Cyclopentadienyl Ring Metathesis with Organocalcium and Organopotassium Compounds

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Cyclopentadienyl ring metathesis occurs between $[Ca(C_5Me_5)_2]$ and $[Ln(C_5H_5)_3]$ complexes in toluene to generate the mixed ring compounds $[Ln(C_5Me_5)_2(C_2H_5)]$ (Ln = **1**-La, **1**-Nd). **1**-Nd has been characterized with X-ray diffraction as a sterically crowded monomer. Only one ring is exchanged between $[Ca(C_5Me_5)_2(thf)_x]$ and $[La(C_5H_5)_3(thf)_x]$ in toluene to yield $[La(C_5Me_5)(C_5H_5)_2(thf)]$ (**2**). In reaction with $[M(C_5H_5)_2]$ (M = Sn, Pb, Mn), $[Ca(C_5M_5)_2(thf)_x]$ yields the corresponding $[M(C_5Me_5)_2]$ complexes. $K[C_5Me_5]$ reacts with $[La(C_5H_5)_3(thf)]$, $[Sn(C_5H_5)_2]$ and $[Pb(C_5H_5)_2]$ in toluene to yield the ring-exchanged products **2**, $[Sn(C_5Me_5)_2]$, and $[Pb(C_5Me_5)_2]$, respectively.

Introduction

Alkali-metal cyclopentadienides (and related $[MgCp'_2]$ and [TlCp] compounds) have long been the most commonly used cyclopentadienylating agents in organometallic chemistry[1,2]. They are efficient transfer reagents with metal halides, owing to the kinetic lability of the Group 1, Mg, and Tl M–Cp′ bonds, and to the low solubility of the metal halide by-products in ethereal media.

Other approaches to transferring cyclopentadienyl rings between metal centers have received less attention. *Cyclopentadienyl ring metathesis* (CRM) between metallocenes was first demonstrated more than 30 years ago in ferrocene derivatives, but because of the stability of the transition metal–Cp′ bond, little use has been made of it in synthesis. For example, $[Fe(C_5(n\text{-}Pr)H_4)(C_5H_5)]$ will undergo ligand redistribution to $[Fe(C_5(n\text{-}Pr)H_4)_2]$ and ferrocene when heated with $AlCl_3$ in CH_2Cl_2 for 2 h[3], and $[Fe(C_5MeH_4)_2]$ and ferrocene will partially react to form $[Fe(C_5MeH_4)(C_5H_5)]$ under prolonged heating (14 d) at high temperature (250°C)[4]. Highly substituted ferrocenes (e.g., $[Fe(C_5Et_5)_2]$), however, have not been observed to undergo CRM reactions, even under forcing conditions[5].

We have been interested in the use of metallocenes and indenyl complexes of the heavier alkaline-earth metals (Ae) calcium, strontium, and barium as CRM reagents. Not only is the lability of the Ae–Cp′ bond high, but the solubility of the compounds also varies markedly with the degree of ring substitution. Many substituted derivatives (e.g., $[Ae(C_5Me_5)_2]$, $[Ae(C_5(i\text{Pr})_4H)_2]$, $[Ae(C_9(i\text{Pr})_2H_5)_2]$[6,7]) have substantial hydrocarbon solubility but the parent compounds ($[Ae(C_5H_5)_2]_x$, $[Ae(C_9H_7)_2]_x$) are both ether- and hydrocarbon-insoluble[8,9]. Thus they could function in CRM reactions in which the precipitation of an isoluble *organometallic* compound is a driving force of the reaction (e.g., eq. 1).

$$n\,[AeCp'_2] + m\,[MCp_x] \xrightarrow{\text{toluene}} [MCp'_{(2n/m)}Cp_{(mx-2n)}] + n\,[AeCp_2]\downarrow \quad (1)$$

As eq. 1 suggests, CRM reactions could provide a controllable route to mixed-ring cyclopentadienyl species, which are uncommon in main-group and f-element chemistry[10,11]. Such complexes allow the effect of changes in the ligand environment around a metal center to be probed in a systematic manner.

We report here the use of alkaline-earth metallocenes as CRM agents with lanthanide and main-group metal complexes, and compare their efficacy with a related potassium reagent in aromatic solvents; these experiments reveal some of the strengths and limitations of this synthetic approach. A portion of this work has been previously communicated[12].

Results and Discussion

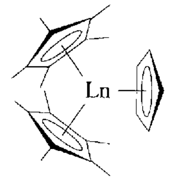
Both $[Ca(C_5Me_5)_2(thf)_x]$ ($x = 0-2$) and $K[C_5Me_5]$ were able to serve as CRM reagents with lanthanide and main-group cyclopentadienyl compounds in toluene, although the organolanthanide products varied depending on whether coordinated THF was present in the reaction.

Synthesis of $[Ln(C_5Me_5)_2(C_5H_5)]$ (Ln = 1-La, 1-Nd)

When unsolvated $[Ca(C_5Me_5)_2]$ was allowed to react in toluene with $[La(C_5H_5)_3]$ ($[Nd(C_5H_5)_3]$), the yellow-green (greenish-brown) complexes **1**-La (**1**-Nd) were obtained in moderate yield.

In practice, a 50% excess of $[Ca(C_5Me_5)_2]$ was used to help offset the low solubility of $[Ln(C_5H_5)_3]$ in toluene. The

$$[Ca(C_5Me_5)_2] + [Ln(C_5H_5)_3] \xrightarrow{\text{toluene}}$$



$$+ [Ca(C_5H_5)_2]\downarrow$$

1

excess does not generate any $[Ln(C_5Me_5)_3]$[13], as might have occurred (eq. 2).

$$3\,[Ca(C_5Me_5)_2] + 2\,[Ln(C_5H_3)_3] \xrightarrow{\text{toluene}} 2\,[Ln(C_5Me_5)_3] + 3\,[Ca(C_5H_5)_2]\downarrow \quad (2)$$

Consistent with this behavior, no further reaction is observed between **1**-Nd and $[Ca(C_5Me_5)_2]$ when they are allowed to stir overnight in toluene. Eq. 2 does not fully describe the course of the reaction, however, as the solid removed by filtration from the reaction contains more than $[Ca(C_5H_5)_2]$. The ^1H-NMR spectrum in [D$_8$]THF displays two resonances [δ = 5.74 (s, C_5H_5), 1.90 (s, C_5Me_5)], one of which suggests the presence of the $[C_5Me_5]^-$ anion, but it is not at the shift expected for $[Ca(C_5Me_5)_2(thf)_2]$ (ca. δ = 2.06)[14]. A mixed-ring complex, such as $[Ca(C_5Me_5)(C_5H_5)]$, which is evidently not soluble in toluene, may be the source of the extra peaks (e.g., as in eq. 3). Pure samples of the compound could not be isolated.

$$4\,[Ca(C_5Me_5)_2] + 3\,[Ln(C_5H_5)_3] \xrightarrow{\text{toluene}} 3\,[ln(c_5Me_5)_2(C_5H_5)] + 2\,[Ca(C_5H_5)_2]\downarrow + 2\,[Ca(C_5Me_5)\,(C_5H_5)]\downarrow \quad (3)$$

It is notable that the lighter group-2 metallocene $[Mg(C_5Me_5)_2]$ fails to serve as a CRM reagent (eq. 4).

$$[Mg(C_5Me_5)_2] + [Nd(C_5H_5]_3] \xrightarrow{\text{toluene}} \mathbf{1}\text{-Nd} + [Mg(C_5H_5)_2] \quad (4)$$

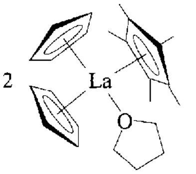
Were eq. 4 to proceed as written, the hydrocarbon-soluble $[Mg(C_5H_5)_2]$ would be formed. The lack of any observable reaction confirms the importance of $[Ca(C_5H_5)_2]$ precipitation as a driving force for the metathesis.

Interestingly, crystals of **1**-Nd are green in artificial (fluorescent) light but salmon-colored in sunlight or under a xenon source. Such photochromic-like behavior does not seem to have been reported for organoneodymium complexes[15].

Metathesis Reactions with Solvated Reagents

The CRM reactions took an appreciably different course when solvated starting materials were used. When 1.7 equivalents of $[La(C_5H_5)_3(thf)_{1.7}]$ were allowed to react with one equivalent of $[Ca(C_5Me_5)_2(thf)_{1.8}]$ in toluene, the mixed-ring product **2** could be isolated; it was characterized by elemental analysis, ^1H and ^{13}C NMR, and an X-ray diffraction study. **2** was also obtained when $[La(C_5H_5)_3(thf)_x]$/$[Ca(C_5Me_5)_2(thf)_x]$ ratios ranging from 2:3 to 2:1 were used. It is notable that only one $[C_5Me_5]^-$ ring is transferred to the lanthanide center.

$$2\,[La(C_5H_5)_3(thf)_x] + [Ca(C_5Me_5)_2(thf)_x] \xrightarrow{\text{toluene}}$$



$$+ [Ca(C_5H_5)_2(thf)_x]\downarrow$$

2

Attempts were made to obtain crystals of **2** suitable for X-ray diffraction, but only weakly diffracting samples could be grown. The lanthanum atom was located on a crystallographic mirror plane; owing to a lack of data and to apparent disorder in the pentamethylcyclopentadienyl and cyclopentadienyl rings, however, the structure could not be successfully refined[16].

A parallel reaction using THF-solvated $[Nd(C_5H_5)_3(thf)_{0.9}]$ and $[Ca(C_5Me_5)_2(thf)_2]$ in toluene produced an inseparable mixture of compounds. The proton NMR spectrum (C_6D_6) contained resonances matching those of the starting material, and also several new peaks at δ = 8.72 (br. s, 15H, C_5Me_5), 2.24 (br. s, 10H, C_5H_5), and −11.81 (br. s, THF). An attempt to purify the mixture by sublimation at 170°C and 2×10^{-4} torr for 4 h was unsuccessful, as was toluene extraction. The integration of the NMR resonances suggests that a species of the form $[Nd(C_5Me_5)(C_5H_5)_2(thf)_x]$ may be present. It is significant in any case that **1**-Nd, which forms from unsolvated reagents, was not produced.

When approximately equal equivalents of $[Ca(C_5Me_5)_2]$ and $[Sn(C_5H_5)_2]$ were allowed to react in toluene, $[Sn(C_5Me_5)_2]$ was isolated in 50% yield; a similar reaction with $[Ca(C_5Me_5)_2(thf)_x]$ and $[Sn(C_5H_5)_2]$ ($[Pb(C_5H_5)_2]$) produced $[Sn(C_5Me_5)_2]$ ($[Pb(C_5Me_5)_2]$) in 55% (59%) yield (eq. 5).

$$[Ca(C_5Me_5)_2(thf)_x] + [(Sn,Pb)(C_5H_5)_2] \xrightarrow{\text{toluene}} [(Sn,Pb)(C_5Me_5)_2] + [Ca(C_5H_5)_2(thf)_x]\downarrow \quad (5)$$

It should be noted that, unlike the case with the organolanthanide compounds, the use of solvated or unsolvated $[Ca(C_5Me_5)_2(thf)_x]$ is not critical to the formation of $[Sn(C_5Me_5)_2]$ or $[Pb(C_5Me_5)_2]$; this likely reflects the fact that THF does not form a stable adduct with either $[(Sn,Pb)(C_5H_5)_2]$ or $[(Sn,Pb)(C_5Me_5)_2]$.

Potassium Pentamethylcyclopentadienide as a CRM Reagent

Owing to its virtual insolubility in hydrocarbons, reactions with $K[C_5Me_5]$ are not usually conducted in such solvents. Nevertheless, we were interested in determining the feasibility of using organopotassium reagents as ring-transfer agents under CRM conditions.

We find that excess $K[C_5Me_5]$ does react with $[La(C_5H_5)_3(thf)_{1.5}]$ in toluene to produce **2**, albeit in low (14%) yield (eq. 6).

$$K[C_5Me_5] + [La(C_5H_5)_3(thf)_{1.5}] \xrightarrow{\text{toluene}} \mathbf{2} + K[C_5H_5]\downarrow \quad (6)$$

Even when using a 3:1 ratio of $K[C_5Me_5]$ to $[La(C_5H_5)_3(thf)_x]$, no more than one $[C_5Me_5]^-$ ring is transferred to the lanthanum center. As observed when using $[Ca(C_5Me_5)_2(thf)_x]$, if the lanthanide reagent is already solvated, only single ring exchange occurs.

When two equivalents of $K[C_5Me_5]$ were allowed to react with one equivalent of $[Sn(C_5H_5)_2]$ in toluene, $[Sn(C_5Me_5)_2]$ was isolated in 58% yield; Similarly, when $[K[C_5Me_5]$ was added to a toluene solution of $[Pb(C_5H_5)_2]$, the solution immediately became orange-red, indicating the formation of $[Pb(C_5Me_5)_2]$ (eq. 7).

$$2\ K[C_5Me_5] + [(Sn,Pb)(C_5H_5)_2] \xrightarrow{\text{toluene}} [(Sn,Pb)(C_5Me_5)_2] + 2\ K[C_5H_5]\downarrow \quad (7)$$

Rapid workup was required to remove the precipitated $K[C_5H_5]$ from the reaction with $[Pb(C_5H_5)_2]$, which if left in contact with the solution would eventually cause reduction and decomposition of the $[Pb(C_5Me_5)_2]$. It is evident that the strong reducing ability of $K[C_5H_5]$ must be taken into account when planning syntheses with redox-sensitive reagents.

It is notable that the main-group compounds $[Sn(C_5Me_5)_2]$ and $[Pb(C_5Me_5)_2]$ were synthesized in relatively good yield by cyclopentadienyl ring metathesis with both $[Ca(C_5Me_5)_2]$ and $K[C_5Me_5]$. As CRM involves the exchange of ion pairs, undoubtedly a major reason for the success with these compounds is that the bonding in Group 14 metallocenes is largely ionic[17–19].

Reactions with Potassium and Calcium Indenides

We attempted to extend the use of the CRM reactions to reagents such as K[Ind] (Ind = $[C_9H_7]^-$) by taking advantage of the low solubility of $K[C_5H_5]$ in toluene (e.g., eq. 8).

$$[La(C_5H_5)_3(thf)_x] + K[Ind] \xrightarrow{\text{toluene}} [La(Ind)(C_5H_5)_2(thf)_x] + K[C_5H_5]\downarrow \text{ (intended)} \quad (8)$$

When equimolar amounts of $[La(C_5H_5)_3(thf)]$ and K[Ind] were allowed to react in toluene, however, the ^{1}H-NMR spectrum of the product indicated that it was a mixture that included starting materials, $[La(Ind)_3(thf)]$[20], and several new resonances that could correspond to species such as $[La(Ind)(C_5H_5)_2(thf)_x]$ and $[La(Ind)_2(C_5H_5)(thf)_x]$. Because of the similar solubilities of the products, separation by solvent extraction was not feasible. The reaction was repeated using equimolar amounts of the solvated indenyl compound $[Ca(Ind)_2(thf)_2]$[7] and $[La(C_5H_5)_3(thf)]$. ^{1}H-NMR spectra of the products in both C_6D_6 and $[D_8]$THF again suggested that a mixture of products was present. Similar results were obtained using a 3:2 ratio of $[Ca(Ind)_2(thf)_2]$ to $[La(C_5H_5)_3(thf)]$.

That complex mixtures are obtained in these reactions but not with the pentamethylcyclopentadienyl compounds may well be a function of relative ligand size. The $[Ind]^-$ ligand is more sterically compact than $[C_5Me_5]^-$, and it is possible to prepare $[Ln(Ind)_3]$ and even solvated $[Ln(Ind)_3(thf)_x]$ complexes[11]. Thus the steric restrictions that prevent the formation of $[Ln(C_5Me_5)_3]$ and $[Ln(C_5Me_5)_3(thf)_x]$ compounds through the CRM route need not apply to the indenyl reactions.

Reactions with Transition-Metal Metallocenes

Several reactions were conducted to survey the extent to which CRM with the calcium and potassium reagents could be extended to transition-metal systems. Approximately equimolar amounts of $[Mn(C_5H_5)_2]$ and $[Ca(C_5Me_5)_2(thf)]$ were allowed to react in toluene; the solution immediately became orange with the formation of $[Mn(C_5Me_5)_2]$ in good yield (eq. 9).

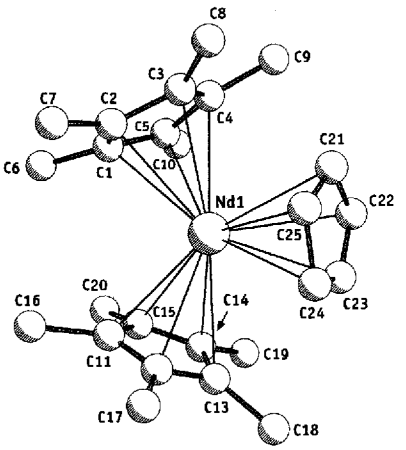
$$[Ca(C_5Me_5)_2(thf)] + [Mn(C_5H_5)_2] \xrightarrow{\text{toluene}} [Mn(C_5Me_5)_2] + [Ca(C_5H_5)_2(thf)_x]\downarrow \quad (9)$$

In contrast, negligible reaction occurred when $[Ca(C_5Me_5)_2(thf)_x]$ was allowed to react with $[Fe(C_5H_5)_2]$ or $[Cr(C_5H_5)_2]$. The facile reaction with $[Mn(C_5H_5)_2]$, which has a high-spin ($^6A_{1g}$) electron configuration[21,22], underscores the importance of appreciable ionic character in a substrate that is to undergo CRM reactions. The covalent metal–ring bonding in $[Fe(C_5H_5)_2]$ and $[Cr(C_5H_5)_2]$ is not easily disrupted under these conditions. The fact that $[Mn(C_5Me_5)_2]$ is exclusively low-spin ($^2E_{2g}$) at room temperature[23], and thus possesses somewhat more metal–ring covalence than does $[Mn(C_5H_5)_2]$, may also contribute to the ease of ring exchange.

Crystal Structure of 1-Nd

The compound consists of monomeric units with two η^5-(C_5Me_5) rings and one η^5-(C_5H_5) ring (Figure 1). Some disorder was evident in the (C_5H_5) ring, and there is a larger than normal spread in the Nd–ring distances (2.69–2.86 Å); the (C_5Me_5) rings were not affected by disorder. **1**-Nd is isostructural with the samarium analog $[Sm(C_5Me_5)_2(C_5H_5)]$[24]; in particular, the $((C_5Me_5)$ centroid)–Nd–((C_5Me_5) centroid) angle of 127.3° is equivalent to the value in $[Sm(C_5Me_5)_2(C_5H_5)]$ (127.0°)[24]. The steric crowding between the rings in **1**-Nd is evident in the displacements of the methyl substituents on the (C_5Me_5) rings by an average of 8.3° and 10.5° from their C_5 ring planes. These are similar to the angles found in the isostructural $[Sm(C_5Me_5)_2(C_5H_5)]$ (8.5° and 8.7°)[24], but are somewhat larger than the displacements typically displayed in a less crowded pentamethylcyclopentadienyl complex (e.g., 5.0° in $[Sm(C_5Me_5)_2]$[25]). Nevertheless, the Nd–ring centroid distances for the (C_5Me_5) rings [2.51(2), 2.52(2) Å] and the (C_5H_5) ligand [2.52(4) Å] are indistinguishable, and are comparable to the distances observed in other (cyclopentadienyl)neodymium complexes [cf. 2.511 Å (av.) in tris(9-methylbicyclo[5.3.0]deca-1(10),8-diene-7-yl)neodymium, $[Nd(C_{11}H_{15})_3]$[26] and 2.48(2) Å (av.) in $[Nd(C_5Me_5)_2CH(SiMe_3)_2]$[27]]. The (C_5Me_5) rings are almost perfectly staggered (twist angle = 32.7°), another consequence of steric congestion.

Figure 1. PLUTO diagram of **1**-Nd[a]



[a] Selected bond lengths [Å] and angles [°]: Nd(1)−Cp'(C1−C5) 2.76(2)−2.81(2), Nd(1)−Cp''(C11−C15) 2.73(2)−2.80(2), Nd(1)−Cp(C21−C25) 2.69(3)−2.86(4), Cp'(centroid)−Nd(1)−Cp''(centroid) 127.3(9), Cp'(centroid)−Nd(1)−Cp(centroid) 117(2), Cp''(centroid)−Nd(1)−Cp(centroid) 116(2).

Conclusion

This initial survey of organocalcium and organopotassium CRM reagents has identified several factors that must be considered in the design of such reactions. As the driving force involves exchange of ion pairs and the precipitation of either $[Ca(C_5H_5)_2]$ or $K[C_5H_5]$, the best candidates for substrates are those in which the metal−ring bonding has a considerable degree of ionic character. This limits its usefulness to organolanthanide (and presumably organoactinide) complexes and to some main-group metallocenes. In the case of the f-element complexes, the extent of ring exchange can be inhibited by the the presence of THF in the reaction mixture, since it is not easily displaced from the strongly oxophilic metal centers. Deliberate manipulation of THF content could provide an additional degree of control over the reactions.

There are also limits to the amount of steric congestion that can be tolerated on the metal centers; i.e., $[Ln(C_5Me_5)_2(C_5H_5)]$ and $[Ln(C_5Me_5)(C_5H_5)_2(thf)]$ are accesible via CRM, but apparently $[Ln(C_5Me_5)_2(C_5H_5)(thf)]$ and $[Ln(C_5Me_5)_3]$ are not. The size of the ring to be exchanged also appears to be critical; if it is relatively sterically compact, as with the indenide anion, there may not be a strong preference for any particular ring exchange product, and complex mixtures can be generated. With the appropriate substrate, however, CRM reactions provide convenient access to mixed-ring systems.

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Experimental Section

General: All manipulations were performed with the rigorous exclusion of air and moisture using high vacuum, Schlenk, or drybox techniques[28]. Unsolvated $[Ca(C_5Me_5)_2]$[12], $[La(C_5H_5)_3]$[29], $[Sn(C_5H_5)_2]$, $[Pb(C_5H_5)_2]$[30], and solvated $[Ca(C_5Me_5)_2(thf)_x]$[14,31] and $[Ln(C_5H_5)_3(thf)_x]$ (Ln = La, Nd)[32] were prepared according to literature procedures. Except for a sample of $[Ca(C_5Me_5)_2(thf)_2]$ prepared immediately before use, the extent of solvation of $[Ca(C_5Me_5)_2(thf)_x]$ and $[La(C_5H_5)_3(thf)_x]$ was determined by ^{1}H-NMR spectroscopy before their use in experiments. Solvents for reactions were dried and degassed using standard methods[33]. − IR: Perkin-Elmer 1600 or ATI Mattson Genesis. KBr pellets prepared as previously described[28]. − NMR: Bruker NR-200 (200 MHz and 50.3 MHz, for ^{1}H and ^{13}C, respectively) or NR-300 (300 MHz and 75.5 MHz, for ^{1}H and ^{13}C, respectively). For ^{1}H NMR, C_6D_6 as solvent, $\delta_H = 7.15$; [D$_8$]THF as solvent, $\delta_H = 3.58$; for ^{13}C NMR, C_6D_6 as solvent, $\delta_C = 128.0$; [D$_8$]THF as solvent, $\delta_C = 67.4$. − Melting points (uncorrected): Mel-Temp melting point apparatus. Elemental analysis by Oneida Research Services, Whitesboro, NY.

X-ray Crystallographic Study[34]: Crystals of **1**-Nd were grown by cooling a saturated hexane solution to −17 °C. Crystal data: $C_{25}H_{35}Nd$, $M = 479.79$, monoclinic, space group $P2_1/n$, $a = 9.374(3)$ Å, $b = 14.238(7)$ Å, $c = 17.429(7)$ Å, $\beta = 102.11(3)°$, $V = 2274(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.401$ g cm^{-3}, Data collection: Rigaku AFC6S diffractometer, graphite monochromated Mo-K_α radiation, crystal size 0.35 × 0.44 × 0.45 mm, all measurements at 20 ± 1 °C, continuous ω-2Θ collecting mode, $6° \leq 2\Theta \leq 50°$, 4467 total reflections measured, 4200 unique, 1905 with $I > 3.0\sigma(I)$, 22.95 cm^{-1} absorption coefficient, absorption correction applied with DIFABS (0.73−1.28 transmission factors). Structural analysis and refinement: Structure solved by direct methods (SHELXS-86 and DIRDIF) and Fourier techniques, and refined using the full-matrix, least-squares method of TEXSAN[35]. Unresolvable disorder was evident in the C_5H_5 ring, but the C_5Me_5 rings were unaffected by the disorder. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated using idealized geometries based on packing considerations and d/(C−H) = 0.95 Å. The positions were fixed for the final cycles of refinement. Data/parameter ratio = 8.11, final $R = 0.062$, final $R_w = 0.084$; max/min peak in final diff map = 0.88/−0.79 e$^-$/Å^3.

1-*(La,Nd):* Into a 125-ml Erlenmeyer flask equipped with a magnetic stirring bar were added $[La,Nd(C_5H_5)_3]$ (0.174 · 10^{-3} mol/ 0.654 · 10^{-3} mol) and toluene (30−50 ml), followed by $[Ca(C_5Me_5)_2]$ (1.5 equiv.). After being allowed to stir for 12 h, the solution was filtered through a glass frit. The solvent was removed from the filtrate under reduced pressure by rotary evaporation to leave yellow-green **1**-La (58%) or bright green **1**-Nd (52%). Data for **1**-La: the material begins to melt at 132−149 °C; decomposition is evident at 222 °C. − IR (KBr): $\tilde{\nu}$ = 2905 cm^{-1} (s), 2856 (s), 2724 (w), 1630 (w), 1437 (s), 1380 (m), 1260 (m), 1017 (s), 874 (w), 766 (s), 537 (br., m). − ^{1}H NMR (C_6D_6): δ = 6.05 (s, 5H, C_5H_5), 1.92 (s, 30H, C_5Me_5). − ^{13}C NMR (C_6D_6): δ = 121.1 (s, C_5Me$_5$), 116.1 (s, C_5H_5), 11.6 (s, C_5Me_5). − $C_{25}H_{35}La$ (474.5): calcd. C 63.29, H 7.44; found C 62.22, H 7.36. Data for **1**-Nd: the solid begins to melt from 154−164 °C; the melting is accompanied by sublimation. − IR (KBr): $\tilde{\nu}$ = 2917 cm^{-1} (s), 1685 (w), 1654 (s), 1560 (s), 1541 (w), 1508 (w), 1458 (m), 1240 (w), 1085 (s), 770 (s). − ^{1}H NMR (C_6D_6): δ = 8.15 (s, 30H, C_5Me_5), −1.29 (s, 5H, C_5H_5). The compound was insufficiently soluble to obtain a ^{13}C-NMR spectrum. Crystals of **1**-Nd are green in artificial (fluorescent) light, but are salmon-colored in sunlight (or xenon illumination). − $C_{25}H_{35}Nd$ (479.8): calcd. C 62.58, H 7.35; found C 62.64, H 7.20.

2 *(Method a):* Into a 125-ml Erlenmeyer flask equipped with a magnetic stirring bar were added $[La(C_5H_5)_3(thf)_{1.7}]$ (0.153 g, 0.335 · 10^{-3} mol) and toluene (35 ml), followed by $[Ca(C_5Me_5)_2(thf)_{1.8}]$ (0.088 g, 0.20 · 10^{-3} mol). After being allowed to stir for 12 h, the off-white solution was filtered through a glass frit. The solvent volume was reduced under vacuum by rotary evaporation at 25°C to leave a slightly damp solid that contained X-ray-quality crystals. After further solvent removal through slow evaporation, white **2** was isolated (0.100 g, 62%). – IR (KBr): $\tilde{\nu}$ = 3091 cm^{-1} (w), 2962 (s), 2894 (s), 2857 (s), 1441 (m), 1014 (s), 861 (m), 765 (s), 662 (w). – ^{1}H NMR (C_6D_6): δ = 6.11 (s, ca. 9H, C_5H_5), 3.34 (m, 4H, THF), 2.00 (s, 15H, C_5Me_5), 1.18 (m, 4H, THF). – ^{13}C NMR (C_6D_6): δ = 119.3 (s, C_5Me$_5$), 113.2 (s, C_5H$_5$), 72.4 (s, THF), 31.9 (s, THF), 12.2 (C_5Me_5). – $C_{24}H_{33}LaO$ (476.4): calcd. C 60.50, H 6.98; found C 61.33, H 6.91.

2 *(Method b):* Into a 125-ml Erlenmeyer flask equipped with a magnetic stirring bar were added K[C_5Me_5] (0.335 g, 1.92 · 10^{-3} mol) and toluene (30 ml), followed by [La(C_5H_5)$_3$(thf)$_{1.5}$] (0.273 g, 0.617 · 10^{-3} mol). After being allowed to stir for 12 h, the beige solution was filtered through a glass frit, which removed unreacted K[C_5Me_5]. The solvent was removed under reduced pressure by rotary evaporation to leave white **2** (0.040 g, 14%), identified by its ^{1}H-NMR spectrum.

[Sn(C_5Me_5)$_2$] from [Ca(C_5Me_5)$_2$] and [Sn(C_5H_5)$_2$]: Into a 125-ml Erlenmeyer flask equipped with a magnetic stirring bar were added [Ca(C_5Me_5)$_2$] (0.061 g, 0.20 · 10^{-3} mol) and [Sn(C_5H_5)$_2$] (0.046 g, 0.18 · 10^{-3} mol), followed by toluene (30 ml). After being allowed to stir for 12 h, the yellow solution was filtered through a glass frit. The solvent was removed under reduced pressure by rotary evaporation to leave a crude material that was washed with hexanes (10 ml). The hexanes were removed under dynamic vacuum to leave bright yellow [Sn(C_5Me_5)]$_2$ (0.036 g, 50%), identified by its ^{1}H-NMR spectrum[36].

[(Sn,Pb)(C_5Me_5)$_2$] from [Ca(C_5Me_5)$_2$(thf)$_x$] and [(Sn,Pb)(C_5H_5)$_2$]: Into a 125-ml Erlenmeyer flask equipped with a magnetic stirring bar were added [Ca(C_5Me_5)$_2$(thf)$_x$] (for Sn, x = 2, 0.22 · 10^{-3} mol; for Pb, x = 0.5, 0.28 · 10^{-3} mol) and [(Sn,Pb)(C_5H_5)$_2$] (0.22 · 10^{-3} mol for Sn; 0.28 · 10^{-3} mol for Pb), followed by toluene (30 ml). After being allowed to stir for 18 (12) h, the yellow (red) solution was filtered through a glass frit. The solvent was removed under reduced pressure by rotary evaporation to leave the metallocene, which may be washed with hexanes. Yield of yellow (red) [Sn(C_5Me_5)$_2$]: 55% ([Pb(C_5Me_5)$_2$]: 59%), identified from its ^{1}H-NMR spectrum in C_6D_6[36,37].

[(Sn,Pb)(C_5Me_5)$_2$] from K[C_5Me_5] and [(Sn,Pb)(C_5H_5)$_2$]: Into a 125-ml Erlenmeyer flask containing a magnetic stirring bar, K[C_5Me_5] (0.84 · 10^{-3} mol) was added to [(Sn,Pb)(C_5H_5)$_2$] (0.42 · 10^{-3} mol) in 30 ml of toluene. The mixture was allowed to stir for 5 min, and then force-filtered through a medium glass frit. Evaporation of the filtrate left a yellow (red) solid, identified as [Sn(C_5Me_5)$_2$] (58%) {[Pb(C_5Me_5)$_2$] (35%)} from its ^{1}H-NMR spectrum in C_6D_6[36,37].

[Mn(C_5Me$_5$)$_2$] from [Ca(C_5Me_5)$_2$(thf)] and [Mn(C_5H_5)$_2$]: Into a 125-ml Erlenmeyer flask equipped with a magnetic stirring bar were added [Mn(C_5H_5)$_2$] (0.102 g, 0.551 · 10^{-3} mol) and toluene (25 ml), followed by [Ca(C_5Me_5)$_2$(thf)] (0.204 g, 0.533 · 10^{-3} mol). After being allowed to stir for 12 h, the orange solution was filtered through a glass frit. The solvent was removed under reduced pressure by rotary evaporation to leave bright-orange [Mn(C_5Me_5)$_2$] (0.106 g, 61%), identified by its IR spectrum[23].

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[15] [Nd(C_5H_5)$_3$] displays similar photochromic-like behavior (P. S. Tanner, T. P. Hanusa, unpublished observation.)

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