Chem. Rev. **2002,** 102, 2119−2136

Chemistry of Tris(pentamethylcyclopentadienyl) f-Element Complexes, $(C_5Me_5)_3M$

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Received January 14, 2002

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I. Introduction

Tris(cyclopentadienyl) lanthanide complexes, $(C_5H_5)_3Ln$, were the first well-characterized organometallic complexes of the lanthanide metals.[1−3] As such these species were crucial to the inception of organolanthanide chemistry: they demonstrated the existence of organometallic complexes of these metals. However, since the C_5H_5 ligands are typically ancillary ligands which stabilize and solubilize but do not participate in organometallic reaction chemistry, the importance of the $(C_5H_5)_3Ln$ complexes was more in their existence than in their reactivity. They did not provide major advances in organolanthanide-based reaction chemistry.[3−11]

Recently another type of tris(cyclopentadienyl) lanthanide complex has been discovered which, in some respects, is the opposite of the $(C_5H_5)_3Ln$ complexes. The tris(pentamethylcyclopentadienyl) complexes, $(C_5Me_5)_3Ln$, were not expected to exist on the basis of known organometallic chemistry, and once discovered,[12] they have contributed significantly to advancing organo−f-element chemistry by revealing new types of reactions and complexes. This review presents a comprehensive summary of the chemistry of these unanticipated species and their impact on the f-element field.

II. Background

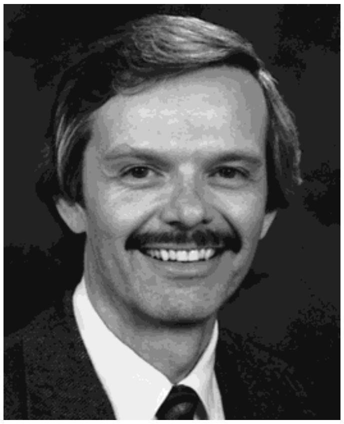
A. Cyclopentadienyl Ligands in Lanthanide Chemistry

Cyclopentadienyl ligands were originally used in f-element chemistry only as part of a broad survey of the chemistry of this ligand with all metals. Metal halides across the periodic table were reacted with alkali-metal cyclopentadienides. For the lanthanides this generated the $(C_5H_5)_3Ln$ complexes according to eq 1.[1,2]

$$LnCl_3 + 3NaC_5H_5 \xrightarrow[-3NaCl]{THF} (C_5H_5)_3Ln \qquad (1)$$

The cyclopentadienyl ligand subsequently proved to be an excellent choice for stabilizing organolan-

10.1021/cr010298r CCC: $39.75 © 2002 American Chemical Society
Published on Web 05/21/2002



William J. Evans was born in Madison, WI, in 1947. He received his B.S. degree in 1969 from the University of Wisconsin, where he did pentaborane research with Donald F. Gaines. He obtained his Ph.D. degree in the area of metallocarborane chemistry at UCLA in 1973 under the direction of M. Frederick Hawthorne. Evans subsequently conducted postdoctoral research at Cornell University with the late Earl L. Muetterties. When Evans joined the faculty of the University of Chicago in 1975, he initiated a research program in an area entirely different from his training or experience: the chemistry of lanthanide elements. Although lanthanide chemistry was not popular at that time and the general view of these metals was that they were not worth studying, Evans felt that the special physical properties of these elements could lead to unique chemistry if the metals could be put in the proper coordination environments. This idea has been realized in many ways since 1975. After promotion to Associate Professor with tenure at Chicago in 1982, he moved to the University of California, Irvine, where he was appointed Professor in 1983. His research has shown from many different perspectives how the unique chemisty of the f elements can be utilized to broaden and expand chemistry.

Benjamin L. Davis was born in Lewiston, ME, in 1975. He received his B.A. degree in 1998 from Bowdoin College, where he worked on the synthesis of C_2-symmetric lanthanocenes with Richard D. Broene. For the past four years he has studied the synthesis and reaction chemistry of sterically crowded lanthanide complexes.

thanide complexes in general.[3−11] As a resonance-stabilized monoanionic group that formally occupies three coordination positions, it meets important requirements necessary for isolating an organolanthanide complex.[13] Anionic ligands are required to electrostatically balance the positive charge of the lanthanide ions, which tend to form rather ionic complexes due to the limited radial extension of the 4f orbitals.[14] Large ligands are useful for the isolation of soluble molecular species, since these metals are some of the largest in the periodic table. The monoanionic nature of the cyclopentadienyl ligand allows it to provide electrostatic and steric stabilization while taking up only one valency of the metal. An extensive review of cyclopentadienyl lanthanide complexes was published in *Chemical Reviews* in 1995 and describes the many examples of the tris-, bis-, and monocyclopentadienyl complexes that have been reported.[3] That review surveys not only simple C_5H_5 ligands, but also a variety of substituted derivatives, C_5H_4R, $C_5H_3R_2$, C_5Me_4H, and C_5R_5, for which much lanthanide chemistry has been developed.

In the hundreds of cyclopentadienyl lanthanide complexes in the literature, the cyclopentadienyl ligand functions almost exclusively as an ancillary ligand, i.e., a group which provides stability and solubility but does not participate in the reaction chemistry. For these reasons, organolanthanide reaction chemistry became more developed with bis(cyclopentadienyl) complexes of general formula $[(C_5H_5)_2LnZ]_n$, in which Z is a monoanionic reactive ligand such as alkyl, aryl, hydride, amide, etc., rather than with tris(cyclopentadienyl) compounds. The tris(cyclopentadienyl) lanthanide complexes have been of interest more from a structural point of view[15−22] or as precursors.[23] The unsolvated $[(C_5H_5)_3Ln]_n$ complexes typically oligomerize in several different ways in order to increase the coordination around the metal. The structures of these $[(C_5H_5)_3Ln]_n$ complexes show that even three C_5H_5 groups do not completely saturate the coordination environment of these large metals. The structures also show that these metal ions can interact with distant electron density in a variety of bonding modes.[3,15−22]

B. Pentamethylcyclopentadienyl Ligands in Lanthanide Chemistry

The C_5Me_5 ligand[24,25] was introduced into lanthanide chemistry in 1980.[26−28] This ligand has all the favorable aspects of the C_5H_5 group plus a larger size and enhanced solubilizing capacity. Its introduction into organolanthanide chemistry had a significant impact on the chemistry of both trivalent and divalent ions. The important class of trivalent $[(C_5H_5)_2LnZ]_n$ compounds had been available only for the later, smaller metals in the series ($Ln = Sm-Lu$).[26,29] Complexes of the larger metals presumably were sterically unsaturated[10] with this ligand set and underwent ligand redistribution reactions to form the more stable $(C_5H_5)_3Ln$ species and generally uncharacterizable Ln/Z combinations.[30,31] The C_5Me_5 ligand allowed $[(C_5Me_5)_2LnZ]_n$ complexes to be synthesized for the larger metals[26] and across the entire lanthanide series.[3] Outstanding organometallic chemistry has resulted as a consequence.[3−10]

The C_5Me_5 group also made possible the isolation of the first soluble organosamarium(II) complex, $(C_5Me_5)_2Sm(THF)_2$, in 1981.[32] The unsubstituted cyclopentadienyl analogue, $(C_5H_5)_2Sm(THF)$, which had been reported in 1969,[33] had limited chemistry due to its insolubility in solvents with which it did not react. $(C_5Me_5)_2Sm(THF)_2$ allowed the powerful reduction chemistry of Sm^{2+} [34−36] to be accessed for the first time in an organometallic environment. This complex also led to the discovery of the surprisingly bent unsolvated metallocene, $(C_5Me_5)_2Sm$.[37] These two metallocene complexes expanded organometallic lanthanide chemistry in many ways. Indeed, just as Kagan's important discovery of the utility of SmI_2 in organic chemistry was being developed on the organic side,[34−36] $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ provided Sm^{2+}-based advances in the organometallic area.

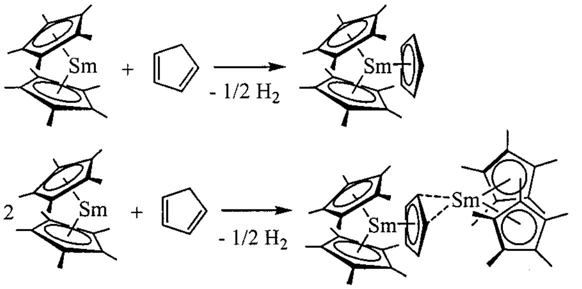
$(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ demonstrated that the lanthanides could be useful in complexing, activating, and transforming many types of unsaturated substrates which previously had been thought to be reactive only with transition metals. This included dinitrogen,[38] olefins,[32,39−42] internal alkynes,[43,44] phosphaalkynes,[45] CO,[46] CO_2,[47] isonitriles,[48] azo compounds,[49−51] imines,[52] and polycyclic aromatic hydrocarbons.[53] These complexes also led to an extensive chemistry with inorganic[54−58] and organometallic substrates as diverse as $Se{=}PPh_3$ and $Al(^iBu)_3$.[41,59,60] These Sm^{2+} organometallics also provided facile synthetic routes to trivalent complexes. For example, the first example of a pentamethylcyclopentadienyl lanthanide hydride, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$, was made via reductive Sm^{2+} chemistry.[43] The convenient synthetic routes to trivalent complexes available via Sm^{2+} reduction have led to a situation in which samarium is often the metal of choice among the 14 possible lanthanides. Examples include studies of polymerization,[41,61−70] thermochemistry,[71] and C−H and Si−H activation.[72−75] This demonstrates the importance of reduction chemistry to the organolanthanide field.

C. Tris(pentamethylcyclopentadienyl) Complexes, $(C_5Me_5)_3Ln$

Although the C_5Me_5 ligand was a great asset to organolanthanide chemistry, it was assumed for years that its importance was in providing mono-C_5Me_5 and bis-C_5Me_5 complexes. Until 1991, it was believed that compounds of the formula $(C_5Me_5)_3Ln$ could not exist. No research advances were expected from such a species much less a *Chemical Review* article devoted entirely to this topic like the present one.

The basis for this belief was 2-fold: the absence of any examples of this type of complex in decades of work on the C_5Me_5 ligand by numerous research groups with nearly all of the metals in the periodic table and the cone angle of this ligand.[76] The cone angle for C_5Me_5 was estimated to be much larger than the 120° needed for a $(\eta^5\text{-}C_5Me_5)_3M$ complex (M = metal).[77−79] Consequently, the ligand was considered to be too large to form $(\eta^5\text{-}C_5Me_5)_3M$ complexes.[80] This seemed quite reasonable since no $(C_5Me_5)_3M$ complexes had been found. Indeed, one rationale considered for the special reactivity of the Sm^{2+} organometallic complexes, $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$, was that they could not form $(C_5Me_5)_3Sm$ as an end product in their reactions. Other soluble Sm^{2+} complexes such as $SmI_2(THF)_2$,[34−36] $Sm[N(SiMe_3)_2]_2(THF)_2$,[81] and $[C_5H_3(SiMe_3)_2]_2Sm(THF)$[82] did not exhibit the spectacular organometallic reaction chemistry of the $(C_5Me_5)_2Sm(THF)_x$ systems,[10] and generally the tris(ligand) complexes, SmI_3, $Sm[N(SiMe_3)_2]_3$, and $[C_5H_3(SiMe_3)_2]_3Sm$, were obtained instead.[82]

Prior to the discovery of $(C_5Me_5)_3Sm$,[12] the tris(cyclopentadienyl) f-element complex containing the largest ligands was $[C_5H_3(SiMe_3)_2]_3Sm$, which had been synthesized using the reductive chemistry of Sm^{2+}.[82] The mixed ligand complexes, $(C_5Me_5)_2Sm(C_5H_5)$ and $[(C_5Me_5)_2Sm]_2(\mu\text{-}C_5H_5)$, also were known. Again, these species were accessed via reductive Sm^{2+} chemistry, eqs 2 and 3.[83]

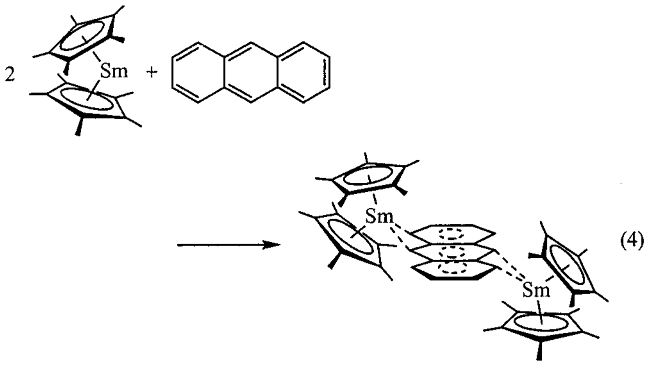


It is interesting to note that it was always conceivable that a tris(mono-hapto) complex, $(\eta^1\text{-}C_5Me_5)_3M$, could exist. However, no examples were found until after $(C_5Me_5)_3Sm$[12] was discovered in 1991. The existence of $(\eta^1\text{-}C_5Me_5)_3Ga$ was discovered in 1994.[84]

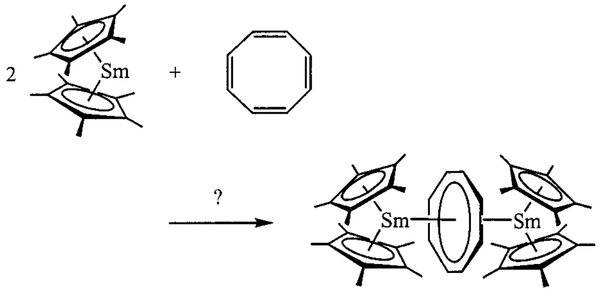
III. Synthesis of $(C_5Me_5)_3Sm$

A. First Synthesis via Exploratory Sm(II) Chemistry

The synthesis of the first $(C_5Me_5)_3Ln$ complex arose from an exploratory synthetic study of the chemistry of $(C_5Me_5)_2Sm$[37,85] with unsaturated hydrocarbons. It had previously been found that 2 equiv of $(C_5Me_5)_2Sm$ reduced anthracene to a dianion, which was unexpectedly planar (to within 0.02 Å) as shown in eq 4.[53]

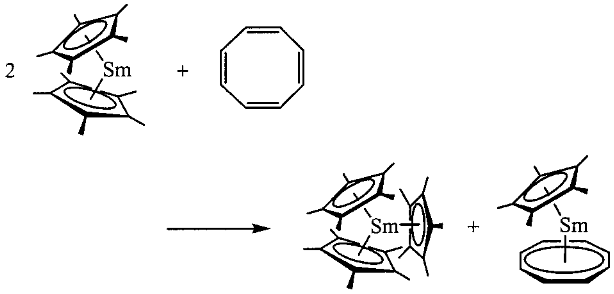


The reaction of $(C_5Me_5)_2Sm$ with 1,3,5,7-cyclooctatetraene was examined in an attempt to set up a reverse situation in which a dianion that is normally planar would be forced to be nonplanar. Reduction of C_8H_8 to $(C_8H_8)^{2-}$ by $(C_5Me_5)_2Sm$ was expected, but it was not clear if there would be room for the planar dianion between two $[(C_5Me_5)_2Sm]^+$ cations, eq 5. The possible distortion that could result and its consequences in chemical reactivity were of interest.



(5)

However, a bimetallic $[(C_5Me_5)_2Sm]_2(C_8H_8)$ product was not isolated from the reaction of $(C_5Me_5)_2Sm$ and C_8H_8. Instead, the mono-C_5Me_5 cyclooctatetraenyl complex, $(C_5Me_5)Sm(C_8H_8)$, was a favored product. Formation of $(C_5Me_5)Sm(C_8H_8)$ from 2 equiv of $(C_5Me_5)_2Sm$ and C_8H_8 left three $(C_5Me_5)^-$ ligands and a Sm^{3+} ion remaining. Surprisingly, these combined to generate the first $(C_5Me_5)_3Ln$ complex, $(C_5Me_5)_3Sm$, eq 6.[12] The reaction occurs immediately on mixing the reagents.



(6)

The formation of this supposedly unattainable $(C_5Me_5)_3Ln$ complex required only the combination of the proper reagents!

How could $(C_5Me_5)_3Sm$ form if the cone angle of C_5Me_5 is much larger than 120°? The complex can exist because the $Sm-C(C_5Me_5)$ distances are substantially longer than those in previously characterized Sm^{3+}/C_5Me_5 complexes.[12,86] A review of C_5Me_5 lanthanide complexes[86] showed that the average $Sm-C(C_5Me_5)$ distance for nine-coordinate Sm^{3+} complexes is 2.75(2) Å with a range of averages for individual complexes of 2.73(2)−2.77(2) Å. $(C_5Me_5)_3Sm$ has an average $Sm-C(C_5Me_5)$ distance of 2.82(5) Å, and the three crystallographically unique $Sm-C(C_5Me_5)$ distances are 2.782(2), 2.817(2), and 2.910(3) Å. Positioning the C_5Me_5 rings at a greater distance reduces the cone angle to the 120° value found in $(C_5Me_5)_3Sm$. The longer Sm−C bonds were consistent with the expectation that this would be a very sterically crowded molecule.

The extreme steric crowding in $(C_5Me_5)_3Sm$ could have been the basis for limited reactivity for this complex, since substrates would not be able to approach the metal center. Alternatively, the long $Sm-C(C_5Me_5)$ distances could provide a basis for high reactivity. These long distances prevented both the C_5Me_5 rings and the samarium from having their normal electrostatic stabilization. This could make the C_5Me_5 rings prone to removal and the metal center highly electrophilic. Moreover, space-filling models, Figure 1, suggested that there was an open channel down the 3-fold axis of the molecule which could allow cylindrical substrates to access the metal.

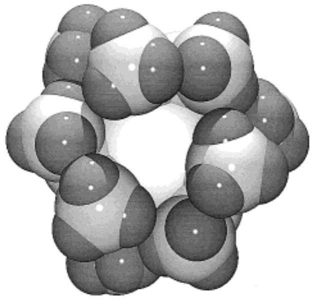
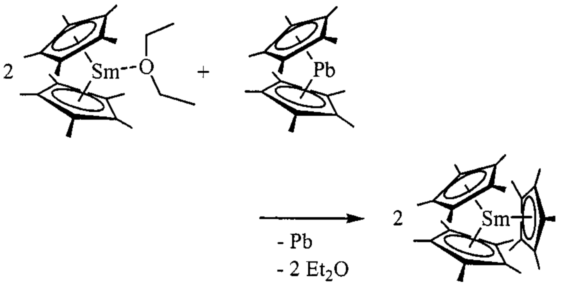


Figure 1. View down the 3-fold axis of $(C_5Me_5)_3Ln$.

Although eq 6 demonstrated that $(C_5Me_5)_3Ln$ complexes could be synthesized, it was not an optimum preparation of $(C_5Me_5)_3Sm$ for subsequent reactivity studies. The synthesis was not efficient in either samarium or C_5Me_5. In addition, $(C_5Me_5)_3Sm$ was isolated only after removal by sublimation of the $(C_5Me_5)Sm(C_8H_8)$ byproduct. $(C_5Me_5)_3Sm$ could also be synthesized from $(C_5Me_5)_2Sm(OEt_2)$ and C_8H_8, but this reaction had the same problems as eq 6. The development of $(C_5Me_5)_3Sm$ chemistry required the discovery of a second type of synthesis as described in the next section. Interestingly, the reaction of the solvated $(C_5Me_5)_2Sm(THF)_2$ and C_8H_8 is reported to give only $(C_5Me_5)Sm(C_8H_8)(THF)$ and $(C_5Me_5)_2$.[87]

B. Efficient Synthesis via Sm(II) and $(C_5Me_5)_2Pb$

The second synthesis of $(C_5Me_5)_3Sm$ also arose from exploratory synthetic studies with $(C_5Me_5)_2Sm$. In this case, the substrates were inorganic rather than organic. $(C_5Me_5)_2Sm$ had been found to make some unusual Zintl ions with antimony,[58] bismuth,[57] and selenium[56,88] reagents. A project to examine reduction of tin and lead compounds was in progress to determine the utility of $(C_5Me_5)_2Sm$ in expanding their Zintl ion chemistry. As part of these studies, the reaction of $(C_5Me_5)_2Sm(OEt_2)$ with $(C_5Me_5)_2Pb$ was suggested as a route to $(C_5Me_5)_3Sm$. $(C_5Me_5)_2Sm(OEt_2)$ was chosen instead of $(C_5Me_5)_2Sm$ since it is easier to prepare. $(C_5Me_5)_2Sm(OEt_2)$ was preferred over $(C_5Me_5)_2Sm(THF)_x$ because $(C_5Me_5)_3Sm$ reacts with THF (section V. B). The $(C_5Me_5)_2Sm(OEt_2)/(C_5Me_5)_2Pb$ reaction was successful as shown in eq 7.[89] The synthesis is efficient in reagents and separation of the Pb byproduct is facile. This synthesis opened up the reaction chemistry of $(C_5Me_5)_3Sm$ described in sections V and VI.

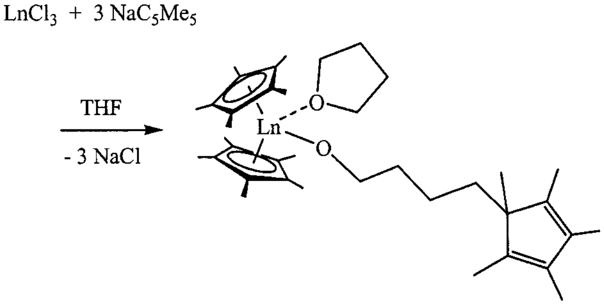


(7)

C. Syntheses from Trivalent Precursors

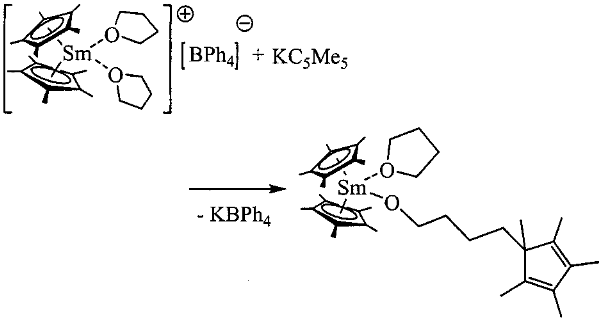
Once the importance of the chemistry of $(C_5Me_5)_3Sm$ was revealed, it was clear that it was desirable to make other $(C_5Me_5)_3Ln$ complexes beyond the single samarium example. This was particularly crucial to the sterically induced reduction chemistry described in sections VI and VII. Neither eq 6 nor 7 was an appropriate synthesis since both relied on the special chemistry of Sm^{2+} which was unavailable to the other lanthanides.[10] General routes to $(C_5Me_5)_3Ln$ complexes required trivalent precursors.

The most obvious trivalent synthetic route to a $(C_5Me_5)_3Ln$ complex, the reaction of a lanthanide trichloride with 3 equiv of a $(C_5Me_5)^-$ salt, the analogue of the Wilkinson preparation of $(C_5H_5)_3Ln$ complexes, eq 1, did not provide isolable $(C_5Me_5)_3Ln$ complexes. Instead, this reaction leads to the THF ring-opened products, $(C_5Me_5)_2Ln[O(CH_2)_4C_5Me_5](THF)$ (Ln = La, Nd, Tm, Lu), eq 8.[90]



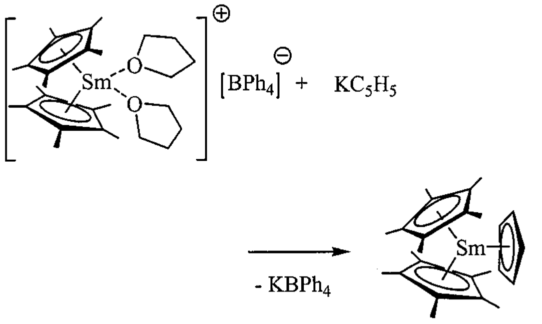
(8)

The first example of a ring-opened complex of this type was isolated from the reaction of $[(C_5Me_5)_2Sm(THF)_2][BPh_4]$ with KC_5Me_5, eq 9.[91]



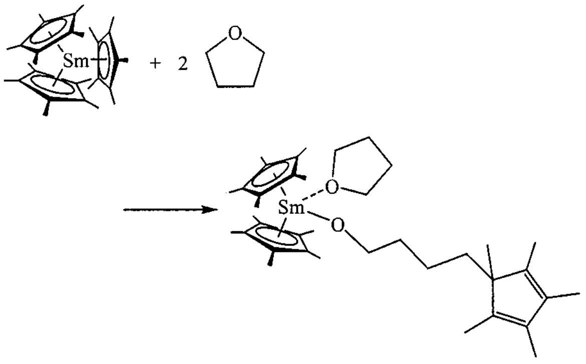
(9)

This reaction also could have been a trivalent route to $(C_5Me_5)_3Sm$, since the reaction of $[(C_5Me_5)_2Sm(THF)_2]^+$ with KC_5H_5 formed $(C_5Me_5)_2Sm(C_5H_5)$,[83] eq 10.



(10)

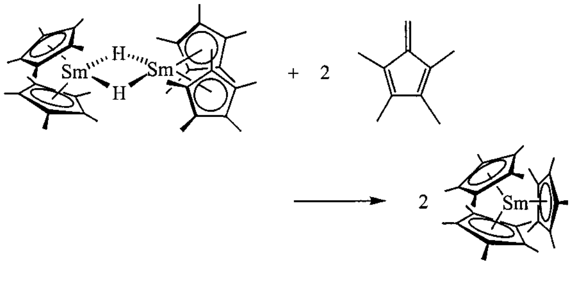
Subsequent reactivity studies, described in section V.B, showed why these routes were not successful: isolated $(C_5Me_5)_3Sm$ ring opens THF, eq 11.[92] Any $(C_5Me_5)_3Ln$ complexes which did form via eq 8 would be expected to immediately ring open the solvent.



(11)

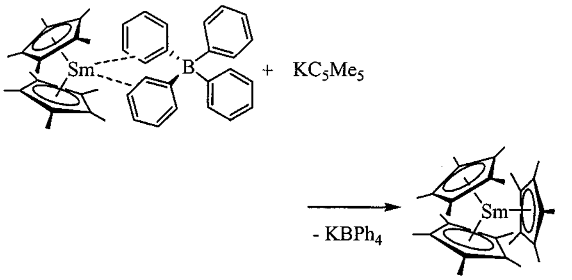
Other conventional trivalent approaches to $(C_5Me_5)_3Ln$ complexes even in the absence of THF were also unsuccessful. For example, deprotonation of C_5Me_5H with trivalent $(C_5Me_5)_2LnZ$ precursors (Z = $CH(SiMe_3)_2$, $N(SiMe_3)_2$, and H) could be done in nonpolar solvents in the absence of THF, and the $(C_5Me_5)_2LnZ$ complexes are known across the lanthanide series. Unfortunately, for Ln = Sm, none of these reactions formed $(C_5Me_5)_3Sm$.[92] Likewise, neither $(C_5Me_5)_2SmPh$ nor $(C_5Me_5)_2Sm(\mu\text{-H})(\mu\text{-}C_5Me_4CH_2)Sm(C_5Me_5)$[93] deprotonated C_5Me_5H.[92] Since the Z ligands in these $(C_5Me_5)_2LnZ$ precursors were sufficiently basic to deprotonate C_5Me_5H, it seemed likely that these reactions failed for steric reasons.

Fortunately, two syntheses of $(C_5Me_5)_3Sm$ from trivalent precursors were discovered which avoided the THF ring-opening problem and the problem of deprotonating C_5Me_5H. One of these arose from examining the $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$-like reactivity of $(C_5Me_5)_3Sm$ described in section V. Since β-hydrogen elimination from a possible $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ intermediate to $[(C_5Me_5)_2SmH]_2$[43] and tetramethylfulvene was not observed, the reverse reaction was attempted. As shown in eq 12, this constituted a third synthesis of $(C_5Me_5)_3Sm$.[94] Since $[(C_5Me_5)_2LnH]_x$ complexes are known across the lanthanide series,[43,95-98] this offered a trivalent route to make $(C_5Me_5)_3Ln$ complexes in general.



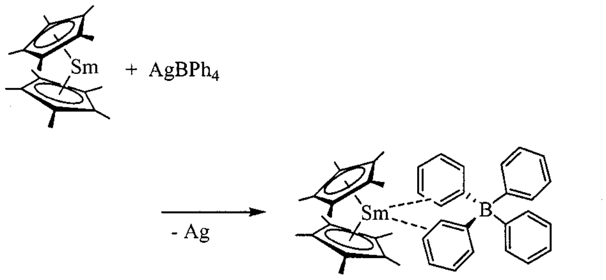
(12)

The fourth synthesis of $(C_5Me_5)_3Sm$ involved the reaction of the unsolvated cation, $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$, with KC_5Me_5, eq 13.[99] This reaction is an



(13)

analogue of eqs 9 and 10 but in the absence of THF. The key to the discovery of this synthesis was identifying the right conditions for the isolation of the unsolvated cation, $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$.[99] Since this samarium cation was originally made via a Sm^{2+} route from $(C_5Me_5)_2Sm$, eq 14, extension of this cation-based synthesis to non-samarium lanthanides required an efficient synthesis of the unsolvated cations, $[(C_5Me_5)_2Ln][BPh_4]$, from trivalent precursors. This was accomplished as shown in eqs 15 and 16.[99] These cations are now readily obtained synthons for all of the lanthanide metals. They allowed new $(C_5Me_5)_3Ln$ complexes to be formed via eq 13, but they are also good precursors for forming $(C_5Me_5)_2LnZ$ complexes in general via eq 17.[99]



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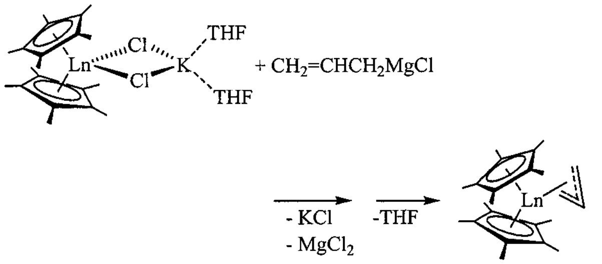

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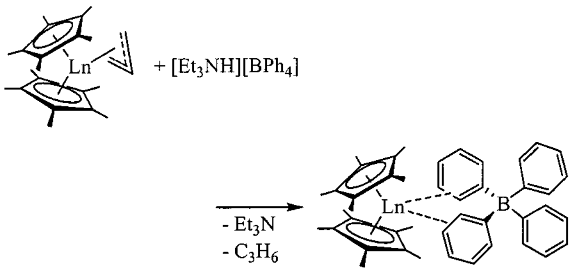

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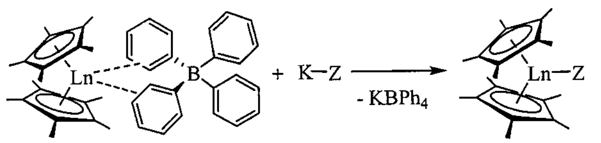
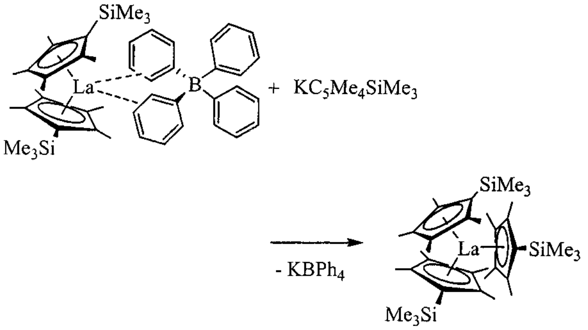


(17)

IV. Synthesis of $(C_5Me_5)_3M$ Complexes beyond M = Sm

A. $(C_5Me_5)_3Ln$ (Ln = La, Ce, Pr, Nd, Gd)

Extension of the routes described above for $(C_5Me_5)_3Sm$ has been challenging. The difficulty in working with the highly reactive $[(C_5Me_5)_2LnH]_x$ complexes[43,95−98] has limited the utility of the Ln−H plus tetramethylfulvene synthesis, eq 12. However, the unsolvated cation route, eq 13, has now been used to make $(C_5Me_5)_3Ln$ for Ln = La−Nd[99,100] and Gd,[101] all of which have been crystallographically characterized. This synthetic approach has also been used to make a series of $(C_5Me_4R)_3Ln$ complexes with cyclopentadienyl rings even larger than C_5Me_5. Hence, the series $(C_5Me_4R)_3La$ (R = Et, ^{i}Pr, SiMe$_3$) has been made by this route and structurally characterized by X-ray crystallography, e.g., eq 18.[102] The tetramethylethylcyclopentadienyl samarium complex, $(C_5Me_4Et)_3Sm$, was also obtainable via eq 7.

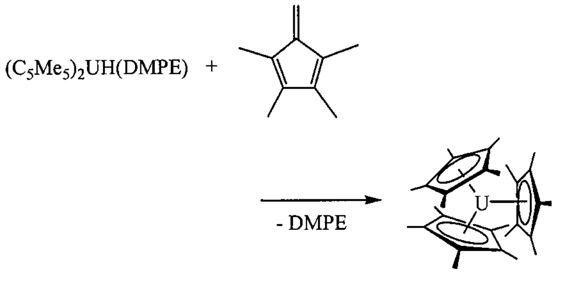


(18)

Surprisingly, $(C_5Me_5)_3La$ and $(C_5Me_5)_3Ce$ were more difficult to synthesize than their *more* crowded analogues, $(C_5Me_5)_3Ln$ (Ln = Pr, Nd, Sm) and $(C_5Me_4R)_3La$ (R = Et, ^{i}Pr, SiMe$_3$). Attempted syntheses of $(C_5Me_5)_3La$ and $(C_5Me_5)_3Ce$ routinely formed the oxides, $[(C_5Me_5)_2Ln]_2O$, analogous to $[(C_5Me_5)_2Sm]_2O$ previously made via Sm^{2+} chemistry.[103] Only by using silylated glassware were these $(C_5Me_5)_3Ln$ compounds isolable in pure form.

B. $(C_5Me_5)_3U$

The trivalent metal hydride plus tetramethylfulvene reaction, eq 12, was useful in the synthesis of the first example of a $(C_5Me_5)_3M$ complex in which M is an actinide, namely, $(C_5Me_5)_3U$, eq 19 (DMPE = $Me_2PCH_2CH_2PMe_2$).[94]



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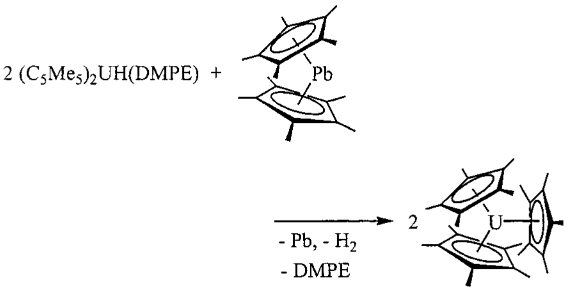
Once the existence of $(C_5Me_5)_3U$ was established, several other synthetic routes were identified, eqs 20−22.[104]



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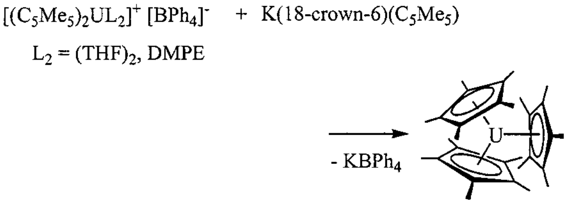

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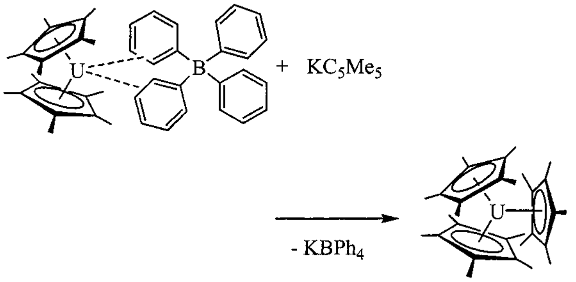


(22)

Equations 20 and 21 were possible since $(C_5Me_5)_3U$ is less reactive with H_2 and THF than $(C_5Me_5)_3Sm$.

C. Synthetic Generalizations

A survey of the successful syntheses of $(C_5Me_5)_3M$ complexes shows that in most cases the reactions involve formation of one highly stable coproduct which leaves the components of a $(C_5Me_5)_3M$ complex. The reactions are set up such that the three $(C_5Me_5)^-$ rings and the trivalent metal combine to make $(C_5Me_5)_3M$ because there is no better option. For example, three of the syntheses of $(C_5Me_5)_3Sm$ involve the formation of the stable byproducts $(C_5Me_5)Sm(C_8H_8)$,[12] Pb,[89] and $KBPh_4$,[99] eqs 6, 7, and 13, respectively. The fourth synthesis of $(C_5Me_5)_3Sm$, eq 12, involves the formation of $(C_5Me_5)^-$, which then functions as one of the $(C_5Me_5)^-$ ligands in $(C_5Me_5)_3Sm$.[94] Equations 19−22 for the synthesis of $(C_5Me_5)_3U$ also involve formation of Pb, $(C_5Me_5)^-$, and $KBPh_4$.

In addition to arranging the syntheses so that formation of $(C_5Me_5)_3M$ is the best option, these syntheses must be done in the absence of compounds with which $(C_5Me_5)_3M$ complexes react. This includes THF, nitriles, isonitriles, some halocarbons, and, in some cases, oxygen functionalities normally as inert as those on glassware. For example, as described above, some preparations require silylated glassware and some $(C_5Me_5)_3M$ complexes will decompose due to the presence of residual THF vapor in a glovebox. As described below, the reactivity appears to depend on the degree of steric crowding. For example, $(C_5Me_5)_3Sm$ reacts with PhCl, but $(C_5Me_5)_3Nd$ can be synthesized using PhCl as a solvent.[105]

It should be noted that there is one complex of composition $(C_5Me_5)_3M$ that can be made from NaC_5Me_5 and a metal trihalide. $GaCl_3$ reacts with 3 equiv of NaC_5Me_5 to form $(C_5Me_5)_3Ga$, but in this case the product has a tris(η^1-C_5Me_5) structure.[84]

D. Structural Generalizations

Table 1 lists structural data on all of the $(C_5R_5)_3M$ complexes crystallographically characterized to date. All of the $(C_5Me_5)_3M$ complexes crystallize in the $P6_3/m$ space group, whereas the $(C_5Me_4R)_3M$ complexes crystallize as either $C2/c$ or $P\bar{1}$. All of the complexes display M−C(C_5Me_5) distances significantly longer than those in previously reported lanthanide and actinide C_5R_5 complexes.[86] All of the complexes also display (C_5R_5 ring centroid)−M−(C_5R_5 ring centroid) angles smaller than those previously reported. For the $(C_5Me_5)_3M$ complexes, these angles are 120° and for the substituted $(C_5Me_4R)_3M$ complexes they range from 119.5° to 120.5°.[102] In comparison, the smallest (C_5Me_5 ring centroid)−M−(C_5Me_5 ring centroid) angle previously reported was was the 127° value in $(C_5Me_5)_2Sm(C_5H_5)$,[83] and the usual range is 130°−138°.[86] Since the values of the M−C(C_5Me_5) distances within a single complex can vary by as much as 0.128 Å, the error limits on the averages are large. This complicates the comparison of the average values in a statistically significant way. However, in general, larger M−C(C_5Me_5) distances are found for the larger metals and larger rings as expected.

V. (η^1-C_5Me_5)−Sm Reactivity of $(C_5Me_5)_3Sm$

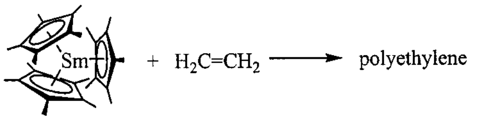
A. Alkyl-like Reactivity

Early studies of the reactivity of $(C_5Me_5)_3Sm$ revealed a series of reactions surprising for a homo-

Table 1. Metrical Data for $(C_5R_5)_3M$ Complexes

	distance (Å)					
		metal−C (ring)			effective ionic radii (9 coordinate)	mean metal−C(ring)] − [ionic radius]
$(C_5Me_5)_3Ln$	metal−centroid	high	low	mean		
$(C_5Me_5)_3Gd$	2.535	2.897 (4)	2.766 (2)	2.80 (4)	1.107	1.693
$(C_5Me_5)_3Sm$	2.555	2.910 (3)	2.782 (2)	2.82(5)	1.132	1.688
$(C_5Me_4Et)_3Sm$	2.568	2.900 (14)	2.787 (12)	2.83 (4)	1.132	1.698
$(C_5Me_5)_3U$	2.581	2.920 (4)	2.813 (3)	2.84 (4)	∼1.19	1.65
$(C_5Me_5)_3Nd$	2.582	2.927 (2)	2.8146(13)	2.86(6)	1.163	1.697
$(C_5Me_5)_3Pr$	2.598	2.938 (3)	2.830 (2)	2.86 (4)	1.179	1.681
$(C_5Me_5)_3Ce$	2.619	2.954 (2)	2.8497 (16)	2.88 (4)	1.196	1.684
$(C_5Me_5)_3La$	2.642	2.975 (3)	2.8732 (19)	2.91 (5)	1.216	1.694
$(C_5Me_4Et)_3La$	2.653	2.973 (3)	2.857 (3)	2.91 (4)	1.216	1.694
$(C_5Me_4{}^iPr)_3La$	2.660	2.971 (3)	2.874 (3)	2.92 (3)	1.216	1.704
$(C_5Me_4SiMe_3)_3La$	2.692	3.0293 (18)	2.8900 (18)	2.95 (4)	1.216	1.734

leptic η^5-cyclopentadienyl complex. These were unexpected because, as mentioned in section II, cyclopentadienyl ligands have been inert ancillary ligands throughout decades of study. Cyclopentadienyl ligands did not have the reactivity of ligands such as alkyls, hydrides, amides, etc. However, $(C_5Me_5)_3Sm$ was found[92] to (a) ring open THF, eq 11, a reaction that usually involves attack by a nucleophile on a bound THF,[91] (b) polymerize ethylene, eq 23, a reaction which, when initiated by a lanthanide complex, usually requires an alkyl or hydride initiating group or a reactive, lower valent metal like Sm^{2+},[61] and (c) react with hydrogen to make the hydride, $[(C_5Me_5)_2SmH]_2$, eq 24, a reaction characteristic of $(C_5Me_5)_2Sm(alkyl)$ complexes.[43,93,95−98,106]



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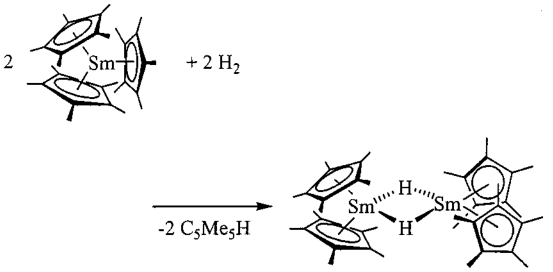
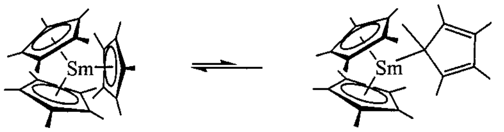


(24)

None of these reactions are known with simple $(C_5H_5)_3Ln$ complexes or their substituted derivatives, and none were expected for η^5-C_5R_5 rings in general. Each of these reactions was typical of alkyl ligands.[3−10] These reactions plus the others discussed in this section indicate that $(C_5Me_5)_3Sm$ can react as if an η^5-$C_5Me_5 \rightleftharpoons \eta^1$-$C_5Me_5$ equilibrium occurs as shown in eq 25. Hence, $(C_5Me_5)_3Sm$ can react like a bulky alkyl complex, $(C_5Me_5)_2SmR$. This reactivity is presumably the result of the steric crowding in the molecule, since it leads to sterically less crowded $(C_5Me_5)_2SmZ$ products and is not observed in C_5Me_5/Sm complexes which have conventional Sm−C(C_5Me_5) bond lengths.



(25)

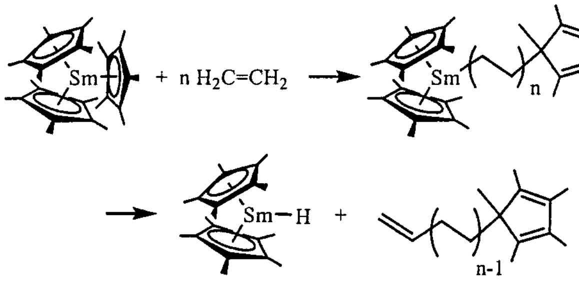
Although all of the reactions presented in this section can be explained with this η^5-$C_5Me_5 \rightleftharpoons \eta^1$-$C_5Me_5$ model, attempts to obtain crystallographic evidence for an η^1-intermediate have not been successful. No evidence for this equilibrium is observable down to −80 °C in toluene by NMR spectroscopy. However, low-temperature NMR studies of $(C_5Me_5)_3Sm$ in the presence of pyridine give peaks suggestive of a $(C_5Me_5)_2Sm(\eta^1$-$C_5Me_5)$(pyridine) adduct at −20 °C. However, the paramagnetism of Sm^{3+} did not allow all of the expected resonances to be observed.[92] Other attempts to trap base adducts of $(C_5Me_5)_2Sm(\eta^1$-$C_5Me_5)$ led to the reductive reactivity discussed in section VI.

B. Ring-Opening Reactions

The ring opening of THF can be rationalized by assuming that THF coordinates to an η^1-C_5Me_5 intermediate to form "$(C_5Me_5)_2Sm(\eta^1$-$C_5Me_5)$(THF)". THF would be activated by coordination to the Lewis-acidic Sm^{3+}, and the ring-opening nucleophile, η^1-C_5Me_5, would be adjacent. Analogous chemistry has been observed for $(C_5Me_5)_2Sm(PPh_2)(THF)$ and $(C_5Me_5)_2Sm(AsPh_2)(THF)$. Each of these complexes can be isolated, but they subsequently form ring-opened products analogous to $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5]$, i.e., $(C_5Me_5)_2Sm[O(CH_2)_4PPh_2]$ and $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2]$.[55] $(C_5H_5)_2Lu(PPh_2)(THF)$, observable only by NMR spectroscopy, behaves similarly.[107] Consistent with this picture, the substituted furan, 2,5-dimethyltetrahydrofuran, does not react with $(C_5Me_5)_3Sm$ even at 75 °C. The sterically more encumbered furan may not be able to coordinate as easily to a $(C_5Me_5)_2Sm(\eta^1$-$C_5Me_5)$ unit. As mentioned in section III.C, THF ring-opened products were observed in $LnCl_3/3KC_5Me_5$ reactions for Ln = La, Nd, Tm, and Lu.[90]

C. Polymerization Reactions

If the polymerization of ethylene by $(C_5Me_5)_3Sm$ proceeds through an η^1-intermediate, the end of the first polymer chain would contain a pentamethylcyclopentadiene terminal group as shown in eq 26.



(26)

After β-hydrogen elimination from the initial polymer chain, subsequent polymerization would occur via the hydride, $(C_5Me_5)_2SmH$, the most likely catalytic intermediate identified by other studies of $(C_5Me_5)_2Sm$-based polymerization.[61] The presence of pentamethylcyclopentadiene in the polymer was not confirmed due to the high molecular weight of the polyethylene formed by this system.

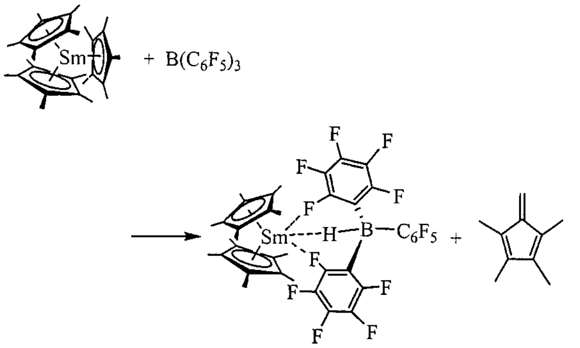
ϵ-Caprolactone is also polymerized by $(C_5Me_5)_3Sm$. Since ϵ-caprolactone is known to coordinate strongly to lanthanides[108] and is readily polymerized by alkyl lanthanide complexes,[109] this reaction can again be rationalized by the intermediacy of a $(C_5Me_5)_2Sm(\eta^1$- $C_5Me_5)L$ species.[92]

D. C_5Me_5 Cleavage Reactions

The reaction of $(C_5Me_5)_3Sm$ with hydrogen, eq 24, was conducted to test the viability of the η^1-alkyl postulate. Since η^5-cyclopentadienyl units are not cleaved by hydrogen, this successful hydrogenolysis is consistent with the idea that $(C_5Me_5)_3Sm$ can display alkyl-like reactivity.

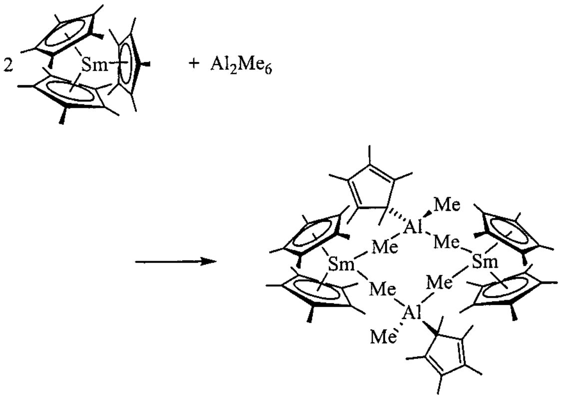
Another characteristic reaction of $(C_5Me_5)_2MR$ complexes of the f-elements and the early transition metals involves removal of an alkyl group with a Lewis acid such as $B(C_6F_5)_3$. Accordingly, $(C_5Me_5)_3Sm$ was treated with $B(C_6F_5)_3$ and Al_2Me_6 to determine if an η^1-C_5Me_5 ligand could be abstracted to form an $[(C_5Me_5)B(C_6F_5)_3]^-$ anion or a $Sm(\eta^1\text{-}C_5Me_5)(\mu\text{-}Me)AlMe_2$ bridging unit, respectively.[110]

$(C_5Me_5)_3Sm$ reacts with $B(C_6F_5)_3$ by loss of a C_5Me_5 ring, but the reaction is not simply an η^1-C_5Me_5 abstraction. As shown in eq 27, tetramethylfulvene is formed and the cationic samarium complex contains an $[\eta^3\text{-}HB(C_6F_5)_3]^-$ moiety.[110] β-hydrogen elimination from a $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ intermediate would provide the observed tetramethylfulvene and a Sm−H, which could be subsequently abstracted by $B(C_6F_5)_3$ to form the $[HB(C_6F_5)_3]^-$ anion. Since no evidence for β-hydrogen elimination from $(C_5Me_5)_3Sm$ alone has been observed, this appears to be a Lewis-acid-assisted β-hydrogen elimination.



(27)

Trimethylaluminum also removes a C_5Me_5 ring from $(C_5Me_5)_3Sm$, but in this case the C_5Me_5 unit stays intact. As shown in eq 28, $[(\mu\text{-}Me)_2AlMe(\eta^1\text{-}C_5Me_5)]^-$ units are formed.[110] These bridge and form a bimetallic complex closely related in structure to that of the previously reported $(C_5Me_5)_2Sm[(\mu\text{-}Me)_2AlMe_2]_2Sm(C_5Me_5)_2$, made from $(C_5Me_5)_2Sm(THF)_2$ and Al_2Me_6.[41] The difference in the $(C_5Me_5)_3Sm$ reaction is that an η^1-C_5Me_5 ligand is attached to each aluminum in place of a methyl group.



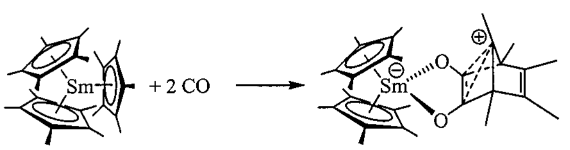
(28)

These reactions of $(C_5Me_5)_3Sm$ with $B(C_6F_5)_3$ and Al_2Me_6 have implications for olefin polymerization reactivity. These reactions indicate that the C_5Me_5 ligand is not necessarily inert in all circumstances in the presence of Lewis acids commonly used as activators in olefin polymerization systems. Since the $(C_5Me_5)^-$ to $(H)^-$ conversion in eq 27 generates a potential initiating site for olefin polymerization,[61,62] such a reaction in a C_5Me_5-based single-site catalyst could lead to another position from which polymerization could occur. Although eq 27 is observed in a complex of special steric crowding, it could conceivably occur in other appropriately crowded complexes in the presence of Lewis acids.

E. Insertion Reactions of CO, Nitriles, and Isocyanates

Space-filling models of the structure of $(C_5Me_5)_3Sm$ suggested that cylindrical substrates could approach the metal center along the axis perpendicular to the plane containing Sm and the three ring centroids as shown in Figure 1. These channels could provide access to a highly electrophilic metal center, since the metal cannot get close to the three rings held distant by the steric crowding. Reactivity with CO was examined in this regard.

CO reacts quickly with $(C_5Me_5)_3Sm$ to form a most unexpected insertion product, $(C_5Me_5)_2Sm(O_2C_7Me_5)$, shown in eq 29.[111] The hydrocarbon part of the new ligand generated in this reaction, $(O_2C_7Me_5)^-$, has all the characteristics of a nonclassical carbonium ion as shown in eq 29. Carbocations are difficult to isolate due to their limited thermal stability and solubility,[112] but this system is soluble in hexane and stable to 60 °C for weeks.

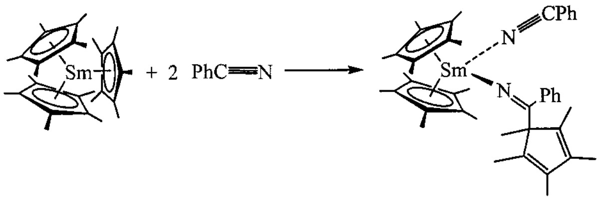


(29)

The reaction which formed $(C_5Me_5)_2Sm(O_2C_7Me_5)$ is as unexpected as the product which was obtained. Formally, the new ligand results from a double insertion of CO into a Sm−(C_5Me_5) unit. Prior to this report there were no cases in which a C_5Me_5 ligand was involved in CO insertion chemistry despite scores of investigations of CO reactivity with C_5Me_5-containing compounds.[25] C_5Me_5 was always an inert ancillary ligand in these CO reactions, as in most other reactions. The mechanistic details of eq 29, which occurs on mixing, are not known, but subsequent studies of the reactivity of $(C_5Me_5)_3Sm$ with nitriles and isocyanates described below show how insertion and coupling can occur.

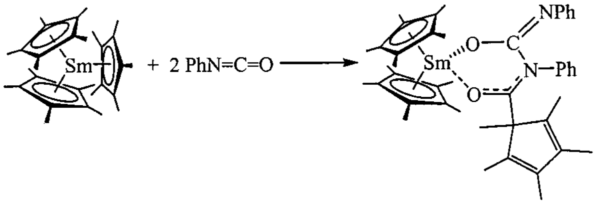
$(C_5Me_5)_3Sm$ reacts with PhC≡N, eq 30, to form a complex in which one PhCN had inserted into a Sm−(C_5Me_5) linkage.[92] Since similar nitrile insertions had been observed with Ti−Me[113] and Y−$CH(SiMe_3)_2$[114] M−C σ-bonded systems, this reaction supported the idea of η^1-C_5Me_5-like reactivity in the $(C_5Me_5)_3Sm$. The insertion product was isolated as a PhCN adduct, such that the overall reaction had a 1:2 $(C_5Me_5)_3Sm$:PhCN ratio.

$(C_5Me_5)_3Sm$ reacts with PhNCO with the same 1:2 stoichiometry, but a more complicated product, $(C_5Me_5)_2Sm[OC(C_5Me_5)N(Ph)C(NPh)O]$, is generated as



(30)

shown in eq 31.[92] As shown in Figure 2, the formation



(31)

of this complex can be envisaged to occur by initial insertion of PhNCO into a Sm(η^1-C_5Me_5) bond and coordination of a second molecule of PhNCO. This would generate a $(C_5Me_5)_2Sm[OC(C_5Me_5)NPh](OCNPh)$ intermediate similar to that of eq 30. In the isocyanate case, this monoinsertion base adduct intermediate would contain a nucleophilic nitrogen from the inserted isocyanate adjacent to the carbon atom of the coordinated isocyanate, a position which is electrophilic.[115] On this basis, the formation of the observed C–N bond and the metallacyclic product is quite reasonable. The nitrile reaction shows how initial insertion and subsequent substrate coordination can occur. The isocyanate reaction shows how two substrates can couple. The CO reaction may occur similarly. Insertion of CO into M–R bonds is known to form reactive MC(O)R acyls which have the capacity to react with additional CO.[25,116,117] Hence, there are reasonable pathways for formation of $(C_5Me_5)_2Sm(O_2C_7Me_5)$, although the specific details are not known.

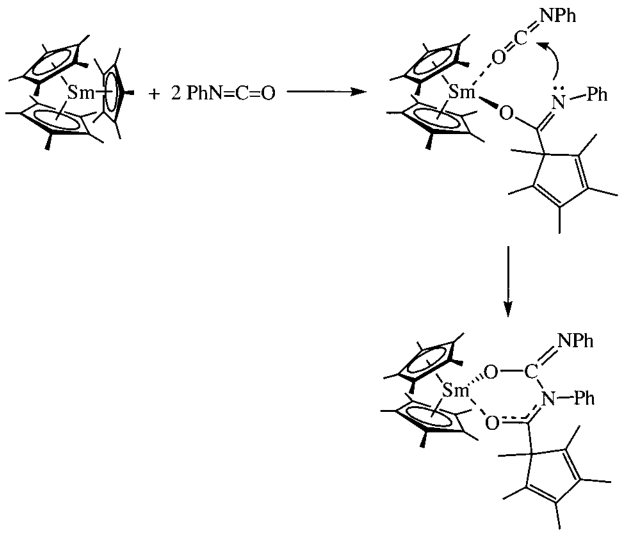


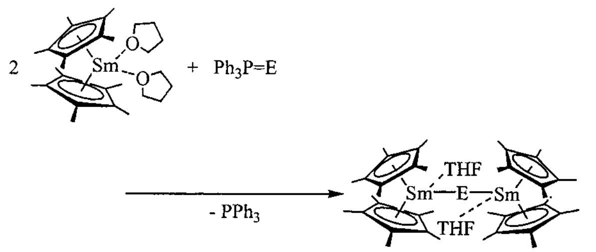
Figure 2. Possible reaction pathway for $(C_5Me_5)_3Sm$ and PhNCO.

VI. Reductive Reactivity of $(C_5Me_5)_3Sm$

A. Similarity of $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm$ Reductions

The observation of $(C_5Me_5)_2Sm(\eta^1$-$C_5Me_5)$-like reactivity described above stimulated efforts to obtain structural information on a Lewis base adduct of the type $(C_5Me_5)_2Sm(\eta^1$-$C_5Me_5)L$. However, a survey of reactions with Lewis bases including $OPPh_3$, $SPPh_3$, and $SePPh_3$ revealed another pattern of reactivity for $(C_5Me_5)_3Sm$, namely, reductive chemistry.[92] Each of these potential ligands was reduced to form $[(C_5Me_5)_2Sm]_2E$ (E = O, S, Se) products containing the $(O)^{2-}$, $(S)^{2-}$, and $(Se)^{2-}$ ions, respectively. The $(C_5Me_5)_3Sm$ reduction products were quickly identified, since they were identical to the products previously generated from the divalent samarium complex $(C_5Me_5)_2Sm$.[10,56,103]

These results led to the discovery of a series of parallel reductions for $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm$. For example, eqs 32–37 (E = S, Se) show three sets of parallel reductions with different types of substrates in which trivalent $(C_5Me_5)_3Sm$[92] and divalent



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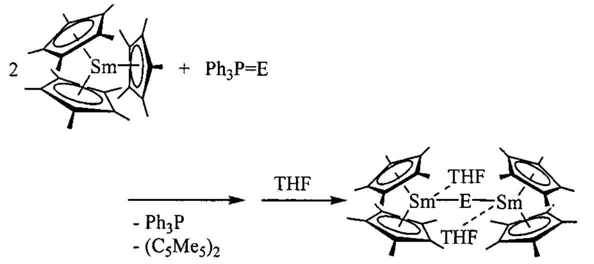
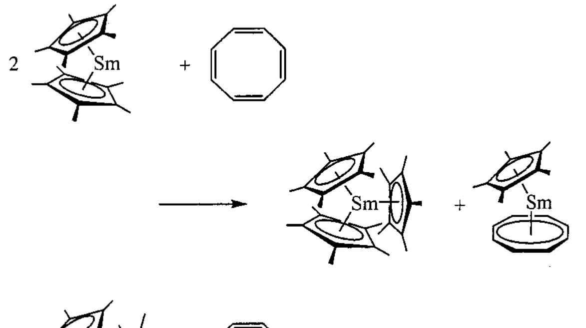


(33)

$$3\,(C_5Me_5)_2Sm + 6\,Me_3CNC \longrightarrow [(C_5Me_5)_2Sm(\mu\text{-}CN)(CNCMe_3)]_3 \quad (34)$$

$$3\,(C_5Me_5)_3Sm + 6\,Me_3CNC \xrightarrow[-3/2\,(C_5Me_5)_2]{} [(C_5Me_5)_2Sm(\mu\text{-}CN)(CNCMe_3)]_3 \quad (35)$$



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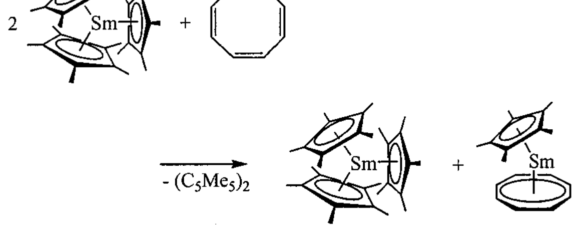


(37)

$(C_5Me_5)_2Sm$[12,48,56,103] each give the same trivalent organosamarium products. Equation 37 is written with $(C_5Me_5)_3Sm$ on both sides of the equation to show the formal similarity to eq 36. This is not meant to imply any mechanistic information.

Since the oxidation state of the metal in the reactant and the product are the same for the above $(C_5Me_5)_3Sm$ reactions, the net reducing agent must be the ligand. Isolation of $(C_5Me_5)_2$[118] as a byproduct in each of the $(C_5Me_5)_3Sm$ reactions indicated that the reductant was one of the $(C_5Me_5)^-$ ligands in $(C_5Me_5)_3Sm$. The appropriate half reaction is shown in eq 38.

$$C_5Me_5^- \rightarrow e^- + 1/2(C_5Me_5)_2 \qquad (38)$$

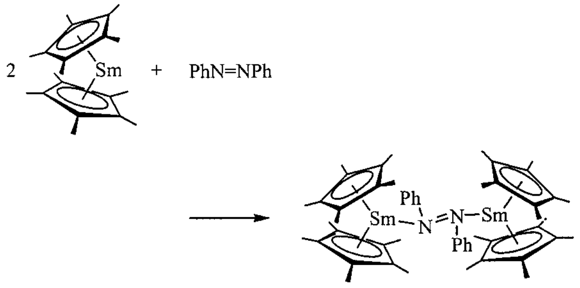
Comparison of the $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm$ half reactions, eqs 39 and 40, shows why each of these compounds gives the same organosamarium product. Both reactions form the same $[(C_5Me_5)_2Sm]^+$ unit, which becomes attached to the reduced substrate in the product.

$$(C_5Me_5)_2Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ \qquad (39)$$

$$(C_5Me_5)_3Sm \rightarrow e^- + [(C_5Me_5)_2Sm]^+ + 1/2(C_5Me_5)_2 \qquad (40)$$

Comparison of $(C_5Me_5)_3Sm$ versus $(C_5Me_5)_2Sm$ reduction of PhN=NPh, eqs 41−43, showed that $(C_5Me_5)_3Sm$ does not display as extensive a reduction chemistry as $(C_5Me_5)_2Sm$. This suggested that the $(C_5Me_5)_3Sm$ reaction was not occurring via a $(C_5Me_5)_2Sm$ intermediate. As shown in eqs 41 and 42, $(C_5Me_5)_2Sm$ can effect both a one-electron reduction[49] and a two-electron reduction[51] of azobenzene depending on the reaction stoichiometry. However, $(C_5Me_5)_3Sm$ reduces azobenzene by only one electron, eq 43.[92] The first and second reduction potentials of azobenzene are in the −1.35 to −1.41 V and −1.75 to −2.03 V (vs SCE) ranges, respectively.[119] Further differences in the reduction chemistry of $(C_5Me_5)_3Sm$ and $(C_5Me_5)_2Sm$ were observed in reactions with anthracene and pyrene, which are reduced by $(C_5Me_5)_2Sm$[53] (e.g., see eq 4), but not by $(C_5Me_5)_3Sm$.[92]

$$(C_5Me_5)_2Sm + PhN{=}NPh \longrightarrow (C_5Me_5)_2Sm(Ph_2N_2) \qquad (41)$$



(42)

$$(C_5Me_5)_3Sm + PhN{=}NPh \xrightarrow[- 1/2\,(C_5Me_5)_2]{} (C_5Me_5)_2Sm(Ph_2N_2) \qquad (43)$$

B. Sterically Induced Reduction

Although ligand-based reductions have previously been observed in lanthanide chemistry, the $(C_5Me_5)_3Sm$ reactions are different. For example, as shown in eq 44, the $(PhS)^-$ ligand in a variety of trivalent lanthanide complexes, $Ln(SPh)_3$, is known to effect reduction with the formation of PhSSPh, the analogue of $(C_5Me_5)_2$ in eq 38.[120]

$$8Ln(SPh)_3 + 6S \xrightarrow{THF} Ln_8S_6(SPh)_{12}(THF)_8 + 6PhSSPh \qquad (44)$$

Even the $(C_5Me_5)^-$ anion has been shown to be a reductant in lanthanide chemistry in the formation of a Eu(II) product from a Eu(III) precursor, eq 45.[28]

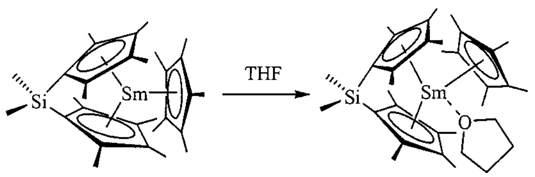
$$EuCl_3 + 3NaC_5Me_5 \xrightarrow{THF} (C_5Me_5)_2Eu(THF) \qquad (45)$$

However, the $(C_5Me_5)^-$-based reductions of $(C_5Me_5)_3Sm$ appear to be unique in that they are only observed in sterically crowded complexes. Hundreds of C_5Me_5/Ln complexes are in the literature, but none have previously displayed $(C_5Me_5)^-$ reduction chemistry.[3]

Since the reductive reactivity arises only in sterically crowded molecules, this type of reduction has been labeled sterically induced reduction (SIR) to distinguish it from other types of processes.[11] SIR may occur when a ligand cannot bind to a metal center at the normal distance necessary for good electrostatic stabilization. Without the usual metal ligand binding, this ligand may be prone to reductive chemistry. In $(C_5Me_5)_3Sm$, the presence of three large C_5Me_5 groups prevents each from achieving normal Sm−C(C_5Me_5) distances. The greater Sm−ring separation may lead to the observed reductive chemistry, which gives products with normal Sm−C(C_5Me_5) bond lengths. This is similar to the steric basis for the $(C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$-like reactivity discussed in section V.

C. Comparison with $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$ Reactivity

This rationale for sterically induced reduction is supported by the chemistry of $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$.[121] This complex was examined because it is very similar but not quite as crowded as $(C_5Me_5)_3Sm$. The Me_2Si bridge in this ansa complex decreases the (ring centroid)−metal−(ring centroid) angle and provides room for the C_5Me_5 ligand to have normal Sm−C(C_5Me_5) bond distances.[121−127] $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$ displays neither the reductive chemistry nor the $(\eta^1\text{-}C_5Me_5)$-Sm reactivity (section V) of $(C_5Me_5)_3Sm$. For example, instead of ring-opening THF, $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$ forms a stable THF adduct, eq 46.[121]



(46)

Since $[Me_2Si(C_5Me_4)_2]Sm(C_5Me_5)$ is electronically similar to $(C_5Me_5)_3Sm$ but slightly less crowded, the special reactivity of $(C_5Me_5)_3Sm$ seems to arise from the steric crowding. Likewise, $(C_5Me_5)_2Sm(C_5H_5)$ (eq 2),[83] which also has normal bond distances, does not have the special chemistry of $(C_5Me_5)_3Sm$. The close similarity of the structures of these tris(cyclopentadienyl)samarium complexes shows that only a small change in steric crowding can lead to sterically induced reduction chemistry.

VII. Expansion of Sm^{2+} Reductive Reactivity to Other Lanthanides via Sterically Induced Reduction

A. Importance of Expanding Sm^{2+} Reduction Chemistry

The idea that the $(C_5Me_5)_2Sm$-like reductive reactivity of $(C_5Me_5)_3Sm$ arose from steric crowding suggested that sterically crowded $(C_5Me_5)_3Ln$ complexes of the other lanthanide metals could have similar reductive chemistry. This would be highly advantageous since it would allow metal size optimization of reductive $(C_5Me_5)_2Sm$ chemistry and it could expand the exceptionally productive divalent reactivity of $(C_5Me_5)_2Sm$[10,11] to all of the lanthanide metals. This is important for the following reasons.

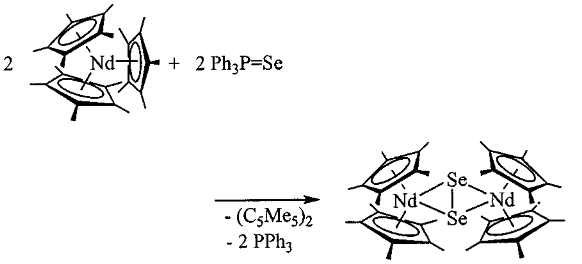
One of the powerful special aspects of lanthanide-based reactivity is that it is often possible to optimize the size of the metal to achieve higher reactivity, selectivity, and yield.[128−130] This metal size optimization can be done in addition to the usual ligand size optimization, which is possible for any metal. The metal size optimization is possible with the lanthanides, since the 4f orbitals have a limited radial extension[14] and the 4f electron configurations consequently do not have a major effect on reaction chemistry. As a result, the chemistry of the ions from La^{3+} to Lu^{3+} is similar in many respects, and the optimum-sized metal for a particular application can be selected from among these 14 metals (excluding radioactive Pm^{3+}). Since these chemically similar metals display a gradual size variation, 0.01−0.02 Å, from metal to metal (the lanthanide contraction),[131] the optimum metal size can be chosen very precisely. In this respect, the lanthanide metals are unique in the periodic table. There is no other extensive set of chemically similar metals which has such a gradual selection of different radial sizes. This situation also allows Y^{3+} to be included in this list of similar ions. Since Y^{3+} has the same charge and a radius as that of the late lanthanides Ho^{3+} and Er^{3+} and since its d^0 electron configuration makes it equivalent to the lanthanides in which electron configurations play a minor role, this ion displays similar chemistry[132] and provides a fifteenth option.

This metal size optimization is possible for the trivalent lanthanide ions, but it has never been possible for Sm^{2+}. Divalent states are not accessible for all of the metals in the series, and the divalent ions that are available have very different reduction potentials.[11,133−137] Although the Sm^{2+} ion has provided a wealth of interesting reductive chemistry,[10,34−36] it is unlikely that samarium is the metal of optimum size for all applications. It would be of great advantage to try with metals of other sizes the Sm^{2+} reductions which did not give characterizable products.[138]

Expanding Sm^{2+} chemistry to the other metals in the series would also be valuable because samarium does not necessarily have the optimum physical properties for all systems. Many types of lanthanide complexes are available only with samarium because they can be made most easily by reductive syntheses using the special properties of Sm^{2+}. Examples include the azobenzene, styrene, stilbene, and diphenylacetylene derivatives $[(C_5Me_5)_2Sm]_2(Ph_2N_2)$,[49] $[(C_5Me_5)_2Sm]_2(PhCHCH_2)$,[39] $[(C_5Me_5)_2Sm]_2(PhCHCHPh)$,[39] and $[(C_5Me_5)_2Sm]_2(Ph_2C_2)$.[44] Complexes readily available only with samarium could be made with metals with other physical properties if Sm^{2+} chemistry could be expanded to the other metals in the series. For example, if luminescence or a high magnetic moment is desirable, Tb^{3+} or Gd^{3+} complexes, respectively, would be preferred. If detailed NMR analysis is necessary, extension of Sm^{2+} chemistry to diamagnetic La^{3+}, Y^{3+}, and Lu^{3+} would be desirable to avoid the paramagnetism of samarium complexes: Sm^{2+} ($\mu = 3.6\ \mu_B$) and Sm^{3+} ($\mu = 1.7\ \mu_B$).

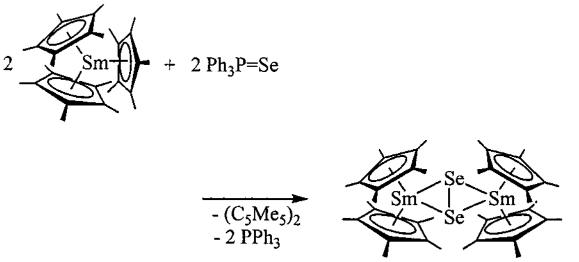
B. $(C_5Me_5)_3Nd$ and $(C_5Me_5)_3La$ Reactivity

Expansion of sterically induced reduction chemistry to other $(C_5Me_5)_3Ln$ complexes was initially examined with $(C_5Me_5)_3Nd$,[99] the first $(C_5Me_5)_3Ln$ synthesized in which Ln ≠ Sm (section IV). The reaction of 2 equiv of $(C_5Me_5)_3Nd$ with $Se{=}PPh_3$ was compared with the analogous reaction of $(C_5Me_5)_3Sm$, eq 33. The Nd reaction, eq 47,[139] generated $(C_5Me_5)_2$, the expected byproduct of sterically induced reduction according to eq 38, as well as PPh_3, the other byproduct of the samarium reaction, but the organometallic neodymium product was different. $(C_5Me_5)_3Nd$ reduces $Se{=}PPh_3$ to a $(Se_2)^{2-}$ complex rather than to the $(Se)^{2-}$ product of the $(C_5Me_5)_3Sm$ reaction, eq 33. The formation of $[(C_5Me_5)_2Nd]_2Se_2$ showed that $(C_5Me_5)_3Nd$ is a reducing agent and that sterically induced reduction can be achieved with metals other than samarium. The reaction also showed that $(C_5Me_5)_3Nd$ does not reduce $Se{=}PPh_3$ to the same extent as $(C_5Me_5)_3Sm$. Since the neodymium complex is not as sterically crowded as the samarium system, this suggested that the reductive reactivity arising from sterically induced reduction would vary depending on the degree of steric crowding.



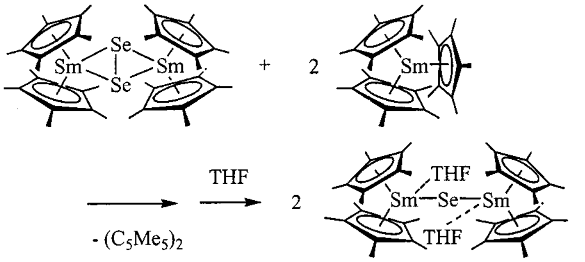
(47)

Consistent with this picture, it was subsequently shown that by controlling the stoichiometry of the more reducing $(C_5Me_5)_3Sm$, an intermediate $(Se_2)^{2-}$ product could be obtained with samarium, eq 48. This $(Se_2)^{2-}$ product had not been available via $(C_5Me_5)_2$-Sm and demonstrated how $(C_5Me_5)_3Sm$-based sterically induced reduction chemistry could even expand reductive $(C_5Me_5)_2Sm$ chemistry.



(48)

Subsequent treatment of the isolated $[(C_5Me_5)_2Sm]_2Se_2$ with additional $(C_5Me_5)_3Sm$ generated the fully reduced $(Se)^{2-}$ product, eq 49.[139]



(49)

Equations 48 and 49 demonstrated that $(C_5Me_5)_3$-Sm can accomplish both one- and two-electron reductions sequentially. This is similar to the reaction chemistry of divalent $(C_5Me_5)_2Sm(THF)_x$ with some substrates, e.g., eqs 41 and 42 above.

The synthesis of $(C_5Me_5)_3La$[102] allowed sterically induced reduction chemistry to be examined further. Although the lanthanum complex is less crowded than either $(C_5Me_5)_3Sm$ or $(C_5Me_5)_3Nd$, it still reduces $Se{=}PPh_3$. The $[(C_5Me_5)_2La]_2Se_2$ product is analogous to that of the neodymium system,[140] i.e., $(C_5Me_5)_3La$ does not reduce $Se{=}PPh_3$ as much as $(C_5Me_5)_3Sm$. A small difference between the La and Nd systems is that this $(Se_2)^{2-}$ product can be isolated as a THF adduct, $[(C_5Me_5)_2La(THF)]_2Se_2$, as well as in the unsolvated form, presumably due to the larger radius of lanthanum. Although this difference may not be very important, it does show the subtle variations that become possible when the size of the metal can be varied in a specific type of complex. If it was desirable to have a base adduct or an open coordination position in the $[(C_5Me_5)_2Ln]_2Se_2$ system (Ln = La, Nd, Sm), La would be the metal of choice. Before the discovery of sterically induced reduction chemistry, Ln = Sm would be the only option.

The fact that $(C_5Me_5)_3La$ and $(C_5Me_5)_3Nd$ are not as reducing as $(C_5Me_5)_3Sm$ supports the idea that these $(C_5Me_5)_3Ln$ reductions do not proceed through $(C_5Me_5)_2Ln$ intermediates formed by homolytic cleavage of a C_5Me_5 radical. If this were the case, the order of reactivity would be expected to be La > Nd > Sm on the basis of the metals' reduction potentials.[141] The fact that $(C_5Me_5)_2Sm$ is more strongly reducing than $(C_5Me_5)_3Sm$, as shown in the azobenzene reactions, eqs 41−43, also argues against a homolytic reaction pathway. The differences in reactivity of the $(C_5Me_5)_3$-Ln complexes (Ln = La, Nd, and Sm) also suggest that this is not a simple heterolytic cleavage of $(C_5Me_5)^-$, which goes on to do the reduction. If this were the case, the reductive capacity would be the same for all of the complexes.

C. Generality of Sterically Induced Reduction

The $(C_5Me_5)_3La$ and $(C_5Me_5)_3Nd$ reductive reactivity demonstrated that sterically induced reduction could bring the one-electron reduction chemistry of Sm^{2+} to other lanthanides if synthetic routes to the appropriately crowded complexes were found. Synthesis of these crowded molecules will always be challenging because they are so reactive. However, this type of reductive reactivity should not be limited only to homoleptic $(C_5R_5)_3Ln$ compounds. Heteroleptic complexes such as $(C_5R_5)_2Ln(C_5R'_5)$ and (large ligand)$_2$-$Ln(C_5Me_5)$ complexes could also be reducing agents if sterically crowded enough. In this regard, it will be interesting to examine the reductive reactivity of complexes such as $(C_5Me_5)_2AlMe$[142] and $(C_5Me_5)_2Sm$-$[PC_4(CMe_3)_2H_2]$.[143] In fact, C_5Me_5-free complexes such as (large ligand)$_3$Ln could also display this chemistry if the large ligand will do reduction. Indeed, it is possible that sterically induced reduction has occurred before in other crowded systems but may not have been identified. Some reactions which would lead to sterically crowded complexes may have "failed" in terms of isolating the crowded complex because the desired sterically crowded complex went on to react via sterically induced reduction pathways to give unexpected products.

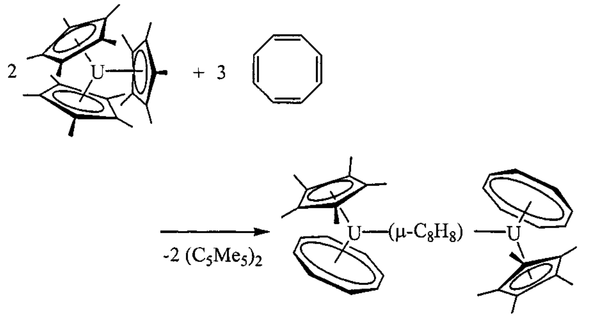
VIII. Multielectron Reduction by Coupling Sterically Induced Reduction with Conventional Metal-Based Reduction

The synthesis of $(C_5Me_5)_3U$,[94] section IV.B, allowed the examination of a complex which had a conventional metal-based redox couple, U(IV)/U(III),[144−148] in a system that was sterically crowded enough to do sterically induced reduction. Hence, $(C_5Me_5)_3U$ could be a net two-electron reducing agent according to eq 50.

$$(C_5Me_5)_3U \rightarrow 2e^- + [(C_5Me_5)_2U]^{2+} + 1/2(C_5Me_5)_2 \quad (50)$$

Two-electron reductions are unusual in f-element chemistry, since most of the redox couples of molecular monometallic species involve one-electron transformations.[11,141,144−147]

The reduction of $(C_5Me_5)_3U$ with 1,3,5,7-cyclooctatetraene, C_8H_8, a substrate which readily undergoes two-electron reduction,[149] produced a surprising result, eq 51. Instead of the 1:1 reaction expected of a two-electron reductant with C_8H_8, a 2:3 reaction stoichiometry was observed with formation of $[(C_5Me_5)(C_8H_8)U]_2(C_8H_8)$.[150] Since 3 equiv of C_8H_8 are reduced by just two molecules of $(C_5Me_5)_3U$ in this reaction, $(C_5Me_5)_3U$ is functioning as a three-electron reductant! One electron arises from U^{3+}, and two



(51)

electrons come from sterically induced reduction by two $(C_5Me_5)^-$ ligands, eq 52.

$$(C_5Me_5)_3U \rightarrow 3e^- + [(C_5Me_5)U]^{3+} + (C_5Me_5)_2 \quad (52)$$

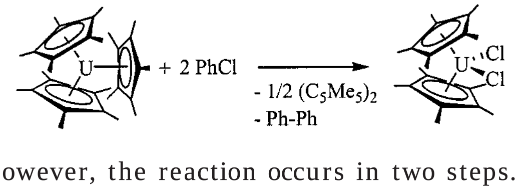
The product of eq 51 was also unusual in that it contained a nonplanar $(C_8H_8)^{-2}$ ligand, one of the original targets which led to the discovery of $(C_5Me_5)_3$Sm (section III.A). In contrast, the less sterically crowded tris(cyclopentadienyl)uranium complex, $(C_5H_4SiMe_3)_3U$, reduces cyclooctatetraene as only a one-electron reductant, eq 53.[151]

$$2(C_5H_4SiMe_3)_3U + C_8H_8 \rightarrow (C_8H_8)U(C_5H_4SiMe_3)_2 + (C_5H_4SiMe_3)_4U \quad (53)$$

Equation 51 demonstrated that multielectron reductions previously not possible with the f elements can be achieved by combining sterically induced reduction chemistry with traditional metal-based redox chemistry. It also showed that a series of reductions can occur which includes two $(C_5Me_5)^-$ sterically induced reduction processes and a traditional metal-based redox electron transfer. Presumably, one of the intermediates in this $(C_5Me_5)_3U/C_8H_8$ reaction was sufficiently sterically crowded to undergo further sterically induced reduction after the initial reduction of C_8H_8 by $(C_5Me_5)^-$ or U^{3+}.

IX. Beyond $(C_5Me_5)_3M$: Synthesis of $(C_5Me_5)_3MX$ Complexes

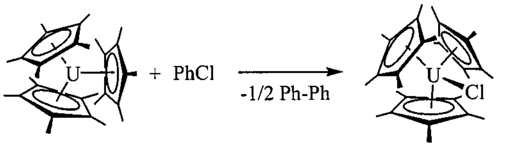
The combined U^{3+} and sterically induced reductions in the $(C_5Me_5)_3U/C_8H_8$ reaction raised the question about the sequence of these electron transfers. The reaction of $(C_5Me_5)_3U$ with PhCl provided information in this regard and also led to a new type of tris(pentamethylcyclopentadienyl) complex.[152] $(C_5Me_5)_3U$ reacts with PhCl as a two-electron reductant to form primarily $(C_5Me_5)_2UCl_2$, eq 54.



(54)

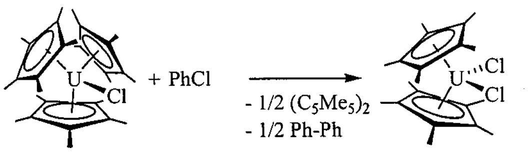
However, the reaction occurs in two steps. Since the intermediate was isolable, this system revealed which reduction occurred first.

Initial reduction of PhCl by sterically induced reduction to form the known U^{3+} product, $[(C_5Me_5)_2UCl]_3$,[153] did not occur. Instead, U^{3+} reduction occurs first to make the unexpected product, $(C_5Me_5)_3UCl$, a complex which not only has the crowding of three C_5Me_5 ligands, but an additional chloride ligand as well, eq 55. The steric crowding in this molecule is



(55)

further exacerbated by the fact that these four ligands are attached to a U^{4+} center that is smaller than the U^{3+} of the precursor.[131] The tetravalent $(C_5Me_5)_3UCl$ intermediate, formed according to eq 55, then subsequently reduces a second equivalent of PhCl via sterically induced reduction, eq 56. Hence, in the overall reaction 54, reduction by U^{3+} precedes sterically induced reduction.

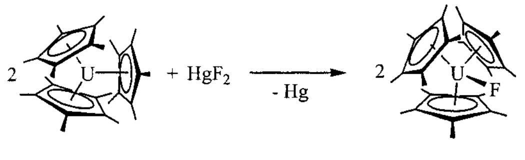


(56)

The isolation of $(C_5Me_5)_3UCl$ shows that the limits of steric crowding in the $(C_5Me_5)_3M$ system have not yet been reached. The structure of $(C_5Me_5)_3UCl$ is rather similar to that of $(C_5Me_5)_3U$, as shown by the overlay of the two structures in Figure 3.

In $(C_5Me_5)_3UCl$, the three ring centroids are still coplanar with the uranium as in $(C_5Me_5)_3U$. The chloride is positioned along the 3-fold axis perpendicular to the plane of the metal and the three ring centroids (cf. Figure 1). The U−C(C_5Me_5) distances in $(C_5Me_5)_3UCl$, Table 2, are long compared to conventional U^{4+}−C(C_5Me_5) distances. In fact, they are similar to those in $(C_5Me_5)_3U$, which has a larger metal center. In addition, the U−Cl length is exceptionally long. It is 2.90(1) Å compared to 2.637 and 2.67(1) Å in the less crowded but compositionally similar complexes $(C_5Me_4H)_3UCl$[154] and $(C_4Me_4P)_3UCl$,[155] respectively.

Once the existence of $(C_5Me_5)_3UCl$ was known, it was clear that the fluoride analogue should also be sterically allowed. This complex, $(C_5Me_5)_3UF$, was obtainable from HgF_2, eq 57.[152] Like its chloride analogue, $(C_5Me_5)_3UF$ has long U−C(C_5Me_5) and U−F bonds. The 2.43(2) Å U−F bond can be compared to the 2.073 and 2.086 Å lengths in $\{[C_5H_3(SiMe_3)_2]_2UF_2\}_2$ and $[C_5H_3(CMe_3)_2]_2UF_2$,[156] respectively.



(57)

As in the case of $(C_5Me_5)_3Sm$ and $(C_5Me_5)_3U$, once the existence of $(C_5Me_5)_3UCl$ was established, several additional syntheses were discovered, eqs 58−61.[152] However, as discussed in section III.C for the $LnCl_3/MC_5Me_5$ reactions, none of these involves the most direct route from UCl_4 and 3 equiv of MC_5Me_5, a

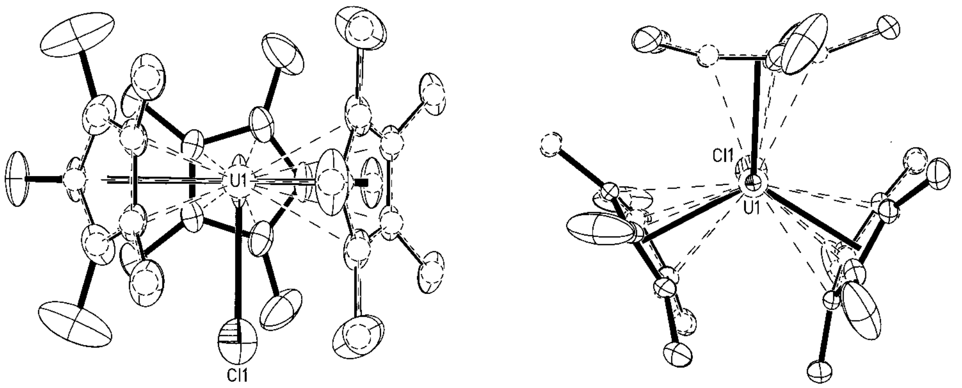
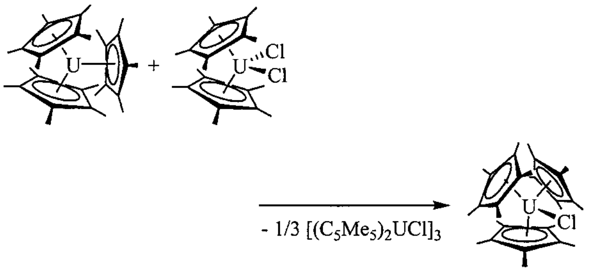


Figure 3. Overlay of $(C_5Me_5)_3U$ (- - -) and $(C_5Me_5)_3UCl$ (—).

Table 2. Metrical Data for $(C_5Me_5)_3MZ$ Complexes

	distance (Å)					
		metal–C (ring)				
$(C_5Me_5)_3Ln$	metal–centroid	high	low	mean	effective ionic radii (10 coordinate)	[mean metal–C(ring)] – [ionic radius]
$(C_5Me_5)_3UCl$	2.551	2.899 (9)	2.780 (6)	2.82 (4)	~1.10	1.72
$(C_5Me_5)_3UF$	2.561	2.908 (6)	2.791 (5)	2.83 (4)	~1.10	1.73
$(C_5Me_5)_3ThH$	2.613	2.946 (3)	2.845 (2)	2.87 (4)	1.13	1.74



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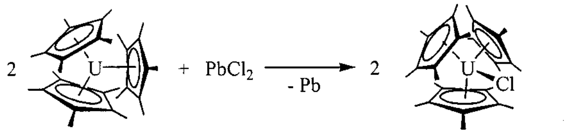

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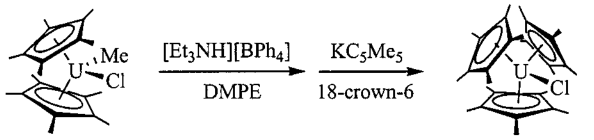
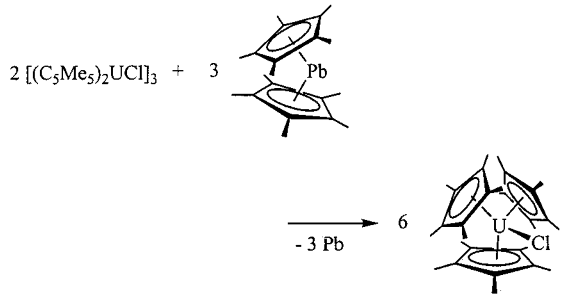


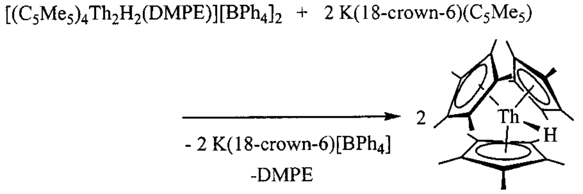
(60)



(61)

route which failed to form tris(pentamethylcyclopentadienyl) complexes.[157]

The existence of $(C_5Me_5)_3UCl$ also implied that analogues of the larger actinide, thorium, should also be sterically possible. Synthesis of $(C_5Me_5)_3ThZ$ complexes which could do sterically induced reduction would be of great advantage due to the limited reductive chemistry available for Th^{3+}, which is difficult to access.[158] The synthesis of a tris(pentamethylcyclopentadienyl) thorium complex was developed as shown in eq 62.[159] In this case, the first tris(pentamethylcyclopentadienyl) hydride complex, $(C_5Me_5)_3MH$, was obtained.



(62)

Structural details on the three $(C_5Me_5)_3MZ$ complexes crystallographically characterized to date are given in Table 2. Each of these complexes crystallizes in the same $P6_3/m$ space group in which the $(C_5Me_5)_3M$ complexes crystallize. In each of the $(C_5Me_5)_3MZ$ systems, the Z ligand is disordered on each side of the plane defined by the metal and the three ring centroids. (Ring centroid)–M–Z angles are 90° and (ring centroid)–M–(ring centroid) angles are 120° in each case. The $M-C(C_5Me_5)$ distances are surprisingly similar to those in $(C_5Me_5)_3M$, despite the presence of the extra Z ligand, Tables 1 and 2. However, this is consistent with the fact that the M–Z distance is quite long.

X. Outlook

The discovery that $(C_5Me_5)_3M$ complexes could be synthesized has transformed tris(cyclopentadienyl) lanthanide chemistry from an area of primarily structural interest to one of unusual and diverse reactivity. Overcoming the long standing assumption that $(C_5Me_5)_3M$ complexes could not exist has opened up many new areas of f-element reactivity.

The chemistry of $(C_5Me_5)_3Sm$ has shown that C_5Me_5 ligands can be reactive species rather than inert ancillary ligands if they are located in sterically crowded coordination environments. Alkyl-like reactivity in ring-opening, polymerization, hydrogenation, β-hydrogen elimination, and insertion reactions is possible. In some cases this can lead to unprecedented types of complexes, e.g., in the formation of a soluble thermally stable nonclassical carbonium ion complex,[111] and unusual types of conversions, such as the $(C_5Me_5)^-$ to $(H)^-$ transformation of eq 27.[110]

Even more surprising is that reductive reactivity is possible with $(C_5Me_5)_3Ln$ complexes and the appropriate substrates. This sterically induced reduction reactivity of the $(C_5Me_5)_3M$ complexes has broad implications. First, it provides a route to obtain reductive reactivity from complexes containing metals that are redox inactive. This is of great importance in lanthanide chemistry in that it provides a method to extend the highly productive Sm^{2+} chemistry to all the lanthanides and to size optimize that reductive chemistry. However, SIR should also be applicable to other types of redox-inactive metal systems. Second, sterically induced reduction provides the opportunity to generate multielectron reducing systems with metals that are redox active. Since multielectron reductants are generally rare, this expands a previously limited area. Finally, since redox chemistry and steric effects are generally not closely connected, sterically induced reduction demonstrates an unusual approach for expanding reductive chemistry.

The synthesis of the $(C_5Me_5)_3MZ$ complexes even more crowded than the $(C_5Me_5)_3M$ systems suggests that the limits of this chemistry have not yet been reached. Both structurally and synthetically, more crowded and reactive species may be accessible. This will require clever syntheses. However, it is clear in retrospect that it is possible to devise and execute the requisite syntheses considering how many $(C_5Me_5)_3M$ complexes have been prepared to date, Tables 1 and 2, and the fact that some 15 different reactions leading to $(C_5Me_5)_3M$ complexes have been identified since the original discovery of the synthesis of $(C_5Me_5)_3Sm$ (eqs 6, 7, 12, 13, 19−22, 55, 57−62). In the most reactive systems, it may not be possible to isolate the sterically crowded complexes. However, if the sterically crowded complexes can be generated in situ such that they can accomplish sterically induced reduction, the most important aspect of this approach will have been achieved. Isolation of the sterically crowded species is less important than achieving the useful reductive reaction chemistry.

Since this review describes the chemistry of a class of molecules that was not expected to exist and since the general class of tris(cyclopentadienyl) complexes was not expected to be very reactive, it is clear that earlier generalizations in this organometallic cyclopentadienyl field were too limited. Future work in the $(C_5Me_5)_3M$ area should not be bound by preconceptions about what may be “sterically allowed”. The structural data on the $(C_5Me_5)_3M$ complexes shows that C_5Me_5 ligands can exist in isolable complexes at distances as much as 0.1 Å longer than normal. Exceptionally long U−Cl and U−F distances were likewise found to be possible in the $(C_5Me_5)_3UX$ systems. Retrospectively, even the early structures of the polymeric $[(C_5H_5)_3Ln]_n$ complexes suggested that long-distance metal−ligand interactions were viable for these systems.[15−22] The possibility that complexes can exist with much longer than normal metal−ligand distances suggests that other types of “nonexistent” compounds may be accessible if the appropriate syntheses can be found. Both exploratory and developmental syntheses should be pursued in this direction as has been successful in developing $(C_5Me_5)_3M$ chemistry.

XI. Acknowledgment

We are grateful to the National Science Foundation for support of this project.

XII. References

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CR010298R