A New Era in Divalent Organolanthanide Chemistry?

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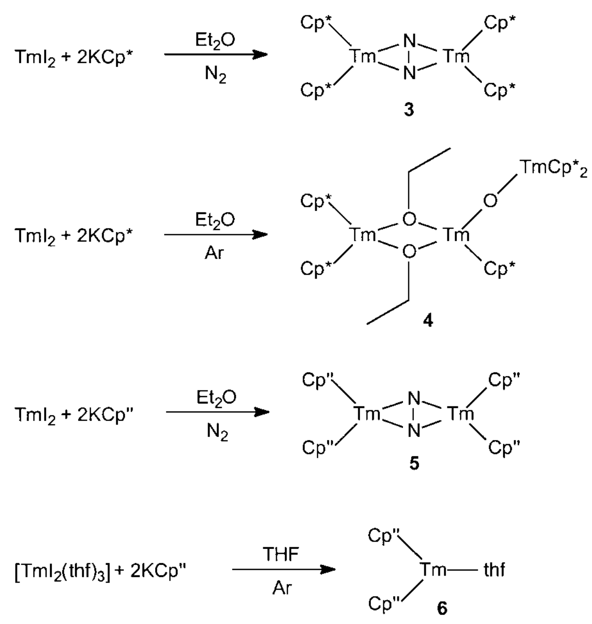
The isolation and structural characterization of the samarium(II) complex $[Cp^*_2Sm(thf)_2]$ (**1**) and its unsolvated analogue $[Cp^*_2Sm]$ (**2**) has proved to be a watershed in the chemistry of the lanthanide elements.[1, 2] In the 20 years since their initial discovery these compounds have been shown to exhibit remarkable chemistries. Their unparalleled reactivities may be illustrated by their mediation of the following selected reactions: 1) the formation of complex heterocycles from the reduction of various unsaturated organic substrates, 2) the multiple reductions of small molecules such as dinitrogen and CO, and 3) the polymerization of ethylene.[3]

In spite of this impressive reactivity, the development of a general organometallic chemistry for divalent lanthanides has been slow to emerge, due to both the highly reducing nature of the majority of these ions and to the lack of suitable starting materials for all but the three most readily accessible Ln^{II} ions (Sm^{2+} (f^6 configuration), Eu^{2+} (f^7), and Yb^{2+} (f^{14})). For these three elements the availability of the diiodides $[LnI_2(thf)_n]$ as thermally stable solids has provided a convenient entry point for the synthesis of organic derivatives. However, recent reports of the isolable and (for limited periods) solution stable diiodides of Tm^{II}, Nd^{II}, and Dy^{II} (and their crystallographically authenticated ether adducts $[TmI_2(dme)_3]$,[4b] $[TmI_2(dme)_2(thf)]$,[4c] $[NdI_2(thf)_5]$,[4c] and $[DyI_2(dme)_3]$[4d](dme = 1,2-dimethoxyethane)) suggest that an extensive organometallic chemistry for these elements may indeed be accessible.[3c, 4] Nevertheless, the highly reducing nature of these metal centers ($E^\circ(Ln^{3+}/Ln^{2+})$ versus NHE: Tm −2.3, Dy −2.6, Nd −2.6 V)[3c] and their large ionic radii require that special care must be taken in the selection of supporting ligands and reaction conditions.

The recent announcement by Evans and co-workers of the synthesis and structural characterization of the first Tm^{II} organometallic compound is testament to the importance of ligand design in the stabilization of such reactive metal centers.[5] Evans and co-workers have previously found that attempts to prepare Tm^{II} complexes supported by the ubiquitous Cp* ligand ($Cp^* = \eta^5\text{-}C_5Me_5$) were hampered by reactions between the desired organothulium(II) compound and dinitrogen to give **3** or, when argon is used as blanket gas, with the ether solvent to give **4** (Scheme 1).[6] Similar problems have also been reported by Fedushkin and co-workers: attempts to obtain an organothulium(II) complex by the alkali metal mediated reduction of $[Cp^*_2TmI(thf)]$ led to Tm^{III} products due to reaction between the Tm^{II} intermediate and the DME solvent.[7]



Scheme 1. $Cp'' = \eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2$.

The major breakthrough in the synthesis of a stable organothulium(II) compound has come through the use of the Cp″ ligand ($Cp'' = \eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_3)_2$), which has different steric and electronic properties to those of Cp*. Metathesis reactions between TmI_2 and KCp″ yield the complex $[Cp''_2Tm(\mu\text{-}N_2)TmCp''_2]$ (**5**) due, once again, to reaction of the desired Tm^{II} complex with dinitrogen.[6] However, in contrast to the formation of **4**, when Ar is used as blanket gas the organothulium(II) complex $[Cp''_2Tm(thf)]$ (**6**) is isolated in high yield (Scheme 1).[5] These reactions clearly demonstrate, not only the high reactivity of organothulium(II) compounds, but the importance of utilizing the appropriate ligands, solvent, and reaction conditions for their synthesis.

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Evans and co-workers also reported the isolation of the Dy^{III} complex $[Cp''_2Dy(\mu\text{-}N_2)DyCp''_2]$ from the reaction between DyI_2 and Cp''K in diethyl ether under nitrogen.[5] This clearly indicates the intermediacy of a Dy^{II} organometallic, although such an intermediate has yet to be isolated. It will be interesting to see whether, using the same reaction conditions as those used for the synthesis of **6**, the first Dy^{II} organometallic compound can be prepared, or whether the greater size and increased reduction potential of Dy^{II} will necessitate changes in the ligand and/or the reaction conditions to effect complex stabilization. The spectroscopic characterization and subsequent crystallization by Lappert and co-workers of compounds formulated as containing La^{II},[8] obtained by alkali metal reduction of $[Cp''_3La^{III}]$, suggests that even highly reducing La^{II} organometallic compounds may be readily accessible, provided that the correct supporting ligands and reaction conditions are chosen ($E^\circ(La^{3+}/La^{2+})$ −3.1 V versus NHE).[3c]

Lanthanide(II) compounds now occupy a special place in the armoury of reagents available to the synthetic organic chemist due to their extremely useful redox potentials, their excellent functional group tolerance and the impressive stereo- and regioselectivities of many of their reactions.[9] Preliminary studies of the reduction chemistry of TmI_2 and DyI_2 have already indicated that these compounds have enormous potential as reagents in organic synthesis.[4d, 10] It remains to be seen whether new organolanthanide(II) compounds such as **6** will one day join the ranks of useful reagents.

Although they represent a significant advance in organolanthanide chemistry, the results outlined above beg several questions: 1) will it be possible to isolate organometallic compounds of the more reducing Ln^{II} ions such as Dy^{II} and Nd^{II} and, if so, to what extent must the ligand environment be modified in order to stabilize these highly reactive metal centers? 2) how will the reaction chemistries of **6** and related complexes compare with those established for **1** and **2**? and 3) will this chemistry be limited to sterically demanding cyclopentadienyl ligands such as Cp'' or will it be possible to further extend this range of compounds to include new σ-bonded organolanthanide(II) compounds?

Whatever the prospects for these new organolanthanide(II) compounds, it is evident that the future holds many challenges for the synthetic lanthanide chemist. We are on the brink of an exciting new era in organolanthanide chemistry which is certain to yield many novel compounds and unusual reactions.

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Catalytic, Enantioselective Syntheses of β-Lactones—Versatile Synthetic Building Blocks in Organic Chemistry

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β-Lactones (2-oxetanones) combine the structural feature of a masked aldol product with the exceptional reactivity of a strained ring system that may be readily opened by nucleophiles.[1] Whereas soft nucleophiles typically add to β-lactones at the C(alkyl)−O bond with inversion of configuration, thereby furnishing chiral β-functionalized carboxylic acids, hard nucleophiles cleave the C(acyl)−O bond and unmask the aldol structure. Considering the significant synthetic value of β-lactones and the presence of this moiety in a number of biologically interesting natural products,[2] it is not surprising that great effort is currently being made to synthesize optically active β-lactones selectively and efficiently.[3]

The most direct synthesis of β-lactones involves the reaction of a ketene and an aldehyde which may proceed

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