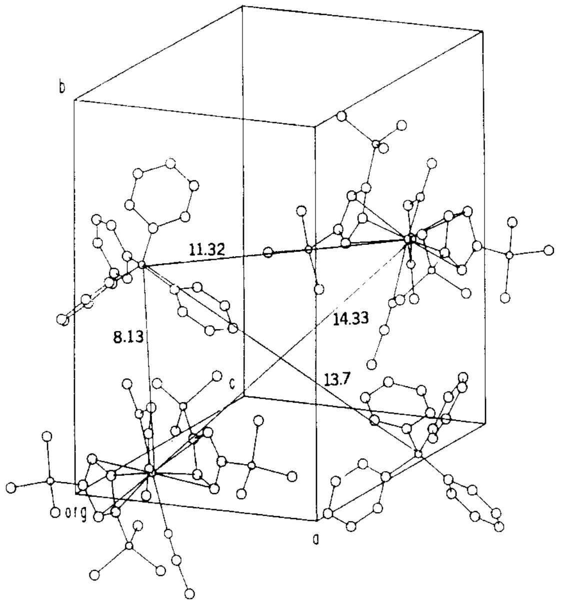

Figure 1. Representation of the unit cell in **5b** indicating the relative disposition of cation and anion fragments. The designation org refers to the origin of the Cartesian coordinate system, and *a*, *b*, and *c* are the crystallographic axes. Cation–anion separations are shown in angstroms.

presence of coordinated BF_4^- is indicated by the spectral data.

The properties described above are highly unusual. On the one hand, the data seem to indicate that the exchange of coordinated BF_4 is slower than is that of THF and MeCN ligands. This would seem to imply a strong interaction between fluoride and the Ln(III) center. At the same time, high-valent metal centers are known to abstract fluoride from tetrafluoroborate anions.[24a,42] The fact that this does not appear to occur here is quite remarkable and suggests that the Cp''_2Ln^{III} center achieves a delicate balance; it is sufficiently acidic (in the Lewis sense) to form tightly bound ion pairs in relatively nonpolar solvents yet is not sufficiently acidic to effect fluoride abstraction.

Synthesis and Solid-State Structure of a Cationic Compound. The ready dissociation of weakly bound ligands in **3** and **4** encouraged us to seek a legitimate organolanthanide cation salt. We chose to use the tetraphenylborate anion as our counterion, even though recent results have indicated that it can coordinate under certain circumstances.[24h,k,43] As such, compounds **2a** and **2b** were reacted with $AgBPh_4$ in THF solution while the temperature was kept at −78 °C. We were unable to crystallize and purify the resulting compound, which we formulate as $[Cp''_2Ln(THF)_2][BPh_4]$. After several attempts in various solvents, we found that compound **5** could be crystallized by slow diffusion of diethyl ether into a solution of the salt in 1,2-dimethoxyethane (DME) containing a few drops of acetonitrile (eq 10). Under these conditions,

$$\mathbf{2} + AgBPh_4 \xrightarrow{THF} [Cp''_2Ln(THF)_2][BPh_4] \xrightarrow{MeCN,\ DME} \mathbf{5} \quad (10)$$

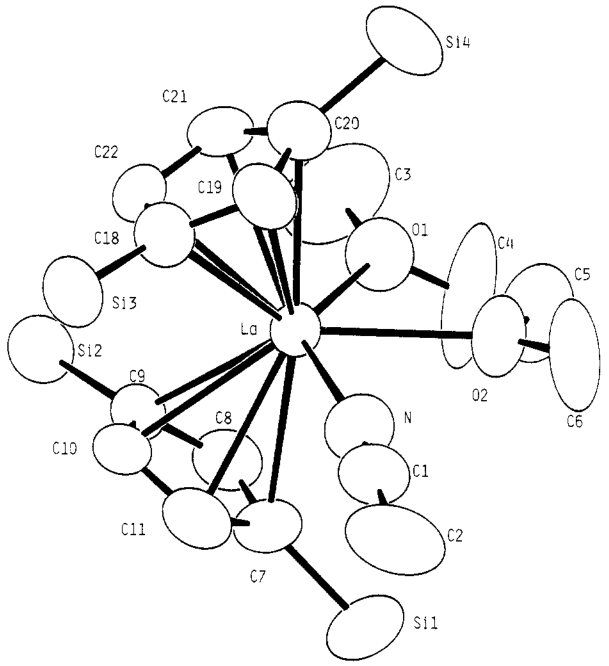

Figure 2. ORTEP drawing of the cation in **5b**. Hydrogen atoms and the silyl methyl groups have been omitted for clarity.

Table II. Selected Bond Lengths and Angles for 5b

	Bond Lengths (Å)		
La–N	2.60 (2)	La–C(19)	2.84 (1)
La–O(1)	2.580 (8)	La–C(20)	2.87 (1)
La–O(2)	2.673 (9)	La–C(21)	2.79 (1)
La–C(7)	2.85 (1)	La–C(22)	2.78 (1)
La–C(8)	2.83 (1)	N–C(1)	1.12 (2)
La–C(9)	2.85 (1)	C(1)–C(2)	1.46 (2)
La–C(10)	2.79 (1)	O(1)–C(4)	1.35 (2)
La–C(11)	2.82 (1)	O(2)–C(5)	1.45 (3)
La–C(18)	2.83 (1)	C(4)–C(5)	1.33 (4)
	Bond Angles (deg)		
O(1)–La–O(2)	61.5 (3)	O(1)–La–N	135.4 (3)
O(2)–La–N	74.1 (3)	La–N–C(1)	171 (2)
N–C(1)–C(2)	176 (2)	La–O(1)–C(3)	128 (1)
La–O(1)–C(4)	117 (1)	La–O(2)–C(5)	114 (1)
La–O(2)–C(6)	130 (1)	La–O(1)–C(3)	128 (1)
La–O(2)–C(6)	130 (1)		

large cubes of composition $[Cp''_2Ln(DME)(NCMe)][BPh_4]\cdot0.5DME$ result. The cerium analogue (**5a**) is orange-brown, while the lanthanum analogue (**5b**) is colorless; both isolated solids are indefinitely stable at low temperature but failed to give satisfactory elemental analyses due to facile loss of the ligands and molecule of crystallization at room temperature.

We undertook an X-ray study of the lanthanum analogue **5b**, the result of which is shown in Figures 1 and 2. The solid-state structure consists of well-separated cations and anions, with a closest interion contact of 3.42 (2) Å between the nitrile methyl carbon (C(2)) and the ortho carbon of a B–Ph group (C(52)). Figure 1 illustrates the disposition of the ions in the unit cell, as well as the calculated La–B, La–La, and B–B separations. The structure of the cation is shown in Figure 2, from which it is clear that the DME ligand exhibits large thermal ellipsoids. This may result from the disorder noted in the Experimental Section or from librational motion operating at 25 °C. However, the metal–ligand and intraligand bond lengths are quite reasonable; key bond lengths and angles are presented in Table II.

The cation is best described as a bent metallocene with three equatorial ligands. The DME chelate ring is puckered with an O(1)–C(4)–C(5)–O(2) dihedral angle of 31

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[42] (a) Reedijk, J. *Comments Inorg. Chem.* **1982**, *1*, 379–389. (b) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 7306. (c) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082–4. Also see: (d) Thomas, B. J.; Mitchell, J. F.; Theopold, K. H.; Leary, J. A. *J. Organomet. Chem.* **1988**, *348*, 333–342.

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(4)°. The essentially linear nitrile ligand (C(2)–C(1)–N angle 176 (2)°) approaches the metal center with a C(1)–N–La angle of 171 (1)° and La–N and N–C(1) distances of 2.61 (1) and 1.12 (2) Å, respectively. The former compares well with the 2.63 (2) Å Ce–N distance in $Cp*_2Ce(I)(NCMe)_2$,[14] and the N–C distance is indicative of a triple bond (typical distance 1.13 Å).[44] The La–Cp″ carbon distances average 2.83 Å, a value that compares with the metal–carbon distances in $Cp*Ce(I)_2(THF)_3$ (2.78 Å)[15] and $Cp*_2Ce(I)(NCMe)_2$ (2.79 Å);[14] the slight differences may in part reflect the difference in Ln(III) ionic radii (La(III), 1.061 Å; Ce(III), 1.034 Å).[1a] The lanthanum–oxygen bonds differ substantially, with La–O(1) and La–O(2) distances of 2.580 (8) and 2.673 (9) Å, respectively. The former compares reasonably well with the Ce–O distances of $Cp*Ce(I)_2(THF)_3$ (2.540 (8) and 2.511 (8) Å), but the O(2) distance is clearly long. Recently, Cramer and Gilje have shown that $Cp*_2UL_3$ compounds exhibit the effects of steric crowding; in $Cp*_2U(Cl)_2(NH–PPh_3)$ the U–Cl distances are nonequivalent (2.730 (4) and 2.658 (5) Å) and longer than the typical value of ca. 2.58 Å.[45] We may be seeing a similar effect here, since it is the DME oxygen nearer the extra (NCMe) ligand that exhibits the long La–O bond.

We should note that when a similar halide abstraction is attempted by treating the chloride analogues $Cp''_2LnCl_2Li(THF)_2$ with 2 equiv of silver salt, there is no evidence for the cations **5**; although some AgCl is precipitated, we are unable to characterize the Ln-containing product. This may reflect the decreased lability of chloride (relative to iodide) ligands in Ln(III) compounds. Also, we were unable to prepare a similar cation salt from the Cp* analogue $Cp*_2Ce(I)(NCMe)_2$. We have no explanation for this observation, which is particularly baffling in light of the recent report by Evans, Caulton, and co-workers of the synthesis of $[Cp*_2Sm(THF)_2][BPh_4]$.[46] This compound results from the oxidation of the divalent $Cp*_2Sm(THF)_2$ with $AgBPh_4$; an attempted synthesis involving chloride abstraction from $Cp*_2Sm(Cl)(THF)$ was unsatisfactory.[47] No divalent precursors exist for the lanthanum and cerium systems studied in our work, so these two synthetic methods are complementary in scope. There are interesting differences in the compounds as well. The 8-coordinate samarium compound is quite resistant to substitution of the THF ligands,[46] whereas we have found that the 9-coordinate **5** will exchange both the chelated DME and MeCN ligands when stirred in THF solution. Our explanation for this is that the larger sizes of the La(III) and Ce(III) ions lower their charge-to-size ratios sufficiently to allow these ligand exchanges to occur. When they are taken together, these two studies indicate that the syntheses of organolanthanide cations should be generally achievable and that the coordination properties of various members of the series may vary substantially.

Conclusions. We have described the interactions of the $[Cp''_2Ln^{III}]^+$ moiety with various Lewis bases, both neutral and anionic. These compounds are accessible from lanthanide–iodide precursors, in which the lability of the iodides may result from unfavorable hard-acid–soft-base interactions or (in some cases) steric crowding introduced by the large halide. The formation of compounds **2**, **4**, and **5** indicates the degree to which lanthanum and cerium favor a 9-coordinate Cp_2LnX_3 geometry, particularly when at least one of the ligands is an acetonitrile molecule. Thus, the organolanthanide fragment is sufficiently electrophilic to bind even relatively weakly coordinating anions such as tetrafluoroborate and the carbonyl group of a formally neutral complexed carbonylmetalate (in **3**). Additionally, however, although neutral ligands such as acetonitrile, THF, and chelated DME are securely bound, they are subject to ligand-exchange reactions. This ligand lability may prove useful in the syntheses of other complexes and in potential catalytic applications of the compounds described herein, and studies of these possibilities are in progress.

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Supplementary Material Available: Tables of diffractometer data, positional and thermal parameters, and bond distances and angles for **5b** and a figure showing the structure of the BPh_4^- anion in **5b** (10 pages); a listing of calculated and observed structure factors for **5b** (26 pages). Ordering information is given on any current masthead page.

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