Synthesis, Structure, and Reactivity of bis(1,2,4-tri-t-butylcyclopentadienyl) Complexes of Cerium

by

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Abstract

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The sterically demanding 1,2,4-tri-t-butylcyclopentadienyl ligand (1,2,4-$(Me_3C)_3C_5H_2$, hereafter Cp’) has been used to prepare monomeric cerium metallocenes, Cp'_2CeX (X = Cl, I, OSO_2CF_3), which are used to synthesize the benzyl, $Cp'_2CeCH_2C_6H_5$. The benzyl is a useful starting material for preparing other complexes in the Cp'_2CeZ system (Z = BF_4, F, NH_2, C_6H_5, H). X-ray crystal structures of $Cp'_2CeOSO_2CF_3$, Cp'_2CeF, $Cp'_2CeCH_2C_6H_5$, and Cp'_2CeH are presented. The benzyl slowly decomposes in solution to toluene and a metallacycle, $[Cp'][(Me_3C)_2C_5H_2(CMe_2CH_2)]Ce$. The ring CMe_3 groups of both the metallacycle and the hydride, Cp'_2CeH, can be fully deuterated by prolonged exposure to C_6D_6, providing a useful labeling tool in mechanistic studies.

The hydride activates C-F and/or C-H bonds in fluorobenzenes, $C_6H_xF_{6-x}$, x = 0 – 5. The reactions are selective, with the selectivity depending on the presence of two

fluorines ortho to the reaction site more than on the type of bond activated. Complexes of the type $Cp'_2CeC_6H_xF_{5-x}$, x = 0 – 4, are formed as intermediates, which slowly decompose in solution to Cp'_2CeF and fluorobenzynes, $C_6H_xF_{4-x}$, x = 0 - 4, which are trapped. The rate at which $Cp'_2CeC_6H_xF_{5-x}$ complexes decompose increases as the number of fluorines decreases. Complexes with one ortho-fluorine decompose much faster than those with two ortho-fluorines. The metallacycle activates only C-H bonds in fluorobenzenes, permitting the synthesis of specific $Cp'_2CeC_6H_xF_{5-x}$ complexes. The crystal structure of $Cp'_2CeC_6F_5$ is presented.

The hydride and the metallacycle react with fluoromethanes, $CH_{4-x}F_x$, x = 1 – 3, through postulated $Cp'_2CeCH_{3-x}F_x$ intermediates to generate Cp'_2CeF and other products. The other products, CH_4, tri-t-butylbenzenes, tri-t-butylfluorobenzenes, and a presumed metallocene cerium fluoride with one Cp' and one $(Me_2EtC)(Me_3C)_2C_5H_2$ ligand, suggest a decomposition pathway for $Cp'_2CeCH_{3-x}F_x$, x = 1 – 3, that involves carbenes or carbenoids, which are trapped.

The hydride polymerizes ethylene, but hydrogenates other olefins. The metallacycle activates C-H bonds in olefins and aromatics to generate new complexes with Ce-C bonds. The hydride reacts with one equivalent of CO in pentane to generate $(Cp'_2Ce)_2CH_2O$, whose crystal structure shows the presence of a bridging η^2-dianionic formaldehyde ligand. $(Cp'_2Ce)_2CH_2O$ reacts H_2 to give the hydride and Cp'_2CeOMe, or with a mixture of H_2 and CO to generate Cp'_2CeOMe exclusively. $(Cp'_2Ce)_2CH_2O$ or the hydride can react with an additional equivalent of CO to generate dimeric enediolate, $(Cp'_2CeCHO)_2$.

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Introduction

Complexes of the lanthanide elements, Ce-Lu in the periodic table, display properties that differ from complexes of the more commonly studied d-block transition metals. The electrons that sequentially fill the 4f orbitals across the lanthanide series do not shield each other well from the nuclear charge. As a result, the radial extension of the 4f orbitals is reduced to near or below the level of the filled 5s and 5p orbitals. This effect greatly limits the extent to which the 4f orbitals can overlap with ligand orbitals because the electrons in them are core electrons. The lack of symmetry constraints imposed by the metal orbitals, and the comparatively large ionic radii of the lanthanide +3 ions,[1] allow organo-lanthanide complexes to attain higher coordination numbers than are typical for d-block metals.[2] The large ion size is also believed to facilitate ligand redistribution in coordinatively unsaturated systems. These differences make the investigation of organo-lanthanide chemistry both challenging and interesting.

Stable organo-lanthanide complexes were first synthesized in 1954, when Birmingham and Wilkinson prepared π-bound Ln-C complexes of the type $Ln(C_5H_5)_3$ (Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb).[3] It was several more years before σ-bound Ln-C complexes of the type $(C_5H_5)_3LnR$ were prepared for some of the later lanthanides (Ln = Gd, Er, Yb, R = C_6H_5, CH_3).[4] Some of the σ-alkyl and hydride complexes of the later lanthanides are capable of useful chemistry such as C-H bond activation,[5] alkene polymerization,[6] and carbonyl activation.[7] However, only a few alkyl complexes of the early lanthanides have been reported.[8-12] All make use of bulky ligands or Lewis base adducts to achieve stable configurations.

In the Andersen laboratories, attempts to synthesize stable σ-alkyls and hydrides of cerium (III) have involved the use of sterically demanding substituted cyclopentadienyl ligands. Stults has prepared $\{[(CMe_3)C_5H_4]_2CeMe\}_2$ and $\{[(Me_3Si)_2C_5H_3]_2CeMe\}_2$.[2] These complexes, which exist as dimers with bridging methyl groups, are unstable in solution. The $\{[(Me_3C)C_5H_4]_2CeMe\}_2$ complex undergoes ligand redistribution at room temperature to give $[(Me_3C)C_5H_4]_3Ce$ and an uncharacterized yellow solid. The $\{[(Me_3Si)_2C_5H_3]_2CeMe\}_2$ complex similarly decomposes to $[(Me_3Si)_2C_5H_3]_3Ce$. The half-lives of these redistributions as determined by ^{1}H NMR spectroscopy are 2-3 hours and 4 days, respectively, and are independent of solvent.[2] As mentioned above, the large ionic radius of the Ce (III) ion (1.15Å)[13] and the tendency of lanthanide ions to maximize their coordination is expected to facilitate the ligand redistribution pathways that lead to $Cp\hat{}_3Ce$ complexes ($Cp\hat{}$ = substituted cyclopentadienyl). The use of bulkier cyclopentadienyl ligands that occupy more of the coordination sphere of the metal should inhibit these processes and permit the isolation of $Cp\hat{}_2CeR$ complexes (R = alkyl) that are stable with respect to redistribution.

Sofield has synthesized $\{[(Me_3C)_2C_5H_4]_2CeMe\}_2$.[14] Though the volume of the CMe_3 group is less than the $SiMe_3$ group (the C-C bond length is 1.54 Å vs. 1.87 Å for C-Si),[15] the stronger C-C bond (81 kcal/mol C-C vs. 69 kcal/mol C-Si)[16] is less susceptible to bending out of the cyclopentadienyl plane. As a result, the di-*t*-butyl-cyclopentadienyl ligand is probably more sterically demanding than the trimethylsilyl analog. Nevertheless, as with the other $(Cp^\wedge{}_2CeMe)_2$ complexes, $\{[(Me_3C)_2C_5H_3]_2CeMe\}_2$ decomposes in solution at room temperature to $[(Me_3C)_2C_6H_4]_3Ce$ and an uncharacterized solid, with a half-life for the decomposition of approximately one week. These results illustrate that the use of more sterically demanding cyclopentadienyl ligands does progressively slow the rate of redistribution to $Cp^\wedge{}_3Ce$ complexes. However, it is clear that still bulkier ligands are required for the isolation of configurationally stable $Cp^\wedge{}_2CeR$ complexes.

The present work focuses on the use of the 1,2,4-tri-*t*-butylcyclopentadienyl ligand (1,2,4-$(Me_3C)_3C_5H_2$, hereafter symbolized Cp') in the synthesis of cerium metallocenes. Chapter 1 describes the methods and machinations required to substitute two Cp' ligands onto cerium halides and pseudohalides, as well as various attempts to synthesize Cp'_2CeR (R = alkyl) complexes. The successful synthesis of $Cp'_2CeCH_2C_6H_5$ and its reactions are discussed, including the synthesis of the monomeric hydride, Cp'_2CeH. The reactions of the hydride and the metallacycle, $[Cp'][(Me_3C)_2C_5H_2(CMe_2CH_2)]Ce$, are the discussed in the remaining chapters. Chapter 2 concerns C-F and C-H activation in a series of fluorobenzenes and the synthesis of complexes of the form $Cp'_2CeC_6H_xF_{5-x}$, $x = 0 – 4$. Chapter 3 addresses reactions of the hydride and the metallacycle with methane and the series of fluoromethanes, $CH_{4-x}F_x$, $x = 1 – 4$. Chapter 4 discusses other reactions of the hydride, including reactions with olefins and CO.

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Chapter 1: Synthesis and Properties of Cp'$_2$CeX and Cp'$_2$CeR complexes (X = halide, pseudohalide; R = alkyl, hydride)

1.1 Synthesis and Properties of the Iodide, Cp'$_2$CeI, and the Triflate, Cp'$_2$CeOSO$_2$CF$_3$

Magnesocenes are useful reagents for transferring cyclopentadienyl rings to lanthanides since they can be purified by crystallization and sublimation, but synthesis of metallocenes of the type Cp'$_2$CeX, X=Cl, I, or OSO$_2$CF$_3$, is hampered by the poor reactivity of the magnesocene, Cp'$_2$Mg, toward CeX$_3$ starting materials. Stirring Cp'$_2$Mg and CeI$_3$ • 3 THF in toluene for one day at room temperature yields unreacted Cp'$_2$Mg and a yellow-green solid that is insoluble in hexane and only sparingly soluble in THF. The low solubility suggests the product could be an organocerium species with a single Cp'-ring, but further characterization was not pursued. The same reactants in THF heated at reflux for one day produce the same sparingly soluble yellow-green solid. In contrast, the reaction of the magnesocene of the less bulky 1,3-di-*t*-butylcyclopentadienyl ligand, Cp$^‡_2$Mg, with CeI$_3$ • 3 THF in toluene at room temperature is complete after just 1 day, yielding orange, hexane-soluble (Cp$^‡_2$CeI)$_2$.[1] Considerably more rigorous conditions are required to synthesize Cp'$_2$CeI: heating a concentrated solution of Cp'$_2$Mg and CeI$_3$ • 3 THF in dibutyl ether at reflux (bp 142°C) for 7 days. The orange solid material crystallizes from a concentrated toluene solution at -15°C, but crystals suitable for X-ray diffraction studies could not be obtained. The EI mass spectrum gave an M$^+$ of 733.

The room temperature ^{1}H NMR spectrum of the Cp'$_2$CeI in C_6D_6 (90MHz) contains two paramagnetic signals attributable to the ring CMe_3 groups, one very broad ($\nu_{1/2}$ = 500 Hz) and one somewhat sharper ($\nu_{1/2}$ = 200 Hz), in a 2:1 area ratio. The signal due to the ring protons could not be located. The resonance of area 2 is presumably due to the pair of CMe_3 groups on adjacent Cp-ring carbons, and its unusual broadness, even for a paramagnetic cerium metallocene, suggests an exchange process may be taking place. A variable temperature ^{1}H NMR study was performed in C_7D_8 to examine this possibility. The resonance of area 2 broadens into the baseline at T_c = 13°C, and at lower temperatures, two resonances of area 1 appear, giving $\Delta G^{\#}_{TC}$ =11 kcal mol^{-1}. Apart from this, the δ vs. 1/T plot showed linear Curie-Weiss behavior for all of the signals.

A physical process that could account for the observed behavior is slowing of the librational motions of the Cp'-rings about their pseudo-C_5 axes. Rapid motion would result in the two rings being related by a time-averaged horizontal mirror plane, giving the molecule idealized C_{2v} symmetry. The two CMe_3 groups on adjacent ring carbons will be related by a vertical plane, making them chemical shift equivalent. At lower temperatures, slowing of the librational motions removes the vertical plane, giving the molecule C_s symmetry and making the two adjacent CMe_3 groups inequivalent.

In the interest of finding a cerium starting material that forms a Cp'$_2$CeX metallocene more readily than CeI_3 • 3 THF, the reactivity of $Ce(OSO_2CF_3)_3$ with Cp'$_2$Mg was tested. No reaction is observed when the reagents are stirred in THF at 25°C for one day, nor at reflux for an equal period of time. The less bulky Cp‡, by contrast, transfers readily from Cp$^‡_2$Mg to $Ce(OSO_2CF_3)_3$, yielding Cp$^‡_3$Ce after one day of stirring in THF at room temperature.[1] $Ce(OSO_2CF_3)_3$ and Cp'_2Mg stirred in refluxing dibutyl ether also failed to react. Similar results were obtained using NaCp' as the cyclopentadienyl ring transfer agent. Cp'_2CeI can be synthesized from $CeI_3 \bullet 3$ THF and NaCp' in refluxing THF, but no reaction is observed between $Ce(OSO_2CF_3)_3$ and NaCp' under the same conditions after 6 days. A solvent combination that does allow the synthesis of $Cp'_2CeOSO_2CF_3$ from cerium triflate and the magnesocene is a 1:10 mixture of freshly dried pyridine and toluene. The Cp'_2Mg and a slight excess of $Ce(OSO_2CF_3)_3$ are suspended in toluene and pyridine is added *via* canula. The suspension slowly turns purple/brown as the pyridine is added. Heating at reflux for one day yields a brown suspension that is taken to dryness and extracted with hexane. The crystals that form from the dark brown hexane solution are also dark brown, and the ^1H NMR spectrum indicates the presence of hexane and other impurities in the crystals. Repeated recrystalizations with hexane ultimately yield brilliant yellow blocks of $Cp'_2CeOSO_2CF_3$ with half an equivalent of hexane included in the crystals. A crystals suitable for X-ray diffraction can be grown in this way; an ORTEP drawing is shown in Figure 1.1, and some bond distances and angles are listed in the figure caption.

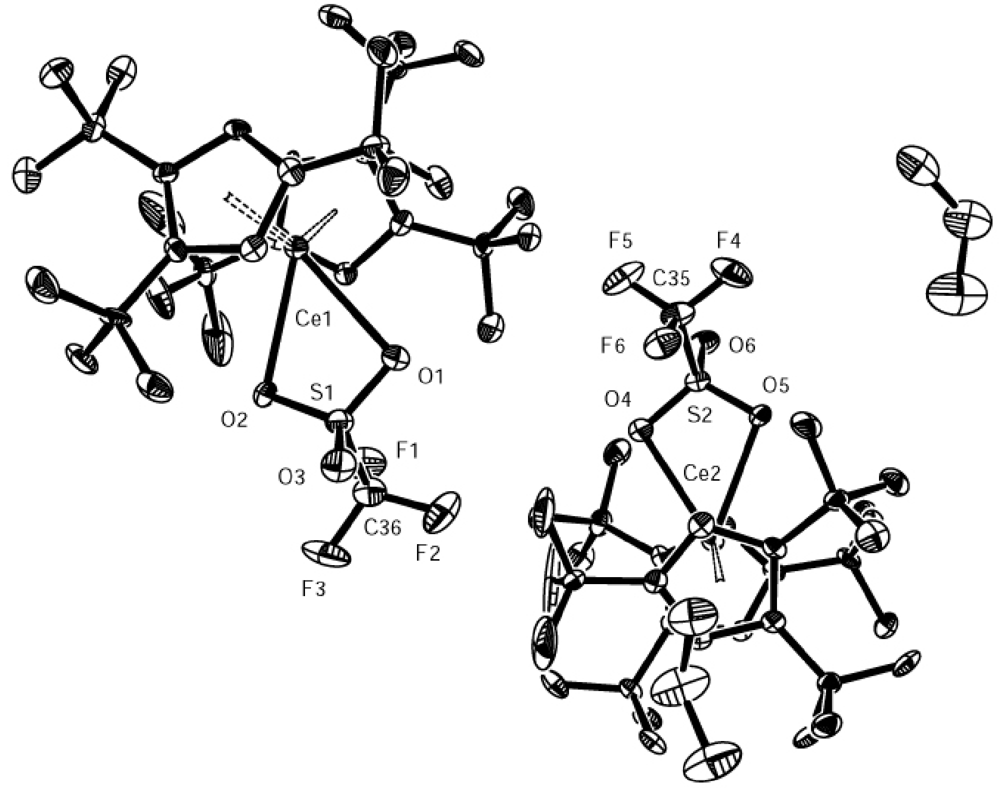


Figure 1.1: ORTEP Drawing of $Cp'_2CeOSO_2CF_3$. Selected Bond Distances and Angles: Ce-O (range): 2.593(4)-2.617(4) Å, Ce-ring C (range): 2.724(5)-2.920(5) Å, Ce-centroid (range): 2.5217(3)-2.5613(3) Å, centroid-Ce-centroid: 142.68(1), 143.06(1)°, O-Ce-O : 54.1(1), 54.5(1)°

The molecule crystallizes in the triclinic space group $P\bar{1}$. The triflate ligand binds in a bidentate fashion, and the rings adopt a staggered orientation that places the unique CMe_3 group of one ring between the pair of adjacent CMe_3 groups on the other. The observation of the same orientation in subsequent structures suggests that this ring orientation is common in bis(tri-t-butylcyclopentadienyl)cerium metallocenes when the centroid-metal-centroid angle is less than approximately 145°. In addition to two molecules of $Cp'_2CeOSO_2CF_3$, the asymmetric unit also contains a well-resolved molecule of hexane. The solvent is not lost upon exposure to vacuum, nor over prolonged storage in solid form.

The room temperature ^1H NMR spectrum of $Cp'_2CeOSO_2CF_3$ in C_6D_6 (90MHz) contains three broad paramagnetic signals of equal area attributable to the ring CMe_3 groups. The ring proton signals again could not be located. Three resonances suggest a molecule with idealized C_s symmetry, where a horizontal mirror plane makes the two rings equivalent, rather than the C_1 symmetry of the solid state structure. A physical process that results in rapid rotational motion about the axis containing Ce and S is required for such a time-averaged horizontal plane to exist, with the triflate ligand either remaining bidentate, or unhooking one of the bound oxygen atoms and rotating about the remaining Ce-O bond.

The ^1H NMR resonances of $Cp'_2CeOSO_2CF_3$ display temperature dependent behavior similar to that of Cp'_2CeI. A δ vs. 1/T plot is shown in Figure 1.2. At T_c = 60°C, two of the CMe_3 signals broaden into the baseline. At higher temperatures, a new, single resonance of area 2 appears at approximately the average chemical shift of the two resonances of area 1 that disappear; the $\Delta G^{\#}_{TC}$ is calculated as 14 kcal mol^{-1}. No further decoalescence of the three CMe_3 resonances is observed down to -92°C, indicating that the process that results in the idealized C_s symmetry in solution cannot not be slowed sufficiently within the temperature range of the experiment to give a spectrum indicative of C_1 symmetry.

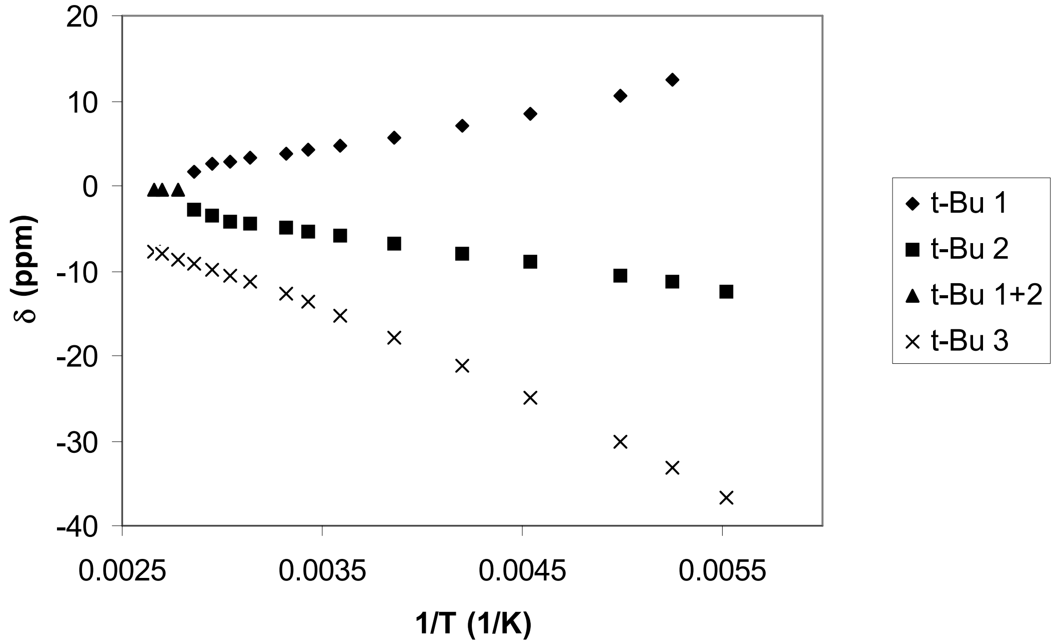


Figure 1.2: ^{1}H NMR δ vs. 1/T plot for $Cp'_2CeOSO_2CF_3$ in C_7D_8

Revisiting the synthesis of the iodide complex, Cp'_2CeI can also be synthesized readily from Cp'_2Mg and $CeI_3 \cdot 3$ THF in 1:10 pyridine/toluene solvent. As with the triflate complex, the reaction is complete after heating at reflux for one day.

Previous work has shown that, while $Cp^{\ddagger}_2CeOSO_2CF_3$ cannot be synthesized directly from $Cp^{\ddagger}_2Mg$ and $Ce(OSO_2CF_3)_3$, it can be synthesized indirectly from $Cp^{\ddagger}_2CeI$ and trimethylsilyl triflate, $Me_3SiOSO_2CF_3$. One equivalent of $Me_3SiOSO_2CF_3$ is used, and the reaction occurs instantaneously.[1] The same reaction is possible in the Cp'-ligand system, but requires 3 equivalents of $Me_3SiOSO_2CF_3$ and three days of stirring to complete the conversion. The steric bulkiness of the Cp' ligand apparently offers a great kinetic barrier to both the synthesis and reactivity of Cp'_2CeX species.

1.2 Attempts to Synthesize Cp'_2CeR, R=alkyl; Synthesis and Properties of the Benzyl, $Cp'_2CeCH_2C_6H_5$

Metallocenecerium methyl complexes with less bulky cyclopentadienyl ligands than Cp' have been synthesized successfully as bridging dimers, but are unstable with respect to ligand redistribution to Cp_3Ce-type species and other unidentified products.[1,2] Adding a solution of CH_3Li to either Cp'_2CeI or $Cp'_2CeOSO_2CF_3$ in diethyl ether cooled in a liquid nitrogen isopropanol bath results in a rapid color change from orange or yellow, respectively, to deep red. When the reaction mixture is taken to dryness, a glassy red solid results which is highly soluble in hexane and resists all attempts at crystallization, even from a concentrated hexane solution at -80°C. During the hexane extraction process, the color of the solution darkens and becomes a deeper red/purple, hinting at possible decomposition or ligand redistribution. The ^1H NMR spectrum of the crude solid contains nearly a dozen paramagnetic resonances, including at least seven large signals attributable to CMe_3 groups. Repeating the reaction and removing the solvent while the reaction flask is still immersed in the liquid nitrogen isopropanol bath, then quickly preparing a ^1H NMR sample of the crude red solid in C_6D_6 results in a ^1H NMR spectrum with two prominent paramagnetic resonances in a 2:1 area ratio and several smaller paramagnetic signals identical to those seen in the previous spectrum. Over time, these smaller resonances increase in area at the expense of the large 2:1 set of resonances. A set of CMe_3 resonances in a 2:1 area ratio would be expected for Cp'_2CeMe, but unfortunately the identity of the species giving rise to the 2:1 pattern in the ^{1}H NMR spectrum not could be confirmed, as once again, no crystals could be obtained from a cooled hexane solution of the red solid product.

The alkyl complex $(Me_5C_5)_2CeCH(SiMe_3)_2$ has been successfully isolated in the laboratories of Teuben.[3] $(SiMe_3)_2CHLi$ was not immediately available, but Me_3SiCH_2Li was. Less than one equivalent of Me_3SiCH_2Li added to $Cp'_2CeOSO_2CF_3$ in C_6D_6 results in a cloudy red solution. The ^{1}H NMR spectrum of the filtered solution contains resonances of unreacted $Cp'_2CeOSO_2CF_3$, a pair of paramagnetic resonances with a 2:1 area ratio, and the same set of small resonances observed in the product of the CH_3Li reaction. As before, the pair of large signals diminishes in size over time as the smaller signals increase, with a half-life for the large signals of roughly 30 minutes at 25°C. Isolation of the presumed $Cp'_2CeCH_2(SiMe_3)$ would have been hampered by the rapid decomposition, and was not attempted.

$(Me_5C_5)_2CeCH_2C_6H_5$ has been prepared successfully, albeit from thermolysis of $(Me_5C_5)_2CeCH(SiMe_3)_2$ in toluene.[4] A diethyl ether solution of benzylmagnesium chloride ($ClMgCH_2C_6H_5$) added to $Cp'_2CeOSO_2CF_3$ in pentane results in a cloudy red/orange solution, and a bright red/orange solid upon removal of the solvent. As the solid is extracted with several portions of pentane, the color of the washings becomes progressively more yellow and less red. Concentrating the filtrate under reduced pressure and cooling to -10°C yields a crop of yellow crystals; concentrating the filtered solution further and cooling yields red crystals. The yellow crystals are only sparingly soluble in C_6D_6, while the red crystals are quite soluble. The ^{1}H NMR spectrum of the yellow crystals in C_6D_6 contains only a pair of paramagnetic resonances in a 2:1 area ratio. The spectrum at 25°C does not change over time nor upon prolonged heating. The spectrum of the red crystals in C_6D_6 contains three prominent resonances in a 1:1:1 area ratio, as well as four smaller paramagnetic resonances. After a day at 25°C, all of these resonances diminish in area, and the same set of resonances that developed in the attempted Cp'_2CeMe and $Cp'_2CeCH_2(SiMe_3)$ syntheses appear, along with resonances of toluene and a new, relatively sharp set of paramagnetic signals in a 2:1 area ratio.

Elemental analysis of the red crystals is consistent with the formulation $Cp'_2CeCH_2C_6H_5$, but the the EI mass spectrum gives only $(M-92)^+$ of 605 instead of the expected M^+ of 697. A single crystals suitable for X-ray diffraction studies can be obtained from concentrated pentane solutions cooled to 15°C; an ORTEP drawing of $Cp'_2CeCH_2C_6H_5$ is shown in Figure 1.3, and some bond distances and angles are listed in the figure caption. The molecule crystallizes in the triclinic space group $P\overline{1}$. The two unique molecules in the asymmetric unit, Molecules A and B, differ markedly from each other. The centroid-metal-centroid angles are more than 10° different (138.3° vs. 149.0°). The Cp' rings of Molecule A adopt approximately the same staggered orientation as in the structure of $Cp'_2CeOSO_2CF_3$. The Ce1-C35-C36 angle between the metal and the benzyl ligand is 93.0°, making the Ce1-C36 distance only 0.44Å longer than the Ce1-C35 distance. The structure of Molecule A is comparable to the $(Me_5C_5)_2CeCH_2C_6H_5$ structure, where the centroid-metal-centroid angle is 137.5°, Ce1-C21-C22 is 86.0°, Ce1-C21 is 2.60Å and Ce1-C22 is 2.89Å.[4] The rings of Molecule B, by contrast, adopt an eclipsed conformation that overlaps two CMe_3 groups on each ring when viewed down the pseudo-C_5 axis. The Ce2-C76-C77 angle between the metal and the benzyl ligand is 130.4°, and the Ce2-C76 distance is 2.58Å. There is little difference between the metal-centroid distances and metal-Cp' ring carbon bond lengths in Molecules A and B. That a single set of time-averaged CMe_3 resonances appears in the ^1H NMR spectrum suggests that there is only a minimal barrier to interconversion between the two conformations in solution.

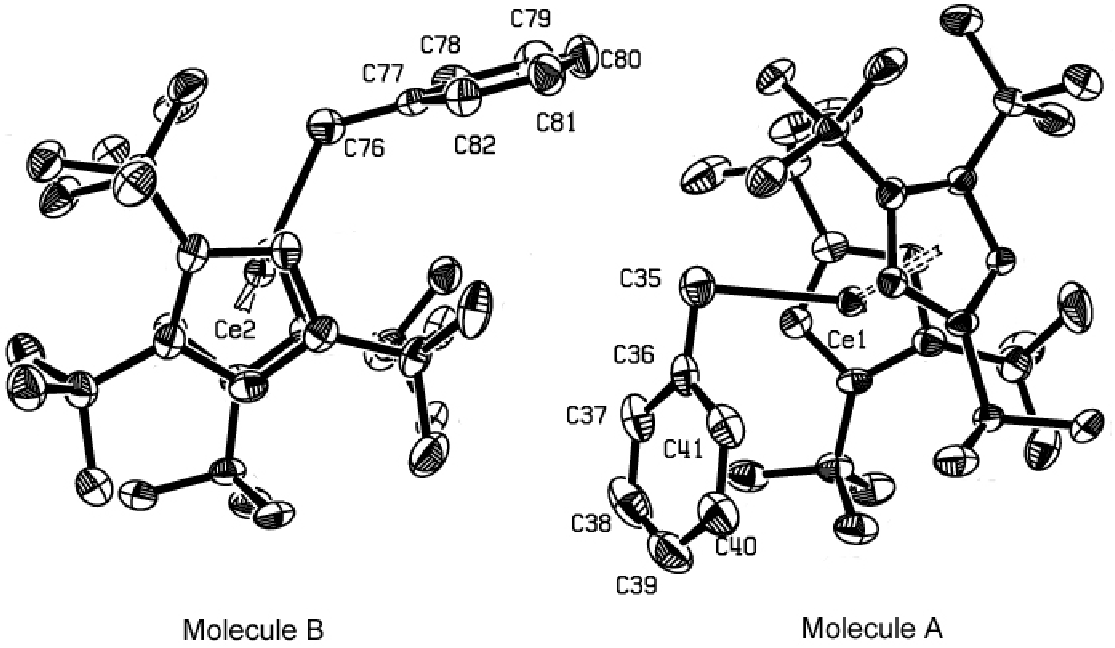


Figure 1.3: ORTEP drawing of $Cp'_2CeCH_2C_6H_5$. Selected distances and angles: **Molecule A**: Ce1-C35: 2.581(5) Å, Ce1-C36: 3.016(5) Å, Ce1-ring C (range): 2.760(5)-3.009(4) Å, Ce1-centroid: 2.5871(3) Å, 2.6384(2) Å, centroid-Ce1-centroid: 138.29(1)°, Ce1-C35-C36: 93.0(3)°. **Molecule B**: Ce2-C76: 2.577(5) Å, Ce-ring C (range): 2.769(5)-2.933(4) Å, Ce2-centroid: 2.5583(3), 2.5664(3) Å, centroid-Ce2-centroid: 148.99(1)°, Ce2-C76-C77: 130.4 (3)°.

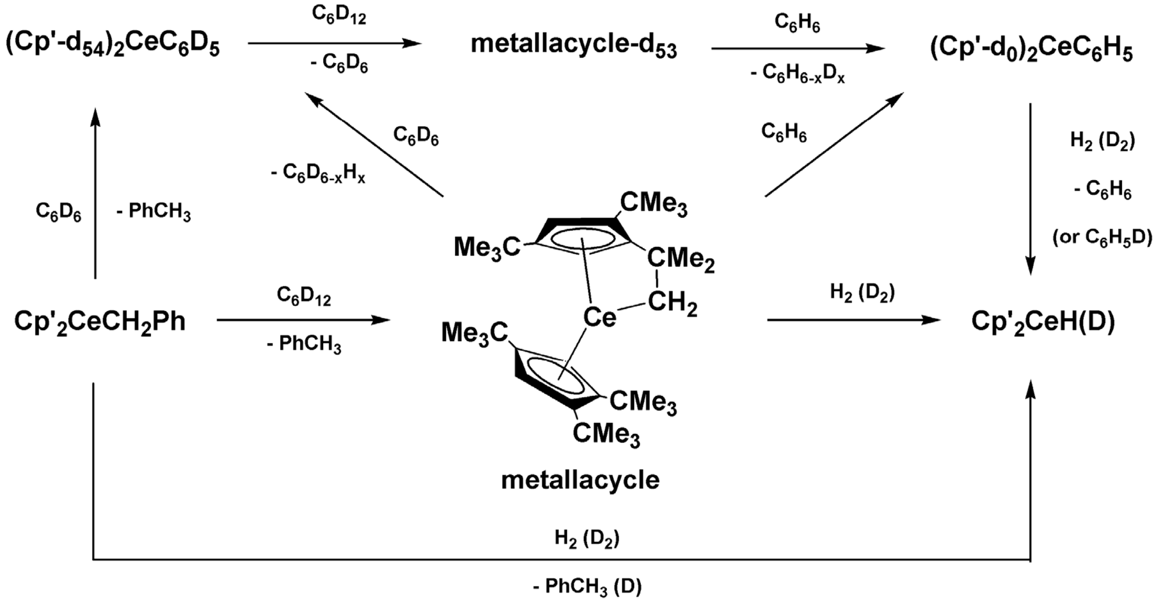
The yellow crystals obtained from the reaction of $ClMgCH_2C_6H_5$ and the triflate likely result from an undesired substitution of the triflate leaving group with the chloride of the Grignard reagent, forming Cp'_2CeCl. The identity of the product is confirmed by independent synthesis of Cp'_2CeCl from Cp'_2Mg and anhydrous $CeCl_3$ in a 1:10 mixture of toluene and pyridine heated at reflux for one day. The yellow product is sparingly soluble in pentane, but crystallizes readily from toluene. Elemental analysis and EI mass spectroscopy are consistent with Cp'_2CeCl, and the ^1H NMR spectrum is identical to that of the yellow crystals obtained from the benzyl reaction.

Neither Cp'_2CeCl nor Cp'_2CeI react with $ClMgCH_2C_6H_5$ to yield $Cp'_2CeCH_2C_6H_5$. As discussed previously, $Cp'_2CeOSO_2CF_3$ can be synthesized from the iodide complex with three equivalents of $Me_3SiOSO_2CF_3$. The chloride complex can also be converted to the triflate by stirring with four equivalents of $Me_3SiOSO_2CF_3$ for two days.

1.3. Reactions of the Benzyl: Synthesis of the Phenyl, $Cp'_2CeC_6H_5$, and Metallacycle

The benzyl, $Cp'_2CeCH_2C_6H_5$, has a considerably longer lifetime in solution at 25°C than the presumed methyl and trimethylsilylmethyl analogs observed in the ^1H NMR spectrum, 1 day instead of a few hours. Over time, the resonances due to the benzyl also disappear from the ^1H NMR spectrum, and the same set of multiple CMe_3 resonances observed in the spectra of the other alkyl complexes appear, along with toluene. Metallocenecerium alkyls with less substituted Cp rings than Cp' usually decompose to give blue, unreactive three ring substances of the form Cp_3Ce as their only readily identifiable product,[1,2] but the dark purple species obtained from the decomposition of the benzyl shows considerable reactivity even toward aromatic solvents. In C_6D_{12} solvent, a set of five large CMe_3 resonances and two smaller signals roughly 1/3rd their size appear in the ^1H NMR spectrum as the resonances due to the benzyl disappear. In C_6D_6 solution, the same CMe_3 resonances appear in equilibrium with another set of CMe_3 resonances with a 2:1 area ratio. On a synthetic scale, a solution of Cp'_2CeCH_2Ph heated at reflux in C_6H_6 for three days gives a red solution, and a red powder upon removal of the solvent. Crystallization from pentane yields a deep red powder whose elemental analysis is consistent with the formulation $Cp'_2CeC_6H_5$. The ^1H NMR spectrum in C_6D_6 is identical to that observed in the NMR tube experiment described above, with the addition of two small resonances whose intensities and coupling pattern (doublet and triplet) are consistent with those expected for the meta and para proton resonances of $Cp'_2CeC_6H_5$. The ortho proton resonance is not observed. In C_6D_{12} solvent, a sample of $Cp'_2CeC_6H_5$ decomposes over several hours at 25°C as resonances due to C_6H_6 and the same seven resonances seen in the decomposition of the benzyl appear. When a sample of $Cp'_2CeC_6H_5$ is heated at 65°C in C_6D_6 over the course of a week, all paramagnetic resonances slowly disappear from the ^1H NMR spectrum as the intensity of the $C_6H_{6-x}D_x$ resonances increase relative to an internal standard. Replacing essentially all of the C_6D_6 by C_6H_6 and heating regenerates the resonances of $Cp'_2CeC_6H_5$. Thus, the CMe_3 groups undergo reversible H/D exchange with C_6D_6 or C_6H_6, with formation of a $Cp'_2CeC_6H_5$ or $Cp'_2CeC_6D_5$ species. These observations suggest that the species giving rise to the seven resonances is the metallacycle

$[(Me_3C)_3C_5H_2][(Me_3C)_2C_5H_2(CMe_2CH_2)]Ce$, a deduction consistent with the reactions shown in Scheme 1.1. A related cerium metallacycle with pentamethylcyclopentadienyl ligands has been observed by heating $(Me_5C_5)_2CeCH(SiMe_3)_2$ in C_6D_{12}. This metallacycle is a tetramer in the solid state.[4]



Scheme 1.1: Reactions of the Metallacycle

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On a synthetic scale, warming the benzyl complex in pentane for 12 hours gives a deep purple solution, which upon removal of the solvent yields a purple glassy solid whose ^1H NMR spectrum in C_6D_{12} is identical to that observed in the NMR tube experiments mentioned above. The solid is highly soluble in pentane and cannot not be persuaded to crystallize; only small amounts of a yellow, insoluble powder, presumed to be the product of reaction of the metallacycle with traces of water (see below) are obtained. Although the metallacycle is not obtained in crystalline form, the sequence of reactions in Scheme 1.1 is consistent with the formulation given. That all of the CMe_3 groups are ultimately deuterated in C_6D_6 indicates that, if the metallacycle is monomeric, the structure shown is one of three possibilities, which in turn would suggest that the ^1H NMR spectrum reflects a time-averaged equilibrium among these three structures. The temperature dependent behavior of the seven principal ^1H NMR resonances of the metallacycle in C_7D_{14} is shown in the δ vs. 1/T plot in Figure 1.4. Three of the large CMe_3 resonances show linear Curie-Weiss behavior, while the other two are curves; these latter two presumably belong to the ring participating in the cycle.

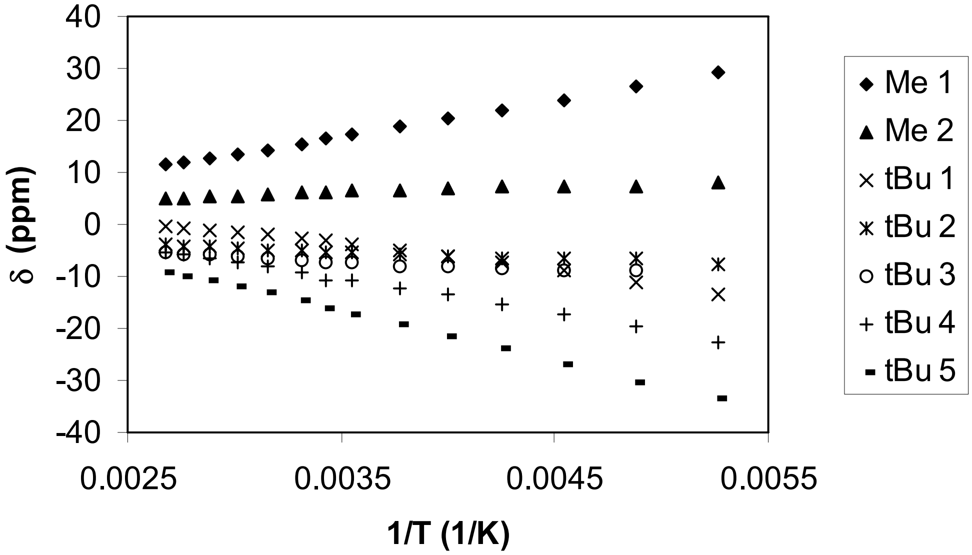


Figure 1.4: ^1H NMR δ vs. 1/T plot for the metallacycle

The temperature dependent behavior of the ^1H NMR resonances of the CMe_3 groups of $Cp'_2CeC_6H_5$ in C_7D_{14} is shown in the δ vs. 1/T plot in Figure 1.5. The compound decomposes rapidly to the metallacycle and benzene above 19°C, so only low temperature data is shown. The ^{1}H NMR spectrum at 19°C contains two large signals in a 2:1 area ratio, attributed to CMe_3 groups, and two smaller resonances, a doublet and a triplet in a 2:1 area ratio, *J* = 7 Hz, attributed to the meta and para-H's, respectively. At -55°C, a resonance emerges from the downfield side of the CMe_3 resonance of area 2. As the temperature decreases to -84°C, the new resonance gradually broadens into the baseline, while the parent resonance remains at ½ its former area. The coupling in the meta and para-H resonances disappears below -55°C, but no new resonances are observed. Apart from the curious behavior of the CMe_3 resonance, all resonances appear to show linear Curie-Weiss behavior.

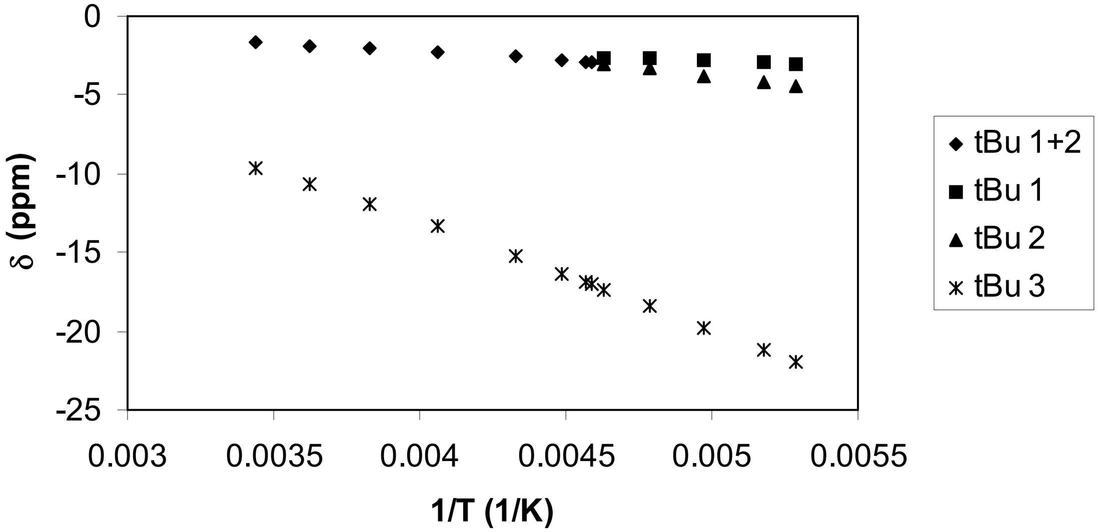


Figure 1.5: ^{1}H NMR δ vs. 1/T plot for the phenyl, $Cp'_2CeC_6H_5$.

1.4. Reactions of the Benzyl: Synthesis of the Hydride, Cp'$_2$CeH

A number of dimeric metallocene hydrides of the lanthanides are known,[5] including two dimeric metallocenecerium hydrides, $(C_5Me_5)_4Ce_2(\mu\text{-}H)_2$ and $[1,3\text{-}(Me_3C)_2C_5H_3]_4Ce_2((\mu\text{-}H)_2$.[6] In the Cp'-ligand system, solutions of the metallacycle or the benzyl in pentane react with 1 atm of H_2 to give a brilliant red-purple solution. The reaction with the metallacycle is essentially instantaneous, while the reaction with benzyl is complete after 30 minutes. Deep purple crystals can be isolated from the concentrated reaction mixture cooled to -15°C. It is necessary to crystallize the product from the reaction, as any extra manipulations or the introduction of additional solvent invariably leads to co-crystallization of the purple product with a yellow, sparingly soluble powder similar to that obtained from the metallacycle crystallization attempts.

The ^{1}H NMR spectrum of the purple crystals dissolved in C_6D_6 clearly shows two types of CMe_3 groups in a 2:1 area ratio and the single resonance of the four equivalent ring methyne protons. Elemental analysis is consistent with the formulation Cp'$_2$CeH, but the EI mass spectrum gives an $(M\text{-}2)^+$ of 605, i.e. the metallacycle. The Ce-H stretching frequency could not be identified in the infrared spectrum, even when directly compared with the deuteride, Cp'$_2$CeD, prepared by exposing the benzyl to an atmosphere of D_2 rather than H_2, nor could the Ce-H resonance be observed in the ^{1}H NMR spectrum. The complex is stable in aliphatic solvents and can be stored indefinitely in solid form under a nitrogen atmosphere, but is extremely sensitive to air and water, hence the need to crystallize the product directly from the reaction mixture. Crystals suitable for x-ray diffraction studies were obtained in this manner; an ORTEP drawing is shown in Figure 1.6 and selected distances and angles are listed in the caption. The molecule crystallizes in the monoclinic space group $P2_1/n$. The hydrogen atoms on the Cp' ligands were placed in calculated positions, while H59, the hydride ligand, was found in the difference Fourier map and refined with isotropic thermal parameters. The structure clearly shows Cp'_2CeH to be a monomer, with no close contacts out to 3.60Å. The centroid-metal-centroid angle is 154.7°, and the cyclopentadienyl rings adopt an eclipsed configuration similar to that observed in the structure of Cp'_2Mg, where one of the two adjacent CMe_3 groups on each ring eclipses another.[7]

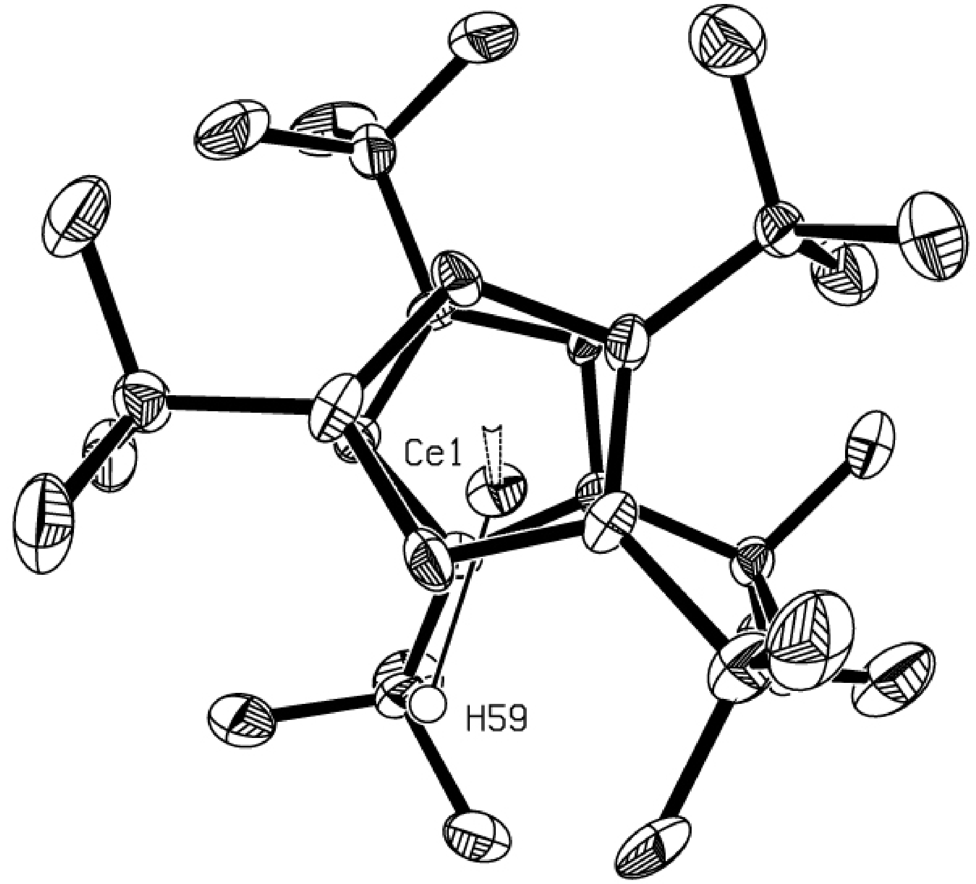


Figure 1.6: ORTEP Drawing of Cp'_2CeH. Selected Bond Distances and Angles: Ce-H: 1.90(5) Å, Ce-ring C (range): 2.757(7)-2.840(6) Å, Ce-centroid: 2.5146(5), 2.5456(5) Å, centroid-Ce-centroid: 154.56(2)°

The ^1H NMR resonances of the hydride follow linear Curie-Weiss behavior. Over the temperature range of the experiment, the CMe_3 resonance of area 2 never decoalesces to two resonances of area 1 as is observed in previous complexes. The δ vs. 1/T plot is shown in Figure.1.7

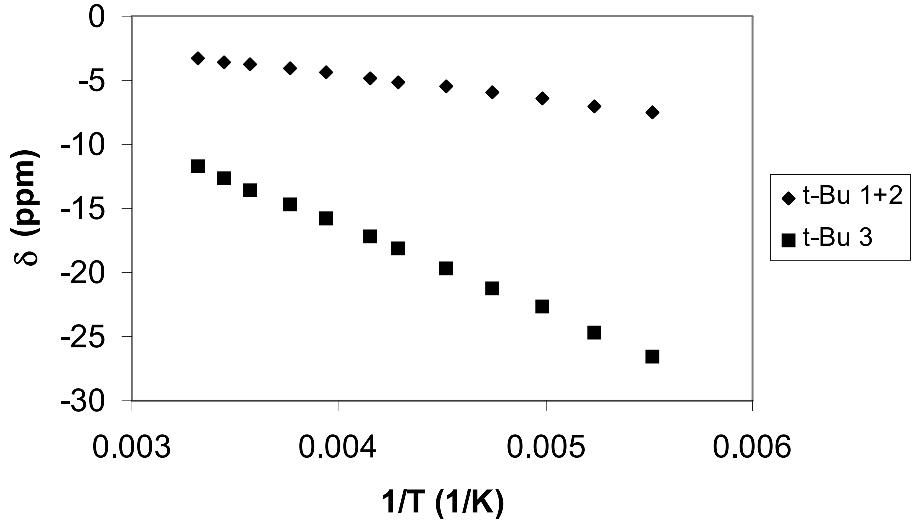


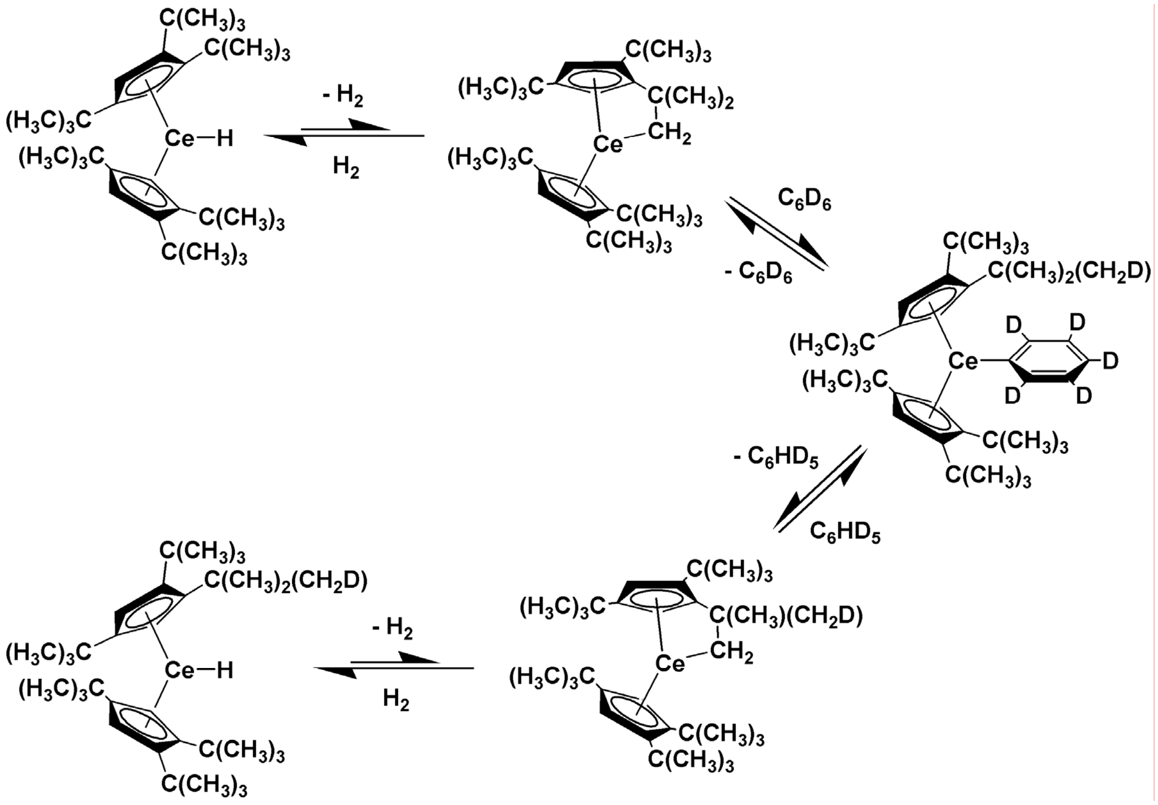
Figure 1.7: ^{1}H NMR δ vs. 1/T plot for the hydride, Cp'$_2$CeH, in C_7D_8.

When a sample of metallacycle is exposed to D_2, small resonances arising from both types of CMe_3 groups of Cp'CeD appear in the ^{2}H NMR spectrum in a 2:1 ratio, mirroring the large resonances that appear in the ^{1}H NMR spectrum. This is further evidence that C-H bonds in both types of CMe_3 groups can be activated to form the metallacycle.

The ^{1}H NMR spectrum of the hydride in C_6D_6 solution shows no direct evidence of reaction to form either the phenyl or the metallacycle. However, upon prolonged exposure to C_6D_6 at 25°C, or more rapidly upon heating to 60°C, the resonances due to Cp'$_2$CeH disappear from the ^{1}H NMR spectrum and appear in the ^{2}H NMR spectrum. The resonances due to $C_6H_{6-x}D_x$ concurrently increase in the ^{1}H NMR spectrum. The

CMe_3 groups of the hydride are clearly undergoing H/D exchange with C_6D_6 analogous to that observed in the metallacycle, at approximately the same rate.

While it cannot be proven, since no intermediates are detected in the ^1H NMR spectrum, a simple process that could account for the H/D exchange observed in the hydride is shown in Scheme 1.2. In the first step, the metallacycle forms and H_2 dissociates. The metallacycle then reacts with C_6D_6 to form the phenyl-d_6, with one CMe_3 proton replaced by deuterium. Elimination of C_6HD_5 gives the metallacycle-d_1, which can then react with another C_6D_6 molecule to continue the deuteration, or with H_2 to reform the hydride-d_1. The process repeats, and the CMe_3 groups are eventually fully deuterated. The equilibrium process shown in Scheme 1.2 would lie in favor of the hydride, as it is the only species observed in the ^1H NMR spectrum during the week-long deuteration process.



Scheme 1.2: Possible scenario for deuteration of ring CMe_3 groups in Cp'_2CeH.

1.5. Other Reactions of the Benzyl

The benzyl reacts readily with ammonia to form Cp'_2CeNH_2. As with the reaction of the benzyl with H_2 to form the hydride, it was necessary to keep manipulations to a minimum and crystallize the product from the reaction mixture to avoid co-crystallization with a yellow, sparingly soluble powder. As previously mentioned, this yellow powder is believed to be a product of the reaction with water.

Attempts to synthesize the hydroxyl compound, Cp'_2CeOH, from the benzyl and water in diethyl ether were unsuccessful. The crude yellow solid obtained when the reaction mixture is taken to dryness is initially soluble in C_6D_6, and gives a pair of CMe_3

resonances in a 2:1 area ratio in the ^{1}H NMR spectrum. Within 10 minutes, a yellow precipitate begins to form, and resonances due to Cp'H increase in the spectrum. The crude solid is likewise initially soluble in hexane, but upon exposure to vacuum or heating, a yellow precipitate appears which cannot be redissolved. A small amount of the precipitate can be dissolved in C_6D_6, and the ^{1}H NMR spectrum contains three new CMe_3 resonances in a 1:1:1 area ratio, along with several smaller resonances. This pattern of resonances is also observed in the ^{1}H NMR spectra of the sparingly soluble yellow powders sometimes obtained from solutions of $Cp'_2CeCH_2C_6H_5$, Cp'_2CeH, Cp'_2CeNH_2, and the metallacycle.

As with the hydrides, the handful of reported base-free metallocene lanthanide fluorides are dimers.[8] Monomeric metallocene fluorides of Yb, Eu, and Sm as THF and diethyl ether adducts have also been reported.[9] With one exception,[10] syntheses of these fluoride complexes make use of divalent lanthanoid complexes as starting materials. $BF_3 \bullet OEt_2$ has been reported as a useful reagent in the synthesis of metalloceneuranium(IV) fluorides from U(IV) starting materials. Examples include $[1,3\text{-}(Me_3Si)_2C_5H_3]_2UF_2$ synthesized from the corresponding bis(dimethylamino) complex, and $[1,3\text{-}(Me_3C)_2C_5H_3]_2UF_2$ from the corresponding dimethoxy and dimethyl complexes. An analogous reaction of $BF_3(OEt_2)$with $Cp'_2CeCH_2C_6H_5$ would be expected to generate Cp'_2CeF. Adding $BF_3(OEt_2)$ to a pentane solution of the benzyl results in a rapid color change from red to yellow. Removal of the solvent results in a yellow powder, which is readily extracted into pentane. Elemental analysis of the yellow crystals obtained from this concentrated pentane solution indicated the formation, not of Cp'_2CeF, but of

Cp'_2CeBF_4. The ^1H NMR spectrum contains two broad ($\nu_{1/2}$ ~ 900Hz) and one somewhat sharper CMe_3 resonance in a 1:1:1 area ratio. The extra BF_3 cannot be liberated by prolonged exposure to dynamic vacuum, nor by sublimation of the solid under static vacuum. Adding an excess of pyridine to a pentane solution of Cp'_2CeBF_4 results in a slightly more orange solution, which upon removal of solvent yields a yellow solid. Crystallization from pentane yields yellow crystals whose ^1H NMR spectrum in C_6D_6 consists of a pair of CMe_3 resonances in a 2:1 area ratio, a resonance of area 4 relative to the CMe_3 resonances presumably corresponding to the ring methyne protons, and two broad resonances of area 2 and 1. The CHN elemental analysis indicates a stoichiometry appropriate for Cp'_2CeF(pyridine). The coordinated pyridine likewise resists removal by heating and exposure to vacuum. Cp'_2CeBF_4 and three equivalents of the benzyl stirred in pentane, followed by crystallization from the orange reaction mixture, ultimately yields an orange powder whose elemental analysis corresponds to base-free Cp'_2CeF.

Crystals suitable for x-ray diffraction studies can be grown *via* sublimation of Cp'_2CeF powder under static vacuum at 118°C in a sealed glass ampoule. An ORTEP drawing is shown in Figure 1.8, and selected distances and angles are listed in the figure caption. Cp'_2CeF crystallizes as a monomer in the monoclinic space group $P2_1/n$. The centroid-metal-centroid angle is 148.9°, and the orientation of the rings and position of the fluoride ligand closely resemble those of the hydride. The temperature dependence of the ^1H NMR resonances of Cp'_2CeF in C_7D_8 solvent also resembles that of the hydride. The CMe_3 resonances maintain a 2:1 area ratio and display linear Curie-Weiss behavior between –80 and 90°C.

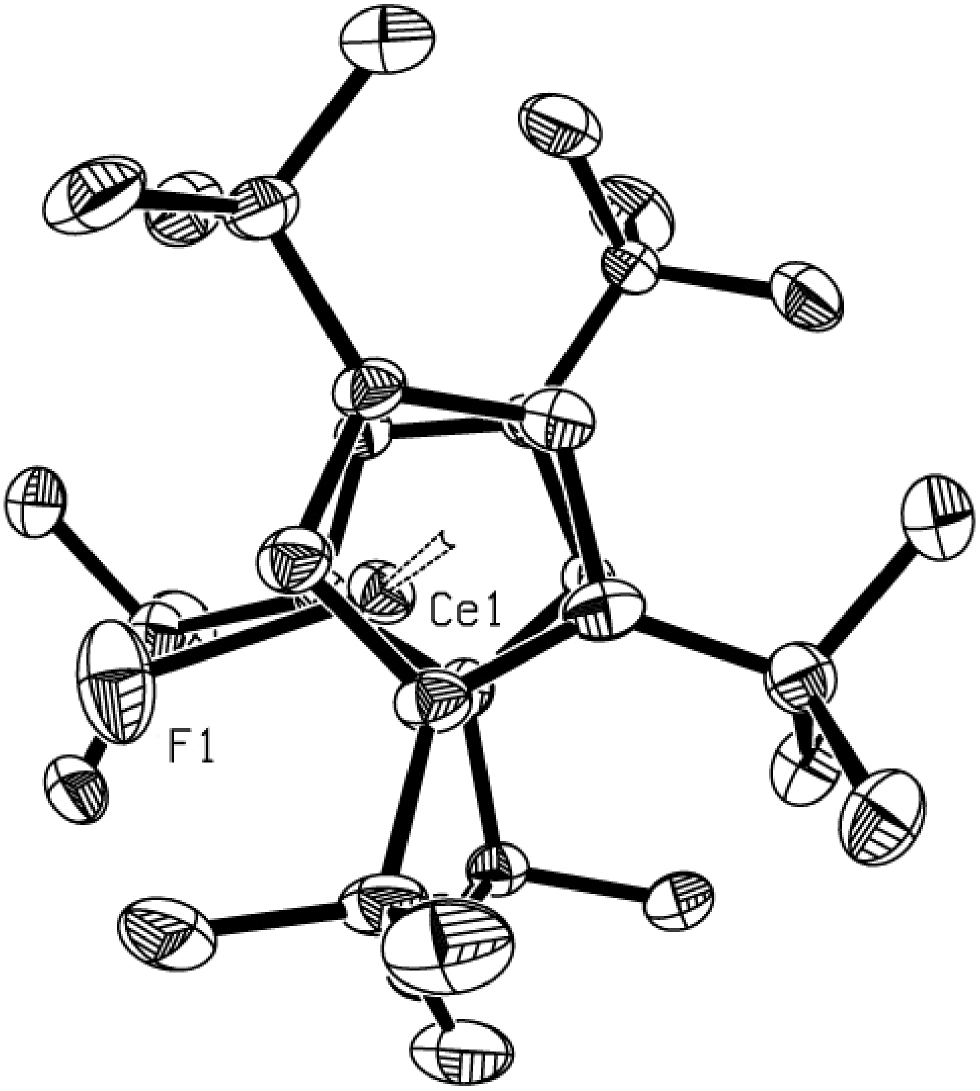


Figure 1.8: ORTEP Drawing of Cp’$_2$CeF. Selected Bond Distances and Angles: Ce-F: 2.165(2) Å, Ce-ring C (range): 2.780(3)-2.878(3) Å, Ce-centroid: 2.5303(2), 2.5683(2) Å, centroid-Ce-centroid: 148.850(7)°

Attempts to recrystallize the fluoride from pentane inevitably lead to co-crystallization with a yellow powder. Unlike the insoluble yellow powders obtained from recrystallization of the hydride, amide, benzyl, or metallacycle, the yellow powder obtained from the fluoride is pentane soluble and gives a pair of CMe_3 resonances with a 2:1 area ratio in the ^1H NMR spectrum. A drop of pyridine-d_5 added to a C_6D_6 solution of the yellow powder shifts the CMe_3 resonances, but the resulting ^1H NMR spectrum is not that of Cp'_2CeF(pyridine). The powder decomposes upon melting, liberating Cp'H. Sublimation of the fluoride therefore requires crude material that is essentially free of this material; otherwise the sublimation fails due to Cp'H from the decomposed powder coating the walls of the ampoule.

In the interest of transferring the chemistry observed in Ce(III) to U(III), a series of exchange reactions were performed by Dr. Jochen Gottfriedsen utilizing Cp'_2CeH and various uranium halides and pseudohalides.[12] When $Cp'_2UOSO_2CF_3$ and Cp'_2CeH are mixed in C_6D_6 solution, the ^1H NMR spectrum indicates the formation of Cp'_2CeF among other products. The analogous experiment of mixing $Cp'_2Ce(OSO_2CF_3)$ and Cp'_2CeH also instantaneously gives Cp'_2CeF, along with a new cerium metallocene thought to be $Cp'_2Ce(OSO_2CHF_2)$, the result of intermolecular H/F exchange. This result prompted the in-depth study of the C-F activation chemistry of the hydride detailed in the next two chapters.

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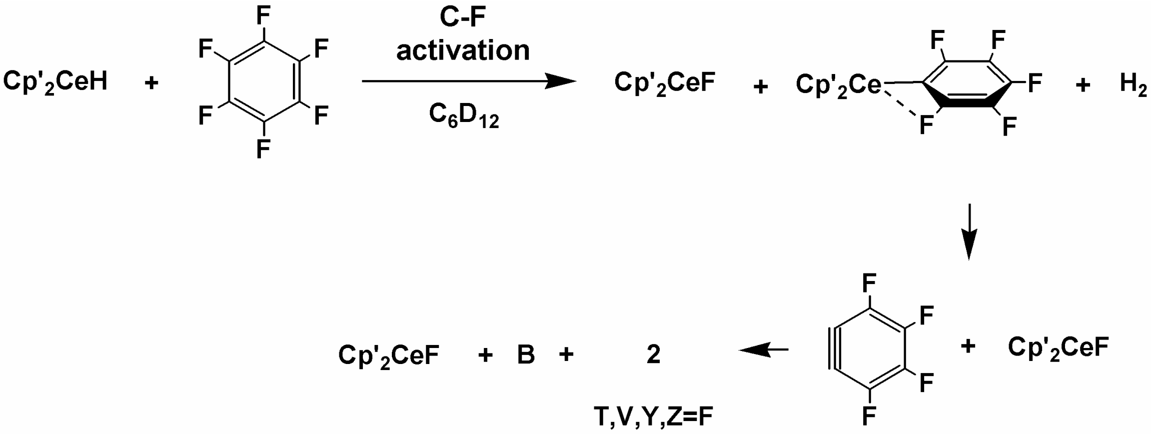
Chapter 2: Reactions of the Hydride and Metallacycle with Fluorobenzenes

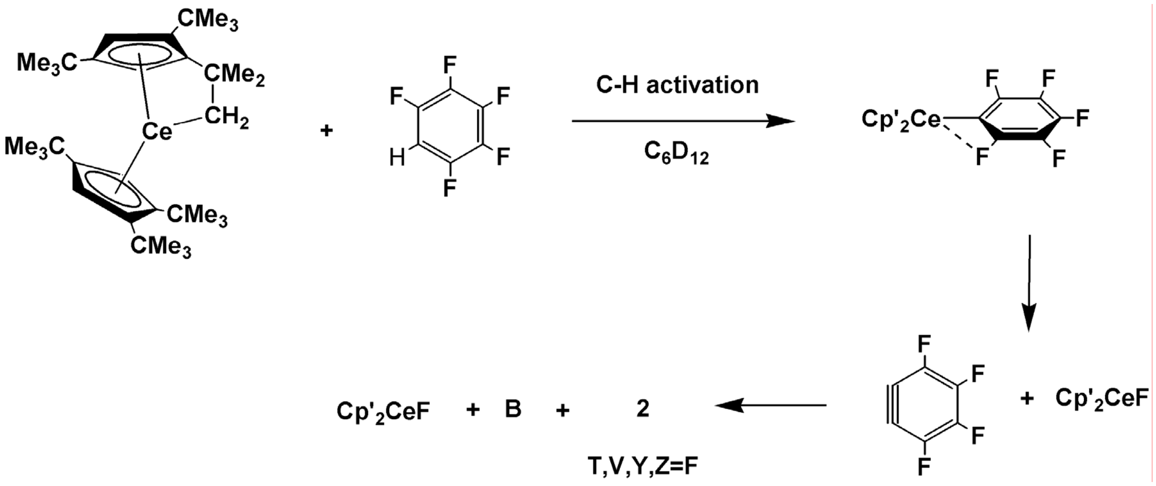
Lanthanide metals in the gas phase will defluorinate fluorocarbons.[1] For example $Ce^{+}(g)$ defluorinates C_6F_6 giving $CeF^{+}(g)$, the radical $C_6F_5\bullet$, $CeF_2^{+}(g)$ and C_6F_4 (a benzyne).[2] In addition, the metallocene $(Me_5C_5)_2Yb$ abstracts a fluorine atom from C_6F_6 giving $[(Me_5C_5)_2Yb]_2(\mu\text{-}F)$,[3] and $(MeC_5H_4)_3UCMe_3$ exchanges the CMe_3 with F in C_6F_6.[4] The general subject of intermolecular C-F activation has been extensively studied and several reviews are available, largely within the framework of oxidative addition reactions.[1,5] Computational studies have shown that the C-F activation may be exothermic but that a high activation barrier is usually observed with late transition metal systems.[6] In the case of early transition metals, the activation barrier is generally lower and several cases of H/F exchange have been observed; it appears that the $C(sp^2)$-F bond is activated more easily than the $C(sp^3)$-F bond.[7] The reactions of bare metal centers have been analyzed by computational methods, showing that electron transfer as well as oxidative insertion paths are possible.[8]

The hydride, Cp'_2CeH, is found to undergo H/F exchange with a series of fluorobenzenes, CH_xF_{6-x}, x = 0 - 5. The reactions never generate Cp'_2CeF exclusively; one or more additional paramagnetic species appear in the ^1H NMR spectra of the reaction mixtures. These are found to be metastable metallocenecerium polyfluorophenyl species of the form $Cp'_2Ce(C_6H_xF_{5-x})$, x = 0 - 4. The multiple products apparently arise from the ability of the hydride to activate both C-F and C-H bonds in fluorobenzenes. In contrast, the metallacycle, $[(Me_3C)_3C_5H_2)][Me_3C)_2C_5H_2(CMe_2CH_2)]Ce$, is found to activate only C-H bonds, generating the $Cp'_2Ce(C_6H_xF_{5-x})$ complexes cleanly and quantitatively. Reactions of the hydride and the metallacycle that give common products are grouped together in the sections that follow, with schemes depicting the proposed reactions at the beginning of each section.

2.1 Hexafluorobenzene and the hydride; pentafluorobenzene and the metallacycle



Scheme 2.1: Proposed reaction of the hydride with hexafluorobenzene.



Scheme 2.2: Proposed reaction of the metallacycle with pentafluorobenzene

When a drop of C_6F_6 (an excess) is added to Cp’$_2$CeH in C_6D_6 in a NMR tube, the red-purple color of the hydride changes upon mixing to the orange of Cp'$_2$CeF, and a gas is evolved. Examination of the ^{1}H NMR spectrum shows that the resonances due to Cp’$_2$CeH are absent and new sets of resonances due to Cp’$_2$CeF, H_2, and a new paramagnetic species with a pair of CMe_3 resonances in a 2:1 area ratio have appeared. A small amount of C_6HF_5 is also observed. Over time, the resonances due to Cp’$_2$CeF increase in intensity at the expense of those due to the new species.

The metallacycle does not react with C_6F_6, even after standing for four days at 25°C in C_6D_{12}. In contrast, a deep purple solution of the metallacycle in C_6D_{12} immediately turns orange when a drop of C_6HF_5 is added. In the ^{1}H NMR spectrum, resonances due to the metallacycle are absent, and a new set of CMe_3 resonances in a 2:1 ratio appear whose chemical shifts are identical to the new species seen in the reaction of the hydride and C_6F_6. On a synthetic scale, adding a stoichiometric amount of C_6HF_5 to a solution of the metallacycle in pentane yields an orange solution from which orange crystals may be obtained. The ^{1}H NMR spectrum of the crystals dissolved in C_6D_{12} is identical to that observed in the mixing experiment. The crystals decompose rather violently on attempted melting in a sealed melting point capillary at about 125°C; extracting the residue into C_6D_6 and examining the ^{1}H NMR spectrum shows resonances due to Cp'_2CeF, as well as several unidentified diamagnetic and paramagnetic resonances. The EI mass spectrum is an incomprehensible collection of peaks, presumably due to this same self-destructive thermal behavior. Fortunately, single crystals of $Cp'_2Ce(C_6F_5)$ suitable for x-ray diffraction studies can be obtained from concentrated pentane solutions. An ORTEP diagram is shown in Figure 2.1, with selected bond distances and angles listed in the caption. The molecule crystallizes in the triclinic space group $P\bar{1}$. The centroid-metal-centroid angle is 146.6°, with the rings adopting a staggered orientation similar to that seen in the triflate, Figure 1.1. The carbon atom of the C_6F_5 group, C35, is located close to the idealized C_2 axis, but the Ce-C35-C36,40 angles are very anisotropic due to a short Ce$\cdots$F-C(ortho) contact of 2.682(2) Å. A pair of close ortho-F$\cdots$Sm contacts of 2.531(8) Å and 2.539(7) Å were found in dimeric $(C_5Me_5)_4Sm_2(C_6F_5)_2$ and in monomeric $(C_5Me_5)Yb(C_6F_5)(thf)_3$ where the ortho-F$\cdots$Yb distance is 3.162 Å.[9]

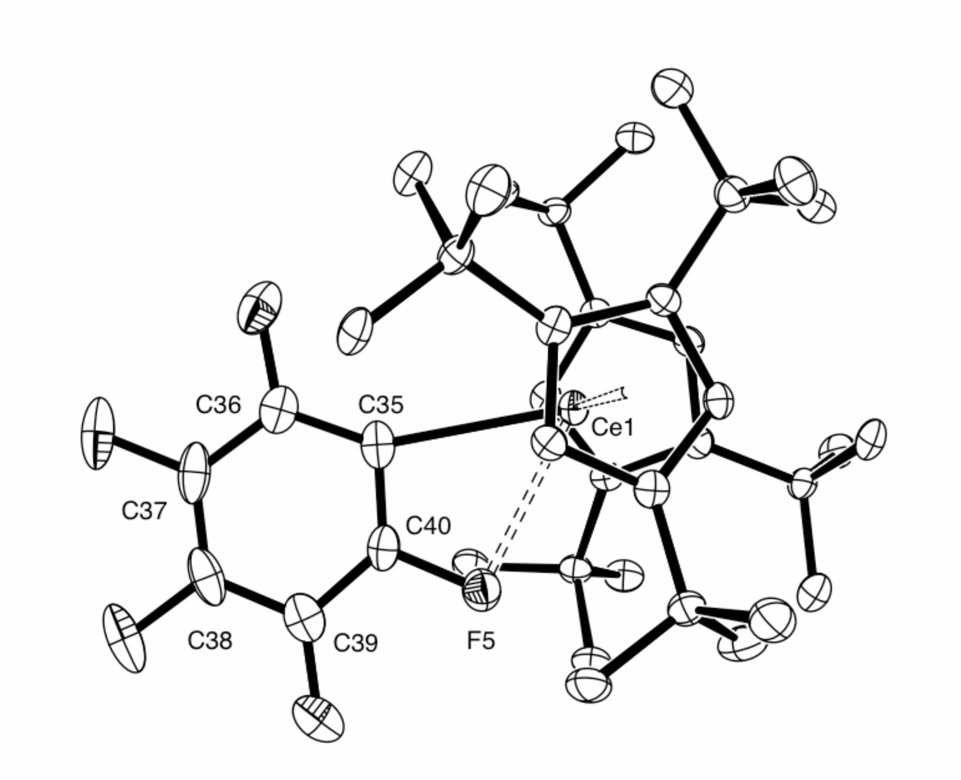


Figure 2.1 ORTEP Diagram of Cp’$_2$Ce(C_6F_5). Selected bond distances and angles: Ce1-ring C (range) = 2.753(4)-2.894(4) Å, Ce1-centroid = 2.5383(3) Å, 2.5430(2) Å, Ce1-C35 = 2.621(4) Å, Ce1···F5 = 2.682(2) Å, centroid-Ce1-centroid = 146.556(8)°, centroid-Ce1-C35 = 104.44(8) °, 108.88(8)°, centroid-Ce1-F5 = 100.10(5)°, 102.24(5)°, Ce1-C35-C36 = 149.7(3)°, Ce1-C35-C40 = 97.5(3)°.

In solution at 25°C, the ^{1}H and ^{19}F NMR spectra are not consistent with the solid state crystal structure, where the idealized symmetry is C_1 and all of the CMe_3 groups and F atoms are inequivalent. The ^{1}H NMR absorptions change as a function of temperature: the CMe_3 resonance of area 2 decoalesces into two equal area resonances at T_c = -25°C, while the other CMe_3 resonance of area 1 has a normal temperature dependence (Figure 2.2), giving a $\Delta G^{\#}_{TC}$ = 10 kcal mol^{-1}. At still lower temperatures, three additional CMe_3

resonances appear out of the baseline as the intensity of the original CMe_3 resonances diminish. The 25°C ^{19}F NMR spectrum consists of three resonances, two of area 2 and one of area 1. One of the area 2 resonances is broad ($\nu_{1/2}$ = 480 Hz), probably corresponding to the ortho-F, and the other two resonances are a doublet and triplet, J = 18Hz, with a 2:1 area ratio, presumably corresponding to the meta and para fluorines, respectively. Lowering the temperature shifts the resonances, and coupling disappears at -25°C as the resonances broaden. Below -50°C, a new resonance emerges from the downfield side of the para-F resonance, labeled para Fa in Figure 2.3, with an area approximately 1/3rd that of its parent (Figure 2.3).

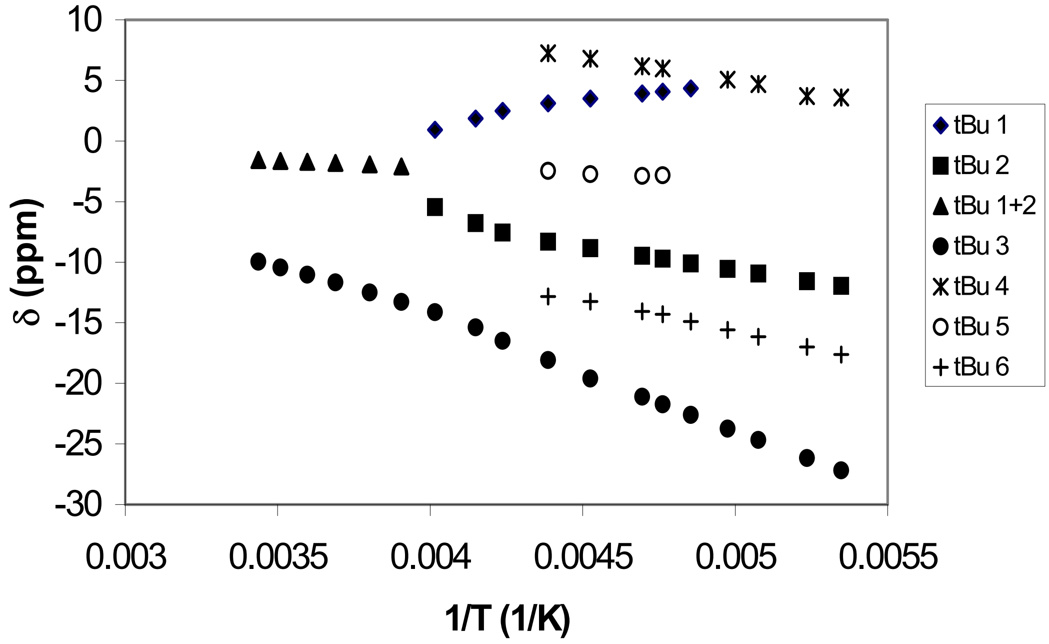


Figure 2.2: ^1H NMR δ vs. 1/T plot for $Cp'_2Ce(C_6F_5)$ in C_7D_{14}.

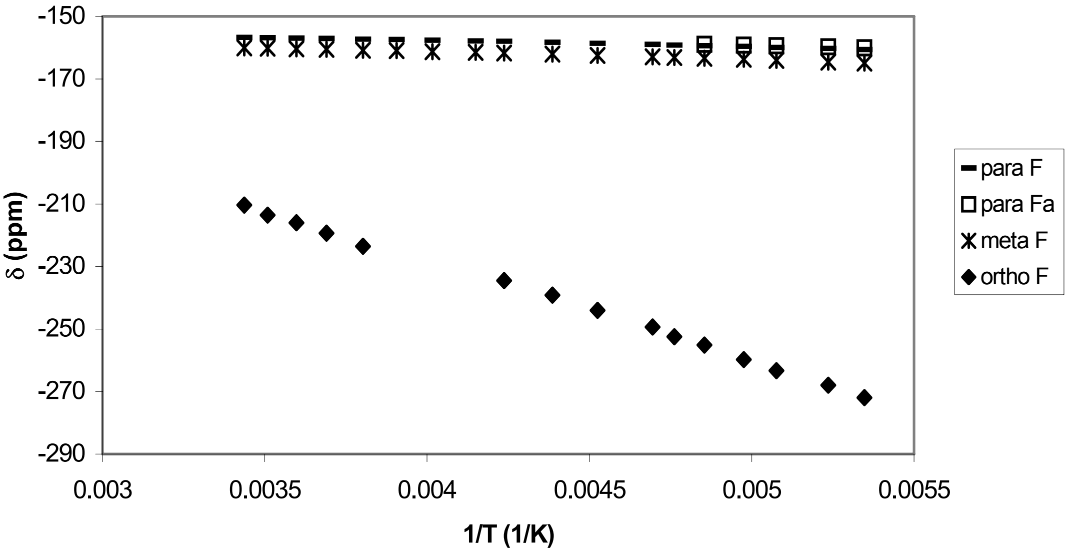
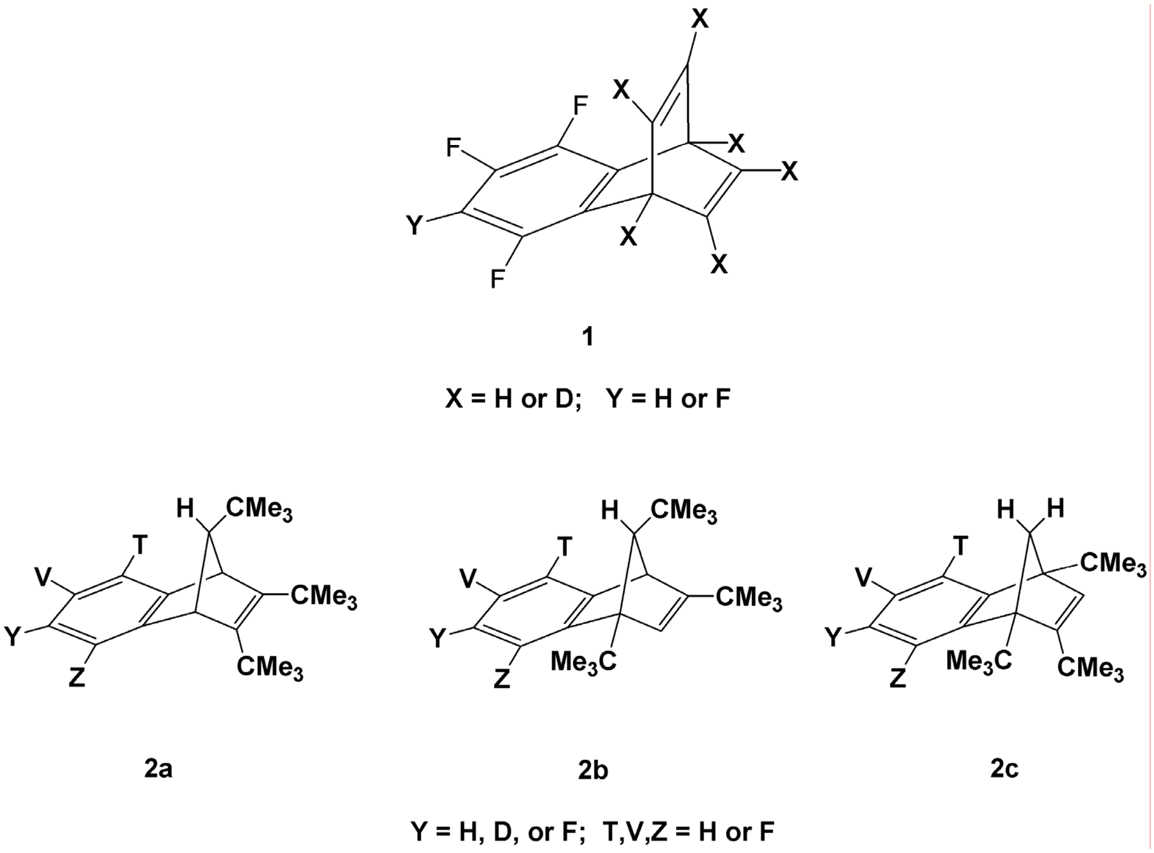


Figure 2.3: ^{19}F NMR δ vs. 1/T plot for Cp'$_2$Ce(C_6F_5) in C_7D_{14}.

The 2:1 pattern of the CMe_3 resonances changing to a 1:1:1 pattern at low temperatures is consistent with a metallocene whose idealized symmetry changes from C_{2v} to C_s, with the C_6F_5 ring lying in the mirror plane. Several physical processes can account for loss of the time averaged C_2-axis and vertical mirror plane that give rise to idealized C_{2v} symmetry, two of which are slowing the librational motion of the Cp'-rings about their pseudo-C_5 axes, and slowing the rocking motion of the C_6F_5 ring in the horizontal mirror plane. The $\Delta G^{\#}_{TC}$ is similar to that observed in Cp'$_2$CeI, where only the librational process is possible. It is more difficult to rationalize a physical process that accounts for the observed temperature dependent behavior below -25°C in the ^{1}H and ^{19}F

NMR spectra. The C_1 symmetry of the solid state structure would be expected to result in six CMe_3 resonances of equal population in the ^1H NMR spectrum and five resonances in the ^{19}F NMR spectrum. In the actual ^1H NMR spectrum, the CMe_3 resonances have unequal population, and only four resonances of unequal population are present in the ^{19}F NMR spectrum. Two distinct conformational isomers with idealized C_s symmetry but of unequal population could account for the six CMe_3 resonances and unequal populations, but would also be expected to produce two sets of five resonances in the ^{19}F NMR spectrum, assuming the ortho-fluorine resonances are observed. The solid state structure shows no close intermolecular contacts, which argues against a monomer/dimer equilibrium.

$Cp'_2Ce(C_6F_5)$ decomposes slowly in a solution of C_6D_6 to give a slightly less than stoichiometric amount of Cp'_2CeF. Examination of the ^{19}F NMR spectrum shows an AA'BB' pattern whose chemical shifts and coupling pattern are identical to the Diels-Alder adduct **1**, X = D, Y = F, between tetrafluorobenzyne and benzene-d_6.[10] Hydrolysis of the mixture with H_2O and injection into a GCMS gives the M^+ for **1**, X = D, Y = F. Repeating the experiment, but replacing the C_6D_6 with C_6H_6 followed by hydrolysis with H_2O and injection into a GCMS gives M^+ for **1,** X = H, Y = F. Thus $Cp'_2Ce(C_6F_5)$ decomposes by forming Cp'_2CeF and tetrafluorobenzyne that is trapped by the solvent benzene, a common decomposition pattern of pentafluorophenyl metal compounds.[11]



Scheme 2.3: Products of [2+4] cycloaddition of benzynes with benzene, **1,** and Cp'H, **2**.

With the identification of Cp'$_2$Ce(C$_6$F$_5$) and **1**, the net reactions symbolized in equations 2-1a through d may be suggested for the reaction of Cp'$_2$CeH and C$_6$F$_6$. Equation 2-1a is an intermolecular C-F activation, 2-1c is a C-H activation, and both yield Cp'$_2$Ce(C$_6$F$_5$), which ultimately decomposes to Cp'$_2$CeF and tetrafluorobenzyne. Equations 2-1b and 2-1d destroy the HF that is formed, producing Cp'$_2$CeF. No intermediates are detected other than Cp'$_2$Ce(C$_6$F$_5$), and in the absence of facilities for dealing with anhydrous HF, only the reaction in 2-1c can be easily tested (see next section). DFT calculations performed by Eisenstein and colleagues suggest that the kinetics of reaction 2-1a is considerably more favorable than a simple H/F exchange through a 4-center metathesis transition state to produce Cp'_2CeF and C_6HF_5.[12]

$Cp'_2CeH + C_6F_6$ -> $Cp'_2Ce(C_6F_5) + HF$ (2-1a)

$Cp'_2Ce(C_6F_5) + HF$ -> $Cp'_2CeF + C_6HF_5$ (2-1b)

$Cp'_2CeH + C_6HF_5$ -> $Cp'_2Ce(C_6F_5) + H_2$ (2-1c)

$Cp'_2CeH + HF$ -> $Cp'_2CeF + H_2$ (2-1d)

Performing the reaction of the hydride with C_6F_6 in the presence of dihydroanthrecene or an atmosphere of H_2 or D_2 does not appear to alter the course of the reaction. No anthracene or hydrogenated products are detected.

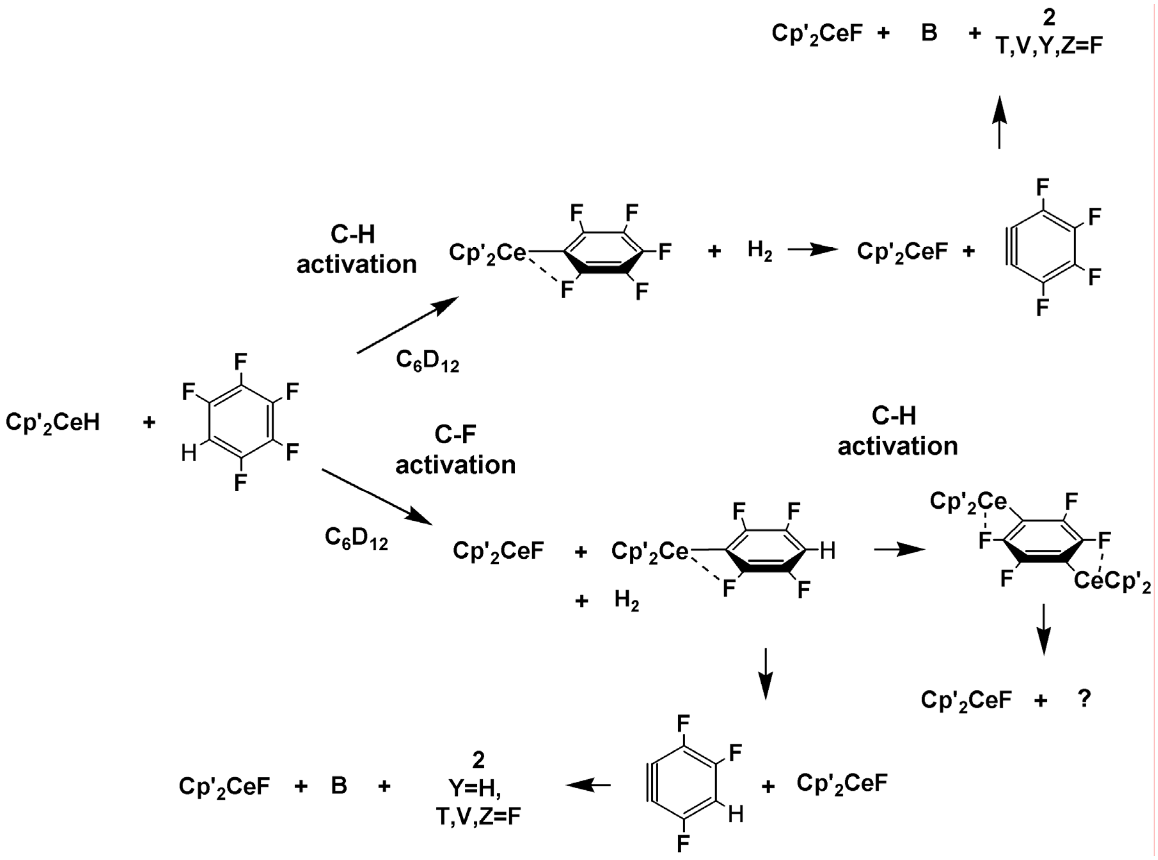
Changing the solvent from C_6D_6 to C_6D_{12} removes the trap for tetrafluorobenzyne. In C_6D_{12}, $Cp'_2Ce(C_6F_5)$ decomposes to Cp'_2CeF, an unknown complex B, and a new organic product over 12 hours at 60°C. Hydrolysis with D_2O or H_2O and injection into the GCMS shows one major fluorinated organic compound with $M^+ = 382$ along with Cp'D or Cp'H. This organic product is likely to be **2a**, T,V,Y,Z = F, the [2+4] cycloaddition product of tetrafluorobenzyne and the substituted cyclopentadienyl ring. The ^{19}F NMR spectrum consists of an AA'BB' pattern similar to that found in **1**, and the ^1H NMR spectrum shows two CMe_3 resonances in a 2:1 area ratio, suggesting that tetrafluorobenzyne adds across the pair of Cp'-ring carbons without CMe_3 groups giving the symmetric structure shown in **2a**, T,V,Y,Z = F. The two other possible isomers **2b** and **2c**, T,V,Y,Z = F, where the [2+4] cycloaddition involves Cp'-

ring carbons bearing CMe_3 groups, may also be formed, as other low intensity absorptions are visible in the ^1H and ^{19}F NMR spectra, and other products observed in the GCMS give mass spectra with $(M-57)^+ = 325$. However, **2a**, T,V,Y,Z = F, is the major isomer formed.

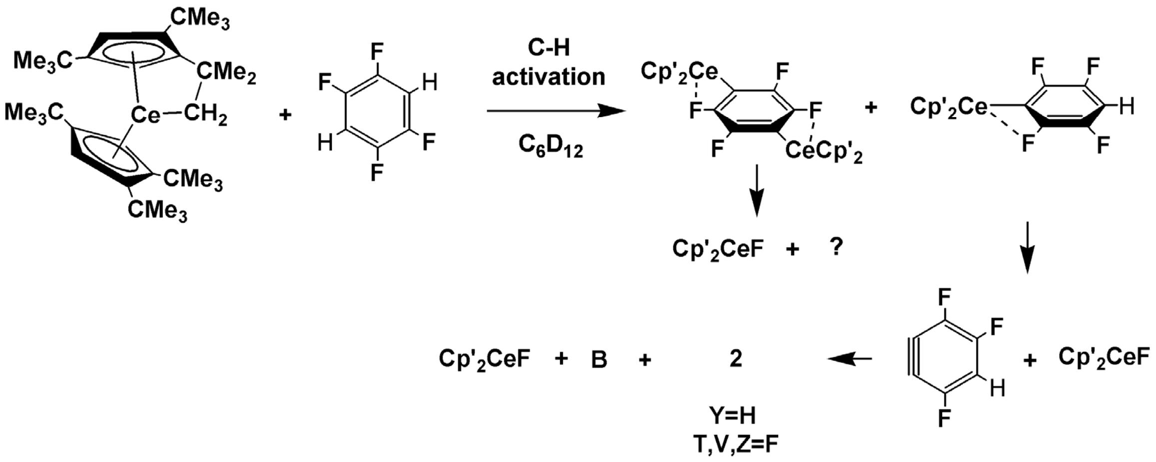
Assuming the tetrafluorobenzyne attacks a Cp'-ring bound to cerium, an extra proton is needed to generate any of the isomers of **2**. When $(Cp'\text{-}d_{27})_2CeC_6F_5$ is allowed to decompose in C_6D_{12} and the residue is hydrolyzed with H_2O and analyzed by GCMS, the M^+ at 410 is observed, implying that the source of the "other" hydrogen is a ring CMe_3. Close inspection of the ^{19}F NMR spectrum resulting from decomposition of $Cp'_2Ce(C_6F_5)$ in C_6D_6 shows that the **2a**, T,V,Y,Z = F, is also present to the extent of about 10%, suggesting that the Cp'-ring can compete with C_6D_6 as a trap for tetrafluorobenzyne. Cyclopentadiene and its anion are capable of trapping benzyne[13] and furan, and other dienes trap tetrafluorobenzyne,[14] so the suggestion that Cp' traps tetrafluorobenzyne is not without precedent.

Complex B, the other cerium-containing product of the decomposition of $Cp'_2Ce(C_6F_5)$, appears as a minor product, accounting for less than 10% of the starting material, in the decompositions of many of $Cp'_2Ce(C_6H_xF_{5-x})$ complexes (see subsequent sections), as well as in the reaction of the hydride with CHF_3 and the metallacycle with CH_2F_2 and CHF_3 (Chapter 3). B has no apparent absorbances in the ^{19}F NMR spectrum, and its ^1H NMR spectrum contains only a pair of CMe_3 resonances in a 2:1 area ratio. Examination of the final ^1H NMR spectra of various NMR tube reactions suggest that greater amounts of B form in reactions where a $Cp'_2Ce(C_6H_xF_{5-x})$ complex is left in contact with excess fluorobenzenes as it decomposes, and where Cp'-rings act as traps for benzynes or carbenoids. B does not react with added hydride or metallacycle, and addition of a drop of pyridine does not give Cp'_2CeF(pyridine). No independent synthesis has been found for B, and it is not possible to isolate and characterize the substance from reaction mixtures, since it only appears as a minor component among a mixture of products. Since B tends to form in reactions where Cp' acts as a trap and demetallates, it could be a one-ring species such as $Cp'CeF_2$.

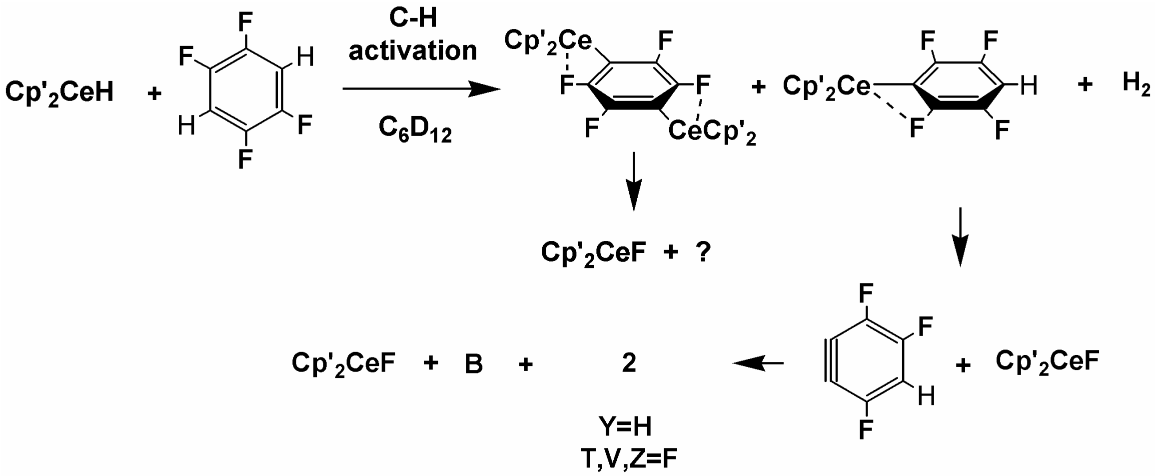
2.2. Pentafluorobenzene and the hydride; 1,2,4,5-tetrafluorobenzene, the metallacycle and the hydride.



Scheme 2.4: Proposed reactions of the hydride with pentafluorobenzene. C-F activation is only observed experimentally at the position para to H. Decomposition products of Cp'$_2$Ce(2,3,5,6-C$_6$F$_4$)CeCp'$_2$ other than Cp'$_2$CeF could not be identified.



Scheme 2.5: Proposed reaction of the metallacycle with 1,2,4,5-tetrafluorobenzene. Decomposition products of Cp'$_2$Ce(2,3,5,6-C_6F_4)CeCp'$_2$ other than Cp'$_2$CeF could not be identified.



Scheme 2.6: Proposed reaction of the hydride with 1,2,4,5-tetrafluorobenzene. Decomposition products of Cp'$_2$Ce(2,3,5,6-C_6F_4)CeCp'$_2$ other than Cp'$_2$CeF could not be identified.

Adding an excess of C_6HF_5 to Cp'_2CeH dissolved in C_6D_6 in an NMR tube changes the color of the solution from red-purple to orange with liberation of a gas. The ^1H NMR spectrum shows new diamagnetic resonances due to H_2 and 1,2,4,5-tetrafluorobenzene, as well as paramagnetic resonances due to Cp'_2CeF, $Cp'_2Ce(C_6F_5)$, and two new sets of paramagnetic resonances in the ratio 6:2:4:1, assuming the resonances are all due to CMe_3 groups. Integration of the initial and final CMe_3 resonances relative to an internal standard shows that the conversion is quantitative. Over time, all of the paramagnetic resonances disappear except those due to Cp'_2CeF, which, along with a trace of complex B, is the only cerium containing metallocene at the end of the reaction.

Addition of 1,2,4,5-tetrafluorobenzene to the metallacycle in C_6D_{12} generates an orange solution whose ^1H NMR spectrum contains the two new sets of resonances observed in the reaction of the hydride with C_6HF_5. Careful control of the experimental conditions permits exclusive formation of one set of resonances or the other. Slow addition of a solution of the metallacycle to an excess of 1,2,4,5-tetrafluorobenzene produces an orange solution whose ^1H NMR spectrum contains one pair of CMe_3 resonances in a 2:1 area ratio and a third resonance whose area corresponds to a single proton. The ^{19}F NMR spectrum contains two resonances, one sharp and one broad. The identity of this metallocene is believed to be $Cp'_2Ce(2,3,5,6\text{-}C_6HF_4)$, with the sharp and broad ^{19}F NMR resonances corresponding to meta and ortho-F's, respectively, and the ^1H NMR resonance of area 1 corresponding to the para-H. A solution of the metallacycle added to an equivalent amount of Cp'$_2$Ce(2,3,5,6-C_6HF_4) in C_6D_{12} generates the other set of resonances observed the ^{1}H NMR spectrum of the original reaction of Cp'$_2$CeH and C_6HF_5. The ^{1}H NMR spectrum consists of a pair of CMe_3 resonances in a 2:1 area ratio, and the ^{19}F NMR spectrum contains only one broad resonance similar to those observed for ortho-F's in Cp'$_2$Ce(2,3,5,6-C_6HF_4) and Cp'$_2$Ce(C_6F_5). The species is considerably less soluble than Cp'$_2$Ce(2,3,5,6-C_6HF_4) in C_6D_{12}, and the synthetic and spectroscopic evidence suggest that the compound is Cp'$_2$Ce(2,3,5,6-C_6F_4)CeCp'$_2$. Hydrolysis with H_2O gives 1,2,4,5-tetrafluorobenzene as the only substance detected by ^{19}F NMR spectroscopy, consistent with this deduction. A stoichiometric mixture of the hydride and Cp'$_2$Ce(C_6F_5) in C_6D_{12} also generates resonances due to Cp'$_2$Ce(2,3,5,6-C_6F_4)CeCp'$_2$ in the ^{1}H and ^{19}F NMR spectra.

The ^{1}H NMR resonances of Cp'$_2$Ce(2,3,5,6-C_6HF_4) display temperature dependence similar to those of Cp'$_2$Ce(C_6F_5). The δ vs. 1/T plots are shown in Figures 2.4 and 2.5. Both CMe_3 resonances in the ^{1}H NMR spectrum broaden into the baseline around -33°C, and four new resonances of varying and unequal population emerge. At -82°C, a new resonance emerges from the downfield side of the para-H resonance, labeled para Ha in Figure 2.4, with an area approximately 1/10th that of its parent. The pair of resonances in the ^{19}F NMR spectrum display linear Curie-Weiss temperature dependence, and no new resonances appear at low temperatures.

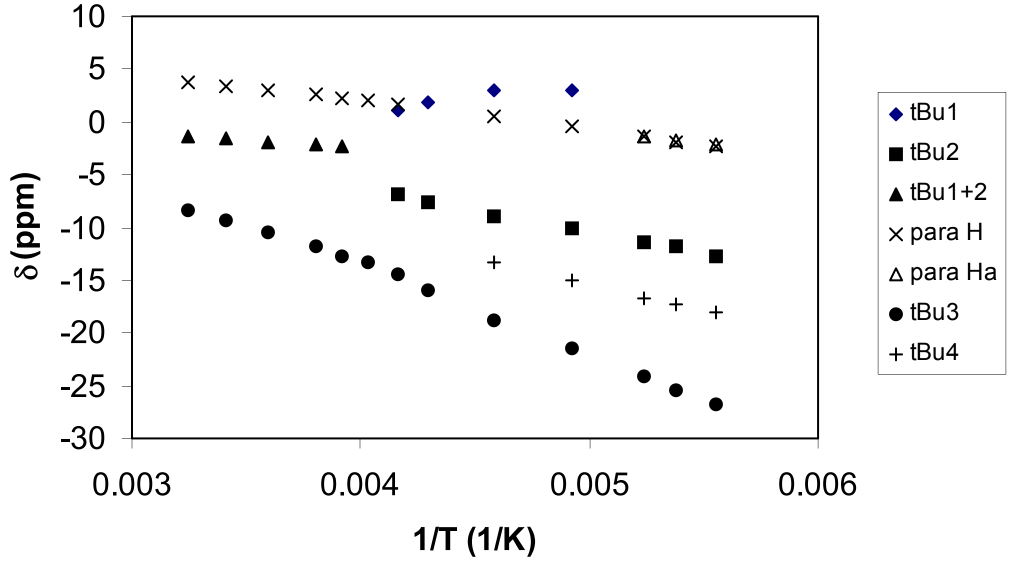


Figure 2.4: ^{1}H NMR δ vs. 1/T plot for Cp'$_2$Ce(2,3,5,6-C_6HF_4) in C_7D_{14}.

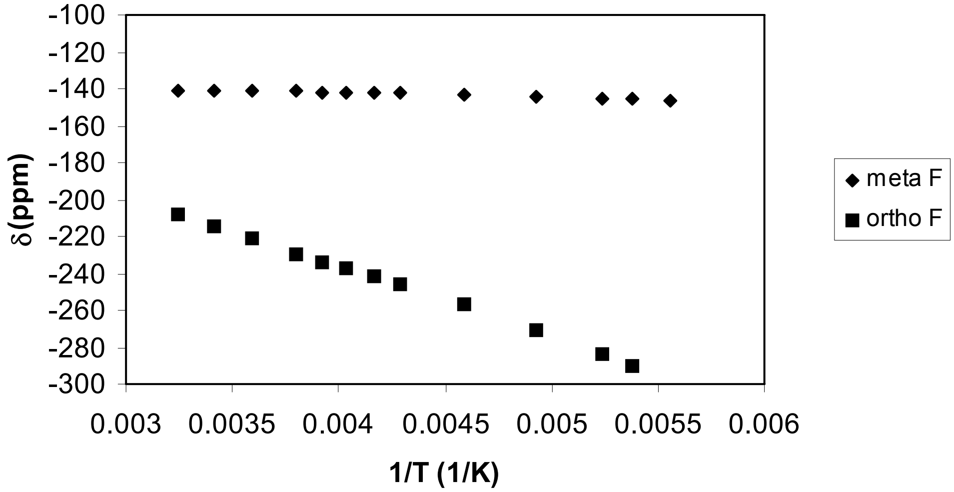


Figure 2.5: ^{19}F NMR δ vs. 1/T plot for Cp'$_2$Ce(2,3,5,6-C_6HF_4) in C_7D_{14}.

When a solution of $Cp'_2Ce(2,3,5,6\text{-}C_6HF_4)$ in C_6D_{12} is heated at 60°C for 12 hours, resonances due to Cp'_2CeF form in the ^1H NMR spectrum. The liberated 3,4,6-trifluorobenzyne is trapped by the Cp’ ring, since the ^{19}F NMR spectrum shows a new ABCX (**2a**, Y = H; T,V,Z = F) pattern as well as resonances in the ^1H NMR spectrum due to **2a**, Y = H; T,V,Z = F. Hydrolysis with H_2O and injection into a GCMS gives one primary isomer with $M^+ = 364$, consistent with **2a**, Y = H; T,V,Z = F, and two minor isomers with $(M\text{-}57)^+ = 307$, presumably due to **2b** and **2c**, Y = H; T,V,Z = F. When the 3,4,6-trifluorobenzyne is trapped with C_6D_6, the NMR spectra and GCMS are consistent with **1**, X = D, Y = H.[15]

The net reactions that account for the products identified in the NMR experiments may be written in equations 2-2a through g.

$Cp'_2CeH + C_6HF_5$ -> $Cp'_2Ce(C_6F_5) + H_2$ (2-2a)

$Cp'_2CeH + C_6HF_5$ -> $Cp'_2Ce(2,3,5,6\text{-}C_6HF_4) + HF$ (2-2b)

$Cp'_2CeH + 1,2,4,5\text{-}C_6H_2F_4$ -> $Cp'_2Ce(2,3,5,6\text{-}C_6HF_4) + H_2$ (2-2c)

$Cp'_2CeH + Cp'_2Ce(2,3,5,6\text{-}C_6HF_4)$ -> $Cp'_2Ce(C_6F_4)CeCp'_2 + H_2$ (2-2d)

$Cp'_2Ce(C_6F_5) + HF$ -> $Cp'_2CeF + C_6HF_5$ (2-2e)

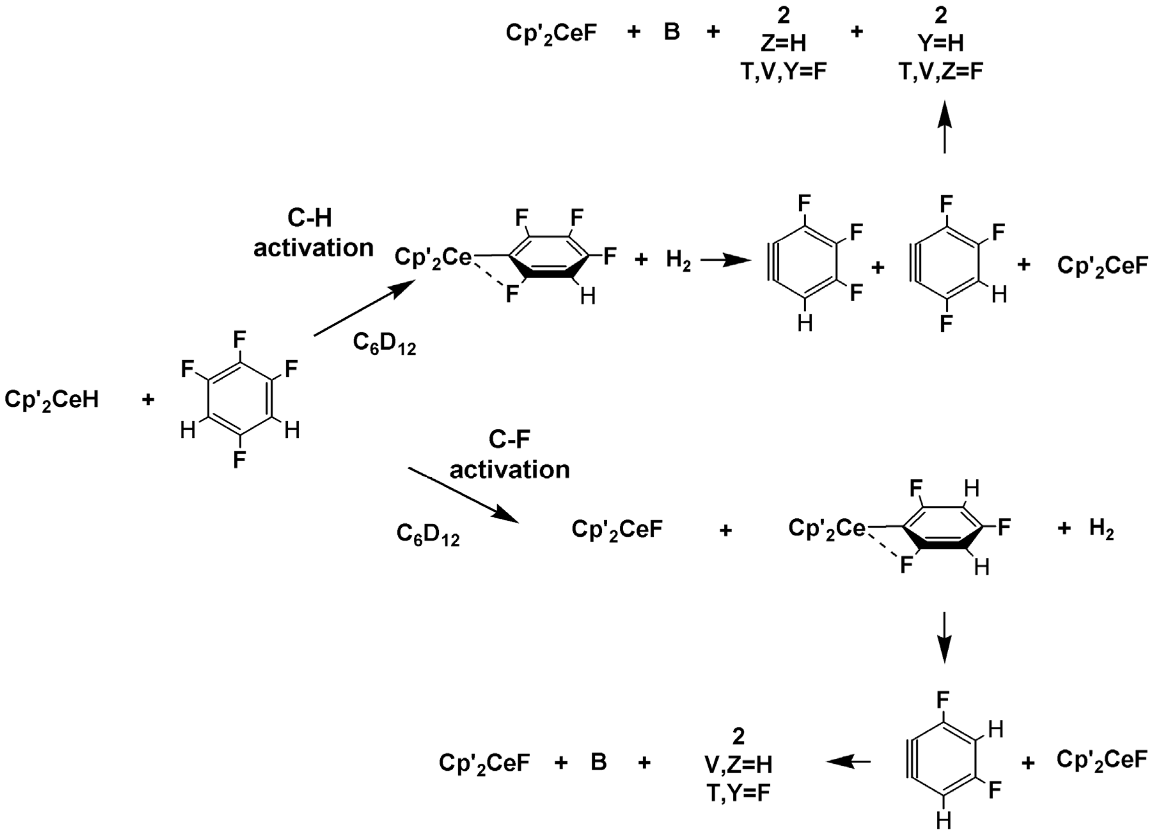
$Cp'_2Ce(2,3,5,6\text{-}C_6HF_4) + HF$ -> $Cp'_2CeF + 1,2,4,5\text{-}C_6H_2F_4$ (2-2f)

$Cp'_2CeH + HF$ -> $Cp'_2CeF + H_2$ (2-2g)

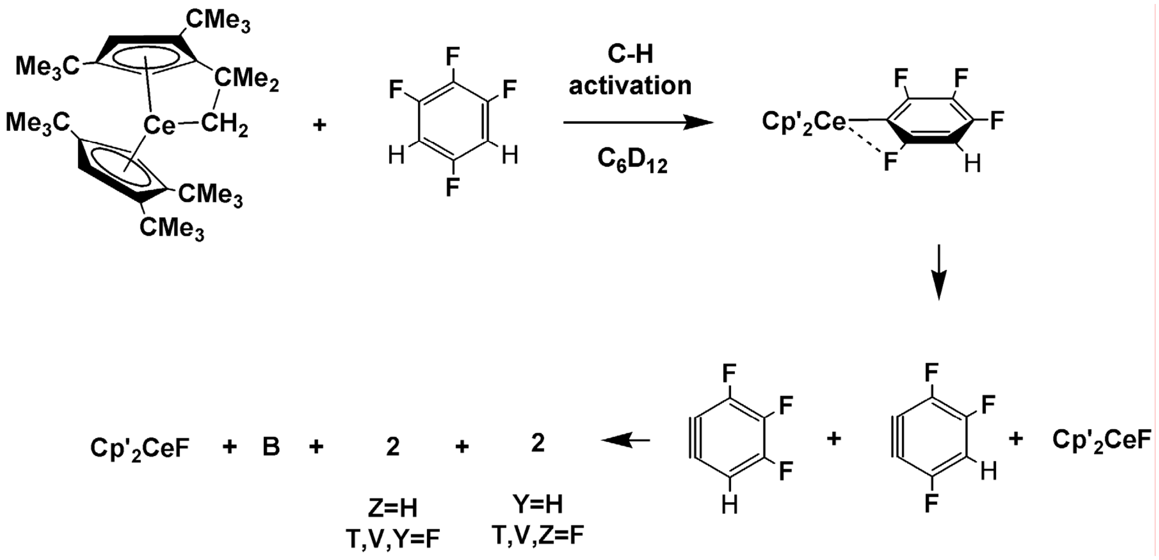
The reactions symbolized in 2-2a and 2-2b are intermolecular C-H and C-F activations, respectively, while those in the remaining equations result from secondary reactions. Since the intermediate HF is never observed, only the net reactions symbolized by equations 2-1 and 2-2 can be written with confidence.

Adding a drop of 1,2,4,5-tetrafluorobenzene to a solution of the hydride in C_6D_6 results in gas evolution and a color change in the solution from purple to orange. If the solution is not sufficiently dilute, copious orange precipitate soon forms. The ^1H NMR spectrum contains resonances due to H_2, $Cp'_2Ce(2,3,5,6\text{-}C_6HF_4)$, $Cp'_2Ce(2,3,5,6\text{-}C_6F_4)CeCp'_2$, and a trace of Cp'_2CeF. The cerium tetrafluorophenyl products all result from C-H activation by the hydride, indicating that this process is far more favorable than C-F activation in 1,2,4,5-tetrafluorobenzene. The resonances due to $Cp'_2Ce(2,3,5,6\text{-}C_6F_4)CeCp'_2$ disappear from the spectrum within a day, due either to precipitation or decomposition of the complex, as the resonances due to Cp'_2CeF increase. Resonances due to $Cp'_2Ce(2,3,5,6\text{-}C_6HF_4)$ diminish slowly over two weeks at 25°C as resonances due to Cp'_2CeF and B increase. At 60°C, a solution of $Cp'_2Ce(2,3,5,6\text{-}C_6HF_4)$ decomposes to Cp'_2CeF and B, in a 2:1 area ratio, in one day.

2.3. 1,2,3,5-Tetrafluorobenzene, the hydride, and the metallacycle



Scheme 2.7: Proposed reactions of the hydride with 1,2,3,5-tetrafluorobenzene. Only the products of the C-H activation pathway are observed experimentally.



Scheme 2.8: Proposed reaction of the metallacycle with 1,2,3,5-tetrafluorobenzene.

Adding an excess of 1,2,3,5-tetrafluorobenzene to the hydride dissolved in C_6D_{12} in an NMR tube changes the solution color from red-purple to orange with liberation of a gas. The ^{1}H NMR spectrum shows new resonances due to H_2, Cp'$_2$CeF, and a new product whose spectrum consists of a set of three equal area paramagnetic CMe_3 resonances and a broadened doublet, J = 7 Hz, whose area relative to the CMe_3 signals corresponds to a single proton. The ratio of Cp'$_2$CeF to this new product is 1:4. Integration of the initial and final CMe_3 resonances relative to an internal standard shows that the conversion is quantitative.

Addition of 1,2,3,5-tetrafluorobenzene to the metallacycle in C_6D_{12} generates an orange solution whose ^{1}H NMR spectrum contains the same set of three CMe_3 resonances and a broadened doublet that were observed in the reaction with the hydride. The ^{19}F NMR spectrum contains four resonances: a broadened doublet of doublets, J_1 = 7 Hz, J_2 = 18 Hz, a broadened doublet, J = 15 Hz, and two broad singlets. Based on these spectra, and the inference from the preceding sections that the metallacycle only activates C-H bonds in polyfluorobenzenes, the identity of this metallocene is proposed to be Cp’$_2$Ce(2,3,4,6-C_6HF_4). The resonances in the ^{19}F NMR spectrum correspond to those expected for the para-F, meta-F, and two ortho-F’s, with the broad singlet in the ^{1}H NMR spectrum corresponding to the meta-H. That this metallocene is formed almost exclusively in the reaction of the hydride with 1,2,3,5-tetrafluorobenzene mirrors the result from the last section, a preference for C-H activation over C-F activation.

The ^{1}H and ^{19}F NMR resonances of Cp’$_2$Ce(2,3,4,6-C_6HF_4) display a slightly more complicated temperature dependence than those of Cp’$_2$Ce(C_6F_5) and Cp’$_2$Ce(2,3,5,6-C_6HF_4). The δ vs. 1/T plots are shown in Figures 2.6 and 2.7. The 1:1:1 pattern of CMe_3 resonances in the 20°C ^{1}H NMR spectrum becomes a 2:1 pattern above 80°C as two of the signals merge. As the temperature is lowered below -20°C, the three CMe_3 resonances broaden into the baseline, and four resonances of varying and unequal population emerge. In the ^{19}F NMR spectrum, coupling disappears below -30°C, and new resonances emerge from the downfield side of the para-F signal and the upfield side of the meta-F signal below -60°C. These new resonances have an area approximately 1/3rd that of their parents, and are labeled meta Fa and para Fa in Figure 2.7. The broad resonances assigned to ortho-F’s broaden into the baseline at -30°C. The further downfield ortho-F resonance re-emerges at -40°C, corresponding to the nonlinearity in the plot of that resonance’s chemical shift.

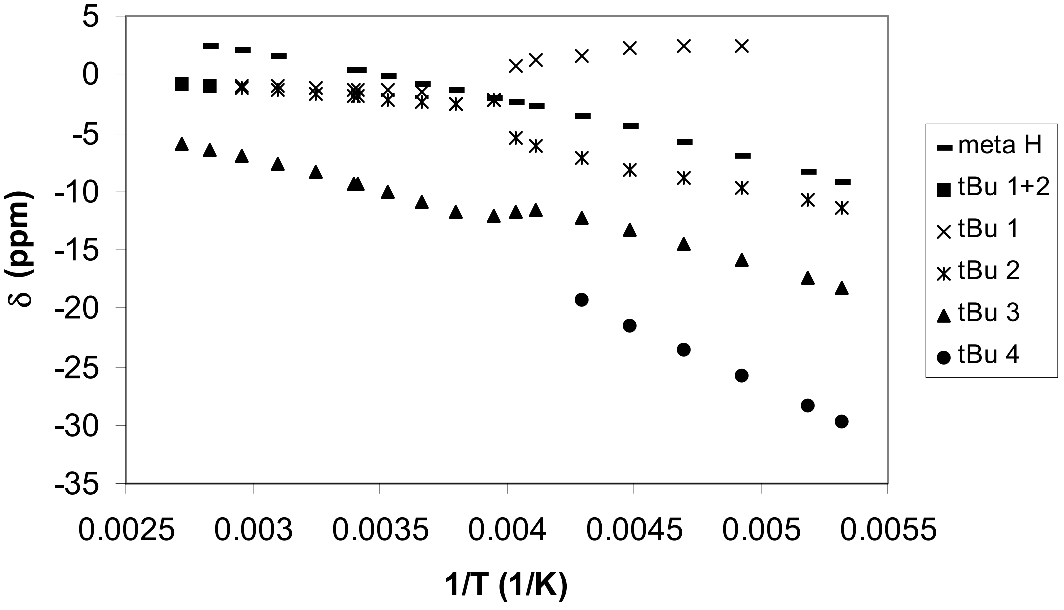


Figure 2.6: ^{1}H NMR δ vs. 1/T plot for Cp'$_2$Ce(2,3,4,6-C_6HF_4) in C_7D_{14}.

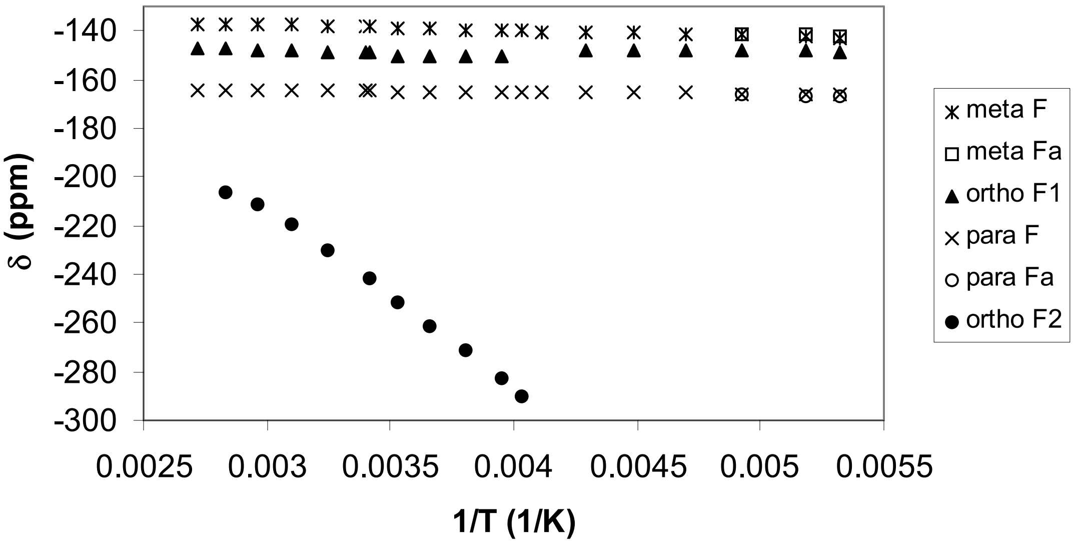
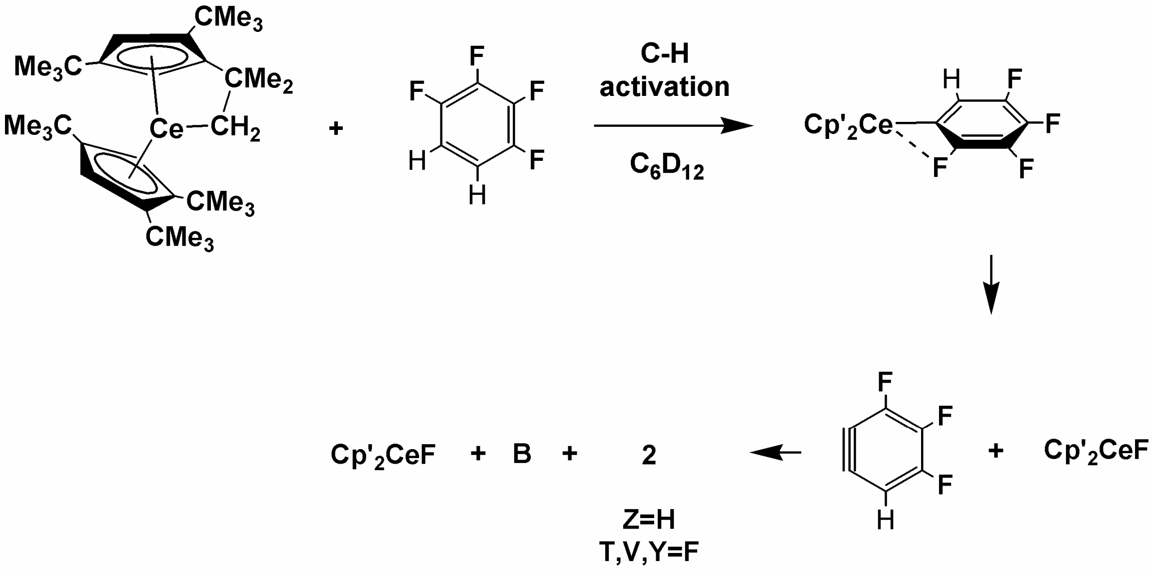


Figure 2.7: ^{19}F NMR δ vs. 1/T plot for Cp'$_2$Ce(2,3,4,6-C_6HF_4) in C_7D_{14}.

In the case of Cp'$_2$Ce(C_6F_5), it was proposed that, despite the C_1 symmetry present in the solid-state structure, librational motions of the Cp-rings and rapid rocking about the ligand Ce-C bond of the C_6F_5 ligand could result in idealized C_{2v} symmetry for the molecule in solution, resulting in the 2:1 pattern of CMe_3 resonances observed in the 25°C ^{1}H NMR spectrum. An additional process is needed to explain the 2:1 pattern observed for the CMe_3 resonances of Cp'$_2$Ce(2,3,4,6-C_6HF_4) above 80°C, since the 2,3,4,6-C_6HF_4 ligand lacks a mirror plane perpendicular to the plane of the ligand. One process that would generate a time averaged vertical plane is rapid rotation about the Ce-C bond. As this motion slows at lower temperatures, the mirror plane is lost, resulting in resonances suggestive of idealized C_s symmetry at 25°C. The appearance of multiple CMe_3 resonances of unequal population at low temperatures is similar to the behavior observed previously for Cp'$_2$Ce(2,3,5,6-C_6HF_4) and Cp'$_2$Ce(C_6F_5).

Cp'$_2$Ce(2,3,4,6-C_6HF_4) decomposes very slowly at 25°C. After 9 days, the integrated intensity of the CMe_3 groups is still 90% of its original value. After heating at 60°C for two days, the only resonances present in the ^{1}H NMR spectrum are those of Cp'$_2$CeF and complex B in a 1:1 area ratio, together accounting for less than 1/4th of the starting material. A large number of diamagnetic resonances have also appeared. Hydrolysis with H_2O and injection into a GCMS show two major products and four minor ones in addition to Cp'H. The two largest peaks give $M^+ = 364$, and the four smaller peaks give $(M-57)^+ = 307$. The two ortho fluorines in Cp'$_2$Ce(2,3,4,6-C_6HF_4) are inequivalent, and ortho-C-F activation can therefore lead to either 3,4,6-trifluorobenzyne or 3,4,5-trifluorobenzyne. Three of the six products observed in the GC have elution times and mass spectra identical to products of the decomposition of Cp’$_2$Ce(2,3,5,6-C_6HF_4), that is, **2a, b,** and **c**, Y = H; T,V,Z = F, the [2+4] cycloaddition products of 3,4,6-trifluorobenzyne and Cp’. The other three products observed in the GC are presumed to be the products of [2+4] cycloaddition between 3,4,5-trifluorobenzyne and Cp’: **2a,b,** and **c**, Z = H; T,V,Y = F.

2.4. 1,2,3,4-Tetrafluorobenzene and the metallacycle



Scheme 2.9: Proposed reaction of the metallacycle with 1,2,3,4-tetrafluorobenzene.

Addition of 1,2,3,4-tetrafluorobenzene to the metallacycle in C_6D_{12} slowly generates an orange solution whose ^1H NMR spectrum contains a pair of CMe_3

resonances in a 2:1 area ratio. The ^{19}F NMR spectrum contains three resonances: two broadened doublets, *J* = 18 Hz, and one broadened triplet, *J* = 18 Hz. The identity of this metallocene is proposed to be Cp'$_2$Ce(2,3,4,5-C_6HF_4), with the doublets in the ^{19}F NMR spectrum corresponding to meta-F's, and the triplet to the para-F. Resonances arising from the ortho-H and ortho-F are not observed.

The rotational process proposed to give rise to the 2:1 pattern of CMe_3 resonances in Cp'$_2$Ce(2,3,4,6-C_6HF_4) at 80°C could also explain the 2:1 pattern observed for Cp'$_2$Ce(2,3,4,5-C_6HF_4) at 25°C. The 2,3,4,5-C_6HF_4 ligand also lacks a mirror plane perpendicular to the plane of the ligand, and rotation about the Ce-C bond is presumably less hindered than in the case of Cp'$_2$Ce(2,3,4,6-C_6HF_4) since the Cp'$_2$Ce(2,3,4,5-C_6HF_4) complex has one proton and one fluorine ortho to the Ce-C bond instead of two ortho-F's.

The absence of an ortho-H resonance is not surprising, as resonances attributable to the pair of ortho-H's in Cp'$_2$CeC_6H_5 are not observed in its ^1H NMR spectrum. Resonances due to ortho-F's are observed in the other Cp'$_2$Ce($C_6H_xF_{5-x}$) complexes discussed thus far, but in those cases, the Ce-ortho-F interaction, as observed in the solid-state structure of Cp'$_2$Ce(C_6F_5), is presumed to exist as a rapid equilibrium involving both ortho-F's as the ligand rocks back and forth, giving rise to a time-averaged vertical mirror plane. The strength of a Ce-ortho-H interaction is likely to be much less than a Ce-ortho-F interaction, which would make the Ce-ortho-F interaction in Cp'$_2$Ce(2,3,4,5-C_6HF_4) less fluxional, and cause the ^{19}F resonance of the single ortho-F to broaden into the baseline due to its close association with the paramagnetic Ce.

The ^1H and ^{19}F NMR resonances of Cp'$_2$Ce(2,3,4,5-C_6HF_4) display a temperature dependence similar to those of Cp'$_2$Ce(C_6F_5). Due to rapid decomposition of the complex above 25°C, only low temperature data can be acquired. The δ vs. 1/T plots are shown in Figures 2.8 and 2.9. Both CMe_3 resonances in the ^1H NMR spectrum broaden into the baseline around -20°C, and five new resonances of varying and unequal population emerge. In the ^{19}F NMR spectrum, coupling disappears below -40°C, and the meta-F resonance furthest upfield (meta F1) broadens, and then sharpens by -60°C as new resonances emerge from the downfield side of the para-F signal and the upfield side of the other meta-F signal. A third new resonance appears out of the baseline between the para-F and the upfield meta-F signal. These new resonances, meta F1a, para Fa, and meta F2a, have integrated intensities approximately 1/3rd that of their parents.

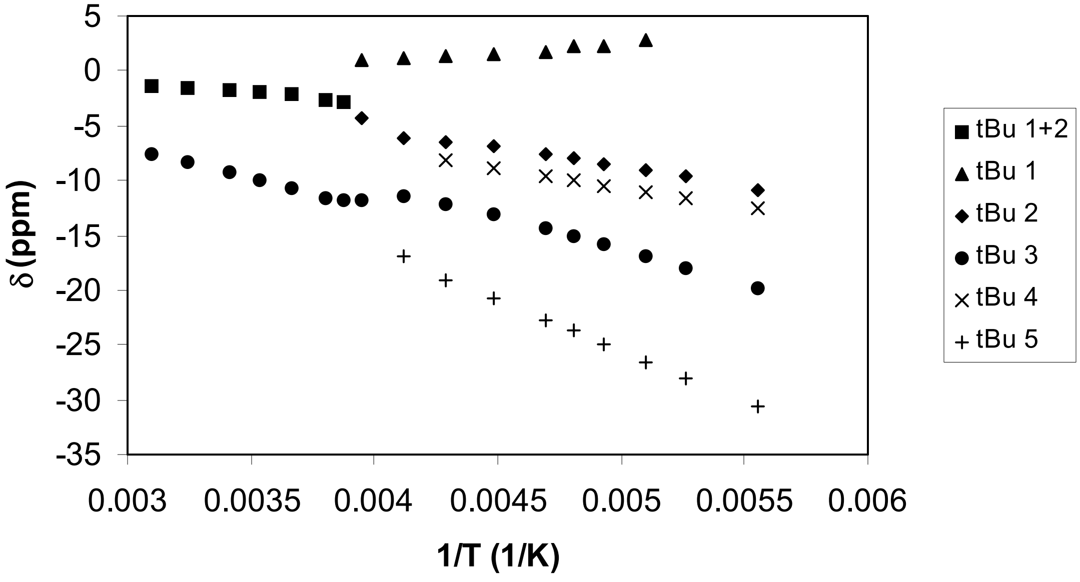


Figure 2.8: ^1H NMR δ vs. 1/T plot for Cp'$_2$Ce(2,3,4,5-C_6HF_4) in C_7D_{14}.

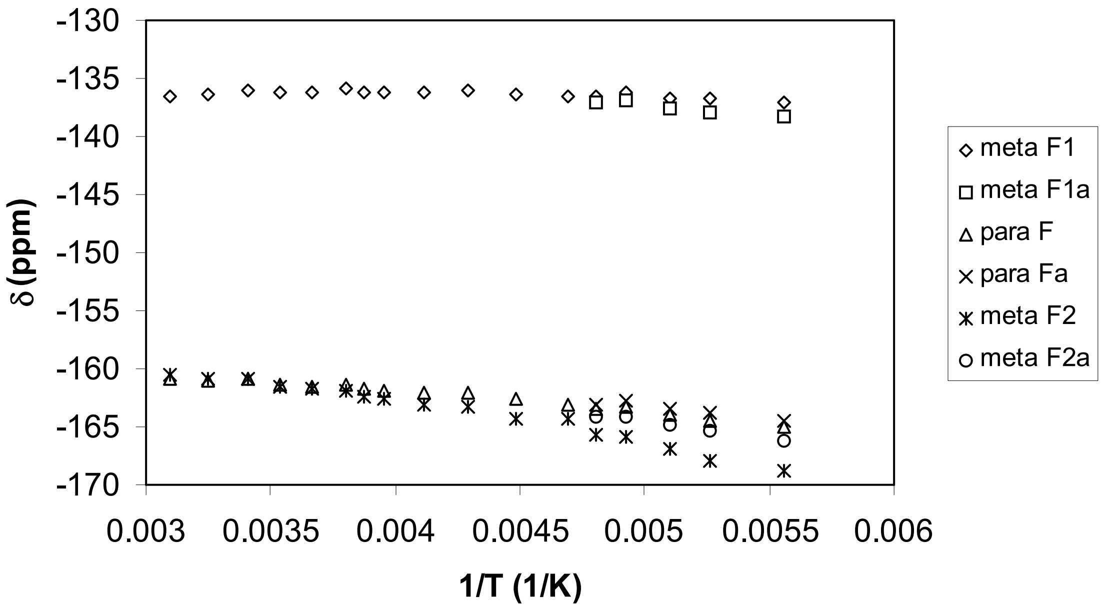
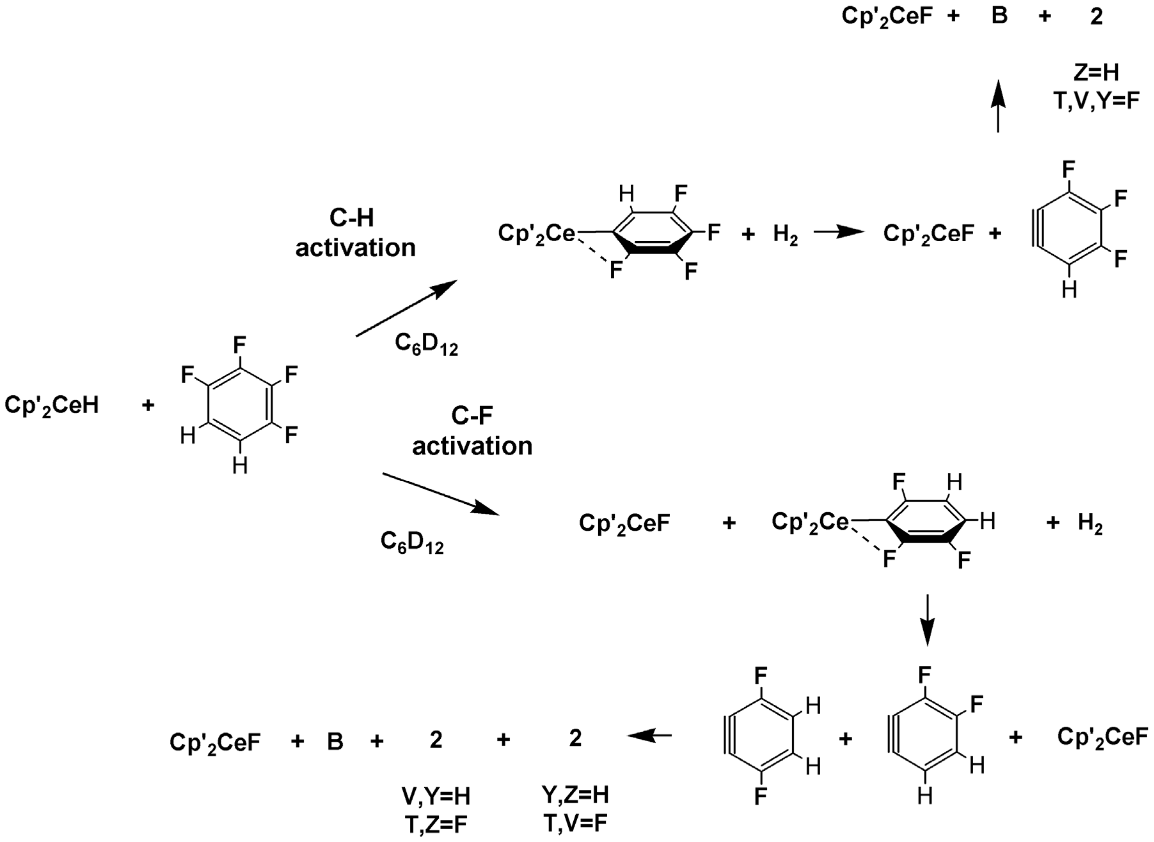


Figure 2.9: ^{19}F NMR δ vs. 1/T plot for Cp'$_2$Ce(2,3,4,5-C_6HF_4) in C_7D_{14}.

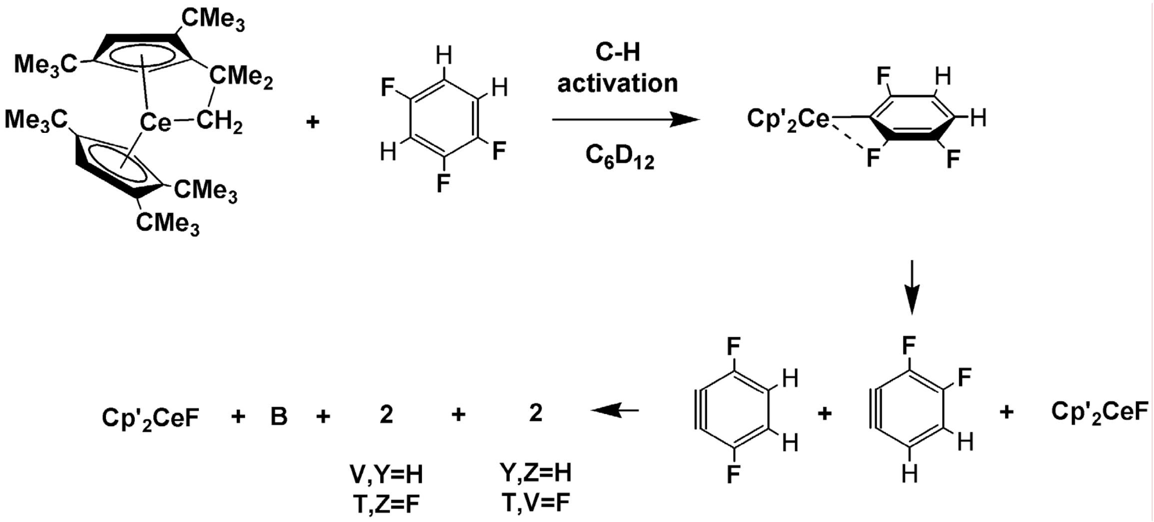
A sample of Cp'$_2$Ce(2,3,4,5-C_6HF_4) in C_6D_{12} in an NMR tube decomposes in one day at 25°C, giving Cp'$_2$CeF and B in a 1:1 area ratio and a variety of diamagnetic products. Hydrolysis with H_2O and injection into a GCMS shows the presence of one major and two minor products in addition to Cp'H. The major peak gives $M^+ = 364$, and the two minor peaks give $(M-57)^+ = 307$. The elution times for these three products match three of the products observed in the decomposition of Cp'$_2$Ce(2,3,4,6-C_6HF_4) and none of the products observed in the decomposition of Cp'$_2$Ce(2,3,5,6-C_6HF_4). Ortho-C-F activation in Cp'$_2$Ce(2,3,4,5-C_6HF_4) would lead to 3,4,5-trifluorobenzyne, and [2+4] cycloaddition with Cp' leads to **2a, b,** and **c**, Z = H; T, V, Y = F.

Several features of the reactions involving 1,2,3,4-tetrafluorobenzene differ markedly from analogous reactions involving the other two tetrafluorobenzenes. The reaction of the metallacycle with 1,2,3,4-tetrafluorobenzene is considerably slower than with the other two tetrafluorobenzenes, taking several minutes instead of seconds. The reaction of the hydride with 1,2,3,4-tetrafluorobenzene, discussed in more detail in the next section, is found to generate products of C-F activation predominently, while the product of C-H activation, $Cp'_2Ce(2,3,4,5\text{-}C_6HF_4)$, appears only as a minor product. In the reactions of the other two tetrafluorobenzenes with the hydride, the products of C-H activation are formed almost exclusively. $Cp'_2Ce(2,3,4,5\text{-}C_6HF_4)$ decomposes in C_6D_{12} solution at 25°C within a day, while the other $Cp'_2Ce(C_6HF_4)$ complexes decompose over the course of a week or more at 25°C to give similar trifluorobenzyne-Cp'-ring cycloaddition products. The results suggest that a proton ortho to only one fluorine is activated less readily than a proton ortho to two fluorines, and $Cp'_2Ce(C_6H_xF_{5-x})$ complexes with only one ortho fluorine are less stable than those with two ortho fluorines. Similar behavior is reported for the reactions of $[Re(\eta^5\text{-}C_5Me_5)(CO)_3]$ with various polyfluorobenzenes: reactions with 1,2,4,5-tetrafluorobenzene[16] and 1,3-difluorobenzene[17] result in C-H activation products with Re bound exclusively to the carbon ortho to two fluorines, while the reaction with 1,4-difluorobenzene[18] gives an η^2-bound difluorobenzene metal complex as the major product; the product of C-H activation, with Re bound to a carbon with only one ortho-F, is a minor product. Relative bond dissociation energy calculations also suggest stronger M-C bonding when two ortho-F's are present compared to just one.[17] It is worth noting that a drop of pentafluorobenzene added to a sample of Cp’$_2$Ce(2,3,4,5-C_6HF_4) in C_6D_{12} results in the formation of a small amount of Cp'$_2$Ce(C_6F_5) after one day at 25°C. After heating for one day at 60°C, **2a**, T, V, Y, Z = F is observed in the GCMS analysis of the hydrolyzate in addition to **2a, b,** and **c**, Z = H; T, V, Y = F.

2.5. 1,2,3,4-Tetrafluorobenzene and the hydride, 1,2,4-trifluorobenzene and the metallacycle



Scheme 2.10: Proposed reactions of the hydride with 1,2,3,4-tetrafluorobenzene.



Scheme 2.11: Proposed reactions of the metallacycle with 1,2,4-trifluorobenzene.

Adding an excess of 1,2,3,4-tetrafluorobenzene to the hydride dissolved in C_6D_{12} in an NMR tube changes the solution color from red-purple to orange with liberation of a gas. The ^{1}H NMR spectrum shows resonances due to H_2, Cp'$_2$CeF, Cp'$_2$Ce(2,3,4,5-C_6HF_4) and a new product whose spectrum consists of a set of three equal area paramagnetic CMe_3 resonances, a broadened doublet J = 8 Hz, and a broadened triplet J = 8 Hz, the latter two integrating to single protons relative to the CMe_3 signals. The ratio of the three paramagnetic products, respectively, is 5:1:2. The ^{1}H NMR spectrum after one day at 25°C contains only resonances due to Cp'$_2$CeF and the new species in a 2:1 ratio. After eight days, the spectrum contains resonances due to Cp'$_2$CeF, the new species, and complex B in a 16:8:1 ratio. Treating another solution of the hydride with 1,2,3,4-tetrafluorobenzene, taking the sample the dryness after 10 minutes, dissolving the orange solid residue in fresh C_6D_{12}, and hydrolyzing the sample results in a ^{19}F NMR spectrum with resonances due to both 1,2,3,4-tetrafluorobenzene and 1,2,4-trifluorobenzene.

Addition of 1,2,4-trifluorobenzene to the metallacycle in C_6D_{12} generates an orange solution whose ^{1}H NMR spectrum contains the same set of three CMe_3 resonances in a 1:1:1 area ratio, the broadened doublet, and the broadened triplet observed in the reaction of the hydride with 1,2,3,4-tetrafluorobenzene. The ^{19}F NMR spectrum contains one sharp and two broad singlets. The identity of this metallocene is proposed to be $Cp'_2Ce(2,3,6\text{-}C_6H_2F_3)$. The resonances in the ^{19}F NMR spectrum correspond to one meta-F and two ortho-F's, with the broad doublet in the ^{1}H NMR spectrum corresponding to the meta-H, and the broad triplet to the para-H.

A sample of $Cp'_2Ce(2,3,6\text{-}C_6H_2F_3)$ in C_6D_{12} heated at 60°C for one day gives a ^{1}H NMR spectrum containing Cp'_2CeF and complex B in a 2:1 area ratio as the only paramagnetic species, together accounting for roughly 1/3rd of the starting material. Multiple diamagnetic signals of significant area are also present. GCMS analysis of the hydrolyzed sample shows five principal products in addition to Cp'H, four with $M^+ = 346$, and one with $(M-57)^+ = 289$, consistent with **2a, b,** and **c**, Y, Z = H; T, V = F and V,Y = H; T, Z = F, formed by the [2+4] cycloaddition of 3,4-difluorobenzyne and 3,6-difluorobenzyne with Cp'. As was the case with $Cp'_2Ce(2,3,4,6\text{-}C_6HF_4)$, the two ortho fluorines in $Cp'_2Ce(2,3,6\text{-}C_6H_2F_3)$ are inequivalent, and ortho-C-F activation can give rise to either of the two difluorobenzynes.

The net reactions that account for the products of the reaction of 1,2,3,4-tetrafluorobenzene with the hydride identified in the NMR experiments may be written in equations 2-3a through f.

$$\mathrm{Cp'_2CeH + 1,2,3,4\text{-}C_6H_2F_4 \rightarrow Cp'_2Ce(2,3,4,5\text{-}C_6HF_4) + H_2} \tag{2-3a}$$

$$\mathrm{Cp'_2CeH + 1,2,3,4\text{-}C_6H_2F_4 \rightarrow Cp'_2Ce(2,3,6\text{-}C_6H_2F_3) + HF} \tag{2-3b}$$

$$\mathrm{Cp'_2CeH + 1,2,4\text{-}C_6H_3F_3 \rightarrow Cp'_2Ce(2,3,6\text{-}C_6H_2F_3) + H_2} \tag{2-3c}$$

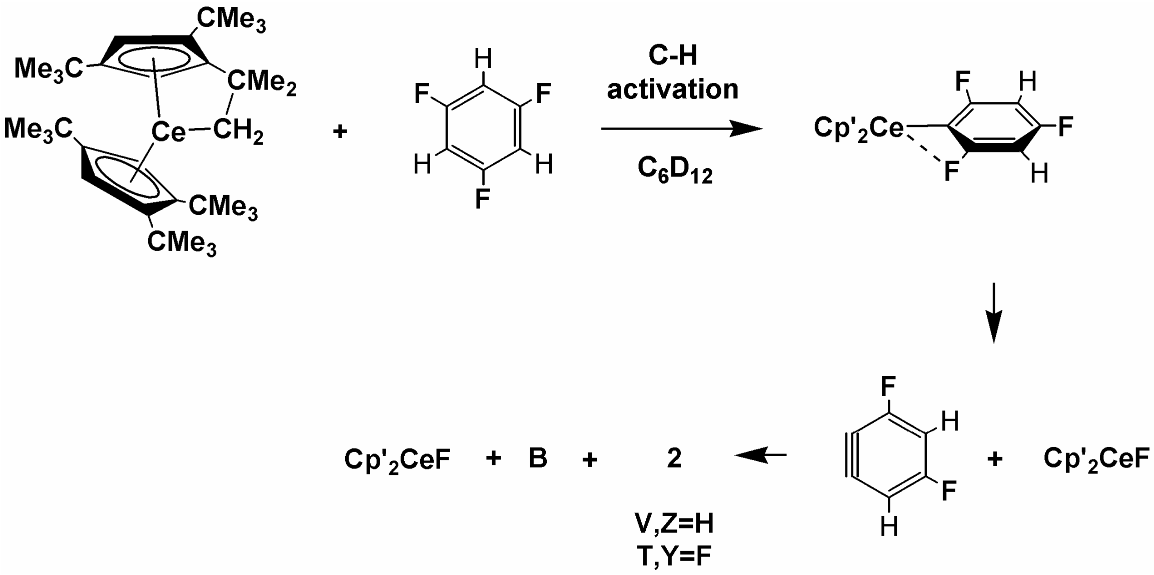
$$\mathrm{Cp'_2Ce(2,3,4,5\text{-}C_6HF_4) + HF \rightarrow Cp'_2CeF + 1,2,3,4\text{-}C_6H_2F_4} \tag{2-3d}$$

$$\mathrm{Cp'_2Ce(2,3,6\text{-}C_6H_2F_3) + HF \rightarrow Cp'_2CeF + 1,2,4\text{-}C_6H_3F_3} \tag{2-3e}$$

$$\mathrm{Cp'_2CeH + HF \rightarrow Cp'_2CeF + H_2} \tag{2-3f}$$

The reactions symbolized in equations 2-3a and 2-3b are intermolecular C-H and C-F activations, respectively, while those in the remaining equations are secondary reactions. The product distribution suggests that C-F activation is competitive with C-H activation in 1,2,3,4-tetrafluorobenzene, in contrast to the results of the reaction of the hydride with the other two tetrafluorobenzenes, where C-H activation analogous to 2-3a appeared to dominate. Moreover, C-F activation appears to occur exclusively at fluorines that are ortho to two other fluorines. C-H activation results in a complex, $\mathrm{Cp'_2Ce(2,3,4,5\text{-}C_6HF_4)}$, with only one fluorine ortho to the Ce-C bond. In the case of the reaction of the metallacycle with 1,2,4-trifluorobenzene, C-H activation likewise occurs exclusively at the proton ortho to two fluorines.

2.6. 1,3,5-Trifluorobenzene and the metallacycle

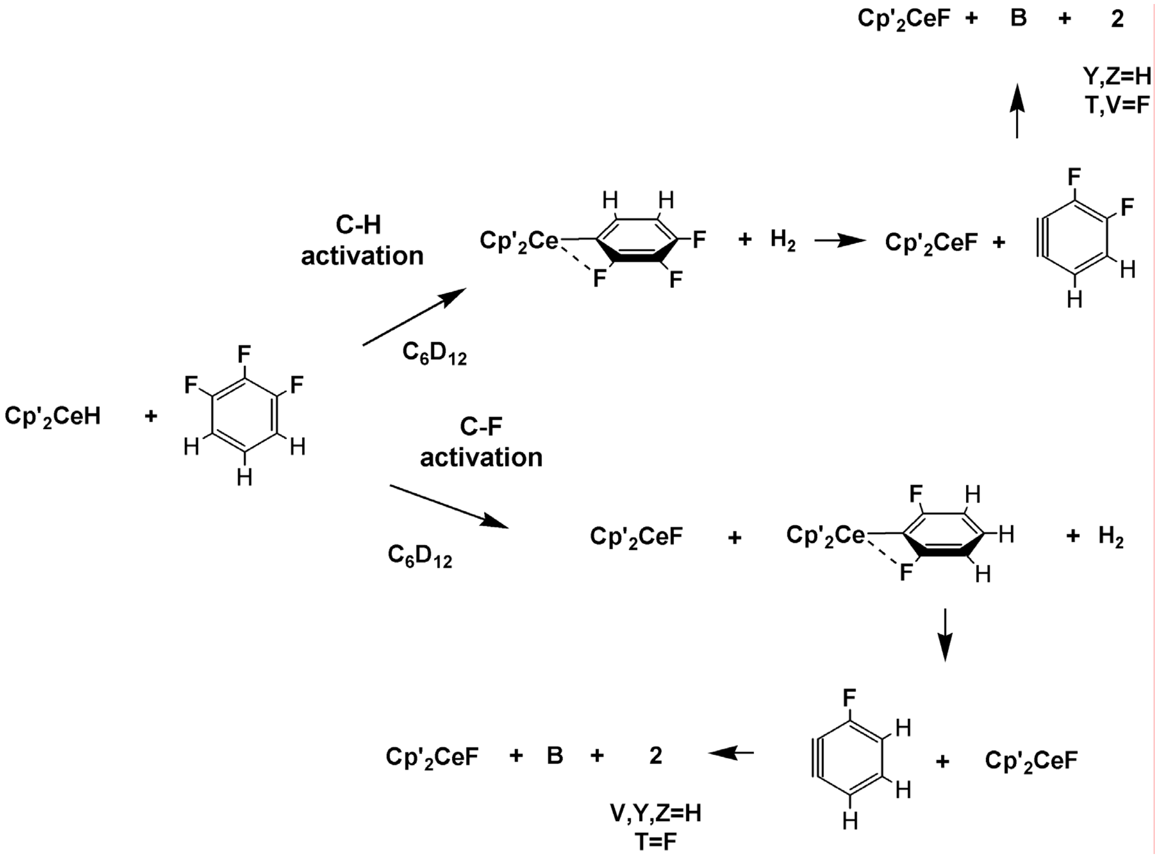


Scheme 2.12: Proposed reaction of the metallacycle with 1,2,3-trifluorobenzene.

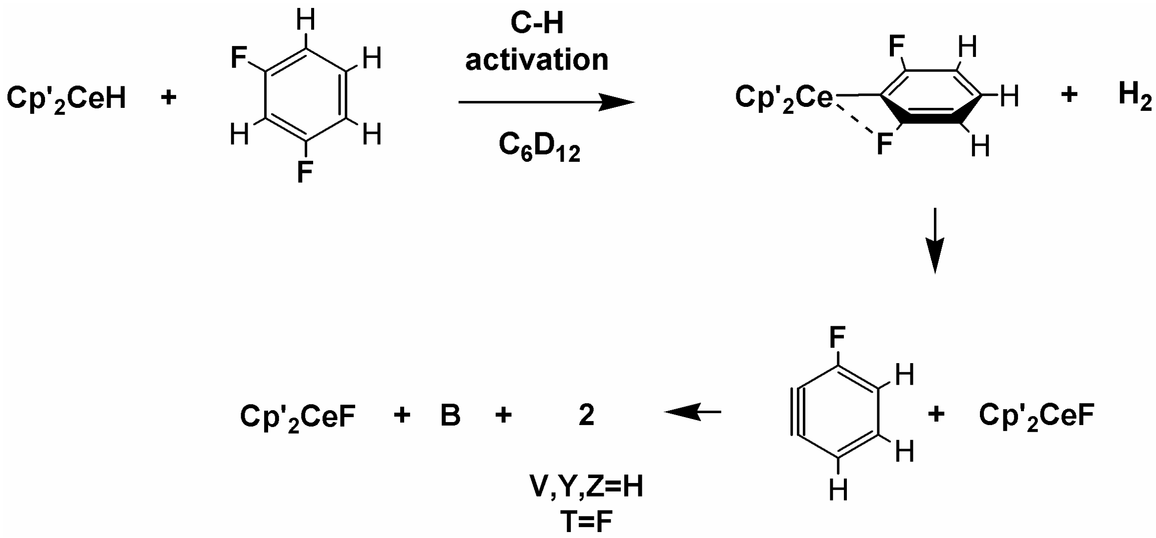
Addition of 1,3,5-trifluorobenzene to the metallacycle in C_6D_{12} results in rapid color change from purple to orange. The ^{1}H NMR spectrum contains a pair of CMe_3 resonances in a 2:1 area ratio and an additional resonance, a broadened doublet, whose integrated intensity corresponds to two protons relative to the CMe_3. The identity of this metallocene is proposed to be Cp'$_2$Ce(2,4,6-$C_6H_2F_3$), with the doublet in the ^{1}H NMR spectrum corresponding to the meta-H's. Heating the sample at 60°C for one day results in a ^{1}H NMR spectrum with paramagnetic resonances due to Cp'$_2$CeF and complex B in a 3:1 area ratio, and many diamagnetic resonances in the 0 to 2 ppm region of the spectrum.

The reaction of the hydride with 1,2,3,5-tetrafluorobenzene would be expected to produce Cp'$_2$Ce(2,4,6-$C_6H_2F_3$) if C-F activation at the lone fluorine ortho to two other fluorines is competitive with C-H activation, but only Cp'$_2$Ce(2,3,4,6-C_6HF_4), the C-H activation product, is detected (Section 2.3).

2.7. 1,2,3-Trifluorobenzene, 1,3-trifluorobenzene, and the hydride



Scheme 2.13: Proposed reaction of the hydride with 1,2,3-trifluorobenzene.



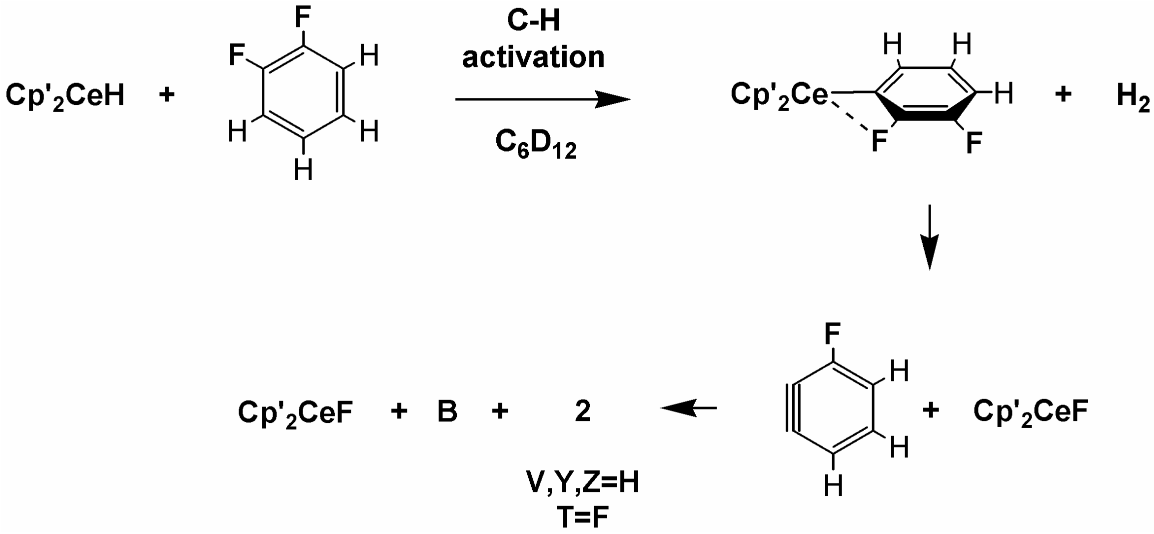
Scheme 2.14: Proposed reaction of the hydride with 1,3-difluorobenzene.

Adding an excess of 1,2,3-trifluorobenzene to a solution of the hydride in C_6D_{12} in an NMR tube results in a slow color change from red-purple to orange over several minutes. After 10 minutes, the ^{1}H NMR spectrum shows the presence of unreacted Cp'$_2$CeH, new resonances due to Cp'$_2$CeF, and three other large paramagnetic resonances that appear to arise from two overlapping 2:1 sets of CMe_3 groups. Three small paramagnetic resonances, a broad singlet, a broadened triplet, and a broadened doublet in a 1:1:2 area ratio, are also present. After one hour, resonances due to Cp'$_2$CeH are absent from the spectrum, and the ratio of Cp'$_2$CeF to the two major new products is 3:2:1. After three hours, only resonances due to Cp'$_2$CeF and one of the new products remain in a 2:1 ratio. The small broad singlet is also absent from the spectrum, and many diamagnetic signals of significant area have appeared in the 0 to 2 ppm region. After one day at 25°C, resonances due to complex B have appeared; the ratio of B to Cp'$_2$CeF and the new product is 1:9:3. Heating the sample to 60°C for one day results in a ^{1}H NMR spectrum containing resonances due to Cp'_2CeF and B in a 9:1 area ratio as the only paramagnetic species, together accounting for approximately 1/3rd of the starting material.

Adding an excess of 1,3-difluorobenzene to a solution of the hydride in C_6D_{12} results in a rapid color change from red-purple to orange. After 20 minutes, the ^{1}H NMR spectrum contains resonances due to Cp'_2CeF and four other paramagnetic resonances: a broadened triplet, a broadened doublet, and two large broad singlets in a 1:2:36:18 area ratio. The pattern of the new resonances is the same as that observed for the more persistent product of 1,2,3-trifluorobenzene and the hydride. The identity of this metallocene is proposed to be $Cp'_2Ce(2,6\text{-}C_6H_3F_2)$, with the doublet and triplet ^{1}H NMR resonances corresponding to the two meta-H's and one para-H, respectively. After one day at 25°C, resonances due to Cp'_2CeF appear in the spectrum; the ratio of Cp'_2CeF to $Cp'_2Ce(2,6\text{-}C_6H_3F_2)$ is 1:2. Many diamagnetic resonances of significant area have also appeared.

The lifetime of $Cp'_2Ce(C_6H_xF_{5-x})$ species at 25°C appears to diminish as the number of fluorines decreases, but the tendency of the hydride to form species with two ortho-F's preferentially persists, whether by C-F or C-H activation. The short-lived product in the reaction of the hydride with 1,2,3-trifluorobenzene may be the C-H activation product $Cp'_2Ce(2,3,4\text{-}C_6H_2F_3)$, though its short lifetime makes identification and study difficult if synthesized from the metallacycle and 1,2,3-trifluorobenzene.

2.8. 1,2-Trifluorobenzene, the hydride, and the metallacycle



Scheme 2.15: Proposed reaction of the hydride with 1,2-difluorobenzene.

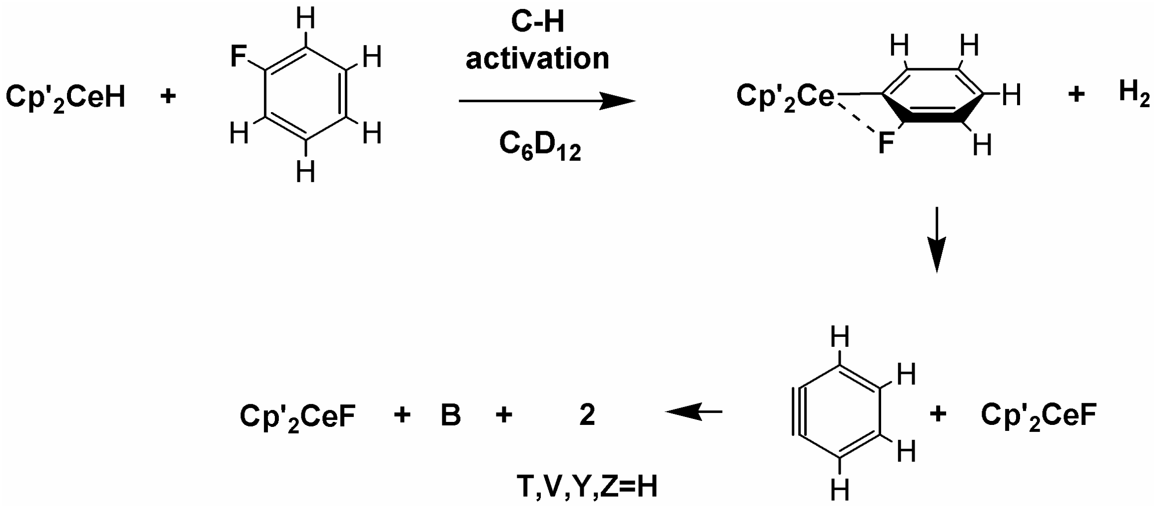
Adding an excess of 1,2-difluorobenzene to the hydride dissolved in C_6D_{12} in an NMR tube slowly changes the solution color from red-purple orange. After five minutes, the ^{1}H NMR spectrum shows the presence of unreacted Cp'$_2$CeH, Cp'$_2$CeF, and five other paramagnetic resonances in a 1:1:1:27:10 area ratio. The spectrum also contains four prominent diamagnetic resonances in a 1:1:9:9 area ratio. A third diamagnetic resonance of approximately the same intensity as those of area 9 appears as a shoulder on the solvent peak. Assuming the peaks of area 9 are due to CMe_3 groups, the ratio of the new diamagnetic product, the new paramagnetic product, Cp'$_2$CeH, and Cp'$_2$CeF after five minutes is 2:1:3.5:2. After 30 minutes, the ratio is 5:1:2:4.5, and after 80 minutes, 88:3:1:27. After one day at 25°C, only resonances due to Cp'_2CeF and the new diamagnetic product remain in the spectrum in a 4.5:1 area ratio.

Adding an excess of 1,2-difluorobenzene to a deep purple solution of the metallacycle in C_6D_{12} gives an orange solution within 10 minutes. The ^1H NMR spectrum contains resonances due to Cp'_2CeF and several other paramagnetic species. After six hours at 25°C, the only distinct resonances are those of Cp'_2CeF. Many small paramagnetic resonances produce a broad, lumpy hump in the baseline between 0 and –10 ppm, and several diamagnetic resonances of considerable intensity appear between 0 and 2 ppm.

The transient paramagnetic species observed in the reaction with the hydride is presumably a metallocenecerium fluorophenyl species, but its concentration is too small and its lifetime too short for its identity to be clearly established. In the preceding sections, the reactions of more highly fluorinated benzenes with the metallacycle resulted in stoichiometric formation of the product of C-H activation, permitting identification of the $Cp'_2Ce(C_6H_xF_{5-x})$ complexes observed in low concentration in reactions of the hydride. In the case of 1,2-difluorobenzene, the reaction with the metallacycle is less clean and more inconclusive than the reaction with the hydride.

The ^1H NMR spectrum of the diamagnetic product that forms rapidly as the reaction with the hydride progresses is considerably more distinct than those seen previously. Its chemical shifts are not those of Cp'H, but are most likely the result of a selective [2+4] cycloaddition of a benzyne with Cp', forming only one isomer, **2b** or **c**, V, Y, Z = H; T = F .

2.9. Fluorobenzene, the hydride, and the metallacycle



Scheme 2.16: Proposed reaction of the hydride with fluorobenzene.

Adding an excess of fluorobenzene to the hydride dissolved in C_6D_6 in an NMR tube slowly changes the solution color from red-purple to orange and then yellow with evolution of a gas. After 10 minutes at 25°C, the ^{1}H NMR spectrum shows the presence of H_2, unreacted Cp'$_2$CeH, Cp'$_2$CeF, a few small paramagnetic resonances, and five prominent diamagnetic resonances. The area ratio of the five diamagnetic resonances is 1:1:9:9:9. Assuming the peaks of area 9 are due to CMe_3 groups, the ratio of the new diamagnetic product, Cp'$_2$CeH, and Cp'$_2$CeF is 1:8:2. After 40 minutes, the ratio is 5:3:1, after 160 minutes, 57:2:1. After one day at 25°C, the only distinct resonances remaining in the spectrum are those due to the new diamagnetic species. Numerous small paramagnetic resonances form a broad hump in the baseline between –3 and –12 ppm.

The ^{1}H NMR spectrum of the solution following hydrolysis with H_2O contains resonances due to the new diamagnetic species as well as isomers of Cp'H. Injection of the sample into a GCMS shows the presence of Cp'H and one other major product with $M^+ = 310$. Performing the reaction in C_6D_{12}, under an atmosphere of H_2, or in the presence of Cp'H, Cp'_2CeF, or dihydroanthracene does not appear to alter the course of the reaction.

The ^{1}H NMR spectrum and GCMS results are consistent with the formation of benzyne and subsequent reaction with Cp' via [2+4] cycloaddition, selectively forming one of the asymmetric isomers **2b** or **c**, T, V, Y, Z = H. The fluorobenzynes that gave rise to the cycloaddition products observed in previous sections were proposed to have resulted from C-F activation at a position ortho to the Ce-C bond. An analogous process in the case of fluorobenzene would require the formation of $Cp'_2Ce(2\text{-}C_6H_4F)$ through C-H activation at a position ortho to the lone fluorine. The ^{1}H NMR spectrum contains several small paramagnetic resonances early in the reaction, but it is unclear whether $Cp'_2Ce(2\text{-}C_6H_4F)$ is among them, or if C-F activation resulting in $Cp'_2CeC_6H_5$ also occurs. The cerium fluorophenyl species produced in the reaction of the hydride with 1,2-difluorobenzene decomposes more rapidly than any seen in previous sections. An even shorter lifetime for a cerium fluorophenyl product of the reaction with fluorobenzene is consistent with the general trend, as is the selective cycloaddition of the resulting benzyne with Cp'. One inconsistent feature is the complete disappearance of resonances due to Cp'_2CeF by the end of the reaction. When fluorobenzene is added to the hydride in the presence of added Cp'_2CeF, the same diamagnetic product appears, and excess Cp'$_2$CeF is still present at the end of the reaction. When the reaction is performed in C_6D_6, the cycloaddition product of benzyne with C_6D_6 is not observed.

Reaction of the metallacycle with excess fluorobenzene in C_6D_{12} produces a complicated ^{1}H NMR spectrum after five minutes at 25°C, with multiple paramagnetic resonances between 10 and –15 ppm. Resonances of Cp'$_2$CeF were not observed. The spectrum was not noticeably different after 6 hours. As was the case with 1,2-difluorobenzene, the reaction of fluorobenzene with the metallacycle does nothing to elucidate the reaction with the hydride.

2.10. General trends

Reactions of Cp'$_2$CeH with CH_xF_{6-x}, x = 1 - 5, favor C-H activation to generate Cp'$_2$Ce($C_6H_{x-1}F_{6-x}$) and H_2 when there are C-H bonds ortho to two fluorines. C-F activation, which generates Cp'$_2$CeF, H_2, and Cp'$_2$Ce($C_6H_xF_{5-x}$), is competitive with C-H activation when there are C-F bonds ortho to two fluorines and no C-H bonds ortho to two fluorines. Reactions of the metallacycle with CH_xF_{6-x} results in C-H activation exclusively to form Cp'$_2$Ce($C_6H_{x-1}F_{6-x}$); C-H bonds ortho to two fluorines are still activated preferentially over C-H bonds ortho to one fluorine.

Complexes of the form Cp'$_2$Ce(CH_xF_{5-x}), x = 0 - 4, decompose *via* ortho-C-F bond activation to generate Cp’$_2$CeF and a benzyne (CH_xF_{4-x}), which is subsequently trapped *via* [2+4] cycloaddition reactions with solvent (C_6D_6) or Cp’ with an additional proton scavenged from another ring CMe_3 group. Complexes with two fluorines ortho to the Ce-C bond have lifetimes considerably longer (days) than complexes with only one fluorine ortho to the Ce-C bond (hours). The lifetimes also diminish as the number of fluorines diminishes, such that $Cp'_2Ce(2,3,4,5\text{-}C_6HF_4)$ persists for several hours at 25°C, while $Cp'_2Ce(2\text{-}C_6H_4F)$ is not observed.

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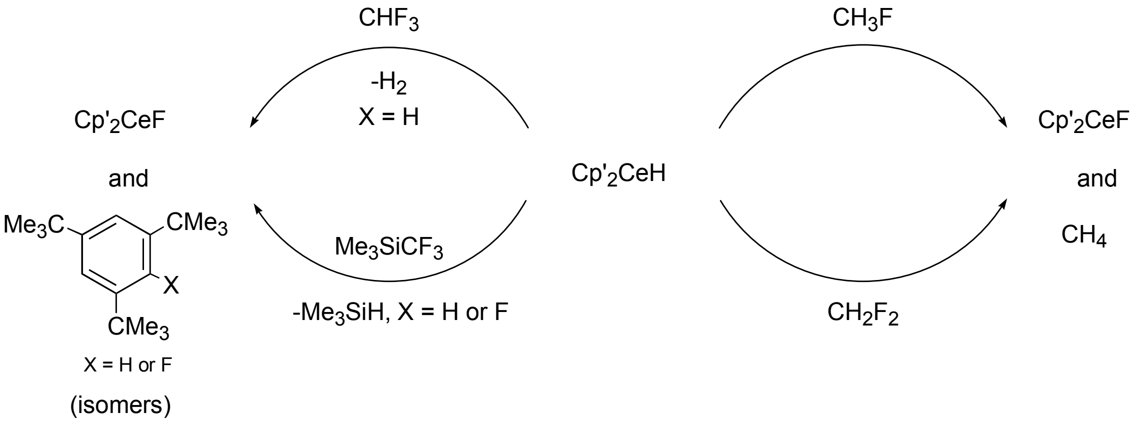
Chapter 3: Reactions of the Hydride and Metallacycle with Fluoromethanes

The hydride, Cp'_2CeH, and the metallacycle, $[(Me_3C)_3C_5H_2)][Me_3C)_2C_5H_2(CMe_2CH_2)]Ce$, react with a series of hydrofluoromethanes, $CH_{4-x}F_x$, x = 1 - 3, to generate Cp'_2CeF and other diamagnetic and paramagnetic products, Schemes 3.1 and 3.3. The reactions are studied by monitoring the changes that occur in the ^1H NMR spectrum in C_6D_6 or C_6D_{12} over time; the t-butyl resonances of the paramagnetic hydride disappear and those of Cp'_2CeF appear. The identity of the non-cerium containing products is deduced by the characteristic resonances in their ^1H and ^{19}F NMR spectra. At the end of the reactions, the samples are hydrolyzed (H_2O or D_2O) and examined by GCMS in order to deduce their identity. In those cases where the reaction is rapid, the reactions are clean and excellent mass balance is observed. In those cases where the reactions are slow, the reactions are less clean. When feasible, labeling and trapping experiments are used to confirm the spectroscopic results.

3.1. Reactions of the hydride with $CH_{4-x}F_x$, x =0-4.



Scheme 3.1. Reactions of Cp'$_2$CeH with fluoromethanes.

Exposure of the hydride, Cp'$_2$CeH, to CH_4 in C_6D_{12} does not change the appearance of the ^{1}H NMR spectrum relative to the individual resonances over a month at room temperature. The lack of exchange is not surprising since the Ce-Me bond enthalpy is likely to be less than that of Ce-H, a trend found in f-block and early d-transition metal metallocenes.[1] (Cp'-d$_{27}$)$_2$CeD in C_6D_{12} in a sealed NMR tube slowly undergoes H for D exchange with an atmosphere of CH_4. Resonances due to CH_3D appear after one week, those due to CH_2D_2 appear after three weeks, and those due to CHD_3 after 10 weeks, with the product ratio gradually shifting in favor of the more deuterated methanes. Presumably CD_4 is also generated, though this cannot be determined conclusively in the ^{2}H NMR spectrum. Over the course of the reaction, the resonances due to (Cp'-d$_{<27}$)$_2$CeH gradually increase in the ^{1}H NMR spectrum, and no new paramagnetic species are observed.

The reluctance of methane to react with the hydride is fortunate, since exposure of the hydride to CH_3F results in a rapid color change from purple to orange, disappearance of the hydride resonances, and appearance of those due to the fluoride and methane, equation 3-1.

$$Cp'_2CeH + CH_3F \quad -> \quad Cp'_2CeF + CH_4 \qquad (3-1)$$

Methane does not react with the hydride, so the net reaction is a simple H/F exchange. Repeating the reaction under an atmosphere of D_2 gives the fluoride and a mixture of CH_4 and CH_3D in approximately equal amounts. This experiment implies that the exchanges symbolized in equations 3-2a and 3-2b are occurring. No multiple H/D exchange in methane is observed, consistent with the lack of reaction between Cp'_2CeD and methane.

$$Cp'_2CeH + D_2 \quad -> \quad Cp'_2CeD + HD \qquad (3-2a)$$

$$Cp'_2CeD + CH_3F \quad -> \quad Cp'_2CeF + CH_3D \qquad (3-2b)$$

Exposure of Cp'_2CeH to an excess of CH_2F_2 in C_6D_{12} ultimately gives the same products shown in equation 3-1 but the rate is much slower, hours rather than seconds. Repeating the reaction in presence of D_2 gives CH_3D and CH_2D_2 in approximately equal amounts. The HD was not detected, presumably because of its low solubility in C_6D_{12}. The labeling result may be rationalized by the net reactions shown in equations 3-1 and 3-3, in which the rate of H/F exchange in eq 3-3 is slower than that in eq 3-1. No CH_3F is detected in the ^1H or the ^{19}F NMR spectrum, consistent with these deductions about the relative rates.

$$Cp'_2CeH + CH_2F_2 \quad \text{->} \quad Cp'_2CeF + CH_3F \qquad (3\text{-}3)$$

The reaction of CHF_3 is much slower than the other two reactions (eqs 3-1, 3-3); weeks rather than hours are required. Although all of the Cp'_2CeH resonances ultimately disappear from the ^1H NMR spectrum and Cp'_2CeF is formed, resonances due to complex B also appear (see Chapter 2). The ratio of Cp'_2CeF to B is 14:1. No methane is observed in the spectrum, although a resonance due to H_2 appears. Under an atmosphere of either D_2 or CH_4, no deuterated methane or ethane is detected. Several CMe_3 resonances appear in the diamagnetic region of the ^1H NMR spectrum; these resonances do not correspond to those of the isomers of free Cp'H, which could have formed *via* hydrolysis from traces of water over the long reaction time. At the end of the reaction, the hydrolyzed reaction mixture analyzed by GCMS shows two products with identical molecular ions in addition to Cp'H, whose fragmentation patterns are identified as being those of the isomeric tri-t-butylbenzenes 1,3,5-$(Me_3C)_3C_6H_3$ and 1,3,4-$(Me_3C)_3C_6H_3$. One set of the new diamagnetic resonances in the ^1H NMR spectrum match those of an authentic specimen of 1,3,5-$(Me_3C)_3C_6H_3$, and the integrated intensities and coupling patterns of the remaining resonances are consistent with the other isomer. The relative intensities show that the isomers form in comparable amounts. The only source of the three t-butyl fragments is the $(Me_3C)_3C_5H_2^-$ ring and the only source of the C_1 fragment is CHF_3. Clearly, the net reaction of CHF_3 is different from that of either CH_2F_2 or CH_3F. The reactions illustrated in equation 3-4a through e may be used to rationalize the identified products. Eq 3-4a is consistent with the detection of dihydrogen and eq 3-4b is consistent with formation of Cp'_2CeF by way of Cp'_2CeCF_3, which is not detected, ejecting difluorocarbene, CF_2. The CF_2 is trapped by a Cp'-ring bound to either Cp'_2CeF or Cp'_2CeH, as illustrated in eqs 3-4c and 3-4d.

$$Cp'_2CeH + CHF_3 \quad \text{->} \quad Cp'_2CeCF_3 + H_2 \qquad (3\text{-}4a)$$

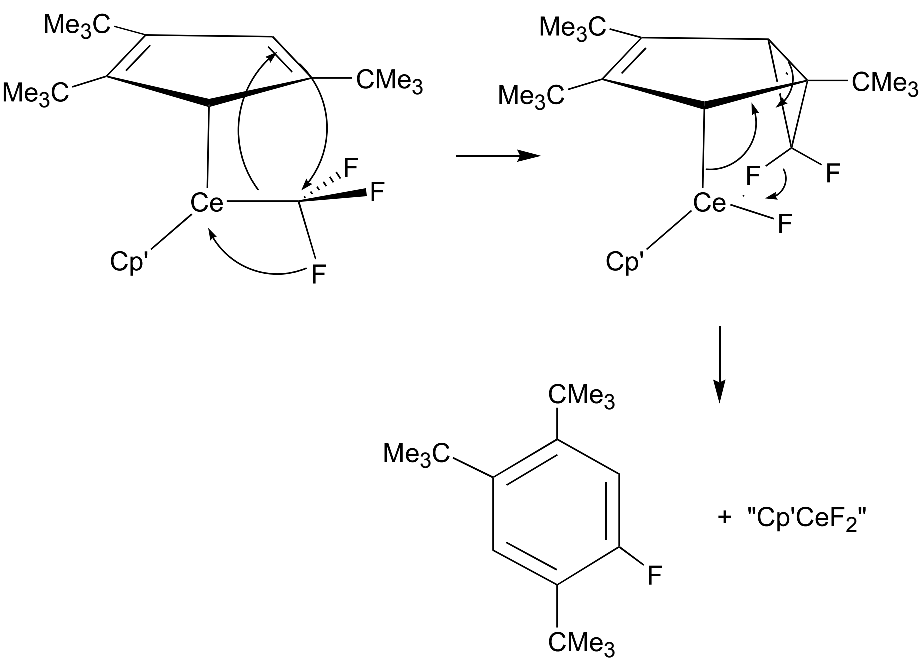
$$Cp'_2CeCF_3 \quad \text{->} \quad Cp'_2CeF + \text{“}CF_2\text{”} \qquad (3\text{-}4b)$$

$$Cp'_2CeF + \text{“}CF_2\text{”} \quad \text{->} \quad Cp'CeF_2 + \text{“}Cp'CF\text{”} \qquad (3\text{-}4c)$$

$$Cp'_2CeH + \text{“}CF_2\text{”} \quad \text{->} \quad Cp'CeHF + \text{“}Cp'CF\text{”} \qquad (3\text{-}4d)$$

$$Cp'_2CeH + \text{“}Cp'CF\text{”} \quad \text{->} \quad Cp'_2CeF + \text{“}Cp'CH\text{”} \qquad (3\text{-}4e)$$

There is literature precedent for carbene insertion into the $(Me_3C)_3C_5H_2^-$ ring. Reaction of $(Me_3C)_3C_5H_3$ and a dihalocarbene generated from $CHCl_3$ or $CHBr_3$ and strong base yields the 1,2,4-tri-t-butyl-5-halobenzenes.[2] Additionally, trifluoromethylmetal species decompose by α-F abstraction to yield CF_2 fragments that are subsequently trapped.[3] The formation of tri-t-butylfluorobenzenes can be rationalized as shown in Scheme 3.2, in which the Cp'-ligand acts as a trap for CF_2.[2]



Scheme 3.2. Formation of an isomer of tri-t-butylfluorobenzene. Insertion of the carbene into the other double bond will generate the other isomer. In the case of CHF insertion, only isomeric tri-t-butylbenzenes will form.

DFT calculations performed by Maron et al. suggest that the most kinetically favorable reaction pathway for all of the hydrofluoromethanes, $CH_{4-x}F_x$, x = 1-3, with an analogous model compound, Cp_2CeH, involves initial C-H activation to generate $Cp_2CeCH_{3-x}F_x$, which then undergoes intramolecular C-F activation to generate Cp'_2CeF and a carbene or carbenoid, which is trapped.[4] Thus the reaction shown in eq 3-4b is reasonable: the difluorocarbene is an electrophile, which can add to the different double bonds of the Cp'-ring, and the resulting cerium compounds decompose to isomeric tri-t-butylfluorobenzenes, "Cp'CF," as illustrated in eq 3-4c and d. However, only isomeric tri-t-butylbenzenes, "Cp'CH," are observed, not the tri-t-butylfluorobenzenes, "Cp'CF." Mixing Cp'$_2$CeH and the isomeric tri-t-butylfluorobenzenes does not give H/F exchange products, i.e., the reaction symbolized in eq 3-4e does not occur. A possible reason for the absence of tri-t-butylfluorobenzenes is suggested by the results of the experiment mentioned at the end of Chapter 1, where Cp'$_2$CeH and Cp'$_2$Ce(OSO$_2$CF$_3$) are mixed and instantaneously give Cp'$_2$CeF and a new paramagnetic cerium metallocene believed to be Cp'$_2$Ce(OSO$_2$CHF$_2$). The products are thought to be the result of intermolecular H/F exchange analogous to the reactions symbolized in eqs 3-1 and 3-3. Mixing Cp'$_2$CeH with (Cp'-d$_{27}$)$_2$CeF in C_6D_{12} instantaneously gives an equilibrium mixture with Cp'$_2$CeF and (Cp'-d$_{27}$)$_2$CeH, the net result of intermolecular H/F exchange. Thus, it is reasonable to suggest that when Cp'$_2$CeCF$_3$ forms (eq 3-4a), in presence of Cp'$_2$CeH, rapid intermolecular H/F exchange generates Cp'$_2$CeF and Cp'$_2$CeCHF$_2$, which forms Cp'$_2$CeF and isomers of tri-t-butylbenzene, the net products observed.

Generating Cp'$_2$CeCF$_3$ by an alternative method and allowing it to decompose is necessary in order to give the reactions in eq 3-4 experimental foundation. Trifluoromethyltrimethylsilane (Me$_3$SiCF$_3$) in presence of CsF is a CF$_3$ transfer reagent for the synthesis of Cp$_2$Ti(CF$_3$)(F).[5] Addition of Me$_3$SiCF$_3$ to Cp'$_2$CeH in an NMR tube instantly gives resonances due to Cp'$_2$CeF, Me$_3$SiH, and the isomeric tri-t-butylbenzenes and a small amount of the isomeric tri-t-butylfluorobenzenes. Repeating the experiment with the (Cp'-d$_{27}$)$_2$CeD gives (Cp'-d$_{27}$)$_2$CeF, Me$_3$SiD, and the isomers of $[(CD_3)_3C]_3C_6H_2D$. The formation of $[(CD_3)_3C]_3C_6H_2D$ implies that (Cp'-d$_{27}$)$_2$CeCF$_3$

undergoes D/F exchange with $(\mathrm{Cp'\text{-}d_{27}})_2\mathrm{CeD}$ to give $(\mathrm{Cp'\text{-}d_{27}})_2\mathrm{CeCDF_2}$, and this yields $(\mathrm{Cp'\text{-}d_{27}})_2\mathrm{CeF}$ and the isomeric deutero tri-t-butylbenzenes.

The net reaction of the hydride with $\mathrm{Me_3SiCF_3}$ may be written as in eqs 3-5a through f.

$$\mathrm{Cp'_2CeH + Me_3SiCF_3} \;\; \text{->} \;\; \mathrm{Cp'_2CeCF_3 + Me_3SiH} \tag{3-5a}$$

$$\mathrm{Cp'_2CeCF_3} \;\; \text{->} \;\; \mathrm{Cp'_2CeF} + \text{“}\mathrm{CF_2}\text{”} \tag{3-5b}$$

$$\mathrm{Cp'_2CeCF_3 + Cp'_2CeH} \;\; \text{->} \;\; \mathrm{Cp'_2CeF + Cp'_2CeCHF_2} \tag{3-5c}$$

$$\mathrm{Cp'_2CeCHF_2} \;\; \text{->} \;\; \mathrm{Cp'_2CeF} + \text{“CHF”} \tag{3-5d}$$

$$\mathrm{Cp'_2CeF} + \text{“}\mathrm{CF_2}\text{”} \;\; \text{->} \;\; \mathrm{Cp'CeF_2} + \text{“Cp’CF”} \tag{3-5e}$$

$$\mathrm{Cp'_2CeF} + \text{“CHF”} \;\; \text{->} \;\; \mathrm{Cp'CeHF} + \text{“Cp’CH”} \tag{3-5f}$$

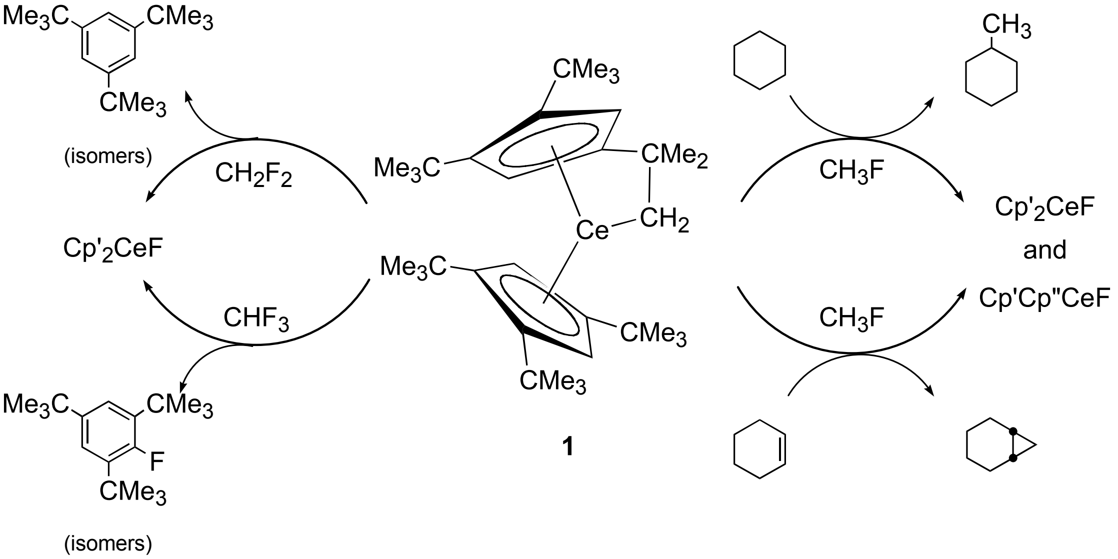
Equations 3-5c, d, and f are also applicable to the reaction of the hydride with $\mathrm{CHF_3}$, replacing reaction 3-4e, which does not occur.

Exposure of $\mathrm{Cp'_2CeH}$ to $\mathrm{CF_4}$ in $\mathrm{C_6D_{12}}$ for a time period of up to a month does not produce any change in the ^{1}H NMR spectrum. Thus, $\mathrm{CF_4}$ does not undergo H/F exchange. Although $\mathrm{CF_4}$ is the most stable fluorocarbon known,[6] the lack of reaction is due to kinetics rather than thermodynamics. A very high barrier to H/F exchange of $\mathrm{Cp_2LaH}$ and $\mathrm{CF_4}$ is obtained from DFT calculations.[7] Support for the kinetic stability of $\mathrm{CF_4}$ is derived by noting that the averaged bond dissociation enthalpy of $\mathrm{CF_4}$ is 130 kcal mol^{-1} while that of $\mathrm{SiF_4(g)}$ is 142 kcal mol^{-1}.[8] Mixing $\mathrm{Cp'_2CeH}$ and $\mathrm{SiF_4}$ generates $\mathrm{Cp'_2CeF}$ and other unidentified compounds instantaneously, showing that the stronger

(Si-F) bond reacts more rapidly than the weaker one (C-F). It is noteworthy that perfluoromethylcyclohexane and Cp'_2CeH does indeed produce Cp'_2CeF, but the reaction time is on the order of a month. Similarly, the $PhCF_3$ and Cp'_2CeH yield resonances due to Cp'_2CeF over three days; several other small paramagnetic resonances due to unknown cerium containing species are also observed in the ^1H NMR spectrum.

The qualitative results show a large variation in the rates of reaction as the H to F ratio changes in the reaction of Cp'_2CeH with hydrofluoromethanes. The reactions of Cp'_2CeH and CH_3F and CH_2F_2 are clean as only two products are formed: Cp'_2CeF and CH_4, (eqs 3-1 and 3-3). The reaction of CHF_3, however, is very slow and produces several products; no methane is detected but products resulting from fluorocarbene are observed. DFT calculations by Maron et al. found facile trapping of insipient CH_2 and CHF carbonoids by H_2, but no such transition state could be located for CF_2, which provides a possible explanation for the alternative trapping by the Cp'-ring in this case.[4]

3.2. Reaction of the metallacycle and $CH_{4-x}F_x$, x =0-4.



Scheme 3.3. Reactions of the metallacycle**,** where Cp' = 1,2,4-$(Me_3C)_3C_5H_2$ and Cp" = $(Me_2Et)(Me_3C)_2C_5H_2$, with fluoromethanes.

Given the general finding of Chapter 2 that reactions of fluorobenzenes, CH_xF_{6-x}, x = 1 - 5, with the metallacycle results exclusively in C-H activation to form $Cp'_2Ce(C_6H_{x-1}F_{6-x})$, the reactions of hydrofluoromethanes, $CH_{4-x}F_x$, x = 1-3, with the metallacycle might be expected to provide another route to the series of hypothetical cerium fluoromethyl complexes, $Cp'_2CeCH_{3-x}F_x$, proposed in the last section. The implication of the reaction symbolized by eq 3-5 is that $Cp'_2CeCH_{3-x}F_x$ in general and Cp'_2CeCF_3 in particular are unstable relative to Cp'_2CeF and a carbene fragment. C-H activation by the metallacycle would not be expected to generate H_2 that could trap these fragments, as was the case in C-H activation by the hydride.

Addition of an excess of CH_4 (1 atm) to the metallacycle in C_6D_{12} does not result in any change in the appearance of the ^{1}H NMR spectrum over the period of a month. However, reaction of the metallacycle-d_{26}, in which all of the hydrogens in the CMe_3 groups are exchanged by deuterium, with methane in C_6D_{12} over the course of a week produces some CH_3D. As in the case of (Cp'-d_{27})$_2$CeD, prolonged exposure gives CH_2D_2, CHD_3, and presumably CD_4. This result implies that the C-H bond of methane can reversibly insert into the Ce-C bond of the metallacycle, a process that is essentially thermoneutral. In Chapter 1, it was noted that experiments aimed at the synthesis of Cp'$_2$CeMe from Cp'$_2$CeX (X = I or O_3SOCF_3) and MeLi give a material whose ^{1}H NMR spectrum is identical to that of the metallacycle. When the reaction and workup is performed at low temperature, the ^{1}H NMR spectrum shows resonances due to the metallacycle and a pair of CMe_3 resonances in a 2:1 area ratio. The latter resonances disappear with time as the metallacycle resonances increase in intensity. This result is understandable if the Ce-C bonds are assumed to be of comparable strength and the increase of entropy drives the methane elimination reaction.

Addition of CH_3F to a solution of the metallacycle in C_6D_{12} in an NMR tube and heating at 60°C over a period of 12 hours results in the appearance of Cp'$_2$CeF and a set of resonances due to a new cerium metallocene C in a 5:1 ratio. Repeating the reaction in presence of cyclohexene results in ^{1}H NMR resonances due to Cp'$_2$CeF, C, and norcarane (Scheme 3.3) though the ratio of Cp'$_2$CeF to C is greater than in absence of cyclohexene.[9]

Analysis of the hydrolyzed reaction mixture of the metallacycle with CH_3F in C_6D_{12} by GCMS shows cyclohexane-d_{12} (solvent), methylcyclohexane-d_{12}, Cp'H and a new cyclopentadiene whose m/z value is 14 amu higher than Cp'H, i.e., Cp'(CH_2)H. Repeating the reaction of the metallacycle with CH_3F in C_6H_{12} rather than C_6D_{12} gives methylcyclohexane in addition to cyclohexane (solvent), Cp'H, and the new cyclopentadiene. These experiments show that CH_2 is trapped by C=C or C-H bonds and provides a clue as to the identity of C, since the metallocene rings have C-H bonds. Exposing the perdeuterometallacycle to CH_3F in C_6D_{12} gives resonances in the ^2H NMR spectrum due to (Cp'-d_{27})(Cp'-d_{26})CeF while the ^1H NMR spectrum contains three new resonances with chemical shifts in the region found for the CMe_3 groups in Cp'_2CeF. Hydrolysis (H_2O) and examination of the hydrolyzate by GCMS shows the presence of two cyclopentadienes: a mixture of the isotopomers (Cp'-d_{26})H, (Cp'-d_{27})H and (Cp'-d_{26})(CH_2)(H), (Cp'-d_{27})(CH_2)(H) *i.e.,* the isotopomers of $\{[(CD_3)_2(CD_2CH_2D)C][(CD_3)_3C][(CD_3)_2(CD_2H)C]C_5H_3\}$. Examination of the ^1H NMR spectrum of the hydrolyzate shows three single resonances in the CMe_3 region for the three possible isotopomers of this new cyclopentadiene. The identity of C is likely $[(Me_2EtC)(Me_3C)_2C_5H_2](Cp')CeF$, the result of insertion of CH_2 into a C-H bond of the ring substituted CMe_3 group. Thus, C-H bonds of the solvent and the ring substituents trap the CH_2 fragment.

There is still an unsettling question, *viz*. photochemical decomposition of CH_2N_2 in presence of cyclohexene gives norcarane and the three isomeric methylcyclohexenes in a ratio of about 2:3.[10] In a later study, singlet CH_2 was found to react with all substrates including C-H bonds of saturated hydrocarbons at diffusion controlled rates.[11] Norcarane is the expected reaction product of singlet methylene, but no evidence of insertion into the C-H bonds of cyclohexene is observed in the products of the reaction of CH_3F and the metallacycle in the presence of cyclohexene. A way around the selectivity issue is to postulate that the carbene generated by the reaction with the metallacycle is not a free carbene, but a carbenoid, that is a methylene in which the metal and leaving group (F) are still attached to the CH_2 fragment. Carbenoid fragments are electrophiles that react much like free carbenes but show greater selectivity.[12] The cerium reaction is therefore related to that observed for various carbenoid precursors like RHCLiX, the Simmons-Smith reagent, RCHIZnI, and $ISmCH_2I$.[13]

A similar set of experiments with the metallacycle and CH_2F_2 gives Cp'_2CeF and B in a 1:1 ratio and the two isomers of tri-t-butylbenzene. The metallocycle with CHF_3 forms Cp'_2CeF and B in a 4:1 ratio, and the isomeric tri-t-butylfluorobenzenes. The presence of cyclohexene does not appear to affect the results obtained from the reactions of either CH_2F_2 or CHF_3, indicating that cyclohexene is not as good a trap as the substituted cyclopentadienyl ring. This set of experiments is consistent with the idea that the C-H bond in $CH_{4-x}F_x$, x = 1-3, inserts into the Ce-C bond of the metallacycle generating $Cp'_2CeCH_{3-x}F_x$, which is not observed by ^1H NMR spectroscopy, but whose identity is inferred by the products of decomposition.

3.3 General Trends

CH_3F and CH_2F_2 react rapidly and cleanly with the hydride to generate Cp'_2CeF and CH_4, presumably *via* C-H activation to generate short-lived intermediates Cp'_2CeCH_2F and Cp'_2CeCHF_2, respectively, and H_2. The intermediates rapidly activate a C-F bond, and the incipient carbenoid fragments are trapped by the H_2 produced in the first step. The products are Cp'_2CeF and CH_4 or CH_3F, which reacts with additional hydride to generate CH_4. The level of deuteration of the methane products when these reactions are performed under an atmosphere of D_2 (CH_3D in the case of CH_3F, CH_2D_2 and CH_3D in the case of CH_2F_2) suggests that the H_2 generated in the first step does not leave the coordination sphere of the complex before it traps the carbenoid fragment. In the slow reaction of CHF_3 with the hydride, H_2 trapping of the CF_2 is proposed to be kinetically unfavorable,[4] so free H_2 is observed and the C=C bonds in the Cp'-ligands act as the carbene trap instead. The isolation of tri-t-butylbenzenes instead of tri-t-butylfluorobenzenes is presumably due to H/F exchange between the proposed intermediate Cp'_2CeCF_3 and Cp'_2CeH. The alternative method for generating Cp'_2CeCF_3, addition of Me_3SiCF_3 to $Cp'_2CeH(D)$, is much faster, and generates the isomeric tri-t-butylbenzenes along with a small amount of tri-t-butylfluorobenzenes. The reactions of CH_3F, CH_2F_2 and CHF_3 with the metallacycle are slow, and lacking H_2 as a trap, the carbenoid fragments are trapped by the C-H or C=C bonds in the Cp'-ligands.

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9. In order to be sure that cyclohexene does not change the course of the reaction, the perdeuterometallacycle was exposed to a large excess of cyclohexene in C_6D_{12}. Over the course of a week, 1,2-dideuterocyclohexene was the only product observed by ^{2}H NMR spectroscopy. This experiment shows that cyclohexene inserts into the metallacycle to give the metallocene cerium cyclohexenyl derivative, and this eliminates cyclohexene-d_1. Since both olefinic C-H bonds

undergo H/D exchange, the process is reversible. The rate of addition is slow, and therefore cyclohexene is present in sufficient excess to act as a trapping reagent. Cyclohexene reacts rapidly with Cp'_2CeH generating the cyclohexyl derivative that yields the metallacycle and cyclohexane. Under H_2 the metallacycle or Cp'_2CeH is a hydrogenation catalyst for cyclohexene. Thus, cyclohexene cannot be used as a carbene trap in reactions of Cp'_2CeH. See also Chapter 4.

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Chapter 4: Small Molecule Insertion by the Hydride

Insertion of small molecules into lanthanide-carbon and lanthanide-hydrogen bonds has been the subject of considerable study, but mostly in the later lanthanides.[1] There are only a few reports on the chemistry of the small family of known cerium alkyls and hydrides.[2] A series of reactions with small molecules was undertaken with the hydride, Cp'_2CeH, and the metallacycle to study alkene polymerization, hydrogenation, and carbonylation.

4.1 Alkene polymerization and hydrogenation

When a hexane solution of the hydride is exposed to an atmosphere of ethylene, the red-purple solution becomes deeper purple, then slowly turns brown as flakes of off-white solid appear. The air-stable solid did not have a clearly defined melting point when heated in a sealed capillary, but did burn when heated in air over an open flame, leaving behind a small quantity of white ash. The ^{1}H NMR spectrum of the mother liquor contained multiple unidentified paramagnetic products. In an NMR tube, exposing a frozen solution of the hydride in C_6D_{12} to ethylene for 10 minutes, then replacing the atmosphere with nitrogen before melting the sample results in a ^{1}H NMR spectrum containing resonances of both the hydride and the metallacycle. A hexane solution of the metallacycle exposed to an atmosphere of ethylene results in a dark brown solution with flakes of off-white precipitate similar to that obtained from the hydride reaction.

A hexane solution of the hydride under an atmosphere of propylene turns from red-purple to a deep red over several hours, but no solid precipitate forms. A solution of the hydride in C_6D_{12} exposed to an atmosphere of propylene for 10 minutes results in a ^1H NMR spectrum containing resonances due to propane, the metallacycle, and a new 2:1 set of broad CMe_3 resonances. The resonances due to the metallacycle also disappear within three hours, leaving the new 2:1 set of CMe_3 resonances as the only paramagnetic product. Reaction of $Cp'_2CeOSO_2CF_3$ with allylmagnesium bromide produces the same set of ^1H NMR resonances, suggesting that the new product is a metallocenecerium allyl, $Cp'_2CeC_3H_5$. Unfortunately, crystals suitable for x-ray diffraction studies could not be obtained, and the binding mode of the allyl ligand is unknown. The integrated intensities of the CMe_3 resonances of $Cp'_2CeC_3H_5$ do not change upon heating in C_6D_{12} for two days at 60°C, but quantitative conversion to Cp'_2CeH and propane is achieved after one day at 25°C under an atmosphere of H_2. When D_2 is used instead of H_2, two resonances appear in the ^2H NMR at chemical shifts corresponding to those of propane-d_n.

While it appears that multiple insertion of ethylene into the Ce-H bond of the hydride is occurring to generate polyethylene, propylene inserts only once. C-H activation on one of the ring CMe_3 groups generates propane the metallacycle, which then activates a C-H bond in propylene to generate the allyl complex. The addition of H_2 regenerates the hydride and expels propane. The hydride thus behaves as a hydrogenation catalyst for propylene in the presence of H_2.

As noted in Chapter 3, the hydride is also a hydrogenation catalyst for cyclohexene. Adding a drop of cyclohexene (an excess) to a solution of the hydride in

C_6D_6 results in the appearance of ^{1}H NMR resonances due to cyclohexane, the metallacycle, and a new 2:1 set of CMe_3 resonances. Dissolving the metallacycle in neat cyclohexene and heating to 60°C for several hours results in a red solution. Removal of the solvent gives a glassy red solid whose ^{1}H NMR spectrum contains the same 2:1 set of CMe_3 resonances observed in the reaction of the hydride with cyclohexene. The new species is presumably a metallocenecerium cyclohexenyl complex. Isolation of this complex is problematic, as it readily loses cyclohexene in solution to reform the metallacycle. In C_6D_{12} solution, the cyclohexenyl complex is observed to be in equilibrium with the metallacycle even in the presence of a large excess of cyclohexene. The binding mode of the cyclohexenyl ligand is not known, but addition of a drop of cyclohexene to a solution of the metallacycle-d_{26} in C_6D_{12} and heating at 60°C for one week results in the appearance of 1,2-dideuterocyclohexene in the ^{2}H NMR spectrum, suggesting that vinylic C-H bonds are being activated reversibly by the metallacycle. This reversibility made cyclohexene a suitable trapping reagent for CH_2 in the reaction of the metallacycle with CH_3F (Chapter 3), while the rapid, irreversible hydrogenation of cyclohexene by the hydride made it unsuitable as a carbene trap in reactions of the hydride with fluoromethanes.

4.2. CO insertion

Exposing a concentrated solution of the hydride in pentane to an atmosphere of CO results in a rapid color change from red-purple to red-orange, followed by the formation of copious orange precipitate. The orange solid crystallizes from toluene, and gives a 1:1:1 pattern of sharp CMe_3 resonances ($\nu_{1/2}$ ~ 20 Hz) in the proton NMR spectrum. Resonances due to toluene are also observed, suggesting included solvent in the crystals. Crystals suitable for x-ray diffraction studies can be grown in this manner; an ORTEP drawing is shown in Figure 4.1 with selected distances and angles listed in the figure caption. The complex is formulated $(Cp'_2Ce)_2CH_2O$, with two Cp'_2Ce units bound in an η^2-fashion to the common dianionic formaldehyde ligand. The molecule crystallizes in the space group P2/n, with the asymmetric unit containing half the molecule as well as half a molecule of toluene. The C and O atoms of the formaldehyde ligand are distinguished by their differing intensities in the difference Fourier map, and the location of Fourier peaks due to hydrogen atoms around the carbon. The interplanar angle of the two Cp'-rings is 134.9(4)°, quite small compared to those of the structures discussed in Chapters 1 and 2.

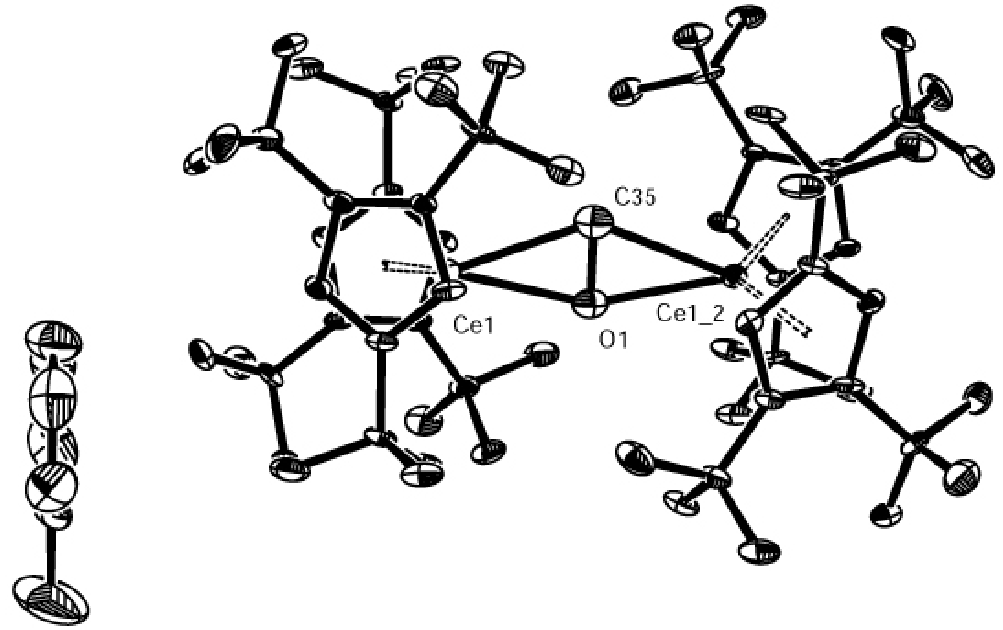
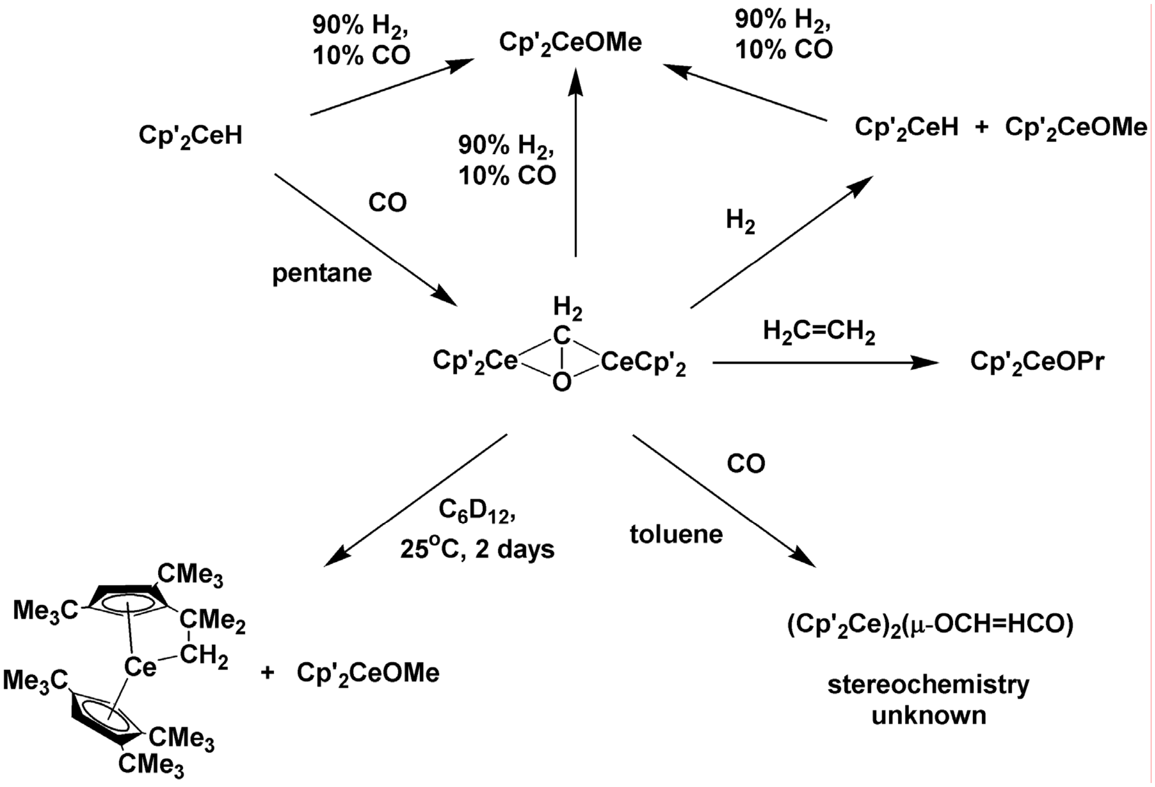


Figure 4.1: ORTEP drawing of $(Cp'_2Ce)_2CH_2O$. Selected distances and angles: Ce1-ring C (range) = 2.773(8)-3.009(8) Å, Ce1-Cp' (perpendicular to l.s. plane) = 2.577(3) Å, 2.597(4) Å, Ce1-O1 = 2.444(2) Å, Ce1-C35 = 2.554(4) Å, interplanar angle of Cp' ligands = 134.9(4)°, O1-Ce1-C35 = 32.2(3)°, Ce1- O1-C35 = 78.2(2)°, Ce1-C35-O1 = 69.5(3)°.

Reactions involving the $(Cp'_2Ce)_2CH_2O$ complex are shown illustrated in Scheme 4.1. The complex is stable in the solid state at room temperature, but melts with decomposition at 212-215°C. The ^{1}H NMR spectrum of the dark red decomposed sample contains a new set of CMe_3 resonances in a 2:1 area ratio, a resonance of area 4 relative to the CMe_3 resonances, presumably due to ring methyne protons, and another resonance of area 3. When a solution of $(Cp'_2Ce)_2CH_2O$ in C_6D_{12} is allowed to stand at 25°C, the 1:1:1 pattern of CMe_3 resonances gradually disappears over the course of two days as resonances of the metallacycle and the same set of resonances observed in the melting point sample appear. The EI mass spectrum of $(Cp'_2Ce)_2CH_2O$ does not give an M^+; rather, $(M-636)^+$ corresponding to the metallacycle and $(M-605)^+$ corresponding to Cp'_2CeOMe are observed.



Scheme 4.1: Reactions involving $(Cp'_2Ce)_2CH_2O$.

Independent synthesis of Cp'_2CeOMe is problematic due to its high solubility and sensitivity to trace quantities of water. $Cp'_2CeOSO_2CF_3$ reacts with dry sodium methoxide to give a red solid whose ^1H NMR spectrum matches that of the major component of the decomposed melting point sample. The solid is highly soluble in pentane and difficult to crystallize without contamination by the sparingly soluble yellow powder mentioned in Chapter 1, presumed to be the product of reaction with traces of water. The conditions that lead to analytically pure Cp'_2CeOMe are suggested by the reaction of $(Cp'_2Ce)_2CH_2O$ with H_2. The color of a solution of $(Cp'_2Ce)_2CH_2O$ under an atmosphere of H_2 rapidly turns from orange to deep red, and the ^1H NMR spectrum indicates the formation of Cp'_2CeOMe and hydride in a 1:1 ratio. Exposing a solution of the hydride in pentane to an atmosphere of a 1:10 mixture of CO and H_2 results in a deep red solution. Cp'_2CeOMe can be crystallized from the reaction mixture as an analytically pure red powder. The ^1H NMR spectrum consists of the same set of resonances as the major component of the decomposed melting point sample and of the decomposition of the $(Cp'_2Ce)_2CH_2O$ in solution at 25°C.

Exposing a solution of $(Cp'_2Ce)_2CH_2O$ to an atmosphere of ethylene results in another new set 2:1 of CMe_3 resonances and three smaller resonances with areas of 2, 2, and 3 relative to the CMe_3 resonances. The pattern of resonances suggests a complex of the formulation Cp'_2CeOPr. Unfortunately, the method used above to synthesize Cp'_2CeOMe cleanly cannot be extended to Cp'_2CeOPr. A solution of $Cp'_2CeOSO_2CF_3$ and dry sodium propoxide stirred in diethyl ether at 25°C for one day in results in a deep red solution. Removal of the solvent yields a glassy red solid that is highly soluble in pentane. Attempts at crystallization were unsuccessful, but the ^{1}H NMR spectrum of the crude solid is identical to that obtained from the reaction of $(Cp'_2Ce)_2CH_2O$ with ethylene.

Exposing a solution of $(Cp'_2Ce)_2CH_2O$ in C_7D_8 to an atmosphere of CO instantly turns the solution color from orange to red. The resonances due to $(Cp'_2Ce)_2CH_2O$ are absent from the ^{1}H NMR spectrum, and a broad set of CMe_3 resonances in a 2:1 area ratio have appeared. On a synthetic scale (0.5 g), a toluene solution of the hydride exposed to an atmosphere of CO initially turns orange and slightly cloudy, gradually clearing and turning darker red within 30 minutes. Crystallization from pentane yields a red powder whose ^{1}H NMR spectrum is identical to that obtained in the reaction of $(Cp'_2Ce)_2CH_2O$ with CO. The EI mass spectrum gives an M^+ of 1270, and the elemental analysis is consistent with the formulation $(Cp'_2CeCHO)_2$. Crystals suitable for x-ray diffraction studies could not be obtained through crystallization. A report of an analogous reaction of $[(C_5Me_5)_2SmH]_2$ with CO results in the isolation of *cis* and *trans* isomers of a binuclear endiolate complex, $[(C_5Me_5)Sm]_2(\mu\text{-OCH=CHO})$, as triphenylphosphine oxide adducts.[3] The samarium complex is stable indefinitely in solution, does not react further with CO, and the *cis* isomer produces a medium intensity band in the IR spectrum at 1600 cm^{-1}, assigned to the C=C stretch in the -OCH=CHO- ligand. $(Cp'_2CeCHO)_2$ is likewise stable in solution and does not react with an atmosphere of either CO or H_2. The IR spectrum contains a strong band at 1620 cm^{-1}. It seems likely that $(Cp'_2CeCHO)_2$ is constituted similar to the samarium complex, with a μ-OCH=CHO ligand bridging two Cp'_2Ce units. $[(C_5Me_5)Sm]_2(\mu\text{-OCH=CHO})$ in the absence of triphenylphosphine oxide has a single ^{1}H NMR resonance attributable to the ring-Me groups, which broadens into the baseline at 233K, and by 213K, two new broad resonances emerge.[3] The temperature dependent behavior of the ^{1}H NMR spectrum of $(Cp'_2CeCHO)_2$ is illustrated by the δ vs. 1/T plot in Figure 4.2. The CMe_3 resonance of area 2 broadens into the baseline at a T_c = 0°C, and at lower temperatures, two new resonances of area 1 emerge at roughly equal distances on either side of the original resonance, giving a $\Delta G^{\#}_{TC}$ =11 kcal mol^{-1}. The three CMe_3 resonances sharpen as the temperature decreases, and at -46°C, a shoulder appears on the upfield side of the resonances that arose from the resonance of area 2, and the downfield side of the unique CMe_3 resonance. By -53°C, the shoulders have separated from their parent signals, with intensities approximately ½ that of their parents. By -78°C, all six resonances are of approximately equal intensity.

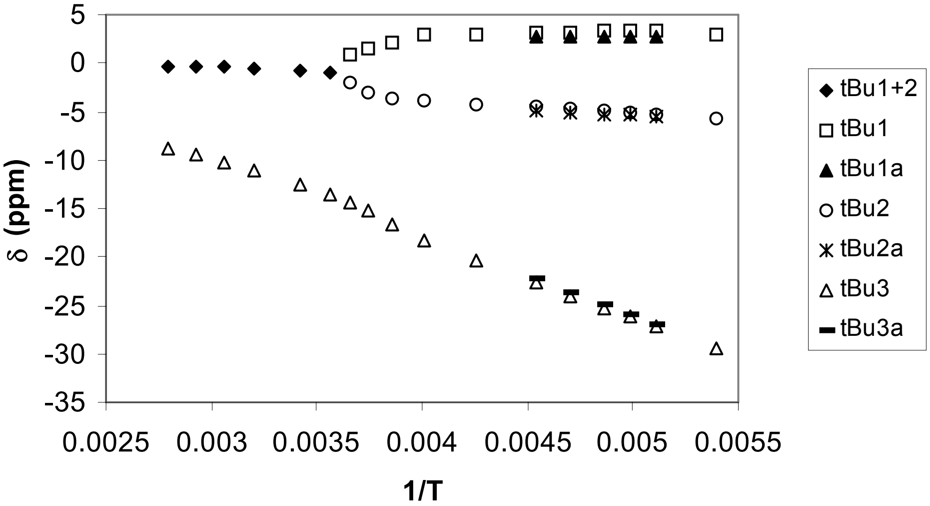


Figure 4.2: ^{1}H NMR δ vs. 1/T plot for $(Cp'_2CeCHO)_2$ in C_7D_8

The physical process proposed for the observed temperature dependent behavior of Cp'_2CeI (Chapter 1), slowing of the librational motions of the Cp' rings about their pseudo-C_5 axes, could also explain the decoalescence of the CMe_3 resonances of $(Cp'_2CeCHO)_2$ from two resonances with a 2:1 area ratio to three resonances with a 1:1:1 ratio. The appearance of six resonances of unequal and varying intensity at still lower temperatures is suggestive of the slowing of an isomerization process. It is unlikely that an intramolecular process could give rise to the observed behavior, as it is difficult to envision a process that would render the Cp'-rings of one Ce-center different from those of the other in unequal populations. The *cis* to *trans* isomerization suggested in the case of the samarium enediolate triphenylphosphine oxide complex is a fascinating possibility, but further study will be needed to determine if this process is actually possible in these systems.[3]

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Experimental Details

General

All manipulations were performed in an inert atmosphere using standard Schenk and dry box techniques. All solvents were dried and distilled from sodium or sodium benzophenone ketyl. Fluoro and hydrofluorobenzenes were dried and vacuum transferred from calcium hydride. Fluoromethane gases were obtained from Scott Specialty Gases in 99.99% purity and used as received. Manipulations were kept to a minimum, and cerium metallocenes were crystallized from their reaction mixtures if possible to minimize their exposure to traces of water in solvent and on glassware. Even so, second crops of crystals were often difficult to obtain due either to co-crystalization with a byproduct or formation of oils. This is the reason for isolated yields in the 50% range.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as Nujol mulls between CsI plates. NMR spectra were recorded on JEOL FX-90Q, Bruker AMX-300, AMX-400, or DRX-500 spectrometers at 19°C in the solvent specified. ^{19}F NMR chemical shifts are referenced to $CFCl_3$ at 0 ppm. J-Young NMR tubes were used for all NMR tube experiments except for variable temperature experiments, which were performed in sealed NMR tubes. Melting points were measured on a Thomas-Hoover melting point apparatus in sealed capillaries. Electron impact mass spectrometry and elemental analyses were performed by the microanalytical facility at the University of California, Berkeley. Samples for GC-MS were prepared from NMR reaction samples by adding a drop of D_2O or H_2O agitating, and allowing the sample to stand closed for 10 min. The samples were then dried over magnesium sulfate, filtered, and diluted ten fold with hexane. A 1 μL sample was injected into a HP6890 GC system with a J&W DB-XLB universal non-polar column, attached to an HP5973 Mass Selective Detector. The abbreviation Cp' is used for the 1,2,4-tri-t-butylcyclopentadienyl ligand, Cp'-d_{27} is used for the same ligand with all t-butyl groups deuterated, and Cp"H is used for the $[Me_2EtC][Me_3C]_2C_5H_2$ ligand.

Chapter 1

Cp'_2CeCl: Anhydrous $CeCl_3$ (1.0 g, 4.1 mmol, dried by heating at reflux in $SOCl_2$) and Cp'_2Mg[1] (1.99 g, 4.1 mmol) were stirred at reflux in a mixture of pyridine (5 mL) and toluene (50 mL) for 24 hours. The yellow-brown suspension was taken to dryness under reduced pressure. The solid residue was extracted with toluene (50 mL). The volume of the solution was reduced until precipitation occurred, warmed to dissolve the precipitate, and then cooled to –15°C. Yield: 1.1 g (1.7 mmol, 42%). MP 233-236°C. ^1H NMR (C_6D_6, 300MHz): δ -2.579 (36H, $\nu_{1/2}$ = 90 Hz), -13.322 (18H, $\nu_{1/2}$ = 80 Hz). MS $(M)^+$ *m/z* (calc, found) 641 (100, 100) 642 (37, 34) 643 (51, 50) 644 (17, 15) 645 (7, 6). Anal. Calcd. for $C_{34}H_{58}CeCl$: C, 63.57; H, 9.10. Found C, 63.72; H, 9.37.

Cp'_2CeI: Method A: $CeI_3 \cdot 3\ THF$[2] (4.0 g, 5.5 mmol) and Cp'_2Mg (2.7 g, 5.5 mmol) were stirred at reflux in dibutyl ether (40 mL) for seven days. The solvent was removed under reduced pressure and toluene (50 mL) was added to the orange solid. The suspension was stirred at reflux for 24 hours, and the toluene was slowly removed under reduced pressure while still hot (~60°C). The orange solid was extracted with hexane (500 mL). The volume of the solution was reduced until precipitation occurred, warmed to dissolve the precipitate, and then cooled to –15°C, yielding orange crystals. Yield, 1.5g (2 mmol, 37%). MP 309-311°C. ^{1}H NMR (C_6D_6, 300MHz): δ 3.20 (18H, $\nu_{1/2}$ = 430 Hz), -8.03 (18H, $\nu_{1/2}$ = 430 Hz), -15.14 (18H, $\nu_{1/2}$ = 220 Hz). MS $(M)^+$ *m/z* (calc, found) 733 (100, 100) 734 (37, 37) 735 (19, 19) 736 (6,5). Anal. Calcd. for $C_{34}H_{58}CeI$: C, 55.65; H, 7.96. Found C, 55.76; H, 8.17.

Method B: CeI_3 • 3 THF (18.1 g, 25.0 mmol) and Cp'_2Mg (12.0g, 24.0 mmol) were stirred at reflux in a mixture of pyridine (10 mL) and toluene (100 mL) for 24 hours. The orange-brown suspension was taken to dryness under reduced pressure. The solid residue was loaded into an extraction thimble (dried at 120°C for three days) and extracted with pentane (200 mL) in a Soxhlet extractor for three days. After 12 hours, orange precipitate appeared in the solvent flask. The extraction was stopped and the flask was exchanged for a flask of fresh pentane (200mL). The initial flask was cooled to –15°C, yielding dirty orange powder. The suspension was filtered, and the flask containing the mother liquor was exchanged for the solvent flask on the extraction apparatus when orange precipitate had appeared in the solvent flask. This process was repeated until the solution around the extraction thimble was colorless. Recrystallization of the accumulated orange powder from toluene (100 mL) yielded small, opaque, bright orange crystals. Yield, 10.2 g (14 mmol, 56%).

Method C: Cp'_2CeCl (0.10 g, 0.15 mmol) was suspended in pentane (20 mL), and Me_3SiI (100 μL, 0.70 mmol) was added *via* syringe. The solution was stirred at room temperature. After one day, an aliquot was taken to dryness for analysis by ^{1}H NMR spectroscopy. The ratio of Cp'_2CeCl to Cp'_2CeI was found to be 3:1. After 7 days, the ^{1}H

NMR spectrum of a second aliquot showed only the resonances of Cp’$_2$CeI; no resonances attributable to Cp’$_2$CeCl were present.

Method D: CeI$_3$ • 3 THF (0.50 g, 0.70 mmol) and NaCp’ (0.35 g, 1.4 mmol) were stirred in THF (20 mL) at room temperature for 3 days, yielding a yellow solution. The ^{1}H NMR spectrum of an aliquot of the solution did not contain resonances attributable to Cp’$_2$CeI. The solition was heated at reflux for 24 hours, which yielded an orange solution. The ^{1}H NMR spectrum of an aliquot of the solution indicated the formation of Cp’$_2$CeI.

Cp’$_2$CeOTf • 0.5 hexane: Method A: Ce(OSO$_2$CF$_3$)$_3$ [3] (15.0 g, 25.5 mmol) and Cp’$_2$Mg (12.0 g, 24.5 mmol) were stirred at reflux in a mixture of pyridine (10 mL) and toluene (100 mL) for 24 hours. The dark brown suspension was taken to dryness under reduced pressure. The residue was extracted with hexane (200 mL). The volume of the solution was reduced until precipitation occurred, warmed to dissolve the precipitate, and then cooled to –15°C. The large brown crystals were recrystallized five times from hexane, until the crystals obtained were bright yellow in color. Yield, 11 g (14 mmol, 55%). MP 300-302°C. ^{1}H NMR (C$_7$D$_8$): δ 4.16 (18H, $\nu_{1/2}$ = 75 Hz), 1.25 (m, hexane), 0.88 (t, hexane, the integrated intensity of these two absorptions indicated about 0.5 hexane per metallocene), -5.36 (18H, $\nu_{1/2}$ = 60 Hz), -13.66 (18H, $\nu_{1/2}$ = 60 Hz). IR: 1340(s), 1240(m), 1220(m), 1210(m), 1190(m), 1180(m), 1170(w), 1020(s), 960(w), 830(m), 780(w), 690(w), 680(w), 640(s), 600(w), 550(w), 520(w), 450(w), 370(w) cm^{-1}. MS (M)$^+$ *m/z* (calc, found) 755 (100, 100) 756 (41, 40) 757 (26, 25) 758 (8,8). Anal. Calcd. for C$_{35}$H$_{58}$CeF$_3$O$_3$S + 0.5 hexane: C, 57.1; H, 8.20. Found C, 57.2; H, 8.32.

Method B: Cp'$_2$CeCl (1.5 g, 2.3 mmol) was suspended in pentane (30 mL), and $Me_3SiOSO_2CF_3$ (1.7 mL, 9.3 mmol) was added *via* syringe. The suspension was stirred at room temperature. After 2 days, the yellow solution was no longer cloudy. An aliquot was taken to dryness for analysis by ^{1}H NMR spectroscopy. The spectrum showed only the resonances of Cp'$_2$Ce OSO_2CF_3; no resonances attributable to Cp'$_2$CeCl were present. The solution was taken to dryness under reduced pressure, and the yellow solid residue was dissolved in hexane (50 mL) and filtered. The volume of the solution was reduced until precipitation occurred, warmed to dissolve the precipitate, and then cooled to –15°C. The ^{1}H NMR spectrum of the resulting yellow crystals was identical to that obtained from the product of Method A. Yield, 0.81g (1.0 mmol, 44%).

Cp'$_2$CeBr: Cp'$_2$CeOTf (0.25g, 0.31 mmol) was dissolved in pentane (10 mL) and Me_3SiBr (120μL, 0.91 mmol) was added *via* syringe. The solution was stirred for one day, then taken to dryness under reduced pressure. The yellow solid was dissolved in pentane and filtered. The yellow solution was concentrated until precipitation occurred, warmed to dissolve the precipitate, then cooled to –15°C, yielding yellow powder. Yield, 0.095 g (0.13 mmol, 42%). MP 266-270°C. ^{1}H NMR (C_6D_6, 300MHz): δ -2.46 (36H, $\nu_{1/2}$ = 550 Hz), -14.03 (18H, $\nu_{1/2}$ = 170 Hz). MS $(M)^+$ *m/z* (calc, found) 685 (86, 85) 686 (32, 30) 687 (100, 100) 688 (36, 31) 689 (17, 13). Anal. Calcd. for $C_{34}H_{58}CeBr$: C, 59.46; H, 8.51. Found C, 59.61; H, 8.36.

Reaction of Cp'$_2$CeOSO$_2$CF$_3$ and CH$_3$Li: Cp'$_2$CeOSO$_2$CF$_3$ (1g, 1.3 mmol) was dissolved in 20 mL of diethyl ether and chilled in a liquid nitrogen/isopropanol bath. CH_3Li (1.8mL of a 0.7M solution in diethyl ether, 1.3 mmol) was added *via* syringe. The yellow solution immediately turned red, and became cloudy after 10 minutes. An aliquot was removed and taken to dryness for quick analysis by ^{1}H NMR spectroscopy. The spectrum of the aliquot showed two new resonances [^{1}H NMR (C_6D_6): δ –2.31 (36H, $\nu_{1/2}$ = 10 Hz), –12.7 (18H, $\nu_{1/2}$ = 16 Hz)], possibly due to Cp'_2CeCH_3, as well as resonances due to $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The latter resonances increased at the expense of the former over time.

NMR tube reaction of $Cp'_2CeOSO_2CF_3$ and Me_3SiCH_2Li: $Cp'_2CeOSO_2CF_3$ was dissolved in C_6D_6 and a small amount of Me_3SiCH_2Li powder was added. The cloudy red solution was filtered into an NMR tube. The ^{1}H NMR spectrum contained resonances of $Cp'_2CeOSO_2CF_3$, $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$, and two new resonances [^{1}H NMR (C_6D_6): δ –1.24 (36H, $\nu_{1/2}$ = 450 Hz), –15.22 (18H, $\nu_{1/2}$ = 50 Hz)], possibly due to $Cp'_2CeCH_2SiMe_3$. The ratio of the three components after 10 minutes was 7:1:3. After 25 minutes at room temperature, the ratio had changed to 3.5:1:1; after 70 minutes, it was 8:4:1. After 1 day at room temperature, only resonances due to $Cp'_2CeOSO_2CF_3$ and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ were present.

$Cp'_2CeCH_2C_6H_5$: The triflate, Cp'_2CeOTf • 0.5 hexane (4.0 g, 5.0 mmol), was dissolved in 30mL of diethyl ether and $C_6H_5CH_2MgCl$ (6.7 mL, 0.75 M in diethyl ether, 5.0 mmol) was added *via* syringe. The solution immediately changed from yellow to red, and became cloudy within 5 minutes. After 5 minutes the solvent was removed under reduced pressure and the red solid was extracted into 20 mL of pentane. The volume of the solution was reduced to 10 mL and cooled to –15°C. After 1 day, yellow crystals of Cp'_2CeCl had formed. The solution was filtered, concentrated further, and cooled to –

15°C, giving red blocks. Yield, 2.1 g (3.0 mmol, 60%). MP 111-113°C. ^{1}H NMR (C_6D_6): δ 13.25 (2H, $\nu_{1/2}$ = 245 Hz), 4.29 (2H, $\nu_{1/2}$ = 20 Hz), 2.47 (1H, $\nu_{1/2}$ = 14 Hz), -0.53 (18H, $\nu_{1/2}$ = 190 Hz), -1.80 (18H, $\nu_{1/2}$ = 195 Hz), -13.19 (18H, $\nu_{1/2}$ = 45 Hz), -32.62 (2H, $\nu_{1/2}$ = 280 Hz). IR: 1590(s), 1490(s), 1370(s), 1360(s), 1240(s), 1220(m), 1210(w), 1170(w), 1160(w), 1030(w), 1000(m), 960(w), 930(m), 890(w), 860(w), 820(m), 810(s), 790(m), 730(s), 720(w), 700(m), 690(m), 680(m), 510(w), 440(w), 360(w) cm^{-1}. Anal. Calcd. for $C_{41}H_{65}Ce$: C, 70.5; H, 9.39. Found C, 70.3; H, 9.32. MS: no $(M)^+$ was observed but $(M-PhCH_3)^+$ was found *m/z* (calc, found) 605 (100, 100) 606 (39, 43) 607 (17, 21) 608 (6, 6).

Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce: Cp'$_2$Ce($CH_2C_6H_5$), (0.7 g, 1.0 mmol) was heated in pentane (10 mL) for 12 hours. The red solution turned deep purple. The solvent was removed yielding a glassy solid. ^{1}H NMR (C_6D_{12}) δ 35.83 (1H, $\nu_{1/2}$ = 200Hz), 33.71 (1H, $\nu_{1/2}$ = 158Hz), 16.24 (3H, $\nu_{1/2}$ = 30 Hz), 5.97 (3H, $\nu_{1/2}$ = 50Hz), -3.40 (9H, $\nu_{1/2}$ = 50Hz), -5.63 (9H, $\nu_{1/2}$ = 45Hz), -7.56 (9H, $\nu_{1/2}$ = 50 Hz), -10.10 (9H, $\nu_{1/2}$ = 10Hz), -16.13 (9H, $\nu_{1/2}$ = 45Hz), -29.25 (1H, $\nu_{1/2}$ = 110 Hz).

Cp'$_2$CeC$_6$H$_5$: Cp'$_2$CeCH$_2$C$_6$H$_5$, (1 g, 1.4 mmol) was heated at reflux in C_6H_6 (20 mL) for 3 days. The solution turned a deeper red and a small amount of yellow precipitate formed. The solvent was removed under reduced pressure and pentane (15 mL) was added. The solution was filtered, the volume was reduced to 10 mL, and the solution was cooled to -15°C, giving a deep red powder. Yield, 123 mg (0.2 mmol, 14%). ^{1}H NMR (C_6D_6): δ 7.88 (1H, t, *J* = 7 Hz), 6.12 (2H, d, *J* = 7 Hz), -1.73 (36H, $\nu_{1/2}$ = 8 Hz) -10.48 (18H, $\nu_{1/2}$ = 11 Hz) the ortho proton resonance was not observed. Anal. Calcd. for $C_{40}H_{63}Ce$: C, 70.2; H, 9.28. Found C, 70.1; H, 9.31.

$\{[C(CD_3)_3]_3C_5H_2\}\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$: The benzyl, Cp'$_2$CeCH$_2C_6H_5$, was dissolved in C_6D_6 in an NMR tube. The sample was heated at 60°C. After 6 days, the solution was taken to dryness. Fresh C_6D_6 was added, and the sample was heated at 60°C for another six days. The solution was taken to dryness, and the deep red solid residue was dissolved in C_6D_{12}. The sample was heated for one day at 60°C to generate the metallacycle. To determine the degree of deuteration of the Cp'-rings, a drop of degassed D_2O was added. GC MS analysis showed a mixture of Cp'D-d$_{28}$, Cp'D-d$_{27}$, and Cp'D-d$_{26}$ in a 40:8:1 ratio, $(M)^+$ *m/z* (calc, found) 260 (1, 1) 261 (18, 18) 262 (100, 100) 263 (19, 17) 264 (2, 2).

NMR tube reaction of Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce and C_6H_6: Cp'$_2$Ce(CH$_2$C$_6$H$_5$) was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce. The solution was taken to dryness and the solid residue dissolved in C_6H_6. The sample was heated at 60°C for 3 days, then taken to dryness and the solid residue dissolved in C_6D_6. The ^{1}H NMR showed resonances characteristic of Cp'$_2$CeC$_6$H$_5$ and the integrated intensities indicated quantitative conversion.

Cp'$_2$CeH: The benzyl, Cp'$_2$CeCH$_2$C$_6$H$_5$ (1.0 g, 1.4 mmol), was dissolved in 10 mL of pentane. The headspace was evacuated and replaced with H_2 (1 atm). The red solution turned purple over 30 minutes. After 2 hours, the volume of the solution was reduced until precipitation occurred, then warmed to dissolve the precipitate. Cooling to -15°C yielded purple crystals. Yield, 0.76 g (1.2 mmol, 85%). MP 152-155°C. ^{1}H NMR (C_6D_6): δ 31.86 (4H, $\nu_{1/2}$ = 220 Hz), -3.44 (36H, $\nu_{1/2}$ = 45 Hz), -12.45 (18H, $\nu_{1/2}$ = 45

Hz). Neither the resonances nor the stretching frequencies of Ce-H were conclusively identified. IR: 2160(m),[5] 1360(s), 1250(s), 1200(s), 1170(m), 1020(s), 1000(s), 960(m), 930(w), 920(w), 870(w), 840(w), 810(s), 800(m), 790(w), 780(w), 680(s), 670(s), 600(m), 520(s), 480(w), 440(m), 360(s) cm^{-1}. MS: no $(M)^+$ was observed but $(M-2)^+$ was found *m/z* (calc, found) 605 (100, 100) 606 (39, 43) 607 (17, 21) 608 (6, 6). Anal. Calcd. for $C_{34}H_{59}Ce$: C, 67.2; H, 9.78. Found C, 67.5; H, 10.11.

Cp'_2CeD was prepared by the same procedure using D_2 instead of H_2. The ^1H NMR and IR spectra of Cp'_2CeD and Cp'_2CeH were found to be identical; a unique Ce-D stretch could not be identified in the IR spectrum.

NMR tube reaction of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ and D_2 in C_6D_{12}: $Cp'_2Ce(CH_2C_6H_5)$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The headspace was evacuated and replaced with D_2 (1 atm). The only paramagnetic resonances in both the ^1H NMR and ^2H NMR spectra were the two CMe_3 resonances of Cp'_2CeD. The resonances were in a 2:1 area ratio in both cases.

Cp'_2CeBF_4: $Cp'_2CeCH_2C_6H_5$ (0.50 g, 0.71 mmol) was dissolved in pentane (10 mL) and $BF_3(OEt_2)$ (0.09 mL, 0.7 mmol) was added via syringe. The red solution turned yellow immediately. The volume of the solution was reduced until precipitation occurred, then warmed to redissolve the precipitate. Cooling to -15^{O}C yielded yellow plates. Yield, 0.29 g (0.42 mmol, 59%). MP 222-225^{O}C. ^1H NMR (C_6D_6): δ 2.53 (18H, $\nu_{1/2}$ = 860 Hz), -6.09 (18H, $\nu_{1/2}$ = 950 Hz), -11.69 (18H, $\nu_{1/2}$ = 85 Hz). IR: 2380(w), 2280(w), 2160(m), 1630(w), 1600(w), 1360(s), 1280(w), 1240(s), 1170(s), 1130(m), 1080(s), 1040(m), 1000(s), 960(s), 920(w), 870(w), 830(s), 780(m), 750(m), 720(w), 700(w), 690(s), 680(s), 600(w), 570(m), 550(s), 510(m), 440(s), 400(m), 360(s) cm^{-1}. Anal. Calcd. for $C_{34}H_{58}CeBF_4$: C, 58.86; H, 8.43. Found C, 58.67; H, 8.43.

Cp'$_2$CeF(pyridine): Cp'$_2$CeBF$_4$ (0.25 g, 0.36 mmol) was dissolved in pentane (10 mL) and pyridine (29 μL, 0.36 mmol) was added *via* syringe. The solution was concentrated until precipitation occurred, then warmed to redissolve the precipitate. Cooling to -15^{O}C yielded yellow powder. Yield, 0.12 g (0.17 mmol, 47%). ^{1}H NMR (C_6D_6): 14.01 (4H, $\nu_{1/2}$ = 60 Hz), 4.79 (1H, $\nu_{1/2}$ = 20 Hz), 3.90 (2H, $\nu_{1/2}$ = 30 Hz), 0.76 (18H, $\nu_{1/2}$ = 30 Hz), -1.30 (36H, $\nu_{1/2}$ = 60 Hz). Anal. Calcd. for $C_{39}H_{63}CeFN$: C, 66.44; H, 9.01; N, 1.99. Found C, 66.36; H, 8.98; N, 2.21. Exposure of the solid to dynamic vacuum for 2 hours and recrystalization from pentane did not change the ^{1}H NMR spectrum. A drop of C_5D_5N added the NMR sample resulted in the disappearance of the resonances at 4.79 and 3.90 ppm.

Cp'$_2$CeF: Cp'$_2$CeBF$_4$ (0.25 g, 0.36 mmol) and Cp'$_2$CeCH$_2$C$_6$H$_5$ (0.75 g, 1.1 mmol) were stirred in pentane (20 mL). The red solution turned orange over 12 hours. The solution was reduced until precipitation occurred, then warmed to redissolve the precipitate. Cooling to -15^{O}C yielded orange powder. Sublimation under static vacuum in a sealed glass ampoule at 118°C yielded small orange crystals. Yield, 0.44 g (0.70 mmol, 48%). MP 164-167°C. ^{1}H NMR (C_6D_6): δ 20.00 (4H, $\nu_{1/2}$ = 70 Hz), -2.50 (36H, $\nu_{1/2}$ = 10 Hz), -6.81 (18H, $\nu_{1/2}$ = 10 Hz). IR: 2380(w), 2280(w), 2180(w), 1630(w), 1590(w), 1350(s), 1270(w), 1260(m), 1240(s), 1200(s), 1170(s), 1110(m), 1090(m), 1020(m), 1000(s), 960(s), 930(w), 920(w), 870(w), 810(s), 780(m), 700(m), 690(m), 680(s), 640(w) cm^{-1}. MS $(M)^+$ *m/z* = (calc, found) 625 (100, 100), 626 (39, 40) 627 (20, 20) 628 (6, 5). Anal. Calcd. for $C_{34}H_{58}CeF$: C, 65.2; H, 9.34. Found C, 65.3; H, 9.46 . Recrystallization of the fluoride from pentane generally lead to co-crystalization with a pentane-soluble yellow powder, possibly a water adduct resulting from traces of water in the solvent. Adding a drop of pyridine-d_5 to a solution of the powder in C_6D_6 shifted the resonances observed in the ^{1}H NMR spectrum, but the resonances due to Cp'$_2$CeF(pyridine) were not observed. Cp'$_2$CeF could not be recovered from the yellow powder, as it decomposed upon heating to give Cp'H. Characterization of the yellow powder: ^{1}H NMR (C_6D_6): δ -2.57 (36H, $\nu_{1/2}$ = 100 Hz), -13.25 (18H, $\nu_{1/2}$ = 90 Hz).

Cp'$_2$CeNH$_2$: Method A: Cp'$_2$CeCH$_2$C$_6$H$_5$ (0.5 g, 0.7 mmol) was dissolved in diethyl ether (50 mL). The headspace was evacuated and replaced with ammonia (dried over sodium). The red solution rapidly turned orange. The volume of the solution was reduced to 20 mL, and the solution was cooled to -15°C, yielding clusters of orange crystals. Yield, 0.13g (0.2 mmol, 30%). MP: ~150°C (decomp). ^{1}H NMR (C_6D_6): δ -0.71 (36H, $\nu_{1/2}$ = 10 Hz), -11.74 (18H, $\nu_{1/2}$ = 10 Hz). IR: 3100(w), 1580(w), 1505(s), 1360(s), 1310(w), 1280(w), 1240(s), 1225(w), 1215(m), 1200(w), 1185(m), 1180(m), 1120(w), 1030(w), 1010(m), 970(m), 950(w), 930(w), 840(w), 810(s), 775(m), 730(m), 685(s), 605(w), 580(w), 560(w), 530(m), 480(s), 450(s), 380(m) cm^{-1}. Anal. Calcd. for $C_{34}H_{61}CeN$: C, 65.6; H, 9.71; N, 2.24. Found C, 65.7; H, 9.93; N, 2.63.

Method B: Cp'$_2$CeOSO$_2$CF$_3$ (1.5 g, 1.9 mmol) and sodium amide (0.09 g, 2.5 mmol) were suspended in diethyl ether (20 mL). The yellow solution turned orange over several hours. The solution was taken to dryness, and the orange solid residue was dissolved in hexane (50 mL). The solution was concentrated and cooled to -15°C, yielding an orange powder. The ^{1}H NMR spectrum contained resonances due to Cp'$_2$CeNH$_2$, along with other small paramagnetic resonances presumably due to reaction of the product with traces of H_2O to produce a yellow, sparingly soluble material. Recrystallization from hexane only increased the amount of this yellow byproduct.

Method C: Cp'$_2$CeCH$_2$C$_6$H$_5$ (0.5 g, 0.7 mmol) was dissolved in cyclohexane (50 mL), and the purple solution was heated at reflux for one day, producing the solution of Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce. The headspace was evacuated and replaced with ammonia (dried over sodium). The deep purple solution rapidly turned orange. The solution was taken to dryness, and the crude orange solid residue was analyzed by ^{1}H NMR spectroscopy. The spectrum contained resonances due to Cp'$_2$CeNH$_2$. Crystallization of the product was attempted from pentane, but it was not possible to separate the product from the yellow byproduct mentioned previously.

Cp'$_2$CeNMe$_2$: Cp'$_2$CeOSO$_2$CF$_3$ (0.5 g, 0.6 mmol) and lithium dimethylamide (0.35 g, 0.7 mmol) were stirred in diethyl ether (20 mL) for 1.5 hours, over which time the solution turn from yellow to deep purple. The solution was taken to dryness under reduced pressure and extracted into pentane (10 mL). The solution was concentrated to 3 mL and chilled to -15°C, yielding an impure purple solid. ^{1}H NMR (C$_6$D$_6$): δ 24.19 (4H, $\nu_{1/2}$ = 300 Hz), 17.22 (6H, $\nu_{1/2}$ = 50 Hz), 3.09 (18H, $\nu_{1/2}$ = 700 Hz), -0.35 (18H, $\nu_{1/2}$ = 700 Hz), -15.99 (18H, $\nu_{1/2}$ = 16 Hz).

Reaction of Cp'$_2$CeCH$_2$C$_6$H$_5$ with H$_2$O: Cp'$_2$CeCH$_2$C$_6$H$_5$ (0.5 g, 0.7 mmol) was dissolved in diethyl ether (10 mL), and water (12 mL of a 0.05M solution in diethyl ether, 0.7 mmol) was added *via* syringe. The solution was stirred for 6 hours, then taken to dryness, giving a yellow-orange solid. Characterization of the crude solid: ^{1}H NMR (90 MHz, C_6D_6): δ 21.09 (4H, $\nu_{1/2}$ = 19 Hz), -2.04 (36H, $\nu_{1/2}$ = 10 Hz), -8.06 (18H, $\nu_{1/2}$ = 10 Hz). The solid was dissolved in hexane (20 mL), and concentrated under reduced pressure until precipitation occurred. The solution was warmed and additional solid was added, but the precipitate could not be redissolved. The solution was cooled to -15°C, yielding a small amount of yellow powder. ^{1}H NMR (C_6D_6): δ 13.15 (2H, $\nu_{1/2}$ = 40 Hz), 12.46 (18H, $\nu_{1/2}$ = 40 Hz), -8.72 (2H, $\nu_{1/2}$ = 50 Hz), -13.85 (18H, $\nu_{1/2}$ = 100 Hz).

NMR tube reaction of $Cp'_2CeOSO_2CF_3$ and Cp'_2CeH in C_6D_6.

Approximately equimolar amounts of $Cp'_2CeOSO_2CF_3$ and Cp'_2CeH were dissolved in C_6D_6 in an NMR tube. The brown solution was stored at room temperature for one day. The ^{1}H NMR spectrum showed the presence of Cp'_2CeF, some residual $Cp'_2CeOSO_2CF_3$, and a new organocerium species with t-butyl resonances in a 2:1 ratio. The ratio of Cp'_2CeF to the new species was 1:1. The new species is presumed to be $Cp'_2CeOSO_2CHF_2$, but due to the unavailability of difluoromethanesulfonic acid, it was not possible to synthesize this material independently.

Chapter 2

$Cp'_2Ce(C_6F_5)$: $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ (0.6 g. 1 mmol) was dissolved in pentane (10 mL) and C_6F_5H (0.18 mL, 1mmol) was added *via* syringe. The purple solution immediately turned orange. The solution volume was reduced to 5 mL and the solution was cooled to -10°C, yielding orange crystals. The low yield was due to the high solubility of the compound. Yield: 0.15g (0.19 mmol), 19%. ^{1}H NMR (C_6D_{12}) δ -1.77 (36H, $\nu_{1/2}$ = 190 Hz), -10.29 (18H, $\nu_{1/2}$ = 55 Hz), ^{19}F NMR (C_6D_{12}) δ -157.64 (1F, t, *J* = 18 Hz), -160.97 (2F, d, *J* = 18 Hz), -210.4 (2F, $\nu_{1/2}$ = 482 Hz). The solid material decomposed rapidly above 135°C, which precludes analysis by EI-MS.

Cp'$_2$Ce(2,3,5,6-C_6HF_4): Cp'$_2$Ce($CH_2C_6H_5$) was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. Three drops of 1,2,4,5-tetrafluorobenzene (an excess) were added to a clean NMR tube and the solution of Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce was slowly added with agitation. The solution turned from purple to orange. The ^{1}H and ^{19}F NMR spectra showed that Cp'$_2$Ce(2,3,5,6-C_6HF_4) formed quantitatively. ^{1}H NMR (C_6D_{12}) δ 3.20 (1H, t, *J* = 3 Hz), -1.84 (36H, $\nu_{1/2}$ = 130 Hz), -9.80 (18H, $\nu_{1/2}$ = 50 Hz), ^{19}F NMR(C_6D_{12}) -140.57 (2F, $\nu_{1/2}$ = 30 Hz), -241.5 (2F, $\nu_{1/2}$ = 410 Hz).

Cp'$_2$Ce(2,3,5,6-C_6F_4)CeCp'$_2$: Two NMR tubes containing equal amounts of concentrated solutions of Cp'$_2$Ce($CH_2C_6H_5$) in C_6D_{12} were heated at 60°C for 12 hours yielding solutions of Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. Three drops of 1,2,4,5-tetrafluorobenzene (an excess) were added to a clean NMR tube and one of the solutions of Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce was slowly added with agitation. The orange solution was taken to dryness to remove excess 1,2,4,5-tetrafluorobenzene, and the second solution of Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce was added. ^{1}H NMR(C_6D_{12}) -1.98 (36H, $\nu_{1/2}$ = 200 Hz), -9.15 (18H, $\nu_{1/2}$ = 65Hz), ^{19}F NMR (C_6D_{12}) -217.06 (2F, broad s). After 10 minutes, a yellow precipitate began to form. The solution was stored at room temperature for one day, then filtered. The insoluble yellow precipitate was suspended in C_6D_6 and heated at 60°C for one day, yielding a clear yellow/orange solution. The ^1H NMR revealed resonances consistent with Cp'_2CeF.

Decomposition of $Cp'_2Ce(2,3,5,6\text{-}C_6F_4)CeCp'_2$ with H_2O: $Cp'_2Ce(2,3,5,6\text{-}C_6F_4)CeCp'_2$ was suspended in C_6D_{12} in an NMR tube, and a drop of degassed H_2O was added. The tube was agitated vigorously, then allowed to stand for 10 minutes. The solution was dried over $MgSO_4$ and filtered. The ^1H and ^{19}F NMR showed the presence of 1,2,4,5-tetrafluorobenzene as the only fluorine-containing product.

Reaction of Cp'_2Mg and $BrMgC_6F_5$: Cp'_2Mg (0.35 g, 0.71 mmol) was dissolved in cyclohexane (5 mL) and $BrMgC_6F_5$ (1.6 mL, 0.22 M in diethyl ether, 0.35 mmol) was added.[49] The cloudy solution was stirred at reflux for 12 hours, by which time the solution had turned bright pink. A drop of degassed water was added to an aliquot of the solution (1 mL). The complicated ^{19}F NMR spectrum contained six major signals, which appeared to correspond to two fluorine containing compounds in a 1:1.5 ratio. GC MS analysis showed two primary components in addition to Cp'H, one with $(M)^+$ *m/z* 382 and one with $(M-57)^+$ *m/z* 325, in a 1:1.5 ratio. These are believed to be the two isomers of the [2+4] cycloaddition product of tetrafluorobenzyne and Cp'H, one symmetric and the other asymmetric, with the asymmetric isomer readily eliminating a t-Bu group. Characterization of symmetric isomer: ^1H NMR (C_6D_6) 4.19 (2H, s), 1.10 (36H, s), 0.63 (18H, s), ^{19}F NMR (C_6D_6) δ -145.32 (2F, m), -158.65 (2F, m). GC MS $(M)^+$ *m/z* (calc, found) 382 (100, 100) 383 (26, 26) 384 (3, 3). Asymmetric isomer: ^1H NMR (C_6D_6) 3.99 (1H, s), 2.04 (1H, s), 0.92 (18H, s), 0.45 (18H, s), ^{19}F NMR (C_6D_6) δ -130.98 (1F, m), -147.20 (1F, m), -157.33 (1F, m), -158.90 (1F, m). GC MS $(M\text{-}57)^+$ *m/z* (calc, found) 325 (100, 100) 326 (21,23) 327 (2, 2).

NMR tube reaction of $\{[C(CD_3)_3]_3C_5H_2\}_2CeC_6F_5$ in C_6D_{12}: A drop of C_6F_5H was added to the solution of the perdeuterated metallacycle. The deep purple solution rapidly turned orange. The ^2H and ^{19}F NMR spectrum showed resonances consistent with $Cp'_2CeC_6F_5$, and the ^1H spectrum showed only traces of undeuterated t-Butyl resonances. The solution was taken to dryness to remove excess C_6F_5H, and the orange residue was dissolved in C_6D_{12}. The sample was heated at 60°C for one day, and then hydrolyzed with a drop of degassed D_2O. The ^{19}F NMR spectrum indicated the formation of a new fluorine containing species whose spectrum was not perturbed by the addition of D_2O. Analysis by GCMS showed one major component in addition to Cp'D-d_{28}, with $(M)^+$ *m/z* 410. This is believed to be the symmetric isomer of the [2+4] cycloaddition of tetrafluorobenzyne and Cp'D-d_{28}, **2**. Characterization of cycloaddition product: ^{19}F NMR (C_6D_{12}) δ -145.46 (2F, m), -158.78 (2F, m). GC MS analysis suggests a mixture of **2**-d_{28} and **2**-d_{27} in a 3:1 ratio, $(M)^+$ *m/z* (calc, found) 409 (34, 32) 410 (100, 100) 411 (25, 33).

NMR tube reaction of $Cp'_2CeC_6F_5$ in C_6D_{12}: $Cp'_2CeC_6F_5$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours. The ^1H and ^{19}F NMR spectra indicated the formation of Cp'_2CeF and an unknown complex (B) in a 1:4 ratio, and a new fluorine containing species whose spectrum was not perturbed by the addition of a drop of D_2O. GC MS analysis showed four primary components in addition to Cp'H, one with $(M)^+$ *m/z* 382 and three with $(M\text{-}57)^+$ *m/z* 325, in a 13:5:1:2 ratio. These are believed to be isomers of the [2+4] cycloaddition product of tetrafluorobenzyne and Cp'H, one symmetric and the others asymmetric, with the asymmetric isomers readily eliminating a t-Bu group. Addition of H_2 at the beginning of the reaction did not appear to change the products of the reaction, but did increase the amounts of the cycloaddition products relative to Cp'H in the GC MS analysis. Characterization of the symmetric isomer: ^{1}H NMR (C_6D_{12}) δ 4.23 (2H, s), 1.22 (36H, s), 0.61 (18H, s), ^{19}F NMR (C_6D_{12}) δ -145.37 (2F, m), -158.72 (2F, m). GC MS $(M)^+$ *m/z* (calc, found) 382 (100, 100) 383 (26, 28) 384 (3, 3). Characterization of complex B: ^{1}H NMR (C_6D_{12}) δ -3.80 (36H, $\nu_{1/2}$ = 30 Hz), -8.06 (18H, $\nu_{1/2}$ = 50 Hz).

NMR tube reaction of $Cp'_2CeC_6F_5$ in C_6H_6: $Cp'_2CeC_6F_5$ was dissolved in C_6H_6 and the solution was heated at 60°C for 12 hours. The ^{1}H and ^{19}F NMR spectra indicated the formation of Cp'_2CeF, the symmetric [4+2] cycloaddition product of Cp'H and tetrafluorobenzyne, and 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene-d_0, the cycloaddition product of tetrafluorobenzyne to C_6H_6.[4] The latter two products were present in a 1:20 ratio. Characterization of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene-d_0: ^{1}H NMR (C_6D_6) δ 6.45 (4H, s) 4.77 (2H, s) ^{19}F NMR δ -149.33 (2F, m), -161.91 (2F, m). GC MS $(M)^+$ *m/z* (calc, found) 226 (100, 100) 227 (13, 12).

NMR tube reaction of $Cp'_2CeC_6F_5$ in C_6D_6: $Cp'_2CeC_6F_5$ was dissolved in C_6D_6 and the solution was heated at 60°C for 12 hours. The ^{1}H and ^{19}F NMR spectra indicated the formation of Cp'_2CeF, the symmetric [4+2] cycloaddition product of Cp'H and tetrafluorobenzyne, and 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene-d_6, the cycloaddition product of tetrafluorobenzyne to C_6D_6.[25] The latter two products were present in a 1:10 ratio. Characterization of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-

methanonaphthalene-d_6: ^{19}F NMR (C_6D_6) δ -149.32 (2F, m), -161.96 (2F, m). GC MS $(M)^+$ *m/z* (calc, found) 232 (100, 100) 233 (14, 13).

NMR tube reaction of Cp'$_2$CeC$_6$F$_5$ and Cp'$_2$CeH in C$_6$D$_{12}$: Cp'$_2$CeC$_6$F$_5$ and Cp'$_2$CeH were dissolved in C_6D_{12}. After 10 minutes, the ^1H and ^{19}F NMR spectra indicated the presence of Cp'$_2$CeC$_6$F$_5$, Cp'$_2$CeH, Cp'$_2$CeF, and Cp'$_2$Ce(2,3,5,6-C$_6$F$_4$)CeCp'$_2$ in a 6.5:1:3:4 ratio. After 20 minutes, the ratio was 23:1:14:18. After one hour, only resonances due to Cp'$_2$CeC$_6$F$_5$, Cp'$_2$CeF, and Cp'$_2$Ce(2,3,5,6-C$_6$F$_4$)CeCp'$_2$ remained in a 2:1:1 ratio. After 16 hours, only resonances due to Cp'$_2$CeC$_6$F$_5$ and Cp'$_2$CeF remained in a 2:1 ratio. After 3 days at room temperature, resonances due to Cp'$_2$CeC$_6$F$_5$, Cp'$_2$CeF, and B were present in a 6:6:1 ratio.

NMR tube reaction of Cp'$_2$Ce(2,3,5,6-C$_6$HF$_4$) in C$_6$H$_6$: Cp'$_2$Ce(CH$_2$C$_6$H$_5$) was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce. After cooling to 25°C, three drops of 1,2,4,5-tetrafluorobenzene were added to a clean NMR tube and the solution of Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce was slowly added with agitation. The solution turned from purple to orange. The ^1H and ^{19}F NMR spectra were consistent with quantitative formation of Cp'$_2$Ce(2,3,5,6-C$_6$HF$_4$). The solution was taken to dryness to remove excess 1,2,4,5-tetrafluorobenzene and the solid residue was dissolved in C_6H_6. The sample was heated to 60°C for 12 hours. The solution was taken to dryness and dissolved in C_6D_6. The ^1H and ^{19}F NMR spectra indicated the formation of Cp'$_2$CeF and B in a 7:1 area ratio, and 5,7,8-trifluoro-1,4,6-trihydro-1,4-methanonaphthalene-d_0, the cycloaddition product of 2,3,5-trifluorobenzyne to C_6H_6.[29] Characterization of 5,7,8-trifluoro-1,4,6-

trihydro-1,4-methanonaphthalene-d_0: ^{1}H NMR δ 6.40 (4H, m) 6.08 (1H, m) 4.89 (2H, m) ^{19}F NMR δ -126.74 (1F, m) -139.48 (1F, m) -152.68 (1F, m). GC-MS $(M)^+$ *m/z* (calc, found) 208 (100, 100) 209 (13,13).

NMR tube reaction of Cp'$_2$Ce(2,3,5,6-C_6HF_4) in C_6D_6: Cp'$_2$Ce($CH_2C_6H_5$) was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. Three drops of 1,2,4,5-tetrafluorobenzene were added to a clean NMR tube and the solution of Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce was slowly added with agitation. The solution turned from purple to orange. The ^{1}H and ^{19}F NMR spectra were consistent with quantitative formation of Cp'$_2$Ce(2,3,5,6-C_6HF_4). The solution was taken to dryness to remove excess 1,2,4,5-tetrafluorobenzene and the solid residue was dissolved in C_6D_6. The sample was heated to 60°C for 12 hours. The ^{1}H and ^{19}F NMR spectra indicated the formation of Cp'$_2$CeF and B in a 6:1 area ratio, and 5,7,8-trifluoro-1,4,6-trihydro-1,4-methanonaphthalene-d_6, the cycloaddition product of 2,3,5-trifluorobenzyne to C_6D_6.[29] Characterization of 5,7,8-trifluoro-1,4,6-trihydro-1,4-methanonaphthalene-d_6 : ^{1}H NMR(C_6D_6) δ 6.06 (1H, m) ^{19}F NMR δ -126.74 (1F, m) -139.48 (1F, m) -152.68 (1F, m) . GC-MS $(M)^+$ *m/z* (calc, found) 214 (100, 100) 215 (14,14).

NMR tube reaction of Cp'$_2$Ce(2,3,5,6-C_6HF_4) in C_6D_{12}: Cp'$_2$Ce($CH_2C_6H_5$) was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. Three drops of 1,2,4,5-tetrafluorobenzene were added to a clean NMR tube and the solution of Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce was slowly added with agitation. The solution turned from purple to orange. The ^{1}H and ^{19}F NMR spectra were consistent with quantitative formation of Cp'$_2$Ce(2,3,5,6-C_6HF_4). The solution was taken to dryness to remove excess 1,2,4,5-tetrafluorobenzene and the solid residue was dissolved in C_6D_{12}. The sample was heated at 60°C for 12 hours. The ^{1}H NMR spectrum indicated the formation of Cp'$_2$CeF and B in a 2:1 area ratio, as well as a significant quantity of diamagnetic material. GC MS analysis showed three primary components in addition to Cp'H, one with $(M)^+$ *m/z* 364 and three with $(M-57)^+$ *m/z* 307, in a 4:1:1 ratio. These are believed to be isomers of the [2+4] cycloaddition product of 3,4,6-trifluorobenzyne and Cp'H, with two of the isomers readily eliminating a t-Bu group.

NMR tube reaction of Cp'$_2$CeH and C_6F_6 in C_6D_6: Cp'$_2$CeH was dissolved in C_6D_6 and a drop of C_6F_6 was added. The solution immediately turned from purple to orange and gas bubbles were evolved. The ^{1}H and ^{19}F NMR spectra showed resonances indicative of Cp'$_2$CeF, and Cp'$_2$Ce(C_6F_5), C_6F_5H and H_2. The cerium containing species were present in a 3:2 ratio and accounted quantitatively for all of the Cp'$_2$CeH starting material. The sample was stored at room temperature for seven days. The ^{1}H and ^{19}F NMR spectra showed resonances indicative of Cp'$_2$CeF and B in a 23:1 area ratio, and 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene-d$_6$, the [2+4] cycloaddition product of tetrafluorobenzyne and C_6D_6.

NMR tube reaction of Cp'$_2$CeH and C_6F_5H in C_6D_6: Cp'$_2$CeH was dissolved in C_6D_6 and a drop of C_6F_5H was added. The solution immediately turned from purple to orange and gas bubbles were evolved. The ^{1}H and ^{19}F NMR spectra showed resonances indicative of H_2, Cp'$_2$CeF, Cp'$_2$Ce(C_6F_5), Cp'$_2$Ce(2,3,5,6-C_6HF_4), Cp'$_2$Ce(2,3,5,6-

C_6F_4)CeCp'$_2$, and 1,2,4,5-tetrafluorobenzene. The cerium containing species were present in a 3.5:2.5:1:4 ratio and accounted quantitatively for all of the Cp'$_2$CeH starting material. The sample was stored at room temperature for seven days. The ^{1}H and ^{19}F NMR spectra showed resonances indicative of Cp'$_2$CeF and B in a 17:1 area ratio, and 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene-d$_6$ and 5,7,8-trifluoro-1,4,6-trihydro-1,4-methanonaphthalene-d$_0$, the [2+4] cycloaddition products of tetrafluorobenzyne and 2,3,5-trifluorobenzyne to C_6D_6, respectively.

NMR tube reaction of Cp'$_2$CeH and 1,2,4,5-tetrafluorobenzene in C_6D_6: A small amount of Cp'$_2$CeH was dissolved in C_6D_6 and a drop of 1,2,4,5-tetrafluorobenzene was added. The solution immediately turned from purple to orange and gas bubbles were evolved. The ^{1}H NMR spectrum showed resonances indicative of Cp'$_2$Ce(2,3,5,6-C_6F_4H), Cp'$_2$Ce(2,3,5,6-C_6F_4)CeCp'$_2$, and H_2. The cerium containing species were present in a 1.5:1 ratio and accounted for nearly all of the Cp'$_2$CeH starting material. Very small but readily observed resonances due to Cp'$_2$CeF were also present. The sample was stored at room temperature for one day, after which time, the ^{1}H NMR spectrum showed resonances due to Cp'$_2$Ce(2,3,5,6-C_6F_4H) and Cp'$_2$CeF in a 18:1 area ratio. After two days, the ratio was 8:1. After 11 days, resonances due to B had appeared, along with diamagnetic resonances of considerable area in the 0 to 2 ppm region. The ratio of B to Cp'$_2$Ce(2,3,5,6,-C_6F_4H) and Cp'$_2$CeF was 1:4:4. After 17 days, the ratio was 1:2:3. The sample was heated at 60°C for two days, after which time, the only paramagnetic resonances in the spectum were those of B and Cp'$_2$CeF in a 1:3 area ratio, accounting for approximately 30% of the area of the CMe_3 resonances present in the starting material.

NMR tube reaction of 1,2,3,5-tetrafluorobenzene and Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce in C_6D_{12}: Cp'$_2Ce(CH_2C_6H_5)$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce. After cooling to 25°C, a drop of 1,2,3,5-tetrafluorobenzene was added, and the sample was agitated. The dark purple sample rapidly turned orange. The ^{1}H NMR spectrum contained four paramagnetic resonances in a 1:18:18:18 area ratio, consistent with a lone proton on the fluoroarene ring and three inequivalent CMe_3 groups, as expected for Cp'$_2$Ce(2,3,4,6-C_6HF_4). The integrated intensity of the CMe_3 groups showed the conversion to be essentially quantitative. The ^{19}F NMR spectrum consisted of four resonances of roughly equal area, two broad corresponding to fluorine atoms *ortho* to the metal, and two sharp corresponding to the fluorine atoms *meta* and *para* to the metal. ^{1}H NMR (C_6D_{12}) δ 0.17 (1H, d, J = 7 Hz), -1.44 (18H, $\nu_{1/2}$ = 100 Hz), -2.09 (18H, $\nu_{1/2}$ = 90 Hz), -9.58 (18H, $\nu_{1/2}$ = 70 Hz), ^{19}F NMR(C_6D_{12}) -138.83 [(2F, dd, J_1 = 7 Hz, J_2 = 18 Hz), -150.47 (1F, $\nu_{1/2}$ = 200 Hz), -165.48 (1F, d, J = 15 Hz), -241.73 (1F, $\nu_{1/2}$ = 500 Hz). After four days at room temperature, small resonances due to Cp'$_2$CeF had appeared, and the resonances attributed to Cp'$_2$Ce(2,3,4,6-C_6HF_4) had decreased slightly in area. Traces of B had also appeared. The sample was heated for two days at 60°C, after which time the resonances attributed to Cp'$_2$Ce(2,3,4,6-$C_6H F_4$) were absent from the spectrum. The resonances due to Cp'$_2$CeF had increased slightly, the resonances due to B had increased to an area equal to that of the Cp'$_2$CeF resonances, and a large number of diamagnetic resonances of significant area had appeared between 0 and 2 ppm. GC MS analysis showed six primary components in addition to Cp'H, two with $(M)^+$ *m/z* 364 and four with $(M\text{-}57)^+$ *m/z* 307, in a 3:11:1:1:6:7 ratio. These are believed to be isomers of the [2+4] cycloaddition products of 3,4,6-trifluorobenzyne with Cp'H and 3,4,5-trifluorobenzyne with Cp'H, with some isomers readily eliminating a t-Bu group. The retention times and isotope patterns for three of the isomers matched those found in the decomposition of Cp'$_2$Ce(2,3,5,6-C_6HF_4) in C_6D_{12}, where 3,4,6-trifluorobenzyne is believed to be produced. The retention times and isotope patterns of the other three matched those found in the decomposition of Cp'$_2$Ce(2,3,4,5-C_6HF_4), where 3,4,5-trifluorobenzyne is believed to be produced. Further characterization of the trapped products was not pursued.

NMR tube reaction of 1,2,3,5-tetrafluorobenzene and Cp'$_2$CeH in C_6D_{12}: Cp'$_2$CeH was dissolved in C_6D_{12} and a drop of 1,2,3,5-tetrafluorobenzene was added. The red-purple sample rapidly turned orange. The ^{1}H NMR spectrum contained a diamagnetic resonance due to H_2 and paramagnetic resonances of Cp'$_2$CeF and Cp'$_2$Ce(2,3,4,6-C_6HF_4) in a 1:4 area ratio. After nine days at room temperature, the ratio was little changed, but traces of B had appeared. The sample was heated for two days at 60°C, after which time the resonances due to Cp'$_2$Ce(2,3,4,6-C_6HF_4) had disappeared from the spectrum, the resonances of Cp'$_2$CeF had not changed in intensity relative to an internal standard, and the resonances due to B had increased to nearly equal the area of the Cp'$_2$CeF resonances. A large number of diamagnetic resonances of significant area had also appeared between 0 and 2 ppm.

NMR tube reaction of 1,2,3,4-tetrafluorobenzene and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6D_{12}: $Cp'_2Ce(CH_2C_6H_5)$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. After cooling to 25°C, a drop of 1,2,3,4-tetrafluorobenzene was added, and the sample was agitated. The dark purple sample gradually turned orange over 15 minutes. The ^1H NMR spectrum contained two paramagnetic resonances in a 36:18 area ratio, presumably due to the CMe_3 groups of a new cerium metallocene. The integrated intensity of the CMe_3 groups showed the conversion to be essentially quantitative. The ^{19}F NMR spectrum consisted of three sharp resonances of equal area corresponding to the fluorine atoms *meta* and *para* to the metal. The resonance for the fluorine *ortho* to the metal was not observed. The new species is presumed to be $Cp'_2Ce(2,3,4,5\text{-}C_6HF_4)$. ^1H NMR (C_6D_{12}) δ -1.90 (36H, $\nu_{1/2}$ = 120 Hz), -9.59 (18H, $\nu_{1/2}$ = 80 Hz), ^{19}F NMR(C_6D_{12}) -136.76 [(1F, d, *J* = 18 Hz), -161.63 (1F, d, *J* = 18 Hz), -161.76 (1F, t, *J* = 18 Hz). After 1.5 hours at room temperature, resonances due to Cp'_2CeF had appeared in the ^1H NMR spectrum, and the resonances attributed to $Cp'_2Ce(2,3,4,5\text{-}C_6H F_4)$ had decreased slightly in area. After one day at room temperature, the resonances attributed to $Cp'_2Ce(2,3,4,5\text{-}C_6HF_4)$ were absent from the ^1H NMR spectrum, the resonances due to Cp'_2CeF had increased slightly, resonances due to B had appeared (roughly 1/4th the area of the Cp'_2CeF resonances) and small resonances attributed to $Cp'_2Ce(2,3,6\text{-}C_6H_2F_3)$ (see below) had appeared where the large $Cp'_2Ce(2,3,4,5\text{-}C_6HF_4)$ resonances had been. A large number of diamagnetic resonances of significant area had also appeared between 0 and 2 ppm. GC MS analysis showed three primary components in addition to Cp'H, one with $(M)^+$ *m/z* 364 and two with $(M-57)^+$ *m/z* 307, in a 4:1:6 ratio. These are believed to be isomers of the [2+4] cycloaddition products of 3,4,5-trifluorobenzyne and Cp'H, with some isomers readily eliminating a t-Bu group. Further characterization was not pursued.

NMR tube reaction of 1,2,3,4-tetrafluorobenzene and Cp'$_2$CeH in C_6D_{12}: Cp'$_2$CeH was dissolved in C_6D_{12} and a drop of 1,2,3,4-tetrafluorobenzene was added. The red-purple sample rapidly turned orange. The ^{1}H NMR spectrum contained a diamagnetic resonance due to H_2 and paramagnetic resonances of Cp'$_2$CeF, Cp'$_2$Ce(2,3,6-$C_6H_2F_3$), and Cp'$_2$Ce(2,3,4,5-C_6HF_4) in a 5:2:1 area ratio. After one day at room temperature, the resonances due to Cp'$_2$Ce(2,3,4,5-C_6HF_4) were absent, small resonances due to B had appeared, and the ratio of the other two components was little changed. The sample was heated for two days at 60°C, after which the resonances due to Cp'$_2$Ce(2,3,6-$C_6H_2F_3$) had disappeared from the spectrum, the resonances of Cp'$_2$CeF had not changed much in intensity relative to an internal standard, resonances due to B had increased to roughly 25% of the area of the Cp'$_2$CeF resonances, and a large number of diamagnetic resonances of significant area had appeared between 0 and 2 ppm. Further characterization was not pursued.

NMR tube reaction of 1,2,3,4-tetrafluorobenzene, Cp'$_2$CeH, and H_2O in C_6D_6: Cp'$_2$CeH was dissolved in C_6D_6 and a drop of 1,2,3,4-tetrafluorobenzene was added. The red-purple sample rapidly turned orange. The ^{1}H NMR spectrum contained a diamagnetic resonance due to H_2 and paramagnetic resonances of Cp'$_2$CeF, Cp'$_2$Ce(2,3,6-$C_6H_2F_3$), and Cp'$_2$Ce(2,3,4,5-C_6HF_4) in a 5:2:1 area ratio. The sample was taken to dryness and redissolved in fresh C_6D_6 to remove residual 1,2,3,4-tetrafluorobenzene. A drop of deoxygenated H_2O was added, and the sample was agitated vigorously. The sample was dried over $MgSO_4$ and filtered into a clean NMR tube. The ^1H NMR and ^{19}F NMR spectra showed the presence of both 1,2,3,4-tetrafluorobenzene and 1,2,4-trifluorobenzene.

NMR tube reaction of Cp'$_2$Ce(2,3,4,5-C_6HF_4) and C_6HF_5 in C_6D_{12}: Cp'$_2$Ce($CH_2C_6H_5$) was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. After cooling to 25°C, a drop of 1,2,3,4-tetrafluorobenzene was added, and the sample was agitated, generating a solution of Cp'$_2$Ce(2,3,4,5-C_6HF_4). A drop of C_6HF_5 was added and the sample was stored at room temperature. After 15 hours, resonances due to Cp'$_2$Ce(2,3,4,5-C_6HF_4) had diminished to 10% their original intensity, and resonances of Cp'$_2$CeF and Cp'$_2$CeC_6F_5 had appeared along with diamagnetic resonances of considerable area in the 2 to 0 ppm region. The ratio of the paramagnetic species, in respective order, was 2:1:1. Resonances due to Cp'$_2$CeC_6F_5 were not discernible in the complicated ^{19}F NMR spectrum. After seven days, the only paramagnetic resonances remaining in the ^1H NMR spectrum were those of B, Cp'$_2$CeC_6F_5, and three other small CMe_3 resonances of an unidentified species. The sample was taken to dryness, the orange solid residue was dissolved in fresh C_6D_{12}, and the sample was heated at 60°C for one day. The ^1H NMR spectrum contained resonances due to Cp'$_2$CeF, B, and another unidentified paramagnetic species with a 1:1:1 set of CMe_3 resonances (^1H NMR (C_6D_{12}): δ -0.91 (18H, $\nu_{1/2}$ = 100 Hz), -1.88 (18H, $\nu_{1/2}$ = 100 Hz), -11.43 (18H, $\nu_{1/2}$ = 120 Hz), along with diamagnetic resonances of significant area in the 2 to 0 ppm region. The ratio of the paramagnetic products, respectively, was 2:1:1.5. GC MS analysis showed the primary components in addition to Cp'H with $(M)^+$ *m/z* 382, $(M)^+$ *m/z* 364, and $(M-57)^+$ *m/z* 307, with elution times that matched those of the products observed in the independent decompositions of $Cp'_2CeC_6F_5$ and $Cp'_2Ce(2,3,4,5-C_6HF_4)$ in C_6D_{12}.

NMR tube reaction of $\mathbf{Cp'_2Ce(2,3,4,5-C_6HF_4)}$ and $\mathbf{H_2}$ in $\mathbf{C_6D_{12}}$: $Cp'_2Ce(CH_2C_6H_5)$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. After cooling to 25°C, a drop of 1,2,3,4-tetrafluorobenzene was added, and the sample was agitated, generating a solution of $Cp'_2Ce(2,3,4,5-C_6HF_4)$. The sample was cooled in a liquid nitrogen isopropanol bath, the headspace was evacuated, and replaced with H_2 (1 atm). The sample was stored at 25°C for four days, and then heated at 60°C for one day. GC MS analysis showed the same products and the same proportions as the reaction without H_2.

NMR tube reaction of 1,2,4-trifluorobenzene and $\mathbf{Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce}$ in $\mathbf{C_6D}_{12}$: $Cp'_2Ce(CH_2C_6H_5)$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. After cooling to 25°C, a drop of 1,2,4-trifluorobenzene was added, and the sample was agitated. The dark purple sample rapidly turned orange. The ^1H NMR spectrum contained five paramagnetic resonances in a 1:1:18:18:18 area ratio, consistent with two inequivalent protons (one *meta*, one *para* to the metal) on the fluoroarene ring and three inequivalent CMe_3 groups, as expected for $Cp'_2Ce(2,3,6-C_6H_2F_3)$. The integrated intensity of the CMe_3 groups showed the conversion to be essentially quantitative. The ^{19}F NMR spectrum consisted of three resonances of roughly equal area, two broad corresponding to fluorine atoms *ortho* to the metal, and one sharp corresponding to the fluorine atom *meta* to the metal. ^{1}H NMR (C_6D_{12}) δ 3.87 (1H, d, $J = 8$ Hz), 0.41 (1H, t, $J = 8$ Hz), -1.46 (18H, $\nu_{1/2} = 70$ Hz), -2.17 (18H, $\nu_{1/2} = 60$ Hz), -9.22 (18H, $\nu_{1/2} = 50$ Hz), ^{19}F NMR(C_6D_{12}) –141.64 [(1F, $\nu_{1/2} = 30$ Hz), -149.48 (1F, $\nu_{1/2} = 200$ Hz), -240.65 (1F, $\nu_{1/2} = 500$ Hz). The sample was taken to dryness and the orange solid residue was dissolved in C_6D_{12} to remove residual 1,2,4-trifluorobenzene. The sample was heated for 2.5 hours at 60°C, after which time resonances due to Cp’$_2$CeF had appeared and the resonances attributed to Cp’$_2$Ce(2,3,6-$C_6H_2F_3$) had decreased to 60% their original area. After heating for 12 hours at 60°C, the resonances attributed to Cp’$_2$Ce(2,3,6-$C_6H_2F_3$) were absent from the spectrum, the resonances due to Cp’$_2$CeF had increased slightly relative to an internal standard, resonances due to B had appeared with roughly 30% the area of the Cp’$_2$CeF resonances, and a large number of diamagnetic resonances of significant area had appeared between 0 and 2 ppm. GC MS analysis showed five primary components in addition to Cp'H, four with $(M)^+$ *m/z* 346 and one with $(M-57)^+$ *m/z* 289, in a 1.5:1.5:1.5:1:1 ratio. These are believed to be isomers of the [2+4] cycloaddition products of 3,6-difluorobenzyne with Cp’H and 3,4-difluorobenzyne with Cp'H, with one isomer readily eliminating a t-Bu group. Further characterization was not pursued.

NMR tube reaction of 1,2,3-trifluorobenzene and Cp’$_2$CeH in C_6D_{12}: Cp’$_2$CeH was dissolved in C_6D_{12} and a drop of 1,2,3-trifluorobenzene was added. The red-purple sample turned orange over several minutes. After 10 minutes, the ^{1}H NMR spectrum contained resonances due to H_2, unreacted Cp'$_2$CeH, Cp'$_2$CeF, and six other paramagnetic resonances in a 1:1:2:85:14:42 area ratio [^{1}H NMR (C_6D_{12}) δ 5.42 (s, $\nu_{1/2}$ = 25 Hz), 4.58 (t, J = 8 Hz), 2.54 (d, J = 8 Hz), -1.77 ($\nu_{1/2}$ = 50 Hz), -9.03 ($\nu_{1/2}$ = 40 Hz), -9.55 ($\nu_{1/2}$ = 50 Hz)] presumably arising from two cerium containing species with overlapping sets of two CMe_3 resonances in 2:1 area ratios. After 3 hours, the spectrum contained only resonances due to Cp'$_2$CeF and one of the two new species [^{1}H NMR (C_6D_{12}) δ 4.58 (t, J = 8 Hz), 2.54 (d, J = 8 Hz), -1.77 (36H, $\nu_{1/2}$ = 40 Hz), -9.03 (18H, $\nu_{1/2}$ = 40 Hz)] in a 2:1 ratio. The resonances are essentially identical to those attributed to Cp'$_2$Ce(2,6-$C_6H_3F_2$) (see below). A number of diamagnetic resonances of significant area had also appeared in the 0 to 2 ppm region of the spectrum. After 1 day at room temperuture, the ratio of Cp'$_2$CeF to the new species was 4:1. The sample was heated at 60°C for one day, after which time only resonances due to Cp'$_2$CeF and B in a 9:1 area ratio, and the diamagnetic species remained in the spectrum.

NMR tube reaction of 1,3,5-trifluorobenzene and Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce in C_6D_{12}: Cp'$_2$Ce($CH_2C_6H_5$) was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding Cp'(($Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. After cooling to 25°C, a drop of 1,3,5-trifluorobenzene was added, and the sample was agitated. The dark purple sample rapidly turned orange. The ^{1}H NMR spectrum contained three paramagnetic resonances in a 1:18:9 area ratio, consistent with two equivalent protons on the fluoroarene ring and two resonances due to the CMe_3 groups of a cerium metallocene, as expected for Cp'$_2$Ce(2,4,6-$C_6H_2F_3$). ^{1}H NMR (C_6D_{12}) δ 1.93 (2H, d, J = 9 Hz), -1.73 (36H, $\nu_{1/2}$ = 50

Hz), -9.51 (18H, $\nu_{1/2}$ = 40 Hz). The sample was heated at 60°C for one day, after which the resonances attributed to $Cp'_2Ce(2,4,6\text{-}C_6H_2F_3)$ had disappeared from the spectrum, and resonances due to Cp'_2CeF and B in a 3:1 area ratio and a considerable quantity of unidentified diamagnetic species had appeared.

NMR tube reaction of 1,3-difluorobenzene and Cp'_2CeH in C_6D_{12}: Cp'_2CeH was dissolved in C_6D_{12} and a drop of 1,3-difluorobenzene was added. The red-purple sample turned orange over several minutes. After 20 minutes, the ^1H NMR spectrum contained four paramagnetic resonances in a 1:2:36:18 area ratio, consistent with the one *para* and two *meta* protons on the fluoroarene ring and CMe_3 groups in a 2:1 area ratio, as expected for $Cp'_2Ce(2,6\text{-}C_6H_3F_2)$. The integrated intensity of the CMe_3 groups showed the conversion to be essentially quantitative. ^1H NMR (C_6D_{12}) δ 4.53, (1H, t, J = 8 Hz), 2.50 (2H, d, J = 8 Hz), -1.77 (36H, $\nu_{1/2}$ = 40 Hz), -9.03 (18H, $\nu_{1/2}$ = 30 Hz). After 1 day at room temperuture, resonances due to Cp'_2CeF had appeared in the spectrum, and the resonances attributed to $Cp'_2Ce(2,6\text{-}C_6H_3F_2)$ had decreased in area relative to an internal standard. The ratio of Cp'_2CeF to $Cp'_2Ce(2,6\text{-}C_6H_3F_2)$ was 2:1. Diamagnetic resonances of significant area had also appeared in the 0 to 2 ppm region.

NMR tube reaction of 1,2-difluorobenzene and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6D_{12}: $Cp'_2Ce(CH_2C_6H_5)$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. After cooling to 25°C, a drop of 1,2-difluorobenzene was added, and the sample was agitated. The dark purple sample slowly turned orange. After 10 minutes, the ^1H NMR spectrum contained resonances due to Cp'_2CeF and several small resonances due to other unidentified paramagnetic species.

After 6 hours at room temperature, only the resonances due to Cp'_2CeF and a new diamagnetic resonances in the 0 to 2 ppm region remained.

NMR tube reaction of 1,2-difluorobenzene and Cp'_2CeH in C_6D_{12}: Cp'_2CeH was dissolved in C_6D_{12} and a drop of 1,2-difluorobenzene was added. The red-purple sample turned orange over half an hour. After 5 minutes, the ^1H NMR spectrum contains resonances due to unreacted Cp'_2CeH, Cp'_2CeF, and five other paramagnetic resonances in a 1:1:1:27:10 area ratio [^1H NMR (C_6D_{12}) δ 6.77 (s, $\nu_{1/2} = 15$ Hz), 5.82 (d, $J = 8$ Hz), 4.66 (t, $J = 8$ Hz), -1.21 ($\nu_{1/2} = 40$ Hz), -9.13 ($\nu_{1/2} = 40$ Hz)], presumably due to a new cerium metallocene. The ratio of Cp'_2CeH to Cp'_2CeF and the new metallocene was 2.5:1.5:1. Four prominent diamagnetic resonances had also appeared [^1H NMR (C_6D_{12}) δ 6.16 (1H, s), 4.27 (1H, s), 1.24 (9H, s), 0.86 (9H, s)], presumably due to a [4+2] cycloaddition product of Cp'H and a fluorobenzyne. After 30 minutes at room temperature, the ratio of Cp'_2CeH to Cp'_2CeF, the new metallocene, and the new diamagnetic product was 2:4.5:1:5. Relative to an internal standard, the resonances due to Cp'_2CeF had not increased, but the resonances due to the new diamagnetic species had increased twofold. After 1 day at room temperature, the only distinct paramagnetic resonances remaining in the spectrum were those of Cp'_2CeF. The ratio of the new diamagnetic species to Cp'_2CeF was 4.5:1.

NMR tube reaction of fluorobenzene and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6D_{12}: $Cp'_2Ce(CH_2C_6H_5)$ was dissolved in C_6D_{12} and the solution was heated at 60°C for 12 hours yielding $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. After cooling to 25°C, a drop of fluorobenzene was added, and the sample was agitated. The dark purple sample slowly turned orange, then yellow over 5 minutes. The ^{1}H NMR spectrum contained a large number of small paramagnetic resonances between 10 and –15 ppm. The spectrum was not significantly different after 6 hours at room temperature.

NMR tube reaction of fluorobenzene and Cp'$_2$CeH in C_6D_6: Cp'$_2$CeH was dissolved in C_6D_{12} and a drop of fluorobenzene was added. The red-purple sample turned orange and then yellow over two hours. After 10 minutes, the ^{1}H NMR spectrum contained resonances due to unreacted Cp'$_2$CeH, Cp'$_2$CeF, a few other small paramagnetic resonances, and five prominent diamagnetic resonances [^{1}H NMR (C_6D_6) δ 6.34 (1H, s), 4.40 (1H, s), 1.40 (9H, s), 1.21 (9H, s), 0.95 (9H, s)]. The ratio of Cp'$_2$CeH to Cp'$_2$CeF to the new diamagnetic species was 8:1:2. After 40 minutes at room temperature, the ratio was 3:1:5. A large number of smaller paramagnetic resonances had also appeared. After 160 minutes at room temperature, the ratio was 2:1:57. After one day at room temperature, the only distinct resonances were due to the diamagnetic species, the large number of small paramagnetic resonances remained in the –3 to –12 ppm region of the spectrum. The addition of H_2, Cp'H, or dihydroanthracene did not appear to alter the course of the reaction. Addition of a drop of D_2O resulted in the appearance of resonances due to Cp'D, but did not alter the spectrum of the diamagnetic species. Analysis of the hydrolyzate by GC MS showed one major component in addition to Cp'D, with a molecular ion of $(M)^+$ *m/z* 310. This is believed to be a [2+4] cycloaddition product of Cp'H and benzyne. The ratio of Cp'H to this new product was 1.5:1.

Chapter 3

NMR tube reaction of CHF_3 and Cp'_2CeH in C_6D_{12}.

Cp'_2CeH was dissolved in C_6D_{12} in an NMR tube. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CHF_3 (1 atm). The tube was warmed to 19°C and allowed to stand. After 20 min. the ratio of Cp'_2CeH to Cp'_2CeF was 32:1, after 3 days it was 1:3.5, and after 6 days it was 1:18. After 26 days, the solution color had changed from purple to orange, all Cp'_2CeH resonances had disappeared from the ^1H NMR spectrum, and small resonances due to B had appeared. The ratio of Cp'_2CeF to B was 14:1. Integration of the t-butyl signal intensities relative to the residual solvent proton signal indicated that slightly less than half an equivalent of Cp'_2CeF had formed relative to the starting material. Resonances due to the two isomers of tri-t-butylbenzene also appeared. GCMS analysis showed two principle components in addition to Cp'H, with $(M)^+$ *m/z* 246 and elution times and fragmentation patterns consistent with isomeric tri-t-butylbenzenes. The isomers were present in approximately a 1:1 ratio, and accounted for most of the remainder of the starting material. [31]

NMR tube reaction of CHF_3 and $(Cp'\text{-}d_{27})_2CeD$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_6 in an NMR tube. The sample was heated at 60°C for 13 days to perdeuterate the ring t-Bu groups; the sample was taken to dryness and the dark red solid residue redissolved in fresh C_6D_6 after 4 days and again after 8 days. After 13 days, the sample was then taken to dryness, and the dark red solid residue was redissolved in C_6D_{12}. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with D_2 (1 atm). The ratio of the unique t-Bu_H to the ring hydrogen resonance in the ^1H NMR spectrum was 1:42. In the ^2H NMR spectrum, both t-Bu_D resonances were observed, and the ring hydrogen resonance was absent. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CHF_3 (1 atm). The sample was heated at 60°C for one day, after which time the ring resonance of $(Cp'\text{-}d_{27})_2CeD$ had disappeared, the ring resonance of $(Cp'\text{-}d_{27})_2CeF$ had appeared in the ^1H NMR spectrum, and resonances consistent with $(Cp'\text{-}d_{27})_2CeF$ had appeared in the ^2H NMR spectrum. GCMS analysis showed two principal components in addition to $(Cp'\text{-}d_{27})H$, with envelopes centered around $(M)^+$ *m/z* 274 and elution times consistent with tri-t-butylbenzene-d_{28}. The extra deuterium is presumed to come from a D for F exchange between $(Cp'\text{-}d_{27})_2CeD$ and an intermediate $(Cp'\text{-}d_{27})_2CeCF_3$, see below.

NMR tube reaction of Me_3SiCF_3, and Cp'_2CeH in C_6D_{12}.

Cp'_2CeH was dissolved in C_6D_{12} in an NMR tube. A drop of Me_3SiCF_3 was added. Upon agitation, the purple solution turned orange. The ^1H NMR spectrum showed the presence of Cp'_2CeF, Me_3SiH, and both isomers of tri-t-butylbenzene. The ^{19}F NMR spectrum contained two new resonances consistent with two isomers of tri-t-butylfluorobenzene. GCMS analysis showed four principal components in addition to Cp'H, two with $(M)^+$ *m/z* 246 and elution times consistent with isomeric tri-t-butylbenzenes, and two with $(M)^+$ *m/z* 264 consistent with isomeric tri-t-butylfluorobenzenes. The ratio of tri-t-butylbenzenes to tri-t-butylfluorobenzenes was approximately 8:1. The symmetric and asymmetric isomers of tri-t-butylbenzene were present in approximately equal amounts (^{1}H NMR), while those of tri-t-butylfluorobenzene were present in a 1.5:1 ratio (^{19}F NMR). Characterization of tri-t-butylfluorobenzene: symmetric isomer: ^{19}F NMR (C_6D_{12}) δ –111.38 (1F, s), GCMS $(M)^+$ *m/z* (calc, found) 264 (100,100) 265 (20,22) 266 (2,3); asymmetric isomer: ^{19}F NMR (C_6D_{12}) δ –95.86 (1F, d, $J_{H\text{-}F}$ = 16 Hz), GCMS $(M)^+$ *m/z* (calc, found) 264 (100,100) 265 (20,34) 266 (2,7).

NMR tube reaction of Me_3SiCF_3 and $(Cp'\text{-}d_{27})_2CeD$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_6 in an NMR tube. The sample was heated at 60°C to perdeuterate the ring t-Bu groups. After 4 days, the sample was taken to dryness, and the dark red solid residue was redissolved in C_6D_6. The sample was heated for an additional 4 days, then taken to dryness, and the dark red solid residue was dissolved in C_6D_{12}. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with D_2 (1 atm). The ratio of the unique t-Bu_H to the ring hydrogen resonance in the ^{1}H NMR spectrum was 1:4. In the ^{2}H NMR spectrum, both t-Bu_D resonances were observed, and the ring hydrogen resonance was absent. A drop of Me_3SiCF_3 was added, and upon agitation, the solution color changed from purple to orange. The ring resonance of $(Cp'\text{-}d_{27})_2CeD$ disappeared and the ring resonance for $(Cp'\text{-}d_{27})_2CeF$ had appeared in the ^{1}H NMR spectrum. Resonances due to $(Cp'\text{-}d_{27})_2CeF$ and Me_3SiD appeared in the ^{2}H NMR spectrum, and resonances due to the two isomers of tri-t-butylfluorobenzene-d_{27} appeared in the ^{19}F NMR spectrum. The sample was twice taken to dryness, redissolved in C_6H_6, and a small amount of Cp'_2CeH was added. After

30 minutes, the ^{19}F NMR spectrum remained unchanged, but the ^{2}H NMR spectrum contained resonances consistent with both (Cp'-d_{27})$_2$CeF and (Cp'-d_{27})$_2$CeH in a 2:1 ratio, implying that H for F exchange occurred. The ^{1}H NMR spectrum likewise contained resonances of Cp'$_2$CeF and Cp'$_2$CeH in the same ratio. GCMS analysis showed four principal components, in addition to Cp'H/(Cp'-d_{27})H, two with envelopes centered around $(M)^+$ *m/z* 274, with elution times consistent with the isomeric tri-t-butylbenzenes-d_{28}, and two with envelopes centered around $(M)^+$ *m/z* 291, with elution times consistent with the isomeric tri-t-butylfluorobenzenes-d_{27}. The extra deuterium in the tri-t-butylbenzene is presumed to come from a D-F exchange between the intermediate (Cp'-d_{27})$_2$CeCF$_3$ and (Cp'-d_{27})$_2$CeD, generating (Cp'$_2$-d_{27})$_2$CeCDF$_2$ and (Cp'$_2$-d_{27})$_2$CeF, see later experiments.

NMR tube reaction of CH_2F_2 and Cp'$_2$CeH in C_6D_6.

Cp'$_2$CeH was dissolved in C_6D_{12} in an NMR tube. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_2F_2 (1 atm). The tube was warmed to 19°C and allowed to stand. After 10 min. the ratio of Cp'$_2$CeH to Cp'$_2$CeF by ^{1}H NMR spectroscopy was 10:1, after 20 min. it was 5:1, and after 1 hour it was 2:1. After one day, all of the resonances due to Cp'$_2$CeH had disappeared and an equivalent amount of Cp'$_2$CeF had formed along with CH_4. Over the time period of the experiment, the color had turned from purple to orange.

NMR tube reaction of D_2, CH_2F_2 and Cp'$_2$CeD in C_6D_6.

Cp'$_2$Ce(CH_2Ph) was dissolved in C_6D_6 in an NMR tube. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with D_2.

The tube was warmed to 19°C and shaken vigorously. Analysis by ^{1}H NMR spectroscopy confirmed the presence of Cp'$_2$CeD. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was partially evacuated, and replaced with CH_2F_2. The sample was stored at 19°C for 1 day, after which time the solution color had changed from purple to orange. Analysis by ^{1}H NMR confirmed the absence of Cp'$_2$CeD and the formation of Cp'$_2$CeF. In addition, the spectrum contained resonances characteristic of CH_4 and CH_3D in an approximately 1:1 area ratio; a trace of CH_2D_2 but no CHD_3 were observed in the spectrum.

NMR tube reaction of D_2, CH_2F_2, and (Cp'-d$_{27}$)CeD in C_6D_{12}.

Cp'$_2$Ce(CH_2Ph) was dissolved in C_6D_6 in an NMR tube. The sample was heated at 60°C for 6 days to perdeuterate the ring t-Bu groups. The sample was taken to dryness, and the solid residue was redissolved in fresh C_6D_6 and heated at 60°C for 2 more days to complete the perdeuteration. Analysis by ^{1}H and ^{2}H NMR confirmed the presence of (Cp'-d$_{27}$)CeC_6D_5.[11] The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with D_2 (1 atm). The tube was warmed to 19°C and shaken vigorously. Analysis by ^{1}H and ^{2}H NMR spectroscopy confirmed the presence of (Cp'-d$_{27}$)CeD. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was partially evacuated, and replaced with CH_2F_2. The sample was stored at 19°C for 1 day, after which time the solution color had changed from purple to orange. Analysis by ^{1}H and ^{2}H NMR spectroscopy confirmed the absence of (Cp'-d$_{27}$)CeD and the appearance of (Cp'-d$_{27}$)CeF. In addition, the ^{1}H NMR spectrum contained resonances characteristic of CH_4, CH_3D, and CH_2D_2 in an approximately 1:29:60 area ratio; no CHD_3 was observed.

NMR tube reaction of CH_3F and Cp'_2CeH in C_6D_{12}.

Cp'_2CeH was dissolved in C_6D_{12} in an NMR tube. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_3F (1 atm). Upon warming to room temperature with agitation, the color of the solution changed from purple to orange. The ^1H NMR spectrum showed that the Cp'_2CeH had been quantitatively converted to Cp'_2CeF. The resonance due to CH_4 was observed.

NMR tube reaction of CH_3F, D_2, and Cp'_2CeH in C_6D_{12}.

Cp'_2CeH was dissolved in C_6D_{12} in an NMR tube. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with D_2 (approximately 0.5 atm) and CH_3F (approximately 0.5 atm). Upon warming to room temperature and agitating the solution, the color changed from purple to orange. The ^1H NMR spectrum showed that the Cp'_2CeH had been quantitatively converted to Cp'_2CeF. Resonances characteristic of CH_4 and CH_3D had also appeared in approximately equal amounts, but no resonances due to CH_2D_2 were observed.

NMR tube reaction of CH_3F and $(Cp'\text{-}d_{27})_2CeD$ in C_6D_6.

Cp'_2CeH was dissolved in C_6D_6 in an NMR tube. The sample was heated at 60°C to perdeuterate the ring t-Bu groups and exchange the hydride with deuterium. After 11 days, the ratio of the unique t-Bu_H to the ring hydrogen resonance in the ^1H NMR spectrum had changed from 9:1 to 1:4. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_3F (1 atm). Upon warming to room temperature with agitation, the color of the solution changed from purple to orange. The ring resonance of (Cp'-d_{27})$_2$CeD had been replaced by that of (Cp'-d_{27})$_2$CeF in the ^{1}H NMR spectrum, and resonances characteristic of CH_4 and CH_3D had also appeared in an approximately 1:2 area ratio; no CH_2D_2 was observed.

NMR tube reaction of CH_4 or CF_4 and Cp'$_2$CeH in C_6D_{12}

Cp'$_2$CeH was dissolved in C_6D_{12} in an NMR. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_4 or CF_4 (1 atm). The sample was heated at 60°C for 30 days. No change was observed in the ^{1}H NMR spectrum.

NMR tube reaction of CH_4 and (Cp-d_{27})'$_2$CeD in C_6D_{12}

Cp'$_2$CeH was dissolved in C_6D_{12} in an NMR tube and heated at 60°C for five days to perdeuterate the ring t-Bu groups. The sample was taken to dryness and the purple solid residue was dissolved in C_6D_{12}. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_4 (1 atm). The sample was heated at 60°C. After 6 days, a 1:1:1 pattern of resonances attributable to CH_3D had appeared just upfield of the CH_4 resonance. The ratio of CH_4 to CH_3D was 5:1. After 15 days, the ratio was 2:1. After 21 days, a 1:3:5:3:1 pattern of resonances attributable to CH_2D_2 had appeared just upfield of the CH_3D signal. The ratio of CH_4 to CH_3D to CH_2D_2 was 4:3:1. After 41 days, the ratio was 1:1.5:1. After 73 days, a 1:3:5:7:5:3:1 pattern of resonances attributable to CHD_3 had appeared just upfield of the CH_2D_2 signal. The ratio of CH_4 to CH_3D to CH_2D_2 to CHD_3 was 1:4:6:2. After 94 days, the ratio was

1:4:8:4. After 127 days, the ratio was 1:9:26:26. After 165 days, the ratio was 1:7:17:18. After 233 days, the ratio was 1:12:62:132.

NMR tube reaction of CHF_3 and Cp'($(Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce in C_6D_{12}.

Cp'$_2$Ce(CH_2Ph) was dissolved in C_6D_{12} and heated at 60°C for 12 hours, yielding a solution of Cp'($(Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CHF_3 (1 atm). The sample was heated at 60°C for 1 day, by which time the resonances for Cp'($(Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce had disappeared from the ^1H NMR spectrum and resonances of Cp'$_2$CeF and B in a 4:1 area ratio and several new diamagnetic products had appeared. Addition of a small amount of Cp'$_2$CeH to the solution did not change the ^1H or ^{19}F NMR spectrum. GCMS analysis showed two primary components in addition to Cp'H, both with $(M)^+$ *m/z* 264, consistent with two isomers of tri-t-butylfluorobenzene, one symmetric and the other asymmetric. The ^{19}F NMR spectrum shows that the isomers are present in an approximately 1.5:1 ratio.

NMR tube reaction of CHF_3, cyclohexene and Cp'($(Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce in C_6D_{12}.

Cp'$_2$Ce(CH_2Ph) was dissolved in C_6D_{12} and heated at 60°C for 12 hours, yielding a solution of Cp'($(Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. A drop of cyclohexene was added. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CHF_3 (1 atm). The sample was heated at 60°C for 1 day, by which time the resonances for Cp'($(Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce had disappeared from the ^1H NMR spectrum and resonances due to Cp'$_2$CeF and B in a 6:1 area ratio and several new diamagnetic products had appeared. The ^{19}F NMR spectrum and GCMS analysis were essentially identical to those from the reaction without cyclohexene present.

NMR tube reaction of CHF_3, 2-methyl-2-heptene, and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_{12} and heated at 60°C for 12 hours, yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. A drop of 2-methyl-2-heptene was added. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CHF_3 (1 atm). The sample was heated at 60°C for 1 day, by which time the resonances for $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the ^1H NMR spectrum and resonances from Cp'_2CeF and B in a 9:1 area ratio and several new diamagnetic products had appeared. The ^{19}F NMR spectrum and GCMS analysis were essentially identical to those from the reaction without 2-methyl-2-heptene present.

NMR tube reaction of CH_2F_2 and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_{12} and heated at 60°C for 12 hours yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_2F_2 (1 atm). The sample was heated at 60°C for 5 days after which time the resonances of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the ^1H NMR spectrum. Resonances due to Cp'_2CeF and B in a 1:1 area ratio and both isomers of tri-t-butylbenzene had appeared in the spectrum. The presence of both isomers was confirmed by GCMS analysis.

NMR tube reaction of CH_3F and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_{12} and heated at 60°C for 12 hours yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_3F (1 atm). The sample was heated at 60°C for 12 hours after which time the resonances of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had disappeared from the ^1H NMR spectrum. Resonances for Cp'_2CeF had appeared, as well as a set of new paramagnetic resonances, presumably due to a new metallocene cerium fluoride, C. GCMS analysis showed the formation of methylcyclohexane-d_{12}, Cp'H, and a new compound with $(M)^+$ *m/z* 248; $Cp'H+CH_2$. When the experiment was repeated and D_2O was used to prepare the GCMS sample instead of H_2O, the molecular ion of the new species was *m/z* 249. The new metallocenes were further identified as described in the next experiment.

NMR tube reaction of CH_3F and $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_6 and heated at 60°C for 4 days to perdeuterate the ring t-butyl groups. The sample was taken to dryness and the solid residue redissolved in fresh C_6D_6. The sample was heated for an additional 7 days, then taken to dryness and the solid residue was redissolved in C_6D_{12}. The sample was heated at 60°C for 1 day, yielding a solution of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_3F(1 atm). The sample was heated at 60°C for 2 days, after which time the resonances of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ had disappeared from the ^1H and ^2H NMR spectra. Resonances for $(Cp'\text{-}d_{27})_2CeF$ had appeared in the ^2H NMR spectum, as well as hints of the signals with chemical shifts similar those in the ^1H NMR spectrum of the unlabeled, unknown metallocene C from the previous experiment. The ^1H NMR spectrum contained three new resonances due to the three isotopomers arising from the insertion of CH_2 into a C-D bond in $(Cp'\text{-}d_{27})_2CeF$. A drop of H_2O was added, and the sample was vigorously shaken. After 10 minutes, the solution was dried and filtered. The filtrate was added to a new NMR tube and heated at 60°C for 1 day to isomerize the substituted cyclopentadienes. The ^1H NMR spectrum contained three single resonances attributed to the three isotopomers of $(Cp''\text{-}d_{27})H$. GCMS analysis showed one major component in addition to $(Cp'\text{-}d_{27})H$ (envelope centered around $(M)^+$ *m/z* 260), with an envelope centered around $(M)^+$ *m/z* 274. Characterization of the new metallocenes: ^1H NMR (C_6D_{12}): δ -0.100 (2H, $\nu_{1/2}$ = 20 Hz), -2.794 (2H, $\nu_{1/2}$ = 20 Hz), -6.129 (2H, $\nu_{1/2}$ = 20 Hz). Characterization of $Cp''H\text{-}d_{27}$: ^1H NMR (C_6D_{12}): δ 1.19 (2H, s), 1.07 (2H, s), 1.00 (2H, s).

NMR tube reaction of CH_3F and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6H_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6H_{12} and heated at 60°C for 12 hours yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_3F (1 atm). The sample was heated at 60°C for 12 hours. GCMS analysis showed the formation of methylcyclohexane, Cp'H, and Cp"H in addition to solvent cyclohexane.

NMR tube reaction of CH_3F, CH_4, and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_{12} and heated at 60°C for 12 hours yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_4 (0.5 atm) and CH_3F (0.5 atm). The sample was heated at 60°C for 12 hours after which time the resonances of Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce had disappeared from the ^{1}H NMR spectrum. The spectrum contained the same resonances as that of the reaction in the absence of CH_4.

NMR tube reaction of CH_3F, cyclohexene, and Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce in C_6D_{12}.

Cp'$_2$Ce(CH_2Ph) was dissolved in C_6D_{12} and heated at 60°C for 12 hours yielding a solution of Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce. A drop of cyclohexene was added. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with CH_3F (1 atm). The sample was heated at 60°C for 12 hours after which time the resonances of Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce had disappeared from the ^{1}H NMR spectrum. Resonances due to Cp'$_2$CeF had appeared in the ^{1}H NMR spectrum along with bicyclo-[4.1.0]-heptane (norcarane) and a small amount of the unknown metallocene C observed previously. GCMS analysis showed the presence of norcarane, Cp'H, and Cp''H; no methylcyclohexane nor methylcyclohexenes were observed.

NMR tube reaction of cyclohexene and Cp'$_2$CeH in C_6D_6.

Cp'$_2$CeH was dissolved in C_6D_{12} in an NMR tube and a drop of cyclohexene (an excess) was added. Within 20 minutes, resonances due to Cp'$_2$CeH had disappeared from the ^{1}H NMR spectrum and resonances of cyclohexane and Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce had appeared.

NMR tube reaction of cyclohexene and Cp'$((Me_3C)_2C_5H_2C(Me_2)CH_2)$Ce.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_{12} and heated at 60°C for 12 hours yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. The sample was taken the dryness and three drops of cyclohexene were added. The sample was heated at 60°C for 2 hours, then taken to dryness. The dark red solid residue was dissolved in C_6D_{12}. A pair of CMe_3 resonances in a 2:1 area ratio had appeared in the ^1H NMR spectrum, along with several smaller paramagnetic signals, including those of the metallacycle. ^1H NMR (C_6D_{12}): δ -1.71 (36H, 160 Hz), -8.98 (18H, 24 Hz). The new product was not further characterized, although it is presumably Cp'_2Ce(cyclohexenyl).

NMR tube reaction of cyclohexene and $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_6 and heated at 60°C for 4 days to perdeuterate the ring t-butyl groups. The sample was taken to dryness and the solid residue redissolved in fresh C_6D_6. The sample was heated for an additional 4 days, then taken to dryness and the solid residue was redissolved in C_6D_{12}. The sample was heated at 60°C for 1 day, yielding a solution of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$. A drop of cyclohexene was added, and the sample was heated at 60°C. After 1 day, a resonance at 5.63 ppm had appeared in the ^2H NMR spectrum, indicating that the protons on the sp^2-carbons of cyclohexene were being exchanged for deuterium. The sample was heated at 60 degrees for 30 days, over which time this signal increased in intensity tenfold. No resonances suggesting H for D exchange on the sp^3 carbons of cyclohexene could be distinguished from the C_6D_{12} solvent signal. GCMS analysis showed that cyclohexene was present in large excess, as the molecular ion at $(M)^+$ *m/z* 82 was present; in addition, the envelope for the (Cp'-d_{27-x})H centered around *m/z* 247 was also observed.

NMR tube reaction of C_7F_{14} and Cp'_2CeH in C_6D_{12}.

Cp'_2CeH was dissolved in C_6D_{12} in an NMR tube and a drop of perfluoromethylcyclohexane was added. The sample was stored at ambient temperature for 5 days, by which time resonances of Cp'_2CeF had appeared in the ^1H NMR spectrum. The ratio of Cp'_2CeF to residual Cp'_2CeH was 3:1. After 22 additional days at ambient temperature, only resonances due to Cp'_2CeF were observed in the ^1H NMR spectrum. Identification of the other organic compounds was not pursued.

NMR tube reaction of $C_6H_5CF_3$ and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)$ in C_6D_{12}.

$Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_{12} and heated at 60°C for 12 hours yielding a solution of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$. A drop of $C_6H_5CF_3$ was added and the solution was stored at room temperature for 24 hours, yielding a red solution. The ^1H NMR spectrum contained resonances for $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$, a small amount of Cp'_2CeF, and two new paramagnetic species with nearly coincident t-butyl resonances in 2:1 ratios. The ratio of products was not significantly changed by heating the solution for 4 days at 60 deg. The new species were not characterized.

NMR tube reaction of $C_6H_5CF_3$ and Cp'_2CeH in C_6D_{12}.

Cp'_2CeH was dissolved in C_6D_{12} in an NMR tube and a drop of $C_6H_5CF_3$ was added. The solution was stored at room temperature for three days, by which time the solution color had changed from purple to orange. The ^1H NMR spectrum contained resonances for Cp'_2CeF and the same two new organometallic species observed in the reaction of

Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce and C$_6$H$_5$CF$_3$. The ratio of Cp'2CeF to the new species was 7:1.

Reaction of SiF$_4$ and Cp'$_2$CeH.

Cp'$_2$CeH (250 mg, 0.41 mmol) was dissolved in pentane (10 mL). The headspace was evacuated and replaced with SiF$_4$ (1 atm). The purple solution immediately turned orange, then cloudy and yellow as copious precipitate formed. The ^{1}H NMR spectrum of the crude product contained four resonances from paramagnetic compounds in a 1:2.5:3.5:3.5 area ratio. The suspension was taken to dryness and the solid residue dissolved in 15 mL of toluene. The volume of the solution was reduced until precipitation occurred, warmed to dissolve the precipitate, and then cooled to -15^{O}C, giving a yellow powder. The ^{1}H NMR spectrum revealed the same four resonances as the crude product and resonances due to Cp'$_2$CeF. In an NMR tube, a dilute solution of Cp'$_2$CeF in C$_6$D$_6$ was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with SiF$_4$ (1 atm). The tube was warmed to 19°C and shaken vigorously. The orange solution turned yellow. The ^{1}H NMR spectrum was identical to that of the crude product of the reaction of Cp'$_2$CeH and SiF$_4$.

Chapter 4

Cp'$_2$CeH and ethylene: Cp'$_2$CeH (0.05 g, 0.08 mmol) was dissolved in hexane (10 mL). The red-purple solution was cooled in a liquid nitrogen isopropanol bath. The headspace was evacuated and replaced with ethylene (1 atm). The sample was warmed to room temperature and stirred. The solution became darker purple, and within 30 minutes, off-white solid began to appear in the solution. After stirring for one day, the dark brown/purple solution was filtered and the cake of off-white solid was washed with hexane. The solid was insoluble in hexane, benzene, and diethyl ether. A clearly defined melting point could not be obtained, but a substantial portion of the solid burned when heated above an open flame, leaving a small quantity of white ash. The ^{1}H NMR spectrum of an aliquot of the mother liquor contained numerous paramagnetic and diamagnetic resonances.

Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce and ethylene: Cp'$_2$CeCH$_2$C$_6$H$_5$ (0.05 g, 0.07 mmol) was dissolved in hexane (10 mL) and heated at reflux for one day, generating a solution of Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce. The purple solution was cooled in a liquid nitrogen isopropanol bath, the headspace was evacuated and replaced with ethylene (1 atm). The sample was warmed to room temperature and stirred. Off-white solid began to appear in the solution within 30 minutes. After stirring for one day, the dark brown/purple solution was filtered and the cake of off-white solid was washed with hexane. The solid was insoluble in hexane, benzene, and diethyl ether. A clearly defined melting point could not be obtained, but a substantial portion of the solid burned when heated above an open flame, leaving a small quantity of white ash. The ^{1}H NMR spectrum of an aliquot of the mother liquor contained numerous paramagnetic and diamagnetic resonances.

NMR tube reaction of Cp'$_2$CeH and deficiency of ethylene: Cp'$_2$CeH was dissolved in C$_6$D$_6$ in an NMR tube and the sample was frozen in a liquid nitrogen isopropanol bath.

The headspace was evacuated and replaced with ethylene (1 atm). After 15 seconds, the headspace was evacuated and replaced with nitrogen. The sample was warmed to room temperature and agitated. The only paramagnetic resonances in the ^{1}H NMR spectrum were those of Cp'$_2$CeH and Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce.

NMR tube reaction of Cp'$_2$CeH and propylene: Cp'$_2$CeH was dissolved in C$_6$D$_{12}$ in an NMR tube, and the sample was cooled in a liquid nitrogen isopropanol bath. The headspace was evacuated, and replaced with propylene (1 atm). The sample was warmed to room temperature. After 10 minutes, the resonance of Cp'$_2$CeH were absent from the ^{1}H NMR spectrum. Resonances for Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce had appeared, as well as a new set of paramagnetic resonances in a 2:1 area ratio, presumably an allyl complex [^{1}H NMR (C$_6$D$_{12}$): δ –0.30 (36H, $\nu_{1/2}$ = 700 Hz), –12.7 (18H, $\nu_{1/2}$ = 150 Hz)]. Resonances of propane had also appeared in the spectrum. The area ratio of Cp'((Me$_3$C)$_2$C$_5$H$_2$C(Me$_2$)CH$_2$)Ce to the new species was 1:1. After 20 minutes, the ratio was 1:6. After 3 hours, only the resonances from the new species were present. The sample was taken to dryness and the red solid residue was dissolved in C$_6$D$_{12}$. Heating the sample for two days at 60°C produced no noticeable change in the ^{1}H NMR spectrum.

Cp'$_2$CeC$_3$H$_5$: Cp'$_2$CeOSO$_2$CF$_3$ (0.38g, 0.48mmol) was dissolved in pentane and allylmagnesium bromide (3.8 mL of a 0.13M solution in diethyl either, 0.49 mmol) was added *via* syringe. The orange solution immediately turned red and cloudy. After five minutes, the solution was taken to dryness, and the red solid residue was extracted with pentane (25 mL). The solution was concentrated and cooled to -15°C, yielding red powder. Yield, 35 mg (0.054 mmol, 11%). MP 212-215°C (decomp) The ^{1}H NMR spectrum was identical to that obtained from the reaction of propylene and the hydride.

NMR tube reaction of $Cp'_2CeC_3H_5$ and H_2: $Cp'_2CeC_3H_5$ was dissolved in C_6D_6 in an NMR tube. The sample was frozen in a liquid nitrogen isopropanol bath, and space was evacuated, and replaced with H_2. After 15 minutes, resonances due to Cp'_2CeH had appeared in the ^{1}H NMR spectrum, along with resonances attributable to propane. After two days at 25°C, resonances due to $Cp'_2CeC_3H_5$ had disappeared from the spectrum, and a quantitative amount of Cp'_2CeH had formed.

NMR tube reaction of $Cp'_2CeC_3H_5$ and D_2 in C_6D_6: $Cp'_2CeC_3H_5$ was dissolved in C_6D_6 in an NMR tube. The sample was frozen in a liquid nitrogen isopropanol bath, and space was evacuated, and replaced with D_2. The sample was heated at 60°C for five hours, after which time, resonances due to $Cp'_2CeC_3H_5$ were absent from the ^{1}H NMR spectrum, and resonances due to Cp'_2CeH had appeared, along with resonances attributable to propane. In the ^{2}H NMR spectrum, two small resonances matching those of propane had appeared, along with small resonances due to Cp'_2CeD with partially deuterated CMe_3 groups.

NMR tube reaction of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ and propylene: $Cp'_2Ce(CH_2Ph)$ was dissolved in C_6D_6 and heated at 60°C for 5 days to perdeuterate the ring t-butyl groups. The sample was taken to dryness and the solid residue redissolved in fresh C_6D_6. The sample was heated for an additional 7 days, yielding a solution of $(Cp'\text{-}d_{27})\{[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]\}Ce$ and $(Cp'\text{-}d_{27})_2CeC_6D_5$. The tube was cooled in a liquid nitrogen isopropanol bath, the head space was evacuated, and replaced with propylene (1 atm). The sample was heated at 60°C. After one day, only resonances due to $(Cp'\text{-}d_{27})_2CeC_3H_5$ were present in the ^1H and ^2H NMR spectra. The sample was heated for 45 days; no resonances attributable to propylene had appeared in the ^2H NMR spectrum.

$(Cp'_2Ce)_2CH_2O$ • toluene: Cp'_2CeH (0.75 g, 1.2 mmol) was dissolved in pentane (5 mL), and the solution was chilled in an ice water bath. The headspace was evacuated and replaced CO (1 atm). The purple solution turned red orange and cloudy as copious yellow-orange solid precipitated. The solution was filtered, and the solid was dissolved in toluene (100 mL). The volume of the solution was reduced to 75 mL, and the solution was cooled to -15°C, yielding small orange crystals. The crystals became opaque upon exposure to vacuum, and the ^1H NMR spectrum indicated the presence of toluene. Yield, 0.56 g (0.42 mmol, 70%). MP 211-215°C (decomp). ^1H NMR (C_6D_{12}, 400MHz): δ 8.95 (18H, $\nu_{1/2}$ = 17 Hz), -3.38 (18H, $\nu_{1/2}$ = 17 Hz), -15.62 (18H, $\nu_{1/2}$ = 31 Hz). IR: 2130(m),[5] 1520(w), 1360(s), 1240(s), 1200(m), 1180(m), 1160(m), 1110(w), 1020(w), 1000(m), 960(m), 920(w), 880(w), 825(w), 810(w), 800(s), 760(w), 720(w), 680(m), 675(m) cm^{-1}. MS: no $(M)^+$ was observed but $(M-605)^+$ corresponding to Cp'_2CeOMe and $(M-636)^+$ corresponding to $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ were found. Anal. Calcd. for $C_{76}H_{118}Ce_2O$: C, 68.32; H, 9.50. Found C, 68.65; H, 9.59.

$Cp'_2CeO(CH_2)_2CH_3$: Cp'_2CeOTf (0.5 g, 0.63 mmol) and sodium propoxide (0.12 g, 1.5 mmol) were suspended in diethyl ether and stirred. The solution slowly turned from yellow to red over the course of an hour. After one day, the solvent was removed under reduced pressure, and the red solid residue was dissolved in pentane (5 mL). The volume of the solution was reduced to 1 mL, and the solution was cooled to - 15°C, but crystallization could not be induced. ^{1}H NMR spectrum of the crude solid (C_6D_6, 300MHz): δ 33.01 (2H, $\nu_{1/2}$ = 50 Hz), 24.63 (4H, $\nu_{1/2}$ = 70 Hz), 11.59 (2H, $\nu_{1/2}$ = 40 Hz), 5.82 (3H, $\nu_{1/2}$ = 20 Hz), -1.42 (36H, $\nu_{1/2}$ = 90 Hz), -11.63 (18H, $\nu_{1/2}$ = 20 Hz).

NMR tube reaction of $(Cp'_2Ce)_2CH_2O$ with ethylene: $(Cp'_2Ce)_2CH_2O$ was dissolved in C_7D_8. The sample was cooled in a liquid nitrogen isopropanol bath, the headspace was evacuated, and replaced with ethylene (1 atm). After four days at room temperature, the orange sample had turned red, resonances due to $(Cp'_2Ce)_2CH_2O$ were absent from the ^{1}H NMR spectrum, and resonances consistent with $Cp'_2CeO(CH_2)_2CH_3$ had appeared. The integrated intensities indicated that the conversion was quantitative.

NMR reaction of $(Cp'_2Ce)_2CH_2O$ with H_2: $(Cp'_2Ce)_2CH_2O$ was dissolved in C_6D_6. The sample was cooled in a liquid nitrogen isopropanol bath; the headspace was evacuated, and replaced with H_2 (1 atm). After four hours, the ^{1}H NMR spectrum contained only resonances due to Cp'_2CeOMe and Cp'_2CeH in an area ratio of approximately 1:1.

$(Cp'_2CeOCH)_2$: Cp'_2CeH (0.5 g, 0.8 mmol) was dissolved in toluene (20 mL). The headspace was evacuated and replaced CO (1 atm). The purple solution turned red orange and became cloudy. After 20 minutes the solution had become clear and red. The headspace was evacuated and replaced with CO (1 atm). After stirring for one hour, the solvent was removed under reduced pressure. The red solid residue was dissolved in pentane (10 mL). The volume of the solution was reduced until precipitation occurred; the solution was warmed to dissolve the solid, and then cooled to - 15°C, yielding red powder. Yield, 0.28 g (0.22 mmol, 55%). MP 232-235°C. ^{1}H NMR (C_7D_8, 400MHz): δ 39.33 (2H, $\nu_{1/2}$ = 80 Hz), 26.94 (4H, $\nu_{1/2}$ = 450 Hz), -0.73 (36H, $\nu_{1/2}$ = 550 Hz), -12.53 (18H, $\nu_{1/2}$ = 100 Hz). IR: 2130(w),[5] 1700(w), 1650(w), 1620(s), 1590(w), 1570(w), 1360(s), 1330(m), 1280(w), 1240(s), 1200(m), 1160(m), 1140(s), 1060(w), 1020(s), 1000(m), 960(m), 920(w), 820(s), 800(s), 760(w), 740(w), 720(w), 680(w), 670(m) cm^{-1}. MS $(M)^+$ *m/z* (calc, found) 1270 (100, 100) 1271 (77, 76) 1272 (55, 54) 1273 (27, 27) 1274 (10, 14). Anal. Calcd. for $C_{70}H_{118}Ce_2O_2$: C, 66.10; H, 9.35. Found C, 66.00; H, 9.43.

NMR reaction of $(Cp'_2Ce)_2CH_2O$ with CO: $(Cp'_2Ce)_2CH_2O$ was dissolved in C_7D_8, and the sample was cooled in a liquid nitrogen isopropanol bath. The headspace was evacuated and replaced with CO (1 atm). The orange solution became redder upon agitation. The ^{1}H NMR spectrum contained only resonances due to $(Cp'_2CeOCH)_2$ and a small amount of Cp'_2CeOMe. The integrated intensities indicated a quantitative conversion.

NMR tube reaction of Cp'_2CeH, CH_4, and CO: Cp'_2CeH was dissolved in C_6D_6, and the sample was cooled in a liquid nitrogen isopropanol bath. The headspace was evacuated and replaced with CH_4 (1 atm). The headspace was evacuated to roughly 0.5 atm and replaced with CO (1 atm). The sample was warmed to room temperature and agitated, or upon it became red orange and cloudy. After one day, the sample was red and clear. The ^{1}H NMR spectrum contained resonances due to $(Cp'_2CeOCH)_2$ and a small amount of Cp'_2CeOMe. The presence of CH_4 did not appear to affect the course of the reaction.

Decomposition of $(Cp'_2Ce)_2CH_2O$ in C_6D_{12}: $(Cp'_2Ce)_2CH_2O$ was dissolved in C_6D_{12} and the sample was monitored by ^1H NMR spectroscopy. After 7.5 hours, resonances due to Cp'_2CeOMe and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ had appeared in the ^1H NMR spectrum, and the resonances due to $(Cp'_2Ce)_2CH_2O$ had diminished relative to an internal standard. The area ratio of the resonances due to Cp'_2CeOMe and $(Cp'_2Ce)_2CH_2O$ was 1:1. After 12 hours, the ratio had changed to 5:1. After 24 hours, only resonances due to Cp'_2CeOMe and $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ were present in the spectrum.

Cp'_2CeOMe Method A: Cp'_2CeH (0.5g, 0.8 mmol) was dissolved in pentane (10 mL). The headspace was evacuated and replaced with a 10:1 mixture of H_2 and CO (1 atm). The solution became cloudy, but gradually cleared over 6 hours. The headspace was again evacuated and replaced with a 10:1 mixture of H_2 and CO (1 atm). After 12 hours, the volume of the solution was reduced to 2 mL, and the solution was cooled to -15°C, yielding red powder. Yield, 0.120g (0.18mmol, 23%). Melts over a wide range, around 150°C. ^1H NMR (C_6D_6, 300MHz): δ 31.04 (3H, $\nu_{1/2}$ = 18 Hz), 23.33 (4H, $\nu_{1/2}$ = 55 Hz), -2.51 (36H, $\nu_{1/2}$ = 11 Hz), -8.62 (18H, $\nu_{1/2}$ = 15 Hz). MS $(M)^+$ *m/z* (calc, found) 637 (100, 100) 638 (38, 48) 639 (20, 24) 640 (6, 8) 641 (1, 3). Anal. Calcd. for $C_{35}H_{61}CeO$: C, 65.89; H, 9.63. Found C, 66.17; H, 9.71.

Method B: $Cp'_2CeCH_2C_6H_5$ (0.53 g, 0.76 mmol) was dissolved in pentane (5 ml) and methanol (20 mL of 0.038M solution in pentane, 0.76 mmol) was added *via* syringe. The red solution was stirred for 20 minutes, and then taken to dryness under reduced pressure. The ^1H NMR spectrum of the crude red solid contained resonances due to

$Cp'_2CeCH_2C_6H_5$ and Cp'_2CeOMe in a 2:1 area ratio. The solid was redissolved in pentane (5 mL) and methanol (40 mL of 0.038M solution in pentane, 1.52 mmol) was added *via* syringe. The red solution was stirred for 20 minutes, and then taken to dryness under reduced pressure. The ^1H NMR spectrum of the crude red solid contained only paramagnetic resonances due to Cp'_2CeOMe, but also a substantial amount of Cp'H. Attempts to crystal the product from pentane were unsuccessful

Method C: Cp'_2CeOTf (1.33g, 1.7 mmol) and sodium methoxide (0.09g, 1.7 mmol) were suspended in diethyl ether (15 ml) and stirred. Within 20 minutes, the yellow solution had turned red. The solution was stirred for one day, and then taken to dryness under reduced pressure. The ^1H NMR spectrum of the crude red solid was consistent with Cp'_2CeOMe. The solid was extracted into pentane (5 mL). The solution was concentrated to 1 mL under reduced pressure and cooled to -15°C. Attempts at crystallization were unsuccessful.

NMR tube reaction of $Cp'((Me_3C)_2C_5H_2C(Me_2)CH_2)Ce$ and $(Cp'\text{-}d_{27})_2CeOMe$: Cp'_2CeH was heated at 60°C in C_6D_6 for 9 days to perdeuterate the ring CMe_3 groups. The sample was taken to dryness, fresh C_6D_6 was added, and the sample was heated at 60°C for an additional five days. The sample was cooled in a liquid nitrogen isopropanol bath; the headspace was evacuated and replaced with a mixture of 10% CO and 90% H_2. The sample was warmed to room temperature and agitated for 10 minutes. It was then returned to the cold bath, headspace was evacuated and replaced with a fresh mixture of 10% CO and 90% H_2. The ^2H NMR spectrum indicated complete conversion to $(Cp'\text{-}d_{27})_2CeOMe$. The sample was taken to dryness. $Cp'_2CeCH_2C_6H_5$ was heated at 60°C in

C_6D_{12} in a separate tube, producing a sample of Cp'($(Me_3C)_2C_5H_2C(Me_2)CH_2$)Ce. The sample is added to the solid residue of (Cp'-d_{27})$_2$CeOMe. The ^{1}H NMR spectrum showed only a trace of Cp'$_2$CeOMe after one hour. The sample was heated at 60°C for one day, after which time prominent resonances due to Cp'$_2$CeOMe had appeared in the ^{1}H NMR spectrum. Resonances due to (Cp'-d_{27}){$[C(CD_3)_3]_2C_5H_2[C(CD_3)_2CD_2]$}Ce had also appear in the ^{2}H NMR spectrum. Additional leading at 60°C did not significantly perturb the relative populations of the species.

NMR tube reaction of (Cp-d_{27})'$_2$CeH and Cp'$_2$CeOMe: Cp'$_2$CeH was heated at 60°C in C_6D_6 for 9 days to perdeuterate the ring CMe_3 groups. The sample was taken to dryness, and a solution of Cp'$_2$CeOMe in C_6D_{12} was added. The relative populations of the species, as indicated by their relative intensities in the ^{1}H and ^{2}H NMR spectra, were not significantly perturbed after the sample was heated for one day at 60°C. After heating for 16 days at 60°C, the perprotio and perdeutero species of both Cp'$_2$CeH and Cp'$_2$CeOMe were present in their respective spectra.

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This absorbance is attributed to an electronic transition arising from the split ^2F ground state of Ce^{3+} ($^2F_{5/2}$ and $^2F_{3/2}$). See: Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495.

Appendix A: X-ray Crystallography Details

General

Neutral atom scattering factors were taken from Cromer and Waber[1]. Anomalous dispersion effects were included in F_{calc}[2]; the values for Δf' and Δf" were those of Creagh and McAuley[3]. The values for the mass attenuation coefficients are those of Creagh and Hubbel[4]. Except as noted, all calculations were performed using the teXsan[5] crystallographic software package of Molecular Structure Corporation.

A1. $Cp'_2Ce(OTf)\bullet(C_6H_{14})_{0.5}$

A fragment of a yellow crystal of $Cp'_2CeOTf\bullet(C_6H_{14})_{0.5}$ having approximate dimensions of 0.11 x 0.13 x 0.16 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART[6] CCD area detector with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 7832 centered reflections with $I > 10\sigma$ in the range $5.00 < 2\theta < 45.00^\circ$ corresponded to a primitive triclinic cell with dimensions:

$a = 10.6082(3)$ Å $\quad \alpha = 76.559(1)^\circ$

$b = 18.9952(6)$ Å $\quad \beta = 82.774(1)^\circ$

$c = 20.2753(5)$ Å $\quad \gamma = 89.274(1)^\circ$

$V = 3941.5(2)$ Å^3

For Z = 4 and F.W. = 799.10, the calculated density is 1.35 g/cm^3. Based on a statistical analysis of intensity distribution,and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (#2). The data were collected at a temperature of -131 ± 1°C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10.0 seconds per frame. Data were integrated by the program SAINT[7] to a maximum 2θ value of 46.5°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP[8]. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[9]. (Tmax = 0.89, Tmin = 0.75). The structure was solved by direct methods[10] and expanded using Fourier techniques[11]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, but not refined. Centroids of the cyclopentadienyl rings (C101-C104) are included, but not refined. The unit cell contains one molecule of n-hexane. The final cycle of full-matrix least-squares refinement was based on 7052 observed reflections ($I > 3.00\sigma(I)$) and 829 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R = 0.033, Rw = 0.031, and GOF = 1.13. The weighting scheme was based on counting statistics and included a factor (p = 0.030) to downweight the intense reflections. Plots of $w\,\Sigma(|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.39 and -0.77 $e^-/Å^3$, respectively.

Empirical Formula	$C_{38}H_{65}CeF_3O_3S$
Formula Weight	799.10
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.11 X 0.13 X 0.16 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.6082(3)Å
	b = 18.9952(6) Å
	c = 20.2753(5) Å
	α = 76.559(1)^o
	β = 82.774(1)^o
	γ = 89.274(1)^o
	V = 3941.5(2) $Å^3$
Space Group	$P\bar{1}$ (# 2)
Z value	4
$D_{\mathbf{calc}}$	1.347 g/cm^3
$F_{\mathbf{000}}$	1672.00
μ(MoKα)	12.54 cm^{-1}
Diffractometer	Bruker SMART CCD

Radiation	MoKα ($\lambda = 0.71069$ Å) graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
2θmax	46.5°
No. of Reflections Measured	Total: 17590 Unique: 10941 ($R_{int} = 0.032$)
Corrections	Lorentz-polarization Absorption (Tmax = 0.89 Tmin = 0.75)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least Squares Weights	$1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$
p-factor	0.030
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	7052
No. Variables	829
Reflection/Parameter Ratio	8.51
Residuals: R; R_w; R_{all}	0.033 ; 0.031; 0.000
Goodness of Fit Indicator	1.13

Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.39 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.77 $e^-/Å^3$

A2. $Cp'_2CeCH_2C_6H_5$

A fragment of a red, block like crystal of $Cp'_2Ce(CH_2C_6H_5)$ having approximate dimensions of 0.30 x 0.27 x 0.10 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on an SMART[6] diffractometer with CCD area detector and graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix obtained from a least-squares refinement using the measured positions of 8192 reflections with $I > 10\sigma$, in the range $4.00 < 2\theta < 46.5^{\circ}$ corresponded to a primitive triclinic cell with dimensions:

a = 13.2277(3) Å α = 96.3770°
b = 16.0800(4) Å β = 105.388(1)°
c = 18.4994(3) Å γ = 96.173(1)°
V = 3731.6(1) $Å^3$

For Z = 4 and F.W. = 698.08, the calculated density is 1.24 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (#2). The data were collected at a temperature of -94 ± 1°C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10.0 seconds per frame. Data were integrated by the program SAINT[7] to a maximum 2θ value of 52.1°. Of the 17828 reflections which were collected, 12450 were unique (R_{int} = 0.023); equivalent reflections were merged. No decay correction was applied. An empirical absorption correction was applied using SADABS[9]. Maximum and minimum effective transmissions were 0.8236 and 0.6757 respectively. The data were also corrected for Lorentz-polarisation effects. The structure was solved by direct methods[10] and expanded using Fourier techniques.[11] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but not refined. Centroids of the cyclopentadienyl rings (C101-C104) were included, but not refined. The final cycle of full-matrix least-squares refinement was based on 9190 observed reflections ($I > 3.00\sigma(I)$) and 757 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R = 0.032, R_W = 0.042, and GOF = 1.37. The weighting scheme was based on counting statistics and included a factor (p = 0.030) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.54 and -0.90 $e^-/Å^3$, respectively.

Empirical Formula	$C_{41}H_{65}Ce$
Formula Weight	698.08
Crystal Color, Habit	red, blocks
Crystal Dimensions	0.30 x 0.27 x 0.10 mm

Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	8192 (4.0 – 46.5^{o})
Lattice Parameters	a = 13.2277(3) Å
	b = 16.0800(4) Å
	c = 18.4994(3) Å
	α = 96.377^{o}
	β = 105.388(1)^{o}
	γ = 96.173(1)^{o}
	V = 3731.6(1) Å^{3}
Space Group	$P\bar{1}$ (# 2)
Z value	4
D_{calc}	1.242 g/cm^{3}
F_{000}	1476.00
μ(MoKα)	12.44 cm^{-1}
Diffractometer	Siemens SMART CCD
Radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
Crystal to Detector Distance	58 mm

Temperature	-94 ^{o}C
Scan Type	ω
Scan Rate	10 second scans 0.3^{o} wide in ω
$2\theta_{max}$	52.0^{o}
No. of Reflections Measured	Total: 17828 Unique: 12450 (R_{int} = 0.023)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.6757 – 0.8236)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^{2}
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.030
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	9190
No. Variables	757
Reflection/Parameter Ratio	12.14
Residuals: R; R_w; R_{all}	0.032; 0.042; 0.050
Goodness of Fit Indicator	1.37
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.54 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.90 $e^-/Å^3$

A3. Cp'_2CeH

A fragment of a purple crystal of Cp'_2CeH having approximate dimensions of 0.12 x 0.33 x 0.05 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a Siemens SMART[6] diffractometer with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix obtained from a least-squares refinement using the measured positions of 5549 reflections with $I > 10\sigma$, in the range $4.00 < 2\theta < 51.61^{\circ}$ corresponded to a primitive monoclinic cell with dimensions:

$a = 9.2454(8)$ Å

$b = 34.141(3)$ Å $\beta = 109.476(2)^{\circ}$

$c = 10.872(1)$ Å

$V = 3235.5(5)$ Å^3

For Z = 4 and F.W. = 607.96, the calculated density is 1.25 g/cm^3. The systematic absences of:

h0l: $h+l \pm 2n$

0k0: $k \pm 2n$

uniquely determine the space group to be $P2_1/n$ (#14). The data were collected at a temperature of -98 ± 1°C. using 10 second scans 0.3° wide in ω. Frame data were integrated using SAINT.[7] Of the 14598 reflections which were collected, 5549 were unique (R_{int} = 0.067); equivalent reflections were merged. No decay correction was applied. An empirical absorption correction was applied using SADABS.[9] Maximum and minimum effective transmissions were 0.934733 and 0.756690, respectively. The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods[10] and expanded using Fourier techniques.[11] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the cyclopentadienyl ligands were calculated based on the expected geometry at each carbon. The hydrogen bound directly to the cerium center (H59) corresponded to the largest peak in the difference Fourier map after all other atoms had been named and refined. Centroids of the cyclopentadienyl rings (C101 and C102) were included, but not refined. The final cycle of full-matrix least-squares refinement was based on 2388 observed reflections ($I > 3.00\sigma(I)$) and 319 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of $R = 0.030$, $R_W = 0.028$, and GOF = 0.80. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.43 and -0.61 $e^-/\text{Å}^3$, respectively.

Empirical Formula	$C_{34}H_{59}Ce$

Formula Weight	607.96
Crystal Color, Habit	purple, prismatic
Crystal Dimensions	0.12 x 0.33 x 0.05 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	5549 (4.0 – 51.61^{o})
Lattice Parameters	a = 9.2454(8) Å b = 34.141(3) Å c = 10.872(1) Å β = 109.476(2)^{o} V = 3235.5(5) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.248 g/cm^3
F_{000}	1284.00
μ(MoKα)	14.25 cm^{-1}
Diffractometer	unknown
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Crystal to Detector Distance	60 mm

Temperature	-98.0^{o}C
Scan Type	ω
Scan Rate	10 second frames
Scan Width	0.3 ^{o}
$2\theta_{max}$	51.4^{o}
No. of Reflections Measured	Total: 14598
	Unique: 5549 (R_{int} = 0.067)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.756690 - 0.934733)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.030
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	2388
No. Variables	319
Reflection/Parameter Ratio	7.49
Residuals: R; R_w; R_{all}	0.030; 0.028; 0.102
Goodness of Fit Indicator	0.80

Max Shift/Error in Final Cycle	0.01
Maximum peak in Final Diff. Map	0.43 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.61 $e^-/Å^3$

A4. Cp'_2CeF

An orange crystal of Cp'_2CeF having approximate dimensions of 0.32 x 0.21 x 0.08 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker APEX[6] CCD area detector with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 5046 centered reflections with $I > 10\sigma$ in the range $4.60 < 2\theta < 49.20^\circ$ corresponded to a primitive monoclinic cell with dimensions:

$a = 9.2297(5)$ Å

$b = 34.078(2)$ Å $\quad \beta = 109.864(1)^\circ$

$c = 10.9325(6)$ Å

$V = 3234.0(3)$ $Å^3$

For Z = 4 and F.W. = 625.95, the calculated density is 1.28 g/cm^3. The systematic absences of:

h0l: $h+l \neq 2n$

0k0: $k \neq 2n$

uniquely determine the space group to be $P2_1/n$ (#14). The data were collected at a temperature of -102 ± 1°C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10.0 seconds per frame. Data were integrated by the program SAINT[7] to a maximum 2θ value of 49.5°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP[8]. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[9]. (Tmax = 1.00, Tmin = 0.87). The structure was solved by direct methods[10] and expanded using Fourier techniques[11]. Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated based on the expected geometry at each carbon. Centroids of the cyclopentadienyl rings (C101 and C102) were included, but not refined. The final cycle of full-matrix least-squares refinement was based on 5515 observed reflections ($I > -10.00\sigma(I)$) and 325 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.044$, $R_w = 0.065$, and GOF = 1.31. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\Sigma\, w\,(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.79 and -0.40 $e^-/Å^3$, respectively.

Empirical Formula	$C_{34}H_{58}FCe$
Formula Weight	625.95
Crystal Color, Habit	orange, block
Crystal Dimensions	0.32 X 0.21 X 0.08 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.2297(5)Å
	b = 34.078(2) Å
	c = 10.9325(6) Å
	β = 109.864(1)^o
	V = 3234.0(3) $Å^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.285 g/cm^3
F_{000}	1316.00
μ(MoKα)	14.32 cm^{-1}
Diffractometer	Bruker APEX CCD
Radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated

Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
$2\theta_{max}$	49.5^{o}
No. of Reflections Measured	Total: 16694 Unique: 5636 (R_{int} = 0.024)
Corrections	Lorentz-polarization Absorption (Tmax = 1.00 Tmin = 0.87)
Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma\ w\ (\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>-10.00\sigma(I)$)	5515
No. Variables	325
Reflection/Parameter Ratio	16.97
Residuals: R; Rw; Rall	0.044 ; 0.065; 0.044
Goodness of Fit Indicator	1.31
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	$0.79\ e^{-}/\text{Å}^3$

Minimum peak in Final Diff. Map -0.40 $e^-/Å^3$

A5. $Cp'_2CeC_6F_5$

A fragment of an orange crystal of $Cp'_2CeC_6F_5$ having approximate dimensions of 0.31 x 0.37 x 0.10 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART[6] CCD area detector with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 6124 centered reflections with $I > 10\sigma$ in the range $4.40 < 2\theta < 49.35^o$ corresponded to a primitive triclinic cell with dimensions:

a =	10.1400(9) Å	α =	85.860(1)°
b =	12.213(1) Å	β =	81.146(1)°
c =	15.632(1) Å	γ =	78.336(1)°

V = 1871.7(3) $Å^3$

For Z = 2 and F.W. = 774.01, the calculated density is 1.37 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (#2). The data were collected at a temperature of -151 ± 1°C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3°counted for a total of 10.0 seconds per frame. Data were integrated by the program SAINT[7] to a maximum 2θ value of 49.3°.The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP[8]. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[9]. (Tmax = 1.00, Tmin = 0.51). The structure was solved by direct methods[10] and expanded using Fourier techniques.[11] Non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated based on the expected geometry at each carbon. Centroids of the cyclopentadienyl rings (C101 and C102) were included but not refined. The final cycle of full-matrix least-squares refinement was based on 5912 observed reflections ($I > -10.00\sigma(I)$) and 415 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.076$, $R_w = 0.101$, and GOF = 1.52. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\Sigma\, w\, (|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.15 and -1.60 $e^-/\text{Å}^3$, respectively.

Empirical Formula	$C_{40}H_{58}CeF_5$
Formula Weight	774.01
Crystal Color, Habit	orange, block
Crystal Dimensions	0.31 X 0.37 X 0.10 mm
Crystal System	triclinic
Lattice Type	Primitive

Lattice Parameters	a = 10.1400(9)Å	
	b = 12.213(1) Å	
	c = 15.632(1) Å	
	α = 85.860(1)^{o}	
	β = 81.146(1)^{o}	
	γ = 78.336(1)^{o}	
	V = 1871.7(3) Å^{3}	
Space Group	P-1 (#2)	
Z value	2	
D_{calc}	1.373 g/cm^{3}	
F_{000}	802.00	
μ(MoKα)	12.66 cm^{-1}	
Diffractometer	Bruker SMART CCD	
Radiation	MoKα (λ = 0.71069 Å)	
	graphite monochromated	
Detector Position	60.00 mm	
Exposure Time	10.0 seconds per frame.	
Scan Type	ω (0.3 degrees per frame)	
$2\theta_{max}$	49.3^{o}	
No. of Reflections Measured	Total: 9440	Unique: 5913
(R_{int} = 0.035)		
Corrections	Lorentz-polarization	

	Absorption (Tmax = 1.00 Tmin = 0.51)
Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	$1/\sigma^2(Fo) = 4Fo^2/\sigma^2(Fo^2)$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>-10.00σ(I))	5912
No. Variables	415
Reflection/Parameter Ratio	14.25
Residuals: R; Rw; Rall	0.076 ; 0.101; 0.076
Goodness of Fit Indicator	1.52
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.15 e$^-$/Å^3
Minimum peak in Final Diff. Map	-1.60 e$^-$/Å^3

A6. $(Cp'_2Ce)_2CH_2O \bullet C_7D_8$

A fragment of an orange block-like crystal of $C_{69}H_{118}Ce_2O \bullet C_7H_8$ having approximate dimensions of 0.28 x 0.18 x 0.05 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART[6] CCD area detector with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 3760 centered reflections with $I > 10\sigma(I)$ in the range $4.46 < \theta < 47.55^{\circ}$ corresponded to a primitive monoclinic cell with dimensions:

$a = 18.566(3)$ Å $\alpha = 90^{\circ}$
$b = 10.453(2)$ Å $\beta = 108.009(2)^{\circ}$
$c = 19.192(3)$ Å $\gamma = 90^{\circ}$
$V = 8876(1)$ Å^3

For Z = 4 and F.W. = 668.00, the calculated density is 1.253 g/cm^3. Analysis of the systematic absences allowed the space group to be uniquely determined to be P 2/n. The data were collected at a temperature of -173(2) K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 20 seconds per frame. Data were integrated by the program SAINT[7] to a maximum θ value of 24.70°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP[8]. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS[9]. (Tmax = 0.9374, Tmin = 0.7107). Of the 14766 reflections that were collected, 5799 were unique ($R_{int} = 0.0883$); equivalent reflections were merged. No decay correction was applied. The structure was solved by direct methods[12] and expanded using Fourier techniques[13]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the cyclopentadienyl ligands were included but not refined. The hydrogen atom on the formyl group was located in the difference Fourier map and refined isotropically. The final cycle of full-matrix least-squares refinement[14] was based on 5799 reflections (all data) and 362 variable parameters and converged (largest parameter shift was 0.012 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo| = 0.0716 \text{ for 3864 data with } I > 2\sigma(I)$$

$$wR_2 = [(\Sigma w (|Fo|^2 - |Fc|^2)^2 / \Sigma w |Fo|^2)]^{1/2} = 0.1424$$

The standard deviation of an observation of unit weight[15] was 1.051. The weighting scheme was based on counting statistics and included a factor (q = 0.0777) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.651 and -1.801 $e^-/Å^3$, respectively. All calculations were performed using the SHELXTL[16] crystallographic software package of Bruker Analytical X-ray Systems Inc.

Empirical Formula	$C_{69}H_{118}Ce_2O$
Formula Weight	668.00
Crystal Color, Habit	orange, block
Crystal Dimensions	0.28 x 0.18 x 0.05 mm
Crystal System	Monoclinic
Lattice Type	primitive

Lattice Parameters	a = 18.566(3) Å
	b = 10.453(2) Å
	c = 19.192(3) Å
	α = 90 °
	β = 108.009(2) °
	γ = 90°
	V = 3541.9(9) $Å^3$
Space Group	P 2/n
Z value	4
D_{calc}	1.253 g/cm^3
F_{000}	1412
μ(MoKα)	1.31 cm^{-1}
Diffractometer	SMART
Radiation	MoKα (λ = 0.71073 Å)
	graphite monochromated
Detector Position	60.00 mm
Exposure Time	20 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	24.70°
No. of Reflections Measured	Total: 14766
	Unique: 5799 (R_{int} = 0.0883)
Corrections	Lorentz-polarization

	Absorption (Tmax = 0.9374, Tmin = 0.7107)
Structure Solution	direct (SHELXS-97 (Sheldrick, 1990))
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2$
Least Squares Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (qP)^2 + 0.000P]$ where $P = [F_o^2 + 2F_c^2]/3$
q-factor	0.0777
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>2.00\sigma(I)$)	3864
No. Variables	362
Reflection/Parameter Ratio	10.67
Residuals: R; wR_2; Rall	0.0716; 0.1424; 0.1207
Goodness of Fit Indicator	1.052
Max Shift/Error in Final Cycle	0.012
Maximum peak in Final Diff. Map	1.651 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.801 $e^-/Å^3$

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8. XPREP:(v 6.12) Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (2001)
9. SADABS: Bruker-Nonius Area Detector Scaling and Absorption v. 2.05 Bruker Analytical X-ray Systems, Inc.: Madison, WI (2003).
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12. XS: Program for the Solution of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99).
13. XL: Program for the Refinement of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)
14. Least-Squares: Function minimized: $\Sigma w\,(|Fo|^2 - |Fc|^2)^2$
15. Standard deviation of an observation of unit weight:

$$[\Sigma w(|Fo|^2 - |Fc|^2)^2/(N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

16. XP: Molecular Graphics program. Part of the SHELXTL Structure Determination Package. Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)