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Received March 17, 2010

Unprecedented tandem insertion/cycloaddition/isomerization reactions of Cp_3Y with diphenylketene have been revealed, by which a general method for assembling one or two anionic side chains to the cyclopentadienyl ring bound to lanthanide metals in a one-pot procedure is established.

Lanthanide complexes containing cyclopentadienyl and related ligands have played a dominant role in the development of organolanthanide chemistry¹ and continue to attract considerable attention because of their great potential as catalysts² or useful intermediates³ in the synthesis of chemicals and materials with interesting properties. The role of cyclopentadienyl ligands in the fine-tuning of the chemical and physical properties of organolanthanide compounds illustrates the need for the development of new functionalized cyclopentadienyl structures and new methods for their construction.^{2c,3c,4} It has been well known that many functionalized cyclopentadienyl complexes of transition metals can be synthesized by direct modification of the corresponding cyclopentadienyl complexes.⁵ In spite of

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considerable additional research efforts along these lines, no viable method for ring modification of lanthanocene complexes has been reported, with the exception of examples based on the side chain modification of prefunctionalized cyclopentadienyl ligands.⁶ The failure is mainly ascribed to the increased Lewis acidity of the lanthanide metals, leading to facile decomposition pathways under the reaction conditions involved.⁷ As a result, the substituents on the cyclopentadienyl ring are generally accreted before application in the lanthanocene synthesis,^{4,8} which not only limits the substituent scope but could also require expensive and/or toxic reagents as well as laborious separations. Therefore, the development of a basic strategy capable of constructing functionalized lanthanocene frameworks, especially the mixed cyclopentadienyl ring systems, directly from a rather simple lanthanocene precursor represents a highly desirable but challenging target.

ORGANOMETALLICS

Although organolanthanide complexes containing cyclopentadienyl and related ligands have been investigated extensively, the parent cyclopentadienyl (C_5H_5) ligand that is most important and ubiquitous in organolanthanide chemistry is usually an inert spectator ligand or a removed group in previously reported reactions of these complexes.^{1,9} As part of a continuing effort in our laboratory toward the development of new methods for synthesis of lanthanocene derivatives,⁹ we became interested in the possibility of developing a one-pot synthesis of functionalized cyclopentadienyl lanthanide complexes from a rather simple lanthanocene

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precursor. Herein, we report the first example of authenticated cyclopentadienyl-based reactions of lanthanocene complexes with ketene and their application in one-pot syntheses of mono- and difunctionalized cyclopentadienyl lanthanide derivatives directly from $(C_5H_5)_3Ln$ precursors, representing a new strategy for functionalization of the Cp rings bound to metals.

Treatment of Cp₃Y with 1 equiv of Ph₂CCO generated the doubly functionalized product **2** as the main metal-containing product with recovery of some Cp₃Y. Employment of Cp₃Y and Ph₂CCO in a 1:2 ratio led to the isolation of **2** in 85% yield (Scheme 1). Complex **2** was characterized by elemental analysis and spectroscopic methods. In the IR spectra of **2**, the carbonyl characteristic stretching frequency was observed at 1712 cm⁻¹. The ¹H NMR data for **2** were consistent with the incorporation of 2 equiv of Ph₂CCO. Furthermore, the formulation of compound **2** (Figure 1) was unambiguously determined via X-ray



Figure 1. Thermal ellipsoid (30%) plot of complex 2. Hydrogen atoms are omitted for clarity. Key bond lengths (Å) and angles (deg): Y(1)-O(1) 2.106(2), Y(1)-O(2) 2.340(2), O(1)-C(24) 1.327(4), O(2)-C(30) 1.208(4), C(17)-C(24) 1.360(4), C(24)-C(25) 1.513(4), C(25)-C(26) 1.513(4), C(26)-C(27) 1.327(4), C(27)-C(28) 1.496(4), C(28)-C(29) 1.544(4), C(29)-C(30) 1.541(4), C(28)-C(31) 1.575(4), C(30)-C(31) 1.541(4); O(1)-Y(1)-O(2) 78.6(1), sum of angles at C(30) 359.5(3).

crystallography analysis. The pseudotetrahedral coordination sphere about Y in **2** is comprised of two η^5 -cyclopentadienyl groups and two oxygen donors of the newly formed bicyclo-[3.2.0]heptenone-substituted enolate ligand. Within the diketone anion ligand, the C-C distances are in the normal range.

To our surprise, the simple coordination of THF can promote **2** to undergo intramolecular insertion of a carbonyl into the Y–O bond, forming the hemiketal complex **3**. The driving force might be from the ease of forming hemiketals and their stability. Compared to the well-known Ln–X (X = H, C, N, S) insertions, ^{8b,9f,9i–9k,10,11} examples of insertions of unsaturated molecules into Ln–O bonds are very rare,^{2a,3b,12} probably due to the high Ln–O bond enthalpy.¹³

It was unexpected that heating a toluene solution of 2 at 110 °C led to the ring-opening of the cyclobutanone, affording 4 in 65% isolated yield. To see if the four-membered-ring unit of complex 3 is also thermally sensitive, the thermal rearrangement of 3 was examined. Interestingly, complex 4could also be obtained by heating 3 in refluxing toluene. Cycloaddition and ring-opening reactions are essential tools for organic synthesis, offering not only substrate flexibility but also rapid increase of molecular complexity. It is unexpected that the cyclopentadienyl ligand bound to a rare earth metal undergoes a tandem insertion/cycloaddition with unsaturated molecules to form highly strained and acylated bicyclo[3.2.0]heptanone. To the best of our knowledge, the ring-opening mode of cyclobutanone shown herein is also unprecedented.¹⁴

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Figure 2. Thermal ellipsoid (30%) plot of complex 3. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)-O(1) 2.082(3), Y(1)-O(3) 2.325(4), O(1)-C(11) 1.324(5), O(2)-C(11) 1.483(5), O(2)-C(18) 1.364(5), C(11)-C(12) 1.599(6), C(12)-C(13) 1.575(6), C(13)-C(14) 1.461(7), C(13)-C(17) 1.560(6), C(11)-C(17) 1.537(6), C(14)-C(15) 1.314(7), C(15)-C(16) 1.503(6), C(16)-C(17) 1.542(6), C(16)-C(18) 1.499(6), C(18)-C(19) 1.340(6); O(1)-Y(1)-O(3) 92.97(14), O(1)-C(11)-O(2) 108.9(3).



Figure 3. Thermal ellipsoid (30%) plot of complex 4. Hydrogen atoms are omitted for clarity. Key bond lengths (Å) and angles (deg): Y(1)-O(1) 2.173(3), Y(1)-O(2) 2.183(3), O(1)-C(11) 1.248(5), O(2)-C(30) 1.246(5), C(29)-C(30) 1.414(6), C(11)-C(25) 1.437(6), C(25)-C(26) 1.371(6), C(26)-C(27) 1.354(6), C(27)-C(28) 1.375(7), C(28)-C(29) 1.400(6), C(25)-C(29) 1.487(6); O(1)-Y(1)-O(2) 80.4(1), sum of angles at C(11) 359.8(5), sum of angles at C(25) 360.0(5).

The molecular structures of **3** (Figures 2) and **4** (Figures 3) were also determined by X-ray structural analysis. Characteristically, the endocyclic C–C distances of the four-memberedring moiety in **3** are between 1.537(6) and 1.599(6) Å, which are similar to the values found in other four-membered-ring compounds(1.533–1.604 Å) and significantly longer than the common C–C single bond lengths due to ring tension.¹⁵ The view of the structure shows that compound **4** has two Ph₂CHC-(O) substituents bonded to the cyclopentadiene ring. The bond parameters of **4** indicate an appreciable degree of π -delocalization across the bifunctional ligands (Figure 3). Metric parameters within the (C₅H₅)₂Y part are unexceptional.



Figure 4. Thermal ellipsoid (30%) plot of 5. Key bond lengths (Å) and angles (deg): Y(1)-O(1) 2.362(3), Y(1)-O(2) 2.292(3), Y(1)-O(3) 2.334(3), Y(1)-O(4) 2.398(3), Y(2)-O(1) 2.296(3), Y(2)-O(3) 2.232(3), Y(3)-O(2) 2.269(3), Y(3)-O(4) 2.224(3), Y(1)-C(1) 2.783(5), Y(1)-C(2) 2.681(5), C(1)-C(6) 1.506(6), O(1)-C(6) 1.380(5), O(2)-C(20) 1.392(6), C(6)-C(7) 1.310(6), O(5)-Li(1) 1.86(1); O(2)-Y(1)-O(1) 83.9(1), O(3)-Y(1)-O(4) 83.4(1), sum of angles at C(6) 360.0(5).

Given the expectation that the cyclopentadiene bridge of **4** might undergo deprotonation, we were interested in the possibility of regeneration of the η^5 -bonding between the metal and the resulting bifunctionalized cyclopentadiene ring and thus developing a basic and versatile strategy for ring modification of cyclopentadienyl ligands bound to rare earth metals. Significantly, treatment of **4** with 2 equiv of LiMe gave a rare trianionic bifunctionalized cyclopentadienyl complex (**5**) in 43% isolated yield (Scheme 1). Single crystals of the byproduct C₅H₅Li (**6**)¹⁶ were also obtained by dissolving the residue in THF and subsequently diffusing hexane into the THF solution.

As shown in Figure 4, compound 5 contains three yttriums, one lithium, four unaltered C5H5 ligands, two trianionic difunctionalized C5H5 ligands, and one coordinated THF molecule. Three Y atoms are coordinated with two types of environments, in which the center Y(1) is bonded to four enolate oxygen atoms, one η^5 -cyclopentadienyl, and one bridging η^2 cyclopentadienyl, while the Y(2) and Y(3) are coordinated to two enolate oxygen atoms and two η^5 -cyclopentadienyl ligands to form a distorted tetrahedral geometry, respectively. The Li⁺ ion is coordinated by a bridging η^5 -C₅H₃(C(O)CPh₂)₂ ligand and one THF molecule. Each of four enolate oxygen atoms bridges two Y atoms. One difunctionalized cyclopentadienyl ligand is bonded to four metals, while another is bonded to three. The Y(1) is respectively linked to Y(2) and Y(3) by two oxygen bridges. The Y-O bond distances are between 2.224(3) and 2.398(3) A, and the average Y-O distance of 2.301(3) A is comparable with the values reported for other Y-O(bridging)distances.¹⁷ The Y(1)-C(1) and Y(1)-C(2) distances of 2.783(5) and 2.681(5) Å are significantly shorter than the corresponding values in $[(C_5H_5)_2Pr(\mu_2-\eta^5:\eta^2-C_5H_5)]_4$ (av 3.04 Å)¹⁸ and

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 $[(C_5H_4Me)_2La(\mu_2-\eta^5:\eta^2-C_5H_4Me)]_4$ (av 3.033(6) Å),¹⁹ when the difference in metallic radii is considered. This difference is due to the chelating effect of the side chains. The structural features within the two enolate units of the bifunctionalized cyclopenta-dienyl ligands are essentially identical.

To confirm that complex 2 was formed by the insertion and subsequent cycloaddition (Scheme 1, path A) rather than by 1,2-cycloaddition of one ketene function to a C5H5 ring followed by insertion of a second ketene function into a Y-C bond (Scheme 1, path B), we first checked the hydrolyzed products of the fast 1:1 reaction of Cp₃Y with Ph₂CCO at -30 °C for 15 min by LC analysis, indicating the presence of a small amount of Ph₂CHCOC₅H₅ without the observation of 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one. However, attempts to isolate the intermediate 1 were unsuccessful. Furthermore, we examined whether the cycloaddition of 1 with Ph2CCO could be prevented by a suitable base (e.g., alkyllithium) and thus if it should offer the opportunity to explore a new simple, one-pot route to assemble linked cyclopentadienyl/enolate lanthanide complexes from a simple Cp₃Ln precursor. To our delight, reaction of Cp₃Y with Ph₂CCO in the presence of LiMe in toluene/THF and subsequent fractional recrystallization in THF/toluene/ hexane gave the first linked cyclopentadienyl enolate lanthanide complex, $[Cp_3Y_2(\mu-O)(\mu-\eta^1:\eta^1:\eta^5-OC(CPh_2)C_5H_4)]_2Li_2(THF)_8$ (8), in 25% isolated yield accompanied by the elimination of C_5H_5Li (6) and unexpected allene product 7. The formation of complex 8 might be interpreted as one PhCCO insertion into the $Y-C_5H_5$ bond and subsequent deprotonation followed by the elimination of CpLi and $Ph_2C=C=C_5H_4$ (7), as shown in Scheme 2. Compound 7 was confirmed by GC-MS analysis of the organic products. It is well known that lithium alkyls do not abstract the hydrogen on the C5H5 ring directly bonded to a lanthanide center;^{7c} therefore, the possibility that compound $\bf 8$ results from the ring metalation and subsequent addition with ketene can be excluded.

An X-ray crystallographic study unambiguously confirmed **8** to be a tetrametallic structure (Figure 5). Coordinated THF molecules allow the lithium ion to be of preferred dissociated state. The linked cyclopentadienyl/enolate dianion ligands coordinate to two yttrium atoms through one bridging oxygen



Figure 5. Thermal ellipsoid (30%) plot of complex 8. Key bond lengths (Å) and angles (deg): Y(1)-O(2A) 2.199(4), Y(1)-O(2) 2.220(5), Y(1)-O(1) 2.769(5), Y(2)-O(1) 2.170(6), Y(2)-O(2) 2.147(4), C(3)-C(6) 1.497(11), C(6)-C(7) 1.364(10), O(1)-C(6) 1.351(9); O(1)-C(6)-C(7) 123.6(8), O(1)-C(6)-C(3) 113.2(7), C(7)-C(6)-C(3) 123.1(8), sum of angles at O(1) 329.0(4), sum of angles at O(2), 359.9(2).

and η^5 -cyclopentadienyl. The coordination geometry at Y(2) is best described as a distorted tetrahedron, while that at Y(1) is a distorted trigonal bipyramid. The average Y–O(μ_3 -oxide) bond length in **8** is 2.189 Å, which is slightly longer than that observed for the μ_3 -oxide group in [(C₅Me₄SiMe₃)Y]₄(μ_3 -O)₂(μ -H)₄-(THF) (av 2.161 Å).²⁰ The Y(2)–O(1) distance of 2.170(6) Å is in the low end of the range (2.206–2.290 Å) typical for [Cp₂Y(μ -OR)]₂.²¹ Characteristically, there is a very weak interaction between Y(1) and O(1).

In summary, a series of unprecedented reactions of $(C_5H_5)_3$ -Ln with diphenylketene have been established. Furthermore, by applying these new reactions as the key step, we have developed an efficient and versatile method for assembling one and two anionic side chains on the sensitive lanthanocene frameworks in a one-pot procedure, which are impossible to carry out by other methods. Further studies into the scope and limitations of the

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functionalization at the cyclopentadienyl and related rings of sensitive lanthanocenes are underway.

Experimental Section

General Procedures. All manipulations were conducted under a nitrogen-filled 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. $(C_5H_5)_3Y^{22}$ and Ph_2CCO^{23} were prepared according to literature methods. Melting points were determined in sealed nitrogen-filled capillaries and were not corrected. Elemental analyses for C and H were carried out on a Rapid CHN-O analyzer. Infrared spectra were obtained on a Nicolet FT-IR 360 spectrometer with samples prepared as Nujol mulls. ¹H NMR data were obtained on a Bruker DRX-400NMR spectrometer.

Preparation of $(C_5H_5)_2Y(\eta^2-[OC(CPh_2-4)-(Ph_2-7,7)-(O-6)-{3.2.0}]$ (2). To a 20 mL toluene solution of $(C_5H_5)_3Y$ (0.375 g, 1.32 mmol) was added Ph₂CCO (0.512 g, 2.64 mmol) at -30 °C. The solution changed color from colorless to red immediately. After being stirred for 30 min, the mixture was warmed to room temperature and continued to stir for 12 h. Then, the solution was concentrated and cooled to -15 °C for several days to afford **2** as orange crystals. Yield: 0.755 g (85%). Mp: 210–212 °C (dec). ¹H NMR (400 MHz, C₆D₆, 25 °C): 7.81(d, 2H, Ph), 7.79 (d, 2H, Ph), 7.38–7.04 (m, 16H, Ph), 6.42 (brs, 5H, C₅H₅), 5.93–4.99 (brs+m, 6H, C₅H₅+CH=C), 5.14 (m, 1H, CH=C), 4.06 (m, 1H, CH), 3.62 (m, 1H, CH), 3.56 (t, 1H, CH). IR (Nujol): 3056 m, 1712vs, 1596s, 1575vs, 1560vs, 1439s, 1327m, 1282s, 1262vs, 1209m, 1008vs, 965m, 912m, 846m, 774vs, 749vs, 704vs, 668s cm⁻¹. Anal. Calcd for C₄₃H₃₅O₂Y (%): C, 76.78; H, 5.24. Found: C, 76.15; H, 5.19.

Preparation of $(C_5H_5)_2$ **Y**(**OCOC**₃₃**H**₂₅)(**THF**) (3). Recrystallization of **2** (0.397 g, 0.59 mmol) in a mixed solvent of THF and *n*-hexane afforded **3** as colorless crystals. Yield: 0.338 g (77%). Mp: 150–152 °C (dec). ¹H NMR (400 MHz, C₆D₆, 25 °C): 7.77(d, 2H, Ph), 7.34–7.01 (m, 18H, Ph), 6.14 (s, 10H, C₅H₅), 5.80 (t, 1H, CH), 5.25 (t, 1H, CH), 4.11 (t, 1H, CH), 3.63 (t, 1H, CH), 3.57–3.43 (m, 5H, CH + THF), 5.84 (m, 4H, THF). IR (Nujol): 3053m, 2927s, 2853s, 1625s, 1598s, 1465m, 1444s, 1314vs, 1255m, 1202m, 1137m, 1040m, 1016m, 958m, 940m, 838m, 778vs, 733m, 704m, 607m cm⁻¹. Anal. Calcd for C₄₇H₄₃-O₃Y (%): C, 75.80; H, 5.82. Found: C, 75.55; H, 5.69.

Preparation of $(C_5H_5)_2Y[\eta^{1:}\eta^{1-}C_5H_3(COCHPh_2)_2-1,2]$ (4). Method A: A 20 mL toluene solution of 2 (0.841 g, 1.25 mmol) was warmed to 110 °C and stirred for another 8 h at this temperature. The solution changed color from red to dark red slowly. Then, the solution was cooled to room temperature and concentrated. After storing at -15 °C for one week, 4 was isolated as yellow crystals (0.549 g, 65%). Mp: 245–247 °C (dec). ¹H NMR (400 MHz, C₆D₆, 25 °C): 7.61 (d, 2H, CH), 7.23 (d, 8H, Ph), 7.11 (t, 8H, Ph), 7.04 (m, 4H, Ph), 6.29 (t, 1H, CH), 5.99 (s, 2H, CHPh_2), 5.84 (s, 10H, C₅H₅). IR (Nujol): 3052m, 1553vs, 1289m, 1254m, 1108s, 1057s, 1031m, 1010s, 941s, 850m, 820m, 778vs, 739vs, 610vs, 628s cm⁻¹. Anal. Calcd for C₄₃H₃₅O₂Y (%): C, 76.78; H, 5.24. Found: C, 76.32; H, 5.20. Method B: Following the same procedure described for method A, heating 3 (0.275 g, 0.37 mmol) in refluxing toluene afforded 4 (0.102 g) in 41% yield.

Preparation of $(C_5H_5)_4Y_3[\mu-\eta^{1}:\eta^{1}:\eta^{5}-C_5H_3(COCPh_2)_2-1,2]$ - $[\mu - \eta^{1}: \eta^{2}: \eta^{5} - C_{5}H_{3}(COCPh_{2})_{2} - 1, 2]Li(THF)$ (5). MeLi (1.6 M in hexane, 1.70 mL, 2.72 mmol) was added dropwise to a toluene solution (20 mL) of 4 (0.915 g, 1.36 mmol) at -30 °C. After stirring for 30 min at -30 °C, the mixture was slowly warmed to room temperature and an orange precipitate was slowly formed. The solution was removed and the precipitate was dissolved in 20 mL of THF. THF was removed under vacuum, and the resulting solid was extracted with 40 mL of toluene. The extraction was evaporated to ca. 10 mL, and pale yellow crystals of 5 · 1/2toluene (0.304 g, 43% based on Y) were obtained at room temperature. The residue was dissolved in THF, and diffusion of *n*-hexane to the solution afforded colorless crystals of $[C_5H_5Li]_n$ (6). Mp: 207–209 °C (dec). IR (Nujol): 3072w, 1616s, 1591s, 1307m, 1264w, 1188s, 1092s, 1041m, 1013m, 941s, 773s, 700m cm⁻¹. Anal. Calcd for C_{93.5}H₇₈-LiO₅Y₃ (%): C, 72.21; H, 5.06. Found: C, 72.02; H, 5.01.

Synthesis of $[(C_5H_5)_3Y_2(\mu_3-O)(\mu-\eta^1;\eta^1;\eta^5-C_5H_4COCPh_2)]_2$ -[Li(THF)₄]₂ (8). To a solution of $(C_5H_5)_3Y$ (0.291 g, 1.02 mmol) in a mixed solvent of THF (10 mL) and toluene (30 mL) was added Ph₂CCO (0.200 g, 1.02 mmol) at 0 °C. After the reaction mixture was stirred for 5 min, LiCH₃ (1.60 M, 0.64 mL) was added at 0 °C. The solution was slowly warmed to ambient temperature and continued to stir for 24 h. The solution was then concentrated to ca. 8 mL under reduced pressure. Yellow crystals of 8 • THF were obtained by vapor diffusion of hexane into the solution. Yield: 0.125 g (25% based on Y). Mp: 242 °C (dec). IR (Nujol): 3054w, 1541s, 1340m, 1260m, 1042s, 1013w, 890m, 764s, 700m cm⁻¹. Anal. Calcd for C₁₀₄H₁₃₀Li₂O₁₃Y₄ (%): C, 63.81; H, 6.69. Found: C, 63.42; H, 6.56.

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.²⁴ SADABS²⁵ 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.²⁶ 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. Two heavily disordered solvated THF in the cationic part of **8** were found. All calculations were performed using the Bruker Smart program.

Acknowledgment. We thank the NNSF of China, 973 program (2009CB825300), NSF of Shanghai, and Shanghai Leading Academic Discipline Project for financial support (B108).

Supporting Information Available: CIF files for complexes of 2–5 and 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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