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A New Strategy for Ring Modification of Metallocenes: Carbodiimide Insertion into the η^5-Y$-$C$_5$H$_5$ Bond and Subsequent Isomerization

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Unusual insertion of carbodiimide into the Y$-$Cp (Cp = C_5H_5) bond and isomerization of the resulting cyclopentadienyl (Cp)-substituted amidinate complex to the amidino-substituted Cp complex have been established, representing an efficient and simple method for ring modification of sensitive metallocenes. All products, including the rare four-center interaction precursor of the insertion, have been characterized by X-ray structural analyses.

Metal complexes containing cyclopentadienyl (Cp) and related ligands have played a dominant role in the development of organometallic chemistry[1] and continue to attract considerable attention because of their great potential as catalysts[2] or useful intermediates in the synthesis of chemicals and materials with interesting properties.[3] It has been proven that variation of the substituents attached to the Cp ring could lead to specific changes in the catalytic activity and chemical and physical properties.[4] Therefore, significant effort has been focused on the development of new functionalized Cp structures and new methods for their construction.

It is well-known that highly stable functionalized Cp complexes of some transition metals can be synthesized by the direct modification of the corresponding Cp complexes via metallacyclopentadienylation,[5] C$-$H addition,[6] or Friedel$-$Crafts reactions.[7] However, attempts to integrate the functionality on lanthanocene frameworks by similar methods proved very difficult because of the increased Lewis acidity of the lanthanides, leading to facile decomposition pathways under the reaction conditions involved.[8] Consequently, exploring the methods for the ring modification of lanthanocene complexes has for a long time been totally neglected. The substituted Cp ligands are generally preformed at the preceding ligand stage in lanthanocene synthesis,[9] with the exception of few examples based on the side-chain modification of prefunctionalized Cp ligands.[10] This not only limits the substituent scope but also could require expensive and/or toxic reagents as well as laborious separations. Thus, the development of a basic strategy for the ring modification of sensitive metallocenes represents a highly valuable but significantly challenging subject.

Several pioneering works have shown that the large steric congestion can impart unusual insertion reactivity to the rings in $(C_5Me_4R)_3Ln$,[11] $(C_{13}H_9)_2Ln(THF)_2$[12] and $(C_9H_7)_2Yb(THF)_2$ (THF = tetrahydrofuran).[13] However, it has been unclear

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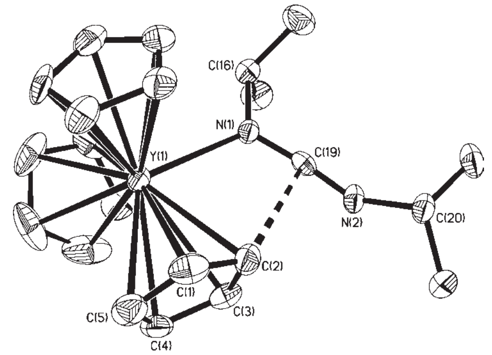


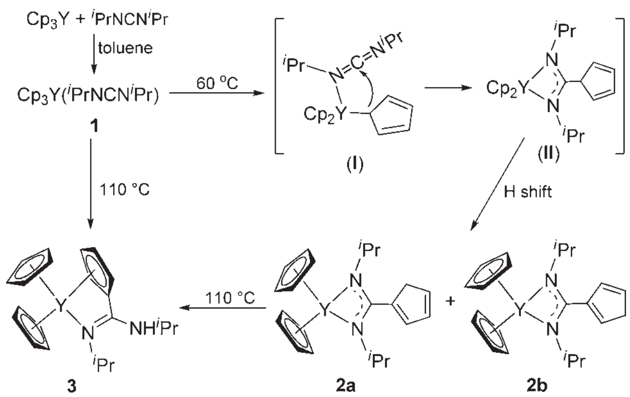
Figure 1. Thermal ellipsoid (30%) plot of **1**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)−N(1) 2.547(6), N(1)−C(19) 1.248(8), N(2)−C(19) 1.203(8), C(19)−C(2) 3.091; C(19)−N(1)−C(16) 114.9(5), C(19)−N(2)−C(20) 136.5(7), N(2)−C(19)−N(1) 172.6(7), C(19)−N(1)−Y(1) 120.3(4), sum of the angles at N(1) 359.8(4).

whether the resulting ring-substituted ligands could regenerate the η^5-Ln−carbocycle bonding. As a part of our continuing research on the insertions of unsaturated substrates into organolanthanides and subsequent hydrogen-shift isomerizations of the related products,[14] we herein report the first insertion of carbodiimide into the η^5-Y−Cp bond and its application in the synthesis of mixed Cp−lanthanide complexes from simple Cp_3Ln, representing a new strategy for functionalization of the Cp rings bound to metals. Furthermore, this work, for the first time, provides the solid-state structural information on the unstable four-center interaction precursor of insertions of organolanthanides.

Treatment of Cp_3Y with 1 equiv of ^{i}PrNCN^{i}Pr in toluene at room temperature gave the adduct Cp_3Y(^{i}PrNCN^{i}Pr) (**1**) in 89% isolated yield. The structure of **1** was determined by single-crystal X-ray diffraction (Figure 1), featuring the donating coordinated ^{i}PrN=C=N^{i}Pr moiety. A significant structural feature is the close proximity of one ring C atom to the carbodiimide C(sp) atom. The C(2)···C(19) distance of 3.091 Å is significantly shorter than the sum of the van der Waals radii of two C atoms (3.4 Å), which clearly prefigures the viability of the migration of the Cp group from Y to C(19) as a synthetic methodology.[15]

Although a four-center interaction has long been postulated as the prerequisite initial step in a variety of insertion reactions of organolanthanides and additional support for this proposal has also been forthcoming from theoretical calculations,[16] there is no information about their solid-state structures because of the high reactivity of the precursors used. Clearly, in the present case, coordination of a metal center to carbodiimide promotes polarization of the N=C=N segment and places the Cp group and the inserting molecule in close proximity, which facilitates the formation of the four-membered insertion transition state.[16a]

Scheme 1



Significantly, heating a toluene solution of **1** at 60 °C gave **2** as colorless crystals in 37% yield. The modest isolated yield reflects the high solubility of **2** rather than the formation of any byproducts. The ^{1}H NMR spectrum indicates that **2** exists as two isomers of the three possible isomers due to double-bond migration in the Cp ring, as shown in Scheme 1.[17] Moreover, it was found that **2a** is in equilibrium with **2b** and the position of equilibrium depends on the temperature. For example, **2a** and **2b** are present in a 2.2:1 ratio at 60 °C, while a 1.78:1 ratio of **2a** and **2b** is observed at ambient temperature.

Remarkably, **2a** and **2b** were quantitatively converted to the amidino-substituted Cp complex **3**, when heated at 110 °C in toluene for 48 h (Scheme 1). Given the fact that either stronger acidic guanidine[14d] or weaker acidic amine[18] compared to amidines abstracts easily one Cp group from Cp_3Ln, the transformation of **2** to **3** was totally unexpected and similar isomerization has not been observed in metallocene chemistry before. Generally, only transmetalation reactions can lead to a change of the bonding mode of the functionalized Cp ligands from a heteroatom to a Cp ring.[19]

Noticeably, the transformation of **1** to **3** can also take place in the solid state at 110 °C. However, the reaction of Cp_3Y with ^{i}PrN=C=N^{i}Pr in THF did not occur even under refluxing conditions; instead, Cp_3Y(THF) was formed. Furthermore, dissociation of **1** to Cp_3Y(THF) and ^{i}PrN=C=N^{i}Pr was observed when it was treated with THF. These results demonstrate that precoordination of carbodiimide to the metal plays a key role in the insertion process. The molecular structures of **2a** (Figure 2) and **3** (Figure 3) were confirmed by X-ray structural analyses.

The conversion of a toluene-d_8 solution of **1** to **2** was monitored by ^{1}H NMR spectroscopy (Figure 4). The ^{1}H NMR spectra of **1** clearly showed that all of the rings retained their η^5-orientation in solution at low temperature. When the sample was warmed to 25−60 °C, **1** was slowly transformed to **2**; in this process, a new peak at 6.1 ppm attributable to the presence of trace amounts of a fluxional η^1-Cp intermediate was observed.[20] The spectroscopic data clearly showed that

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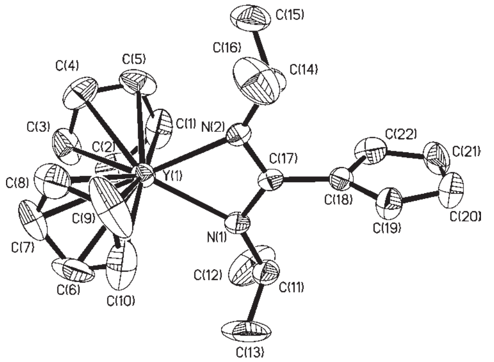

Figure 2. Thermal ellipsoid (30%) plot of **2a**. H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Y−N(1) 2.311(4), Y−N(2) 2.318(4), C(17)−C(18) 1.495(7), C(18)−C(19) 1.379(7), C(19)−C(20) 1.432(7), C(20)−C(21) 1.394(8), C(21)−C(22) 1.441(8), C(18)−C(22) 1.434(7), N(1)−C(17) 1.325(6), N(2)−C(17) 1.318(5); N(1)−Y−N(2) 58.1(1), sum of the angles at C(17) 360.0(5), sum of the angles at C(18) 360.1(5).

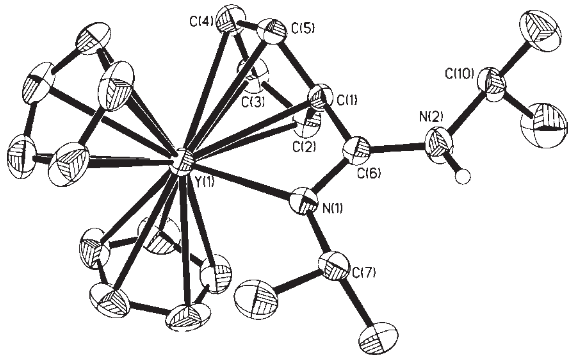

Figure 3. Thermal ellipsoid (30%) plot of **3**. H atoms [except at N(2)] are omitted for clarity. Selected bond distances (Å) and angles (deg): Y−N(1) 2.503(3), N(1)−C(6) 1.289(4), N(2)−C(6) 1.349(5), C(1)−C(6) 1.478(5), C(1)−C(2) 1.395(5), C(2)−C(3) 1.394(5), C(3)−C(4) 1.378(6), C(4)−C(5) 1.388(5), C(1)−C(5) 1.399(5); N(1)−Y−C(1) 54.16(11), C(6)−N(1)−C(7) 118.3(3), C(7)−N(1)−Y 141.1(2), C(6)−N(1)−Y 100.5(2), sum of the angles at C(6) 360.1(4).

two different resonance sets for the ^{i}Pr, η^5-C_5H_5, and pendent C_5H_5 groups, which correspond respectively to **2a** and **2b** with ca. a 2.2:1 molar ratio of **2a**/**2b**, appeared and their strength increased with time, while the resonances at 6.00 and 1.00 ppm, which are respectively assigned to the η^5-C_5H_5 and CH_3 protons of **1**, weakened gradually. Furthermore, the clean transformation of **2a** and **2b** to **3** was also established by heating the resulting mixture at a elevated temperature of 80 °C, where the peaks at 6.2, 6.0, 5.4, 4.14, 3.06, 2.41, 1.0, and 0.98 ppm of relative intensity 2:10:2:1:1:1:6:6 consistent with the presence of **3** appeared in company with the disappearance of the resonances attributable to **2a** and **2b**.

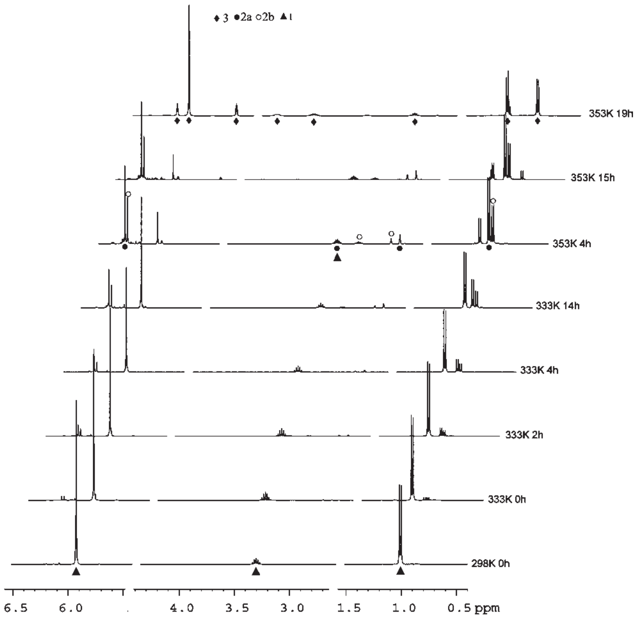

Figure 4. Time- and temperature-dependent ^{1}H NMR study for the progress of conversion of **1** to **2a**, **2b**, and **3** in toluene-d_8.

In summary, we have demonstrated, for the first time, that insertion of carbodiimide into the sterically less demanding Cp ligand attached to lanthanides is a viable fundamental reaction type for Cp_3Ln complexes. The identification of intermediate species indicates that insertion proceeds by the initial coordination of carbodiimide to the lanthanoene center, causing a close proximity to one Cp group and the subsequent $\eta^5 \leftrightarrow \eta^1$ interconversion of the ring ligand. Tandem insertion and isomerization provides an efficient and convenient method for the synthesis of heteroleptic lanthanocenes directly from simple Cp_3Ln precursors. The present strategy for the modification of Cp ligands provides potential advantages over the classical electrophilic metallocene substitution routes when the complex is sensitive to acids or contains a functional group that has a preference for reaction with the electrophiles over the C−H bond of the Cp rings.

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Supporting Information Available: Detailed experimental procedures, full characterization data, and X-ray data for **1**, **2a**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.