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Facile Reversible Benzophenone Insertion into Rare-Earth Metal Pyrazolato Complexes

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Abstract: Treatment of the homoletic CeIV pyrazolato complex \([\text{Ce}{{(\text{Me}_2\text{pz})}_2}]_2\) (\(\text{Me}_2\text{pz} = 3,5\)-dimethylpyrazolato) with benzophenone (bp) led to the formation of an \(\text{Me}_2\text{pz}\)-substituted diphenylmethoxy-(N,O)-chelating ligand (pdpm), possibly metal-templated through initial coordination of bp to the cerium atom and subsequent bp insertion into the Ce–N(\text{Me}_2\text{pz}) bond. This coordination/insertion process was shown to be reversible, leading to a complex sequence of equilibria involving multiple degrees of insertion/de-insertion and association/dissociation. The dependency on temperature and the amount of bp of all equilibria was revealed, with insertion/association of bp being favored at low temperatures and de-insertion/dissociation preferentially occurring at elevated temperatures. Such sets of equilibria were also observed for the treatment of trivalent complexes \([\text{Ln}{{(\text{Me}_2\text{pz})}_3}{}_{(\text{thf})}]_2\) (\(\text{Ln} = \text{La}, \text{Ce}, \text{Lu}\)) with bp. Through structural analysis, the trivalent complexes were shown to be less effective in the bp-to-pdpm conversion than the CeIV derivative, giving direct evidence of how an increase in rare-earth Lewis acidity aids in ketone anchorage and concomitant conversion. The observed equilibria seem to also apply to the more illustrious organocerium systems. The conversion of bp into the corresponding tertiary alcohol by the routinely employed reagent \(\text{CeCl}_3/\text{nBuLi}\) is the most selective when termination of the reaction by hydrolysis is performed at lower temperatures, with a reagent ratio \(\text{bp}/\text{CeCl}_3/\text{nBuLi}\) of 1:1:1.

Introduction

With the ability to readily access both trivalent and tetravalent oxidation states, cerium stands out from the other rare-earth elements (Ln), especially regarding its versatile application in organic transformations.[1] Aside from the ubiquitous use of ceric ammonium nitrate (CAN) as a strong single-electron oxidant,[1c,2] CeIII reagents have also been shown to be highly effective in the conversion of ketones to alcohols (prominent reagents involve CeCl3/LIR mixtures where \(R = \text{alkyl}\)).[3] It is generally accepted that the Lewis-acidic CeIII center draws the ketone into coordination, which weakens the C=O bond, thus encouraging nucleophilic attack by coligands.[4] However, this reasoning does not explain why cerium outperforms other more Lewis-acidic trivalent rare-earth elements of smaller ionic radii,[3a,3b] even if the increase in performance is only slight. Considering that treatment of CeIII complexes with 1,4-benzoquinone can give CeIV hydroquinolate complexes[5] by two single-electron-transfer processes (which have been recently shown to be reversible),[6] it is conceivable that (ordinary) ketone anchorage at CeIII similarly occurs. Nevertheless, based on the Lewis acidity criterion alone, CeIV complexes would be superior reagents to anchor ketones in such transformations. However, as CeIV complexes are generally strongly oxidizing agents of varied stability,[6d,6f] the presence of reducing coligands applied in these transformations (e.g., alkyl, hydrido), would cause spontaneous reduction of the CeIV ion, making such investigations infeasible.

We recently introduced dialkyl-substituted pyrazolato ligands to CeIV chemistry,[6] isolating the dimeric complex \([\text{Ce}{{\text{IV}}-\text{(Me}_2\text{pz})}_2}]_2\) (1; \(\text{Me}_2\text{pz} = 3,5\)-dimethylpyrazolato). Complex 1 was remarkably stable under argon, and as pyrazolate/pyrroles are known nucleophiles,[8] it was envisioned that this complex would provide an excellent platform to study ketone anchorage and subsequent nucleophilic attack at CeIV. In contrast to paramagnetic CeIII-based systems,[9] the diamagnetic nature of CeIV also permits detailed NMR spectroscopic investigations, providing deeper insight into rare-earth-metal-based insertion processes.[10a,1d] Benzophenone (bp) was selected as the ketone, not only because it does not engage in any obvious redox chemistry with cerium,[10b] but also because its role in insertion reactions is of wider interest, especially in F-block chemistry.[11]

We found that addition of bp to a solution of \([\text{Ce}{{(\text{Me}_2\text{pz})}_2}]_2\) generates a complex series of equilibria (Scheme 1), involving association/dissociation of bp into the coordination sphere of cerium, and insertion/de-insertion of bp into the cerium–N(\text{Me}_2\text{pz}) bond. Such equilibria are not exclusive to the tetravalent oxidation state and could be observed for the trivalent complexes \([\text{Ln}{{(\text{Me}_2\text{pz})}_3}{}_{(\text{thf})}]_2\) (\(\text{Ln} = \text{La}, \text{Ce}, \text{Lu}\)), as well. The equi-
libria were further shown to be relevant to the CeCl₃/nBuLi-mediated conversion of bp into the corresponding tertiary alcohol.

Results and Discussion

Initial Identification of the Equilibrium Sequence

Treatment of 1 with 1 equiv. of bp in C₆D₆ caused a color change from dark red to red-orange. Analysis by ¹H NMR spectroscopy at 25 °C indicated a mixture of species, namely [Ce(Me₂pz)₂(bp)] (1·bp), the anticipated [Ce(Me₂pz)₂(pdpm)] [2·pdpm = (3,5-dimethylpyrazol-1-yl)diphenylmethanolate], and a di-pdpm species [Ce(Me₂pz)₂(pdpm)₂] (3), in a ratio of approximately 3.5:34:1 (Scheme 1, Figure S1). Apparently, the formation of 2 involved a nucleophilic attack of an Me₂pz ligand on the carbonyl group, generating this new N,O ligand – a result of bp association (1·bp) and coordination to the cerium atom and concomitant bp insertion into the Ce–N(Me₂pz) bond.

Underpinning the Equilibrium Sequence

It was observed that the choice of solvent dramatically influenced the association/dissociation of the pdpm ligand; for example, when bp is added to 1 in [D₈]THF, no formation of pdpm was observed (Figure S4). This is likely due to saturation of the coordination sphere of the cerium atom by THF, inhibiting bp coordination and subsequent insertion into the Ce–N(Me₂pz) bond. Therefore, the equilibria were only studied in non-coordinating solvents. If the C₆D₆ reaction mixture was warmed, the resonances for 3 decreased (giving 2 and 1·bp, pushing the equilibrium to the left; Scheme 1) and were completely removed at 45 °C. Continued heating, above 75 °C, caused complete bp de-insertion (Figure S5), with the broadened signals indicating that a degree of bp association to and dissociation from the coordination sphere of the cerium atom is likely occurring. In contrast to heating, cooling of the reaction mixture to 10 °C gave an increase in both 2 and 3 at the expense of 1·bp, giving a total ratio of 1·bp/2/3 of 1.4:23:1.

To further examine the equilibria at even lower temperature, C₆D₆ was displaced by [D₈]toluene (giving the same total volume). It was revealed that, upon cooling to –15 °C, the resonance attributable to 1·bp decreased, and resonances for both 2 and 3 increased (Figure S6). At –35 °C, all 1·bp was consumed, leaving a 2/3 ratio of 2:1. Upon further cooling to –65 °C, the integrations for 3 increased along with resonances for dimeric [Ce(Me₂pz)₂]₂ (1), while those of 2 decreased, indicating that once the source of bp is exhausted, the equilibrium sequence (1 → 1·bp, 1·bp → 2 etc) comes to a halt. However, at this point, the system can undergo a ligand exchange process to generate the two more stable species 1 and 3, rather than intermediate compounds (1·bp, 2, and 2·bp).[14] This is further evident from the observation that, although 2 was the major

Scheme 1. Equilibria occurring from the reactions between [Ce(Me₂pz)₄] (1) and benzophenone (bp) in C₆D₆ or [D₈]toluene: cerium–bp association (1a–3a) and dissociation (1d–3d), and bp insertion (1i–3i) and de-insertion (1ii–3ii) into the Ce–N(Me₂pz) bond.
species in solution at ambient temperature, attempted crystallization of 2 from an n-hexane solution failed, giving only crystalline 3 and 1. The solid-state structure of 1 was different from that of the toluene solvate reported previously,[6] featuring Me2pz ligands with different bridging modes, namely 1k(N,N’):2k(N) and 1k(N,N’):2k(N,N’), as opposed to two 1k(N,N’):2k(N,N’) Me2pz ligands in 1-toluene (Figure S7). The structural elucidation of 3 confirmed an eight-coordinate cerium atom, featuring two cisoid-η3(N,N,N′) Me2pz ligands and two N,O-chelating pdpm ligands (Figure 1). Analysis of the pdpm bond lengths confirmed the reduction of the C=O bond of bp (2 or 4 equiv.), crystallization at ambient temperature only gave bp: 196.5 ppm).[18]

For single crystals of 3 dissolved in [D8]toluene, the temperature-dependent equilibria were examined between –80 and 80 °C by 1H NMR spectroscopy. At 10 °C in [D8]toluene, the ratio of complexes 2/3 was approximately 1:1 (Figure S10), highlighting the influence of the additional equivalent of bp on the equilibrium sequence. When cooled to –80 °C, only the resonances of 3 were identified (Figures S11, S12), while heating to –80 °C afforded complete bp de-insertion from the Ce–N bonds, but there appeared to be some degree of bp association with the cerium center (Figures S13, S14). Furthermore, there were obvious color changes observed when the sample was held at different temperatures, corresponding to different positions of the equilibria. At lower temperatures, the solution lightened in color, giving either an orange solution (corresponding to the color of crystals of 3), or a light-yellow one, when more bp was added. At higher temperatures, the solution was dark-red, indicating the absence of pdpm ligands. This was also evident by UV/Vis spectroscopy (Figure S15), where, at 80 °C, the reaction mixture of 3 in toluene gave a spectrum almost identical to that of neat 1 at the same temperature, further supporting the complete de-insertion of bp and reformation of the Ce–N(Me2pz)2 bond at 80 °C.

Considering complex 3 was isolated from the reaction between 1 and bp (4 equiv.), it appears that bp/Me2pz→pdpm conversion by 1 is limited to two bp units upon crystallization. Due to the high stability of 3, neither an additional association/insertion (Scheme 1; 3a/3i) nor ligand rearrangement to form [Ce(Me2pz)2(pdpm)2](4) is feasible at these temperatures. It was initially assumed that this was due to steric constraints at the CeIV center; however, we were curious if either putative [Ce(Me2pz)2(pdpm)2](4), or even perhaps the product of exhaustive insertion, [Ce(pdpm)3]5, could form in solution at lower temperatures in the presence of additional amounts of bp. Thus, reaction mixtures containing 3 and bp (1 equiv. bp: Figures S16–S19; 2 equiv. bp: Figures S20, S21) were dissolved in [D8]toluene, in the presence of an innocent standard (FeCp2). The reaction mixtures were then incrementally cooled to –80 °C and analyzed by 1H NMR spectroscopy. In either case, complex 3 appeared to be the major species at lower temperatures; however, resonances attributable to two other species could be detected as well. From their respective integrations, one set of resonances was ascribed to targeted 4, but the other species had a pdpm/Me2pz ratio of 1:3, with the presence of 1 equiv. of coordinated bp (signal at δ = 7.60 ppm), next to the resonance of free bp (δ = 7.65 ppm). This suggested the formation of a [Ce(Me2pz)2(pdpm)(bp)]-type species (2-bp, as shown in Scheme 1, 2a). This is surprising, considering it is not formed when a solution of crystalline 3 is cooled to –80 °C. When more bp was added, the resonances attributable to 2-bp increased, and with 10 equiv. of bp, 2-bp was the major species at –80 °C (Figure S23). We had a closer look at the reaction mixture of 3 and bp (2 equiv.), to possibly explain why 2-bp is favored in

![Figure 1. Molecular structure of [Ce(Me2pz)2(pdpm)2](3). Ellipsoids are shown at the 50 % probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ce1–O1 2.173(2), Ce1–N1 2.564(2), Ce1–N3 2.026(5) and 2.023(5), Ce1–N4 2.371(2), C6–O1 1.378(3); O1–Ce1–N1 63.78(5), Cent(N3/4)–Ce1–N3(Me2pz) 93.66(7). Despite the formation of a favorable CeIV–alkoxide bond, and a five-membered ring, either the addition of another equivalent of bp to 2 (in C7D6: Figures S8, S9), or the dissolution of crystals of 3 in [D8]toluene (Figure S10), caused rapid de-insertion (Scheme 1, 2ii) and dissociation (Scheme 1, 2d) of bp from the second pdpm ligand, supporting the proposed complicated sequence of equilibria. Again, 2 appeared to be the major species in solution at ambient temperature, with a ratio for complexes 2/3 of 4.5:1, and at these temperatures, only trace amounts for 1-bp were observed (Figure S8).

Thus, in the absence of 1, and as the formation/disassembly of transient 2-bp is rapid at ambient temperature, the remaining bp stays unbound to the cerium atom. This is supported by both 1H and 13C NMR spectroscopic analysis of the C6D6 solution, with the ortho-H resonance for the liberated bp (δ = 7.69 ppm) matching that of free bp (cf. 7.56 ppm in 1-bp), and the C=O resonance being detected at δ = 196.1 ppm (Figure S9; further comparisons: [Ce4+YC1(bp)]: C=O: δ = 206.6 ppm vs. free bp: 196.5 ppm).[18]
this system over the dissolution of crystalline 3 at the same temperature. Warming the reaction mixture from −80 to −70 °C showed decreases in both 3 and bp (Figure 2, orange and blue lines), whereas 2-bp and 4 increased only slightly (Figure 2, green and yellow lines). Thus, as not all of 3 is being converted into 4 or 2-bp, and as the integrations for bp also decreased, there is likely another intermediate species present, such as $[\text{Ce}(	ext{Me}_2\text{pz})_3(\text{pdpm})_2(\text{bp})](3\text{-bp}, \text{not shown in Figure 2}). The broadened features in the NMR spectrum could be attributed to 3-bp, due to the rapid dissociation/association of bp. It is not until the solution is warmed beyond −70 °C that resonances for 4 significantly increase[19] and those of 2-bp decrease. Therefore, between −80 and −70 °C, bp can coordinate to the cerium atom, but only above −70 °C can rapid bp activation occur. Further, the resonances of 1 were not observed, indicating that ligand-exchange processes are absent in the presence of bp.

$\text{Fig. 2.} \ ^1\text{H} \text{NMR spectroscopic integrations of complexes 2, 2-bp, 3, 4, and bp from the reaction mixture between 3 and bp (2 equiv.) at various temperatures (integrations were calculated relative to FeCp}_2\text{, for easier comparison; integrations shown for bp are presented with one less equivalent, e.g., at −40 °C, shown ratio = 0.2, actual ratio = 1.2).}$

The entire equilibrium sequence can be rationalized by two distinct processes (Figure 2), one involving the coordination of bp to the cerium atom (i.e., the bp association processes, $1 \rightarrow 1\text{-bp, } 2 \rightarrow 2\text{-bp, } 3 \rightarrow 3\text{-bp}$) and the other involving the bp/Me$_2$pz → pdpm conversion (i.e., the bp insertion processes, $2\text{-bp} \rightarrow 3, 3\text{-bp} \rightarrow 4$). However, although the third equivalent of bp allows the formation of 4 at low temperatures, it also plays an additional role, which undermines the insertion process. When more bp is present, the likelihood of bp coming into the coordination sphere of the cerium atom increases (i.e., $3 \text{+ bp} \rightarrow 3\text{-bp}$), and upon coordination, it can either form pdpm (for one pdpm ligand, Scheme 2; $3 \text{+ bp} \rightarrow 2\text{-bp + bp}$), namely the free bp initiates a bp exchange process, which is promoted in the presence of additional bp. This is assumed to be rapid and unnoticeable above −40 °C, but at lower temperatures, this bp exchange process outruns the insertion process, leading to an increased formation of 2-bp when more bp is present (Scheme 2; iii). Further, it should be noted that under no conditions the product of exhaustive insertion $[\text{Ce}(\text{pdpm})_4]$ was observed. However, examination of this equilibrium is limited, as when the sample is warmed beyond −60 °C, the bp insertion equilibrium proceeds (slowly removing 2-bp and forming 4 via 3; Scheme 2; iii), and above −50 °C, the typical temperature-dependent behavior of these equilibria dominates (Scheme 1; 3a/3d). Also notably, the formation of the pdpm ligand appears to occur only in the presence of a metal center (templating effect), as treatment of Me$_2$pzH with bp resulted in no reaction (Figure S24).

$\text{Scheme 2. Possible path for the formation of 2-bp and 4 from 3, and the bp-induced de-insertion and exchange: (i) bp exchange within the pdpm ligand; (ii) pdpm dissociation induced by incoming bp and the consequential association/dissociation equilibrium; (iii) formation of 4.}$

Comparisons with Trivalent Complexes

To further determine the capacity of Ce$^{IV}$ in ketone conversion, and whether such equilibria are restricted to the tetravalent oxidation state, we compared the activation ability of the corresponding trivalent pyrazolate complex species toward bp. Accordingly, $[\text{Ln} \text{(Me}_2\text{pz})_2(\text{thf})](\text{Ln} = \text{La (6a), Lu (6b)})[20]$ and $[\text{Ce} \text{(Me}_2\text{pz})_3] \text{[7]}$ were treated with bp (3 equiv. for Ce; 2 equiv. for La, Lu). Unfortunately, complexes 6 and 7 were poorly soluble in non-coordinating solvents and thus were treated with bp in THF prior to crystallization from n-hexane (Ln = La, Ce) or cyclohexane (Lu). Indeed, bp insertion also occurred for all Ln$^{III}$ derivatives, affording dimeric species $[\text{Ln}_2 \text{(Me}_2\text{pz})_2(\text{pdpm})_n]$, $[\text{Ln} = \text{La (8La), Ce (8Ce)}]$, the solid-state structures are shown in Figure 3 (left; Ln = Ce) and Figure S28 (Ln = La) and $[\text{Lu} \text{(Me}_2\text{pz})_2(\text{pdpm})_n]$ (9Lu, Figure 3 (right)), with pdpm/Me$_2$pz ratios of 1:1 and 1:2, respectively. The pdpm ligands are located exclusively in bridging positions, with either three bridging pdpm and three terminal Me$_2$pz ligands (8La, 8Ce) or two bridging pdpm and Me$_2$pz ligands ($\mu$-$\eta^1$-$\eta^1$)$^1$ and two terminal Me$_2$pz ligands (9Lu). Attempted $^1\text{H} \text{NMR spectroscopic investigations for 8La and 8Ce were difficult because of their poor solubility, but it was observed that both complexes rapidly liberate bp, indicative of equilibrium sequences similar to those of 1. In the case of lanthanum, complete bp de-insertion and dissociation occurred at ambient temperature, giving $[\text{La} \text{(Me}_2\text{pz})_2]$ as determined by elemental analysis. It was only complex 9Lu, featuring the strongest Lewis acid center of the Ln$^{III}$ derivatives, that re-

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Figure 3. Molecular structure of \([\text{Ce}_2(\text{Me}_2\text{pz})_3(\text{pdpm})_3]\) (8Ce, left) and \([\text{Lu}(\text{Me}_2\text{pz})_2(\text{pdpm})_2]\) (9Lu, right). Ellipsoids are shown at the 50 % probability level; hydrogen atoms and phenyl rings of pdpm are omitted for clarity. Selected bond lengths [Å] and angles [°] for 8Ce: Ce1–O1 2.441(3), Ce1–O2 2.373(3), Ce1–O3 2.481(3), Ce1–N1 2.615(4), Ce1–N3 2.586(4), Ce1–N7 2.474(5), Ce1–N8 2.456(4), Ce2–O1 2.380(3), Ce2–O2 2.543(3), Ce2–O3 2.502(3), Ce2–N5 2.595(4), Ce2–N9 2.587(4), Ce2–N10 2.435(4), Ce2–N11 2.470(5); Ce1–O1–Ce2 98.20(12), Ce1–O2–Ce2 95.62(12), Ce1–O3–Ce2 93.99(11), Ce1–O1–C6 109.6(3), O1–Ce1–N1: 62.88(5). Selected bond lengths [Å] and angles [°] for 9Lu: Lu1–O1 2.194(2), Lu1–N1 2.390(2), Lu1–N3 2.419(2), Lu1–N4 2.392(2), Lu1–N6 2.297(2), C6–O1 1.386(3); Lu1–O1–Lu1′ 94.785(4), N1–Lu1–O1 68.46(7).

tained its constitution in solution, although it was poorly soluble. The \(^1\)H NMR resonance for the pdpm \([\text{C}(4)–\text{H of the Me}_2\text{pz component}]\) ligand in complex 9Lu appeared at a value identical to that of 2, suggesting that the pdpm ligand of 2 may also be bridging in solution, as these resonances are distinct from the equivalent pdpm C–H resonance observed in mononuclear 3.

The decreased pdpm/Me\(_2\)pz ratios observed for the trivalent species give direct evidence of increased reactivity of the Ce\(^{IV}\) cation in ketone anchorage and ergo emphasize the importance of Lewis acidity on ketone anchorage. However, the difference between La\(^{III}\)/Ce\(^{III}\) and Lu\(^{III}\) can be rationalized by the following: the larger ions can accommodate more bp units into their coordination sphere, but their weaker Lewis acidity (compared with that of Lu) makes their associated bp units more labile in solution. Thus, upon crystallization, when these larger ions are starved of donor solvent molecules, another bp unit can coordinate and form pdpm, but it immediately undergoes de-insertion and is dissociated upon dissolution. For the smaller lutetium ion, the increased Lewis acidity enables retention of one pdpm ligand in solution. Crucially, the Lu\(^{III}\) center is still not acidic enough to anchor and convert two bp units, thus being less effective at the higher-oxidation-state species, Ce\(^{IV}\). Nucleophilic attack on carbonyl groups by Me\(_2\)pz\(^-\) is known, but it has been only observed from ligand degradation processes.[21,22] Nevertheless, although experiments were limited, due to the poor solubility of complexes 6 and 7, it appears that such complex sequences of equilibria are not exclusive to the tetravalent oxidation state, and therefore, they may be relevant to other systems involving such insertion processes.

Do Similar Equilibria Exist in the CeCl\(_3\)/nBuLi Reaction Mixture?

To determine if such bp/L + bp equilibria (L = monoanionic ligand) are restricted to only the pyrazolate system, we revisited the commonly used CeCl\(_3\)/LiR mixture on the conversion of bp into 1,1-diphenylpentan-1-ol (Hdppo, after hydrolysis). Although the reaction between \(n\)BuLi and bp has been well-known for over 40 years [giving a mixture of Hdppo and diphenylmethanol (Hdpdm) upon hydrolysis],[23] to the best of our knowledge, it has not yet been performed in the presence of CeCl\(_3\) reagents [though CeI\(_3\) was shown to selectively convert (PhCH\(_2\))\(_2\)CO into the tertiary alcohol].[3d] Accordingly, similar association/dissociation and insertion/de-insertion phenomena within the system CeCl\(_3\)/nBuLi/bp would involve equilibria like CeCl\(_2\)(nBu) + bpâ†’CeCl\(_2\)(dppo) (dppo = 1,1-diphenylpentan-1-olate; see Scheme 3, Table 1), dependent on temperature and reagent ratio parameters.

Assuming that such equilibria exist, we expected that the hydrolysis of a reaction mixture containing a reagent ratio of 1:1:1 at lower temperatures (method a, see Scheme 3) should outperform ambient-temperature hydrolysis (method b, see Scheme 3). However, if no equilibrium is present in this system, then the highest selectivity should be achieved by hydrolysis of a reaction mixture containing a reagent ratio of 1:3:3 (CeCl\(_3\)/nBuLi/bp, respectively; method c) at lower temperatures (as at ambient temperatures, organocerium decompositions prevail; method d, see Exp. Sect.), since this mixture should favorably form [Ce(dppo)]\(_3\). Thus, CeCl\(_3\) and bp (ratio of 1:1), were stirred...
Scheme 3. A simplified CeCl₃/nBuLi/bp system; the penultimate organocerium complex prior to hydrolysis (by pOH and H₂O, followed by acetic acid) is considerably more complicated than presented.

Table 1. Summary of the reactions between CeCl₃, bp, and nBuLi, and the ratio of the obtained organic products (Hdpoo: Hdpdm/bp).

<table>
<thead>
<tr>
<th>Method</th>
<th>CeCl₃/bp/nBuLi</th>
<th>T hydrolysis (°C)</th>
<th>Hdpoo</th>
<th>Hdpdm</th>
<th>bp</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1:1:1</td>
<td>-55°</td>
<td>44</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>b</td>
<td>1:1:1</td>
<td>0°</td>
<td>10</td>
<td>3.6</td>
<td>1</td>
</tr>
<tr>
<td>c</td>
<td>1:3:3</td>
<td>-55°</td>
<td>3.6</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

[a] Stirred at −65 to −55 °C in THF for 40 min before hydrolysis. [b] Slowly warmed to 0 °C in THF and then hydrolyzed.

at −78 °C in THF, and a slight excess of nBuLi was added. Although the reaction was not as selective as other systems,[24] the lower-temperature hydrolysis favored Hdpoo formation. In all reactions, bp was the limiting reagent; thus, it was recovered in varying amounts after hydrolysis, supporting the idea that a dppo/nBu de-insertion/dissociation equilibrium is indeed present. Although this is only a preliminary analysis and the experiment does contain problems (such as the necessity to use THF as a solvent, which will induce a degree of dissociation), the results support the presence of a dissociation/de-insertion equilibrium in these systems, as well as CeCl₃(nBu)-type components as the likely active species in 1:1:1 ratio reaction mixtures.

**Conclusion**

The current rare-earth metal-templated Ph₂CO association/insertion de-insertion/dissociation equilibria, as well as the dependence of successful activation on oxidation and temperature, appear to be new. In solution, pyrazolato ligands and dependence of successful activation on oxidation and temperature, high temperature, which ensures maximal ketone anchorage and insertion into the Ce–X bond.

**Experimental Section**

**General Experimental Procedures and Instrumentation:** All manipulations were performed using glovebox (MBraun 2008; < 0.1 ppm O₂, < 0.1 ppm H₂O) or Schlenk-line techniques under purified argon in oven-dried glassware. Solvents (THF, n-hexane, and toluene) were purified by Grubbs columns (MBraun SPS, solvent purification system) and stored inside a glovebox. Benzophenone, nBuLi (2.5 M in hexanes), and Me₂P₂H₂ were purchased from Sigma–Aldrich and used as received. CeCl₃ was purchased from Sigma–Aldrich and converted into CeCl₃(thf)₁.₀₅ through Soxhlet extraction. Compounds [Ce(Me₂pz)₂(thf)₂] (6a), [Ce(Me₂pz)₃(thf)] (7), and [Ln(Me₂pz)₂(thf)]₂ (Ln = La (6a), Lu (6b)) were synthesized according to published procedures.[25,26] The NMR spectra of air- and moisture-sensitive compounds were performed in predried (with NaK) [D₆]benzene (C₆D₆), [D₈]toluene, or [D₈]THF with J. Young valve NMR spectroscopy tubes. Analyses were performed at 25 °C with either a Bruker AVII+400 (¹H: 400.13 MHz; ¹³C: 100.16 MHz), Bruker-Avance II 500 (¹H: 500.13 MHz; ¹³C: 125.76 MHz), or a Bruker DRX250 (¹H: 250 MHz; ¹³C: 63 MHz) spectrometer. Infrared spectra were recorded with a Nicolet 6700 FTIR spectrometer (ν = 4000–600 cm⁻¹) using a DRIFT chamber with dry KBr/sample mixtures and KBr windows, or as Nujol mulls between (CsI plates). Magnetic susceptibilities and μ_eff values were calculated by the Evans method.[27] UV/Vis measurements were performed with a Perkin–Elmer Lambda 35 UV/Vis instrument as dilute toluene solutions. Elemental analyses (C, H, N) were performed on the bulk sample with an Elementar Vario MICRO cube. Reported yields are given for compounds after a satisfactory elemental analysis was obtained from the bulk sample.

**Experimental Details:**

Note: Dimeric complexes [Ce(Me₂pz)₂]₂ and 0.25(toluene) (1) and [Ce(Me₂pz)₂(thf)]₂ were treated as a monomeric species, for example, [Ce(Me₂pz)₂]₂(toluene) after drying, for stoichiometric calculations. From one synthesis, complex 1 was obtained as [Ce(Me₂pz)₂]₂(toluene), and was used as [Ce(Me₂pz)₂]₂(toluene) for stoichiometric calculations, as indicated below.

**Experimental Details Concerning the Treatment of** [Ce(Me₂pz)₂]₂(toluene) (1) with Benzenophene (bp) and Identification of [Ce(Me₂pz)₂(pdpdm)] (2)

**Method a.** By ¹H NMR Spectroscopy at Various Temperatures: [Ce(Me₂pz)₂]₀.₁₂₅(toluene) (0.0120 g, 0.0225 mmol) was dissolved in C₆D₆ (0.5 mL); bp (0.0043 g, 0.0235 mmol) was added, and the solution changed color to red-orange. FeCl₃ (0.0019 g, 0.0102 mmol) was added as an internal standard to assist in ratio determination. ¹H NMR spectroscopic analysis indicated an equilibrium between Ce(Me₂pz)₂(pdpdm) (7); see Figure S1) and 1-bp, with trace amounts of [Ce(Me₂pz)₂(pdpdm)] (3). **Figure 1** NMR (C₆D₆, 500 MHz; trace impurities and specific resonances for 3 are not included, integrals are set to 1 equiv. of FeCl₃, see Figure S1 for assignments): δ = 1.31 (s, 10 H, CH₃-pdpdm (2)), 2.05 (s, 10 H, CH₃-pdpdm (2)), 2.20 (s, ca. 73 H, CH₃-Me₂pz (1–3)), 4.00 (s, 10 H, FeCl₃), very limited understanding of what is occurring in the transition states [22] or reaction mixtures [29] involved. At the same time, our observations were shown to relate to more illustrious organocerium systems, like the classical CeCl₃/nBuLi-promoted ketone transformations. There, similar equilibria might prevail, and product (= alcohol) selectivity may be enhanced by using a reagent ratio of 1:1:1 and terminating hydrolysis at a lower temperature, which ensures maximal ketone anchorage and insertion into the Ce–X bond.
Method d. Variable-Temperature 1H NMR Spectra: 

[D8]Toluene was added to a 1H NMR tube containing crystalline [Ce(Me2pz)4]2 and bp (0.0116 g, 0.0176 mmol). The sample was analyzed by 1H NMR spectroscopy at temperatures between –30 and +60 °C (see Figure S14).

Attempted Isolation of [Ce(Me2pz)(pdpm)]2

Method a. 1H NMR Scale Reaction of [Ce(Me2pz)4]2 (0.0045 g, 0.0076 mmol) and bp (0.0092 g, 0.0178 mmol) were dissolved in toluene (giving a total volume of 0.4 mL). The mixture was added to an NMR tube and analyzed by 1H NMR spectroscopy, which showed the presence of 3 (see Figure S3).

Method b. 1H NMR Spectroscopic Analysis with an Excess of [Ce(Me2pz)2(pdpm)]2 (1): [Ce(Me2pz)2]0.25(toluene) (0.0178 g, 0.0203 mmol) was dissolved in [D8]THF, 400 MHz, 300.15 K; δ = 2.32 (br. s, 26 H, CH3), 6.09 (br. s, 4 H, Ar-H). The supernatant solution was discarded. The material was repeatedly washed with minimal amounts of cyclohexane, and the solvents were evaporated to dryness (in vacuo). C46H48CeN8O2 (885.06 g mol–1): calcd. C 62.43, H 5.47, N 12.66; found C 62.06, H 5.20, N 12.73.

Method c. Treatment of [Ce(Me2pz)4]2 (1) (in Excess) with bp (4 equiv.): [Ce(Me2pz)2(pdpm)]2 (0.0292 g, 0.0162 mmol) was dissolved in toluene (giving a total volume of 0.7 mL). The sample was analyzed by 1H NMR spectroscopy at temperatures between –30 and +60 °C (see Figure S14).
Method b. Attempted Crystallization of [Ce(Me2pz)(pdpm)]$_2$ (3): [Ce(Me2pz)$_2$.0.125$(toluene) (0.0164 g, 0.0327 mmol) and bp (0.0165 g, 0.0905 mmol) were dissolved in toluene and stirred for several minutes. The light-orange reaction mixture was concentrated to a light oil, and n-hexane was added. Upon storage at –35 °C, the light-yellow solution gave orange crystals of 3 (identified by unit-cell comparisons with a genuine sample, a = 110.9°, b = 19.16°, γ = 19.88°; after separation from the crystals of 3, crystallization from the supernatant solution at –35 °C gave more crystals of 3.

Method c. $^1$H NMR Scale Reaction of 2 with bp (2 equiv.): [D$_8$]Toluene was added to a $^1$H NMR tube containing crystalline 2 (0.0085 g, 0.0096 mmol), FeCp$_2$ (0.0028 g, 0.0151 mmol), and bp (0.0032 g, 0.0175 mmol). The sample was analyzed by $^1$H NMR spectroscopy at various temperatures (see Figures S20, S21). At ambient temperature, 2 was the major species in a 1:2 ratio of 2/1 (see Figure S20). At lower temperatures, resonances for [Ce(Me2pz)$_2$.pdpm)]$_2$ (3) were identified (see Figure S20). UV/Vis spectroscopic analysis was also performed on 2 and (2 equiv.) in toluene at various temperatures (see Figure S22).

Method d. $^1$H NMR Scale Reaction of 3 with bp (10 equiv.): [D$_8$]Toluene was added to a $^1$H NMR tube containing crystalline 3 (0.0092 g, 0.0103 mmol), FeCp$_2$ (0.0040 g, 0.0214 mmol), and bp (0.0175 g, 0.0960 mmol). The reaction mixture was analyzed at various temperatures, and the spectra are displayed in Figure S23. At ambient temperatures, the only Ce-containing species was [Ce(Me2pz)$_2$.pdpm)]$_2$ (3); at lower temperatures, the presence of 3, and 2 and bp was observed.

Reaction of Trivalent Species [Ln(Me2pz)$_3$(thf)]$_2$ (Ln = La, Ce, Lu) with bp

Treatment of [La(Me2pz)$_3$(thf)]$_2$ (6a) with bp (2 equiv.) and Isolation of [La$_2$(Me2pz)$_2$.pdpm)]$_2$ (6la): [La$_2$(Me2pz)$_2$.pdpm)]$_2$ (6la) (0.0306 g, 0.0616 mmol) and bp (0.0220 g, 0.1207 mmol) were dissolved in THF and stirred. The colorless solution was concentrated to an oil, and cyclohexane was added. Colorless crystals of [La$_2$(Me2pz)$_2$.pdpm)]$_2$ were identified (see Figure S24). UV/Vis spectroscopic analysis of the starting materials. Addition of LuCl$_3$(THF)$_3$ (0.0097 g, 0.0195 mmol) and bp (0.0085 g, 0.0497 mmol) were added. $^1$H NMR ([D$_8$]THF, 300 K, 400 MHz): δ = 6.04 (s, 21 H, Me$_2$pz-Bu), 3.07 (m, 6 H, bp), 2.71 (m, 6 H, bp), 1.21 (m, 18 H, n-hexane). 19La and 1H NMR spectroscopy of the starting materials.

Treatment of [Lu(Me2pz)$_3$(thf)]$_2$ (6b) with bp and Isolation of [Lu$_2$(Me2pz)$_2$.pdpm)]$_2$ (9la): [Lu$_2$(Me2pz)$_2$.pdpm)]$_2$ (9la) (0.0335 g, 0.0629 mmol) and bp (0.0220 g, 0.1207 mmol) were stirred in Cs$_6$(thf).

Control Reaction. Treatment of Me2pzH with bp: Me2pzH (0.0342 g, 0.3557 mmol) and bp (0.0655 g, 0.3600 mmol) were combined in Cs$_6$(thf) and analyzed by $^1$H NMR spectroscopy showing only starting materials. Addtion of LuCl$_3$(THF), (0.0097 g, 0.0195 mmol) and heating did not give any significant changes to the NMR spectrum.

General Procedures for Reactions between CeCl$_3$$_2$, Benzoephone, and nBuLi: Two different ratios of reactants (CeCl$_3$, bp, nBuLi) were employed, either 1:1:1 (methods a and b) or 1:3:3 (methods c and d). At ambient temperature, CeCl$_3$ and bp were stirred in THF for ca. 1 h. The reaction mixture was cooled to –78 °C, and nBuLi was added dropwise. The reaction mixture was either stirred at –65 to –55 °C for 40 min (methods a and c) or warmed to 0 °C (methods b and d) where for method d decomposition was noted by a color change to dark brown. For methods a and c, hydrolysis was performed in the following manner: at –55 °C a cold mixture of 2-propanol and toluene was added, then after a few minutes, cold water was added, the solution changed from light-yellow to colorless, and a white precipitate formed. The reaction mixture was warmed to 20 °C, and acetic acid (1 mL) was added. For method b, hydrolysis was performed at 0 °C, where ice-cold 2-propanol and toluene were added, followed by ice-cold water, and then, after 10 min, acetic acid was added. After hydrolysis, the mixtures were dried in vacuo, and diethyl ether and water were added. The diethyl ether layer was extracted, dried with MgSO$_4$, and concentrated to an oil (in vacuo); CCl$_3$ was added, and a small amount was extracted; it was analyzed by $^1$H NMR spectroscopy, giving the ratio of products listed in Table 1.
Method a. 1:1:1 Ratio, Hydrolysis at Low Temperature: CeCl₃(thf)₃ (0.2650 g, 0.3104 mmol), bp (0.1487, 0.8160 mmol), and nBuLi (0.1000 g, 0.3104 mmol) were employed. The solution turned light green upon nBuLi addition, and then it quickly changed color to light yellow. ¹H and ¹³C NMR spectroscopy indicated a product ratio of 1,1-diphenyl-1-pentanol (dppo)/diphenylmethanol/bp of 44:15:1.

Method b. 1:1:1 Ratio, Hydrolysis at Ambient Temperature: CeCl₃(thf)₁.05 (0.0800 g, 0.2483 mmol), bp (0.1639, 0.8999 mmol), and nBuLi (1.000 mmol) were employed. The solution turned light green upon nBuLi addition, and then it slowly changed color to light yellow. Warming to 0 °C showed no sign of color change. ¹H and ¹³C NMR spectroscopy indicated a product ratio of 1,1-diphenyl-1-pentanol (dppo)/diphenylmethanol/bp of 3.6:3:1.

Method c. 1:3:3 Ratio, Hydrolysis at Low Temperature: CeCl₃(thf)₁.05 (0.0800 g, 0.2483 mmol), bp (0.1341, 0.7360 mmol), and nBuLi (0.75 mmol) were used. The solution turned light green upon nBuLi addition, and then it slowly changed color to light yellow; upon warming, the mixture turned to orange, then brown, suggesting decomposition occurred. The solution was filtered, concentrated, and stored at –35 °C; however, no crystallization occurred.

Method d. 1:3:3 Ratio, Attempted Hydrolysis at Ambient Temperature: CeCl₃(thf)₁.05 (0.0800 g, 0.2483 mmol), bp (0.1341, 0.7360 mmol), and nBuLi (0.75 mmol) were used. The solution turned light green upon nBuLi addition, and then it slowly changed color to light yellow; upon warming, the mixture turned to orange, then brown, suggesting decomposition occurred. The solution was filtered, concentrated, and stored at –35 °C; however, no crystallization occurred.

X-ray Diffraction Crystallography: All compounds were examined with a Bruker Apex-II CCD diffractometer at 100.15 K (3, ⁸Ce⁶, ⁸⁴Lu) or 150.15 K (¹H, ⁹⁴Sm), mounted on a fiber loop in paratone crystallography oil. Absorption corrections were completed using the Apex II program suite.[28] Structural solutions were obtained by charge-flipping methods (3, ⁸Ce⁶, ⁸⁴Lu) or direct methods (¹H, ⁹⁴Sm) and were refined using full-matrix least-squares methods against F² using SHELX2013.[29] Within the OLEX2 graphical interface.[30] A list of the parameters are found in Table 2. Notes: ⁸Ce⁶: Three n-hexane molecules were within the lattice, two of which were of half occupancy and disordered, and one of which required DFIX commands. One carbon atom (C16s) on one half of an n-hexane molecule was not modelled with hydrogen atoms, hence 1 H atom is missing from the formula. The ISOR command was used on one disordered carbon atom on a phenyl ring of pdpm. ⁸⁴Lu: Crystals were slightly twinned, giving large residual g peaks close to the metal centre. The ISOR command was used on the NPD atoms. SQUEEZE[31] was used on the solvent-accessible voids to remove low-occupancy hexane within the cell. CCD: 1541213 (for ¹H), 1441016 (for ⁸Ce⁶), 1533910 (for ⁸⁴Lu), 1441021 (for ⁸Ce⁶), and 1533909 (for ⁹⁴Sm) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): Spectra of reported complexes.

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References


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