

Reactions of Cp₃Y with Benzophenone: A Simple and Efficient Method for Transformation of Unsubstituted Cyclopentadienyl to Bridged *ansa*-Cyclopentadienyl/Alkoxyl Ligand

Xiaoqing Li,[†] Jianquan Hong,[†] Ruiting Liu,[†] Linhong Weng,[†] and Xigeng Zhou^{*,†,‡}

[†]Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, People's Republic of China, and [‡]State Key Laboratory of Organometallic Chemistry, Shanghai 200032, People's Republic of China.

Received August 2, 2010

Insertion of benzophenone into the Y–Cp (Cp = C_5H_5) bond and two new reactivity patterns of the Cp-substituted alkoxide complexes have been established, by which an efficient and convenient method for conversion of the unsubstituted cyclopentadienyl group to the single-carbon-bridged *ansa*-cyclopentadienyl/alkoxyl ligand by using a simple ketone as the functionalizing reagent is developed. All products including the four-center interaction precursor of the insertion have been characterized by X-ray structural analyses.

Controlling metal coordination environment and reactivity through modification of supporting ligation is a common theme in organometallic chemistry. Cyclopentadienyl and substituted cyclopentadienyl groups are ubiquitous functional ligands in organometallic compounds that have been extensively used as catalysts in organic synthesis¹ and olefin polymerizations.² In addition, metallocene complexes are also valuable as synthetic intermediates in organic synthesis,³ as precursors to a wide range of functional materials,⁴ and as potential pharmaceuticals;⁵ thus considerable effort continues to be directed toward the development of new substituted cyclopentadienyl ligands and new methods for their construction.⁶ The major goal is to obtain new functionalized metallocenes with required properties and develop simpler and even cheaper methods for synthesis of metallocenes. Among a variety of approaches for their preparation, the preparation of functionalized cyclopentadienyl complexes directly from simple cyclopentadienyl complexes and unsaturated substrates is arguably one of the best possibilities from both economic and environmental viewpoints, because it avoids the initial synthesis of substituted cyclopentadienes that undergo easily dimerization, an additional step that sometimes involves expensive or toxic reagents and requires chemical separations. Although many viable methods for ring modification of metallocene complexes of late transition metals have been developed, including functionalization via metallacyclopentadienylation,⁷ direct C-H addition,⁸ and Friedel-Crafts reactions,⁹ they usually require the use of additives such as Lewis acids and strong bases and/or generate the acidic byproducts, which are not suitable for sensitive metallocene complexes having labile metalcyclopentadienyl bonds.¹⁰ Thus, the development of a fundamental strategy capable of functionalizing the unsubstituted

^{*}To whom correspondence should be addressed. E-mail: xgzhou@ fudan.edu.cn.

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cyclopentadienyl ligand of sensitive organometallic compounds represents a highly desirable but significantly challenging target.

Recently, precedent for insertion of carbodiimide into the η^1 -indenyl-zirconium bond of $\{\sigma: \eta^5 - (C_9H_6)C_2B_9H_{10}\}Zr\{\eta^2 - \eta^2 - \eta^2$ (RN)₂C(NMe₂)}(THF) and subsequent regeneration of the η^1 -substituted indenyl-zirconium bond has shed light on ring modification of sensitive metallocenes.¹¹ However, attempts to expand upon this class of reaction to the η^5 cyclopentadienyl system have been unsuccessful.12 In addition, whether the resulting ring-substituted ligands could regenerate the η^{5} -bonding mode remains unexplored in organometallic chemistry of main and rare earth metals, although it has proven successful for a few large sterically crowded lanthanocenes such as $(C_5Me_4R)_3Ln$,¹³ (Flu)₂Ln(THF)₂ (Flu = fluorenyl),¹⁴ and $(Ind)_2 Yb(THF)_2 (Ind = indenyl)^{15}$ and a variety of metallocene complexes of main metals¹⁶ to undergo insertions with unsaturated substrates. During our research into the reactivity of organolanthanides toward ketenes,¹⁷ we observed in one case that Cp₃Y can undergo unusual tandem insertion/cycloaddition/ isomerization reactions with diphenyl ketene (Scheme 1).¹⁸ These reactions have proven to be efficient as the key step in

the synthesis of the bifunctionalized cyclopentadienyl ($C_5H_3(C-(O)=CPh_2)_2$) trianion yttrium complex. However, very poor yield is obtained for the synthesis of the monofunctionalized cyclopentadienyl ($C_5H_4C(O)=CPh_2$) dianion complex by this protocol. Furthermore, there is little information concerning the insertion intermediates.

In order to obtain further insight into the insertion reactivity of Cp₃Y and to develop the synthetic strategy for the one-pot synthesis of bridged ansa-cyclopentadienyl/alkoxy complexes from aunsubstituted cyclopentadienyl complex precursors, we became interested in the possibility of inserting a ketone into the η^5 -Y-C₅H₅ bond and the in situ transformation of the resulting insertion products to functionalized cyclopentadienyl complexes and hoped that an investigation of the difference between ketones and ketenes might lead to the development of conditions for the insertions of Cp₃Y in improved yield, selectivity, substrate scope, and avoidance of the use of strong bases. Herein, we report an efficient direct conversion of the Cp group bound to the yttrium into the single-carbon-bridged ansa-cyclopentadienyl/ alkoxyl dianion ligand with Ph₂CO as a functionalizing reagent.

Treatment of Cp₃Y with 1 equiv of Ph₂CO in toluene at room temperature clearly indicated the formation of the adduct Cp₃Y(OCPh₂) (1), albeit in a low yield with a large amount of Cp₃Y recovered (Scheme 2). Attempts to obtain the ¹H NMR information of 1 were impaired due to the partial dissociation of coordinated Ph₂CO molecules in common lab solvents. The molecular structure of 1 is shown in Figure 1, featuring the donating coordinated Ph₂CO moiety. The C(1)···C(27) distance is 3.675 Å, which clearly prefigures the possibility of 1 as a precursor of the welldocumented four-centered insertion transition state.¹⁹

In marked contrast to $Ph_2C=C=O$,¹⁸ heating a 1:1 mixture of Cp₃Y and Ph₂CO in toluene at 85 °C for 8 h, after recrystallization in THF, gave the Cp-substituted alkoxide complexes 2 as colorless crystals in 67% yield, indicating that one Ph₂CO molecule inserts into a Y-Cp bond to afford the initial product (2c), which subsequently undergoes tautomerization via a formal 1,3- or 1,5-hydrogen shift of cyclopentadiene, forming the stable alkoxide complexes 2a and **2b**, as shown in Scheme 2. However, the reaction of Cp_3Y with Ph₂CO in THF did not occur even with prolonged heating at 70 °C. Furthermore, the dissociation of 1 to Cp₃Y(THF) and Ph₂CO was observed when it was treated with THF. This demonstrates that the precoordination of ketone to the metal plays a key role in the insertion process. Clearly, in the present case the coordination of a metal center to Ph₂CO not only promotes the polarization of the carbonyl but also places the Cp group and the inserting molecule into close proximity, which facilitates the formation of the fourmembered insertion transition state.¹⁹

The ¹H NMR spectrum indicates that **2** exists mainly as two isomers, **2a** and **2b** (ca. 1.38:1), of the three possible isomers due to double-bond migration in the cyclopentadiene ring. Furthermore, the structure of **2a** (Figure 2) was unambiguously determined via X-ray crystallography analysis. The pseudotetrahedral coordination sphere about Y in **2a** is composed of two centers of η^{5} -Cp rings, one oxygen atom from the newly formed alkoxide ligand and one THF

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DC(20)

C(20')



Figure 1. Thermal ellipsoid (30%) plot of 1. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): $C(1)\cdots C(27)$ 3.675, Y(1)-O(1) 2.342(3), O(1)-C(1) 1.222(4), Y(1)-C(24) 2.682(5), Y(1)-C(25) 2.686(5), Y(1)-C(26) 2.715(5), Y(1)-C(27) 2.688(5), Y(1)-C(28) 2.680(5), C-(1)-O(1)-Y(1) 170.3(3).

oxygen. The 1.408(5) Å O(2)–C(11) distance is in the normal range of C–O single-bond distances. The bond angles around C(18) are consistent with sp² hybridization, while those around C(11) are consistent with sp³ hybridization.

To our delight, reaction of **2** with *n*-BuLi in THF gave selectively the *ansa*-bridged cyclopentadienyl/alkoxyl yttrium derivative $[CpY(\mu-\eta^{1}:\eta^{1}:\eta^{5}-OCPh_2C_5H_4)]_2$ (**3**) in 71% isolated yield. The formation of complex **3** might be interpreted as metalation of the free cyclopentadiene moiety of **2** followed by intramolecular ligand exchange between Y³⁺ and Li⁺, as shown in Scheme 2. The eliminated CpLi is structurally confirmed by X-ray diffraction analysis.²⁰ A view of the crystallographic structural data for **2a** (Figure 2) indicates that during crystal packing there is no positional preference for the pendent cyclopentadienyl group and the second phenyl

Figure 2. Thermal ellipsoid (30%) plot of 2a. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): O(2)-C(11) 1.408(5), Y(1)-O(2) 2.046(3), Y(1)-O(3) 2.345(3), C(11)-O(2)-Y(1) 171.6(3).

group, and both are disordered over two sites, related by a rotational displacement.

Assembling the anionic substituent on the cyclopenta dienyl ring judiciously has become an attractive strategy for the fine-tuning of stability, catalytic activity, selectivity, and reactivity of organometallic compounds.²¹ Despite significant recent advances in this field, examples of metal complexes bearing linked *ansa*-cyclopentadienyl/alkoxyl dianion ligands remain scarce.²² This is somewhat surprising, considering both the extensive use of the amido analogues^{2a,b,21} in organometallic chemistry and the expectation that the nature of the related ligand system may be adjusted by variation of either the cyclopentadienyl moiety, the alkoxyl

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Figure 3. Thermal ellipsoid (30%) plot of 3. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)-O(1) 2.326(2), Y(1)-O(1A) 2.262(2), O(1)-C(11) 1.436(4), C(6)-C(11) 1.530(6), O(1A)-Y(1)-O(1) 74.7(1), O(1)-C(11)-C(6) 105(1).

group, the ansa-bridge, or a combination thereof. There does not appear to be a large effort to expand upon this class of compounds, which is probably due to the lack of viable synthetic methodologies to access these complexes. The anionic side chains of cyclopentadienyl ligands are mainly introduced before application in the synthesis of constrained geometry complexes (CGCs). The approach of introducing an ansa-bridge by a reaction in the ligand sphere of a suitable metallocene precursor to create CGCs is much less developed and gives access only to a limited variety in terms of prefunctionalized cyclopentadienyl complexes.²³ To the best of our knowledge, there are as yet no generally satisfactory routes to the direct introduction of the anionic substituent on the unsubstituted Cp ring. Obviously, the present reaction provides an efficient means of obtaining CGCs containing the bridged ansa-cyclopentadienyl/alkoxyl ligands.

An X-ray crystallographic study unambiguously confirmed **3** to be a dimer structure (Figure 3). The newly formed *ansa*-bridged cyclopentadienyl/alkoxyl (C₅H₄CPh₂O) ligand interacts with the two yttrium atoms in a μ - η^1 : η^1 : η^5 -bonding mode. The average Y–O distance of 2.294(2) Å is comparable to the corresponding value in Cp₄Y₃[C₅H₃(COCPh₂)₂-1,2][C₅H₃(COCPh₂)₂-1,2]Li(THF), 2.301(3) Å.¹⁸ The O–Y–O and Y–O–Y angles are in the normal range.²⁴

Considering that the use of *n*-butyllithium as a deprotonating reagent should set limit for the utility of this reaction when the system contains another functional group that is sensitive to ^{*n*}BuLi, together with the inspiration of the intramolecular thermal proton migration between the guanidinate ligands,²⁵ we decided to try to deprotonate the pendant cyclopentadiene



Figure 4. Thermal ellipsoid (30%) plot of 4. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)-O(2) 2.207(4), Y(1)-O(3) 2.386(4), Y(1)-O(1) 2.444(4), Y(2)-O(2) 2.183(4), Y(2)-O(1) 2.222(4), O(1)-C(1) 1.430(6), C(1)-C(14) 1.511(7); O(2)-O(4) 2.90(1); O(2)-Y-(1)-O(3) 78.2(2), O(2)-Y(1)-O(1) 70.6(2), O(3)-Y(1)-O(1) 138.6(2), O(2)-Y(2)-O(1) 75.4(2), C(1)-O(1)-Y(2) 142.8(4), Y(2)-O(1)-Y(1) 102.1(2), Y(2)-O(2)-Y(1) 111.7(2), O(1)-C-(1)-C(14) 104.2(5).

of 2 by intramolecular cyclopentadiene abstraction. Gratifyingly, heating 2 in refluxing toluene, after recrystallization in THF, gave one new bridged cyclopentadienyl/alkoxyl complex, $Cp_{3}Y_{2}(\mu-OH)(\mu-\eta^{1}:\eta^{1}:\eta^{5}-OCPh_{2}C_{5}H_{4})(THF)_{2}$ (4), accompanied with the liberation of diphenylfulvene and cyclopentadiene. The formation of 4 might be interpreted as the tandem intra- and interligand hydrogen migration of 2, for which the former led to the elimination of diphenylfulvene, while the latter led to deprotonation and recoordination of the pendant cyclopentadiene substituent, as shown in Scheme 2. Complex 4 can also be obtained by directly heating a 1:1 mixture of Cp₃Y and Ph₂CO in refluxing toluene followed by recrystallization in THF. The results demonstrate that the resulting cyclopentadienesubstituted alkoxyl ligand can undergo intramolecular proton exchange with the unsubstituted cyclopentadienyl ligand, and thus direct functionalization of unsubstituted cyclopentadienyl ligand with ketone without the presence of any additive is also feasible. In addition, the reaction provides the first authentic structural evidence for the transformation of an alkoxide ligand to a hydroxide one.

The formation of diphenylfulvene and cyclopentadiene was identified by GC-MS analysis of the organic products. The X-ray analysis shows that complex 4 is a dinuclear structure (Figure 4), and one $Ph_2C(O)^-$ anion functionality is appended to a cyclopentadienyl ring via a formal hydrogen substitution. The structural features of the newly formed *ansa*-bridged cyclopentadienyl/alkoxide ligand are essentially identical to those of complex 3. The presence of the hydroxyl is also confirmed by the hydrogen-bond interaction between it and the THF molecule.

In summary, the insertion of benzophenone into the η^{5} -Ln–Cp bond and two new reactivity patterns of Cp-substituted alkoxyl complexes have been revealed, by which an efficient and convenient conversion of an unsubstituted cyclopentadienyl ligand into a single-carbon-bridged *ansa*-cyclopentadienyl/ alkoxyl ligand is developed. The results described here not only provide good insight into the versatility of insertions of

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Cp₃Ln but also demonstrate that the tandem insertion and hydrogen transfer reaction of Cp₃Ln with unsaturated substrates is a practical and versatile strategy for the direct introduction of the *ansa*-bridge on the cyclopentadienyl ring in the synthesis of CGCs, which are difficult to achieve by other means, from the viewpoints of operational simplicity and assembly efficiency.¹⁸ Furthermore, this work presents authentic structural evidence for the transformation of an alkoxide to a hydroxide. Further investigations on the scope and limitations of the functionalization of the cyclopentadienyl and related rings of sensitive lanthanocenes and synthetic applications of this reaction are underway in our laboratory.

Experimental Section

General Procedures. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or glovebox techniques. All organic solvents (including deuterated solvents for the NMR measurements) were predried over sodium wire and distilled from sodium/benzophenone under dinitrogen prior to use. Benzophenone and *n*-BuLi (2.5 M in *n*-hexane) were purchased from Aldrich Chemical Co. and used as received. Elemental analyses for C and H were carried out on a Rapid CHN-O analyzer. ¹H NMR data were obtained on a Bruker DRX-400 NMR spectrometer.

Preparation of Cp₃Y(OCPh₂) (1). Ph₂CO (0.169 g, 0.93 mmol) was added to a solution of Cp₃Y (0.264 g, 0.93 mmol) in toluene (20 mL). The color changed from colorless to red immediately. After stirring for 24 h at room temperature, the solution was concentrated to ca. 8 mL under reduced pressure and allowed to stand at -15 °C for several days. Red crystals of 1 (0.023 g, 5%) were separated with a large amount of Cp₃Y recovered. Anal. Calcd for C₂₈H₂₅OY (%): C, 72.10; H, 5.40. Found: C, 71.92; H, 5.23.

Preparation of Cp₂Y[(OCPh₂(C₅H₄)](THF) (2). Ph₂CO (0.182 g, 1.00 mmol) was added to a solution of Cp₃Y (0.284 g, 1.00 mmol) in toluene (20 mL). After stirring at 85 °C for 8 h, THF (10 mL) was added and the solution continued to stir for another 2 h. Then the solvents were removed under vacuum. The residue was washed with hexane and was redissolved in THF. Diffusion of hexane into the solution afforded complex 2 as colorless crystals. Yield: 0.361 g (67%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 7.59–7.18 (m, 10H, Ph), 6.76–6.38(m, 3H, C₅H₅_{suncoord}), 6.14 (s, 0.58 × 10H, C₅H₅), 6.12(s, 0.42 × 10H, C₅H₅), 3.34(t, 4H, THF), 3.10 (br s, 0.42 × 2H, C₅H₅_{suncoord}), 2.85 (br s, 0.58 × 2 H, C₅H₅_{suncoord}), 1.26–1.23 (m, 4H, THF). Anal. Calcd for C₃₂H₃₃O₂Y (%): C, 71.37; H, 6.18. Found: C, 71.21; H, 6.05.

Preparation of $[CpY(\mu-\eta^{1}:\eta^{1}:\eta^{5}-OCPh_{2}C_{5}H_{4})]_{2}$ (3). *n*-BuLi (2.5 M in hexane, 0.64 mL, 1.60 mmol) was added dropwise to a THF solution (20 mL) of 2 (0.862 g, 1.60 mmol) at -30 °C. After stirring for 30 min at -30 °C, the mixture was slowly warmed to room temperature and stirred overnight. THF was removed under vacuum, and the resulting solid was extracted with 20 mL

of toluene. Toluene was then removed under vacuum, and the resulting solid was redissolved in 3 mL of THF. Diffusion of hexane into the solution afforded complex **3** as colorless crystals. The residue was dissolved in THF, and diffusion of hexane to the solution afforded colorless crystals of $[C_5H_5Li]_n$. Yield: 0.455 g (71%). ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ 7.65–7.55 (m, 4H, Ph), 7.11–6.91 (m, 16H, Ph), 6.43 (s, 10H, C_5H_5), 5.93 (s, 2H, $-C_5H_4$), 5.69(s, 2H, $-C_5H_4$), 5.47 (s, 2H, $-C_5H_4$), 4.69(s, 2H, $-C_5H_4$). Anal. Calcd for $C_{46}H_{38}O_2Y_2$ (%): C, 69.01; H, 4.78. Found: C, 68.89; H, 4.63.

Preparation of Cp₃Y₂(μ-OH)(μ - η ¹: η ¹: η ⁵-OCPh₂C₅H₄)]-(THF)₂ (**4**). Ph₂CO (0.166 g, 0.91 mmol) was added to a stirred solution of Cp₃Y (0.258 g, 0.91 mmol) in toluene (20 mL). After stirring at 110 °C for 8 h, all volatile substances were removed under vacuum, and the residue was redissolved in THF and allowed to stand at -35 °C for several days. Colorless crystals of **4** were separated. Yield: 0.231 g (65%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 7.14–7.01 (m, 10H, Ph), 6.52 (s, 5H, C₅H₅), 6.24 (s, 1H, -C₅H₄), 6.07 (s, 5H, C₅H₅), 5.91(s, 1H, -C₅H₄), 5.86 (s, 1H, -C₅H₄), 5.75 (s, 1H, -C₅H₄), 5.60 (s, 5H, C₅H₅), 3.45 (t, 8H, THF), 1.40–1.33 (m, 8H, THF), 0.82 (s, 1H, OH). Anal. Calcd for C₄₁H₄₆O₄Y₂ (%): C, 63.08; H, 5.94. Found: C, 62.89; H, 5.82.

Crystal Structure Determination. Suitable single crystals were sealed under N₂ in thin-walled glass capillaries. X-ray diffraction data were collected on a SMART APEX CCD diffractometer (graphite-monochromated Mo K α radiation, $\phi-\omega$ scan technique, $\lambda = 0.71073$ Å). The intensity data were integrated by means of the SAINT program.²⁶ SADABS²⁷ was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package.²⁸ All non-hydrogen atoms were found from the difference Fourier syntheses and refined anisotropically. All hydrogen atoms were assigned in idealized positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program.

Acknowledgment. We thank the National Natural Science Foundation of China, 973 Program (2009CB825300), Shanghai Science and Technology Committee (No. 08dj1400100), and Shanghai Leading Academic Discipline Project (B108) for financial support.

Supporting Information Available: X-ray data for 1–4 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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