

Chemistry of the Lanthanides Using Pyrazolylborate Ligands

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I. Introduction

As a result of the large size of the lanthanide ions and the predominant ionic bonding, steric saturation is a critical factor in controlling the coordination number, the geometry, and the architecture of their complexes. The isolation of well-defined molecular species often requires the use of sterically demanding ligands. The pyrazolylborate ligands, first introduced by Trofimenko,¹ represent an attractive and versatile alternative (Chart 1). The facile manipulation of the 3- and 5-substituents of the pyrazolyl rings allows the fine-tuning of the ligand size and thereby implies the possibility of controlling the metal coordination sphere to an unprecedented degree. This review updates the previous comprehensive review by

Santos and Marques, which covered both lanthanide and actinide chemistry.² Some aspects of lanthanide Tp chemistry have also been highlighted recently by Edelmann.³ To provide some context to much of the current work, there is some overlap between this review and its predecessors.

II. Preparation of Lanthanide Pyrazolylborate Complexes by Metathesis

Salt metathesis offers a simple and straightforward method for the preparation of pyrazolylborate complexes. Thus, reaction of lanthanide halide or triflate with the potassium or sodium salts of a range of pyrazolylborates results in the synthesis of mono-, bis-, or even tris-ligand complexes depending on the reaction conditions and the steric demand of the ligand.

A. Trivalent Complexes

1. Tris and Bis $\text{Tp}^{\text{R,R'}}$ Complexes

1.1 The Unsubstituted Tp Ligand. Although discussed in the previous review of this area,² it is worth recapping on the earliest work. Bagnall is normally credited with the introduction of the poly-pyrazolylborate ligands into the chemistry of the f-elements.^{4,5} However, for historical accuracy, it should be noted that in the late 1960s M. T. Flood and H. B. Gray prepared several lanthanide poly-pyrazolylborate complexes and studied their emission spectra.⁶ In addition, the fluorescence spectra of $[\text{Tb}(\beta\text{-dike})_x(\text{Tp})_y]$ complexes were also reported around that time.⁷

Reaction of lanthanide chlorides in water with KTp gave good yields of $[\text{LnTp}_3]$, (eq 1).^{5,8,9}

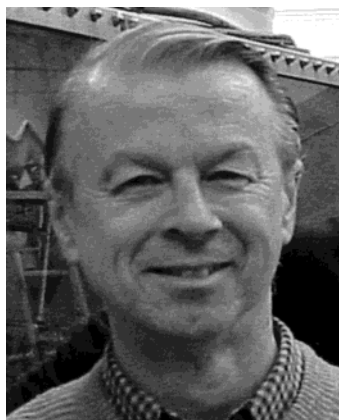


On the basis of IR spectroscopy and solubility behavior, it was postulated that the structure of the early ($\text{Ln} = \text{La-Tb}$) and late ($\text{Ln} = \text{Dy-Lu}$) $[\text{LnTp}_3]$ complexes were different.^{5,9} The late $[\text{LnTp}_3]$ complexes were found to be rigid in solution and the structure of the Yb complex was determined both by X-ray crystallography (Figure 1a) and by paramagnetic NMR spectroscopy.^{10,11} The eight-coordinate bicapped trigonal prismatic structure provided an explanation for the solution rigid behavior. As shown in Figure 1a, it is the B–H of the bidentate Tp ligand

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Josef Takats was born in Budapest, Hungary. He emigrated to Canada and obtained his B.Sc. degree from the Université de Montreal in 1965. He carried out his graduate work at M.I.T. under the supervision of Professor F. A. Cotton and received his Ph.D. degree in 1969. After a year as Instructor at M.I.T. and Assistant Professor at the University of Minnesota, he moved to the University of Alberta in 1971 where he is a Professor of Chemistry. It was at M.I.T. that he developed a lifelong interest in organometallic chemistry and a fascination with fluxional molecules. Over the years, his research focused mainly on the synthesis and reactions of cycloheptatrienyl bridged heterobimetallic complexes, iron-group carbonyl-olefin, and alkyne compounds and, of course, polypyrazolylborate complexes of lanthanides and actinides.



Dr. Noemia Marques was born, raised, and educated in Lisbon. After postgraduate work in Physical Inorganic Chemistry at the Universidade Nova de Lisboa, she received her Ph.D. from the Technical University of Lisbon in 1987, under the supervision of Professor K. W. Bagnall. She is a senior researcher at Instituto Tecnológico e Nuclear. Her main research interests are in the field of inorganic and organometallic chemistry of lanthanides and actinides.

rather than the uncoordinated pyrazolyl ring that points toward the uncapped face of the trigonal prism. Therefore, fluxionality of the complex would require a more elaborate ligand rearrangement than mere decoordination and recoordination of capping ligands. The ^1H and ^{13}C NMR spectra of the other late $[\text{LnTp}_3]$ complexes could be satisfactorily analyzed with reference to the same $[\text{YbTp}_3]$ structure.⁹ More recently, Apostolidis and co-workers have repeated these syntheses with a view to establishing the structures of the remaining complexes in the series. For the larger ions, 9-coordinate structures are obtained, as illustrated by the tricapped trigonal prismatic structures of the Pr and Nd complexes, Figure 1b. For ions smaller than Ho, the eight coordinate structure determined previously for Yb are obtained.¹²



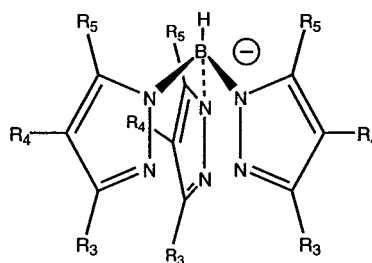
Dr Andrea Sella was born in Milan, Italy, but grew up in the US and Kenya. After undergraduate studies at the University of Toronto, Canada, he was saved from a fate worse than death by Professor Bob Morris at the same university, with whom he began his postgraduate studies. In 1986, he moved to Professor Malcolm Green's group at Oxford where was awarded a D.Phil. in 1990. He is now a Senior Lecturer in the Chemistry Department at University College London where he has interests in lanthanide chemistry and in the public understanding of science.

Mixed ligand complexes $[\text{LnTp}_2\text{Cl}(\text{THF})]$ have been prepared by reacting lanthanide trichlorides with KTp or NaTp in a 1:2 molar ratio. Although no structural information exists on the THF adducts, the X-ray crystal structures of several complexes of the form $[\text{LnTp}_2\text{Cl}(\text{L})]$ ($\text{L} = \text{pzH}, \text{H}_2\text{O}$) are known. Reger reported the X-ray crystal structure $[\text{YTp}_2\text{Cl}(\text{H}_2\text{O})]$,¹³ obtained from the reaction of $\text{YCl}_3(\text{H}_2\text{O})_n$ with NaTp . More recently, Sun and Wong showed that metathesis of anhydrous NdCl_3 with KTp gives the base-free seven-coordinate chloride (eq 2). However, in the presence of moisture the eight coordinate aquo complex is formed (eq 3). The aquo complex was characterized crystallographically (Figure 2a) and found to adopt a square antiprismatic structure.¹⁴ Closely related work has also been described by Onishi. Complexes of the type $[\text{LnTp}_2\text{Cl}(\text{L})]$ were synthesized for $\text{Ln} = \text{Lu}, \text{Nd}, \text{Yb},$ and Y .¹⁵ The structures of $[\text{NdTp}_2\text{Cl}(\text{pzH})]$ (Figure 2b)¹⁶ and $[\text{SmTp}_2\text{Cl}(\text{pzH})]$ ¹⁷ have been established by X-ray crystallography.



Substitution of the chloride ligand in $[\text{LnTp}_2\text{Cl}]$ complexes was successful with anionic bidentate ligands such as oxalates, carboxylates, tropolonates, and β -diketonates. Jones and co-workers have carried out an extensive program of synthesis and structural characterization of eight coordinate complexes of general structure $[\text{LnTp}_2(\text{L})]$, where L was a bidentate ligand,^{18–26} most of which were discussed in detail in a previous review.² Related complexes have been synthesized by Takats²⁷ and Reger.²⁸ The samarium complexes $[\text{SmTp}_2(\beta\text{-dike})]$ ($\beta\text{-dike} = \text{CH}(\text{CO})_2\text{R}_2$, $\text{R} = \text{Me}, \text{CF}_3$) and the mixed ligand $[\text{SmTp}_2\text{Bp}]$ were also prepared from $[\text{SmTp}_2\text{Cl}(\text{L})]$ complexes by metathesis. The NMR spectra and X-ray crystal structure indicate the latter complex to contain a 9-coordinate metal center with an agostic B-H-Sm

Chart 1



Abbreviation ^a	Structure	R ₃	R ₄	R ₅
Tp	HB(pz) ₃	H	H	H
Tp ^{Me2}	HB(dmpz) ₃	Me	H	Me
Tp ^{Me2-4Et}	HB(3,5-dimethyl-4-ethylpyrazolyl) ₃	Me	Et	Me
Tp ^{tBu,Me}	HB(3-Bu ^t -5-methylpyrazolyl) ₃	Bu ^t	H	Me
Tp ^{2-Pyr}	HB(3-(2-pyridyl)pyrazolyl) ₃	2-pyridyl	H	H
Tp ^{Ms}	HB(3-mesitylpyrazolyl) ₃	mes	H	H
Tp ^{Ms*}	HB(3-mesitylpyrazolyl) ₂ (5-mesitylpyrazolyl)	(mes) ₂ ,H	H	H ₂ (mes)
Tp ^{Ms,Me}	HB(3-mesityl-5-methylpyrazolyl) ₃	mes	H	Me
Tp ^{Ms,Me*}	HB(3-mesityl-5-methylpyrazolyl) ₂ - (3-methyl-5-mesitylpyrazolyl)	(mes) ₂ ,Me	H	Me ₂ (mes)
Tp ^{Ph}	HB(3-phenylpyrazolyl) ₃	Ph	H	H
Tp ^{Tn}	HB(3-thienylpyrazolyl) ₃	2-thienyl	H	H
Tp ^{CF3,CF3}	HB(3,5-bis(trifluoromethyl)pyrazolyl) ₃	CF ₃	H	CF ₃

^a The starred ligands are ones that have undergone a borotropic rearrangement such that one pyrazolyl group has the opposite substitution pattern to the other two.

interaction. Curiously, the authors describe the polyhedron only in terms of the positions of the nitrogen atoms (bicapped trigonal prismatic). The authors also note that attempts to prepare the corresponding [SmTp₂Bp^{Me2}] were not successful.²⁹ A recent paper from Jones reports further structural studies on related Eu(III) and Gd(III) complexes and analysis of the solid angle sum (sas) as a measure of the steric saturation at the lanthanide center. It was found that in the series of [LnTp₂(β-dike)] (Ln = Ce, Eu, Yb) the sas vary linearly with the Ln³⁺ ionic radius.³⁰

Finally in this section, pyrazolylborate ligands have been used to bind lanthanide ions in mixed 3d/4f complexes. Trinuclear complexes [(Tp₂Ln)₂NiL] (Ln = Sm-Lu; L = trimethylenebisoxamide, ethylenebisoxamide) were prepared. The Yb and Lu complexes of the two different ligands were structurally characterized. The geometry round each Ln center was found to be square antiprismatic while the Ni remained square planar. No magnetic interaction was observed between the well-separated Ln(III) ions.³¹ In related work, a set of oxalate-bridged complexes [Tp₂Ln(μ-C₂O₄)Cr(acac)₂] (Ln = Eu, Gd, Tb, Yb, Lu) were prepared.³² The Gd complex shows very weak antiferromagnetic coupling to the Cr(III) center. The Yb complex was structurally characterized (Figure 3). The crystal contained enantiomeric pairs of diastereomers, Δ,Λ and Λ,Δ (where the Δ and Λ refer

to the absolute configurations about Ln and Cr, respectively). Analogous preparations using resolved Λ-[Cr(acac)₂(C₂O₄)⁻] as the building block, resulted in the isolation of the complexes [Tp₂Ln(μ-C₂O₄)Cr(acac)₂] (Ln = Gd, Yb). The Yb complex was shown by X-ray crystallography to exist as the Δ,Λ diastereomer. Comparison of the near-infrared circular dichroism spectra of the dimeric complexes with that of a diastereomeric mixture of Δ- and Λ-[Tp₂Ln(S-pba)] (S-pba = S-(+)-2-phenylbutanoate) gave no evidence for the presence of the Λ configuration at Ln in the dimers. These observations imply that these complexes form stereospecifically and exhibit a remarkable configurational stability for normally labile lanthanide centers. Interestingly, crystals of [Tp₂Ln(S-pba)] contained both the Δ,S and Λ,S diastereomers in the asymmetric unit.³³

1.2 The Tp^{Me2} Ligand. Significantly more work has been carried out in recent years using the Tp^{Me2} ligand because of the greater steric control afforded by the methyl groups in the 3 position of the pyrazolyl rings.

A series of complexes of the lanthanide elements, of general formula [Ln(Tp^{Me2})₂OTf], has been prepared by metathesis of Ln(OTf)₃ in THF. The complexes fall into two distinct classes—those soluble in THF and those that are not. Careful examination of the IR spectra showed that in the former case the

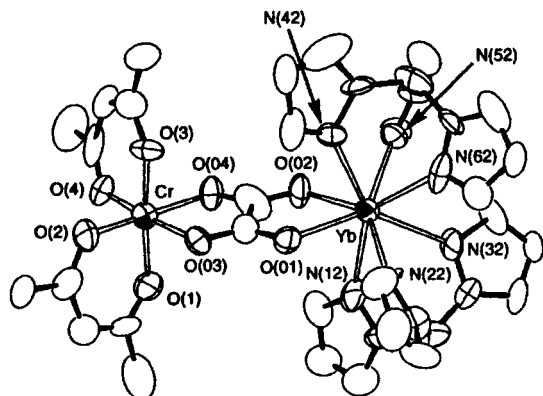


Figure 3. The molecular structure of Δ, Δ -[Tp₂Yb(μ -C₂O₄)-Cr(acac)₂]. Reproduced from ref 33 by permission of The Royal Society of Chemistry. Copyright 2001.

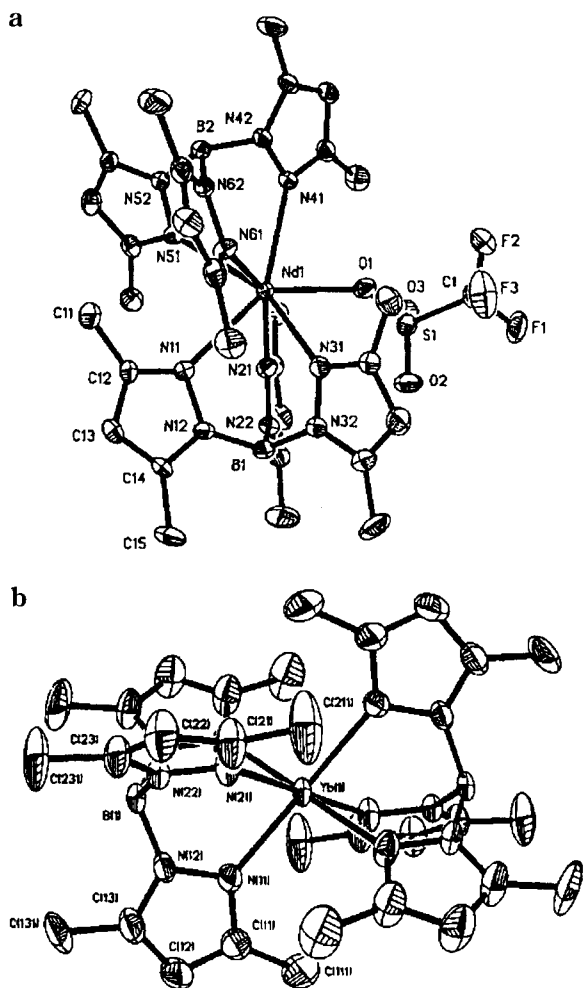
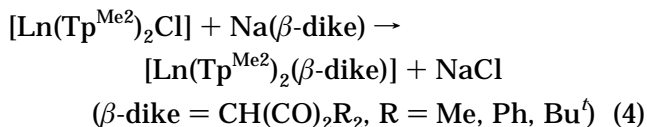


Figure 4. Molecular structures of (a) [Nd(Tp^{Me2})₂OTf] and (b) [Yb(Tp^{Me2})₂]OTf. Reprinted with permission from ref 35. Copyright 1996 American Chemical Society.

the fluxionality decreases as the steric bulk of the substituents on the β -diketonate increases.



Reaction of [Sm(Tp^{Me2})₂Cl] with KR in the presence of protic substrates Y (Y = HOPh, HOC₆H₂-2,4,6-

Bu^t, HNPh₂, HCp, HCCPh, and dmpzH) gives the corresponding [Sm(Tp^{Me2})₂Y] compounds (Figure 5).³⁹ However, attempts to isolate the alkyl itself by a variety of methods have been unsuccessful^{39,40} due primarily to facile reduction of the metal center to Sm(II) and subsequent precipitation of insoluble [Sm(Tp^{Me2})₂] (see section II.B.1 below). The use of larger and less reducible Ln(III) ions may make the synthesis of analogous [Ln(Tp^{Me2})₂R] possible.

2. Mono Tp^{R,R'} Complexes

2.1 The Tp and Tp^{Me2} Ligands.

The preparation of mono-Tp^{R,R'} complexes is problematical as a result of the potential for ligand redistribution reactions. The only known "half-sandwich" complexes of the unsubstituted Tp ligand are [YTpX₂(THF)₂] (X = Cl, Br) and [NdTpI₂(THF)₂]; the latter has been structurally characterized (Figure 6).⁴¹ The compounds were prepared at room temperature, since higher temperatures were found to encourage redistribution of ligands. Since bulky substituents in the 3-position of the Tp ligand can be expected to suppress such redistribution, it is not surprising that most attempts have focused on such ligands.

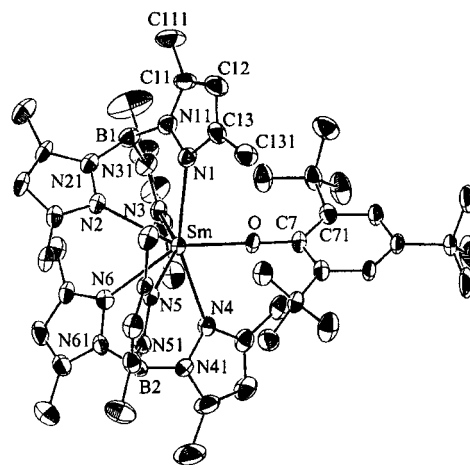


Figure 5. The molecular structure of [Sm(Tp^{Me2})₂-(OC₆H₂tBu₃)]. Reprinted with permission from ref 39. Copyright 2001 Elsevier Science.

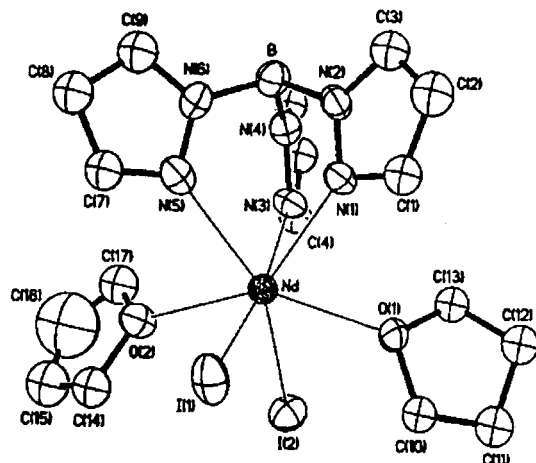


Figure 6. The molecular structure of [NdTpI₂(THF)₂]. Reprinted with permission from ref 41. Copyright 2000 American Chemical Society.

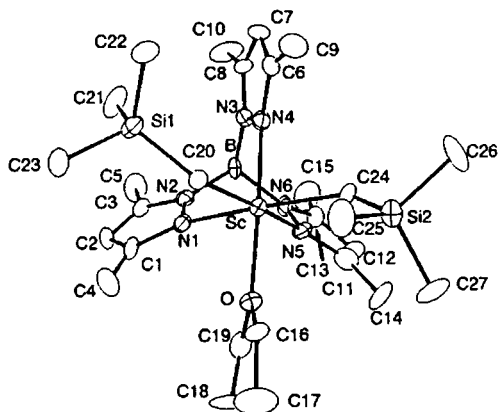
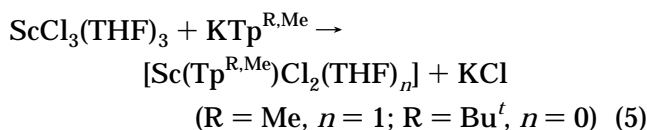
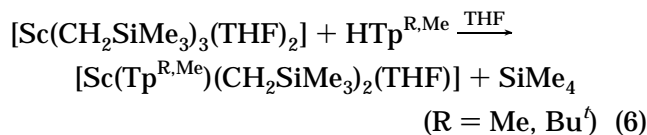


Figure 7. The molecular structure of $[\text{Sc}(\text{Tp}^{\text{Me}_2})(\text{CH}_2\text{-SiMe}_3)_2(\text{THF})]$. Reprinted with permission from ref 42. Copyright 1997 National Research Council of Canada.

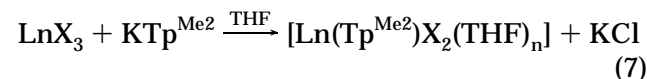
Piers and co-workers successfully prepared half sandwich complexes of scandium by metathesis with $\text{ScCl}_3(\text{THF})_3$ (eq 5).⁴²



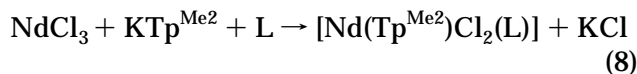
However, attempts to prepare the corresponding alkyls, by reaction with the appropriate alkyl lithium reagent resulted in the isolation of $\text{LiTp}^{\text{R,Me}}$ rather than the desired complexes. Only in the case of Tp^{Me_2} could any of the desired product, $[\text{Sc}(\text{Tp}^{\text{Me}_2})(\text{CH}_2\text{-SiMe}_3)_2(\text{THF})]$, be isolated and, even then, contaminated with 10% of $\text{LiTp}^{\text{Me}_2}$, which proved to be inseparable. The use of the alternative protonolysis route led to the isolation of the alkyl derivatives (eq 6). Crystal structures of the hydrocarbonyl compounds with both ancillaries have been obtained (Figure 7). No further work on this system has since been published.



Bianconi and co-workers have reported high yield syntheses of complexes of the type $[\text{Ln}(\text{Tp}^{\text{Me}_2})\text{X}_2(\text{THF})_n]$ (Ln = Y, Nd) by careful addition of one equivalent of KTp^{Me_2} to a suspension of LnX_3 in THF (eq 7).^{41,43} The structure of $[\text{Nd}(\text{Tp}^{\text{Me}_2})\text{I}_2(\text{THF})]$ (Figure 8a) was determined. The presence of only one coordinated THF ligand in $[\text{Nd}(\text{Tp}^{\text{Me}_2})\text{I}_2(\text{THF})]$, as opposed to two in $[\text{NdTpI}_2(\text{THF})_2]$, clearly demonstrates the greater steric demand imposed by Tp^{Me_2} compared to the unsubstituted Tp ligand.



In the presence of a substituted bipyridyl, Sun and Wong have prepared the $[\text{Nd}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{L})]$ (L = 4,4'-di-*tert*-butyl-2,2'-bipyridine) by metathesis (eq 8).¹⁴ The complex was structurally characterized, but no further reports of reactivity were given.



Several workers have noted that these complexes are somewhat unstable in solution (resulting from Tp^{Me_2} fragmentation, section IV) over extended periods, although they are quite stable in the solid state. The synthesis and structural characterization of $[\text{Yb}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{THF})]$ have been reported.⁴⁴ However, attempted crystallizations of this complex over a prolonged period gave crystals of two different

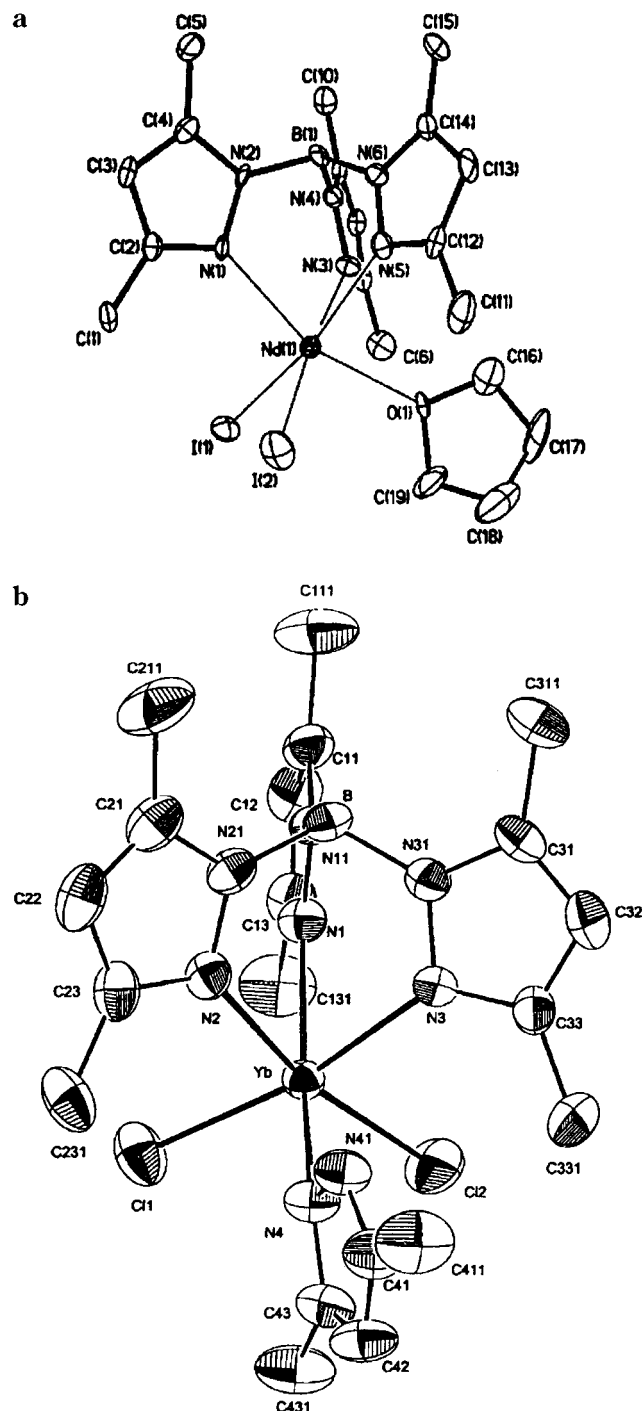
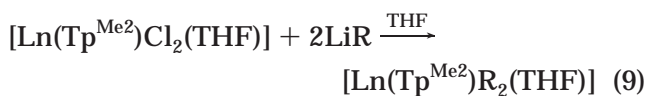


Figure 8. The molecular structures of (a) $[\text{Nd}(\text{Tp}^{\text{Me}_2})\text{I}_2(\text{THF})]$ (Reprinted with permission from ref 41. Copyright 2000 American Chemical Society) and (b) $[\text{Yb}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{dmpzH})]$. Reprinted with permission from ref 44. Copyright 1998, Elsevier Science.

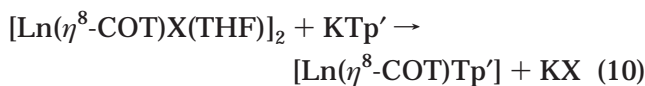
compounds, $[\text{Yb}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{dmpzH})]$ (Figure 8b) and $(\text{dmpzH}_2)[\text{Yb}(\text{Tp}^{\text{Me}_2})\text{Cl}_3]$. Similar observations were made with $[\text{Ln}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{THF})]$ ($\text{Ln} = \text{Y}^{41}, \text{Lu}^{45}$), and the structures of both $[\text{Ln}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{dmpzH})]$ have been determined.

Attempts to derivatize the half-sandwich halides using OR^- , Cp^- , and Et_2N^- , and R^- have proved difficult, and several groups have reported such reactions to be unsuccessful.^{8,46–48} Bianconi, on the other hand, has reported that careful addition of LiR ($\text{R} = \text{Ph}, \text{CH}_2\text{SiMe}_3$) gave the corresponding hydrocarbyls ($\text{Ln} = \text{Y}, \text{La}, \text{Nd}$)⁴³ (eq 9). These hydrocarbyls were found to be active ethylene polymerization catalysts, as were the analogous Tp and Tp^{Ph} complexes. Furthermore, hydrogenolysis of the hydrocarbyls gave trimeric hydrides said to be analogous to those prepared in the 1980s by Evans using Cp^* as the ancillary.⁴⁹ The structures have not, however, been definitively established. These hydride compounds were also reported to act as polymerization catalysts.⁴³



More recently, Bianconi has demonstrated that the half-sandwich halides $[\text{Ln}(\text{Tp}^{\text{R}})\text{X}_2(\text{THF})]$ ($\text{Ln} = \text{Y}, \text{Nd}$; $\text{R} = \text{H}, \text{Me}, \text{Ph}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) are labile, undergoing fast THF dissociation in solution. The halides can undergo substitution to yield mixed $[\text{Y}(\text{Tp}^{\text{R}})(\text{Bp}^{\text{R}})\text{X}]$ ($\text{R} = \text{Me}, \text{R}' = \text{Me}, \text{X} = \text{Cl}$; $\text{R} = \text{H}, \text{R}' = \text{Ph}, \text{X} = \text{Br}$) complexes. The complexes appear to be nonfluxional in solution.⁴¹

Edelmann has prepared a number of mixed $\text{Tp}^{\text{R}_2}/\text{COT}$ ($\text{R} = \text{H}, \text{Me}$) complexes by reaction of $[\text{Ln}(\eta^8\text{-COT})\text{X}(\text{THF})_2]$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$; $\text{X} = \text{Cl}$; $\text{Ln} = \text{Y}$, $\text{X} = \text{OTf}$) with KTp or KTp^{Me_2} (eq 10).^{50,51} The THF-free nature of the complexes demonstrates the ability of the Tp^{R_2} ligand to saturate the coordination sphere of the lanthanides. The structures of the Y and Pr complexes have been determined and show the expected parallel arrangement of the Tp and COT planes. Amberger and co-workers have investigated the electronic structure of $[\text{Pr}(\eta^8\text{-COT})\text{Tp}]$ by a combination of luminescence and magnetic measurements. The crystal field parameters have been determined and compared with those of other COT -containing complexes.^{52–55}



2.2 The $\text{Tp}^{2\text{-Pyr}}$ and Related Ligands. In work aimed at the construction of luminescent and/or magnetically interesting complexes, Ward and McCleverty have been building an extensive range of podand ligands, using a range of pyridine and bipyridyl groups in the 3-position of the pyrazole ring. Their starting point was the potentially hexadentate $\text{Tp}^{2\text{-Pyr}}$ ligand, which yielded both 1:1 and 1:2 complexes. Reaction of hydrated LnCl_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Ho}, \text{Yb}$) with $\text{KTp}^{2\text{-Pyr}}$ in methanol in the presence NH_4PF_6 gave the unexpected cationic half-sandwich fluoride complex $[\text{Ln}(\text{Tp}^{2\text{-Pyr}})\text{F}$ -

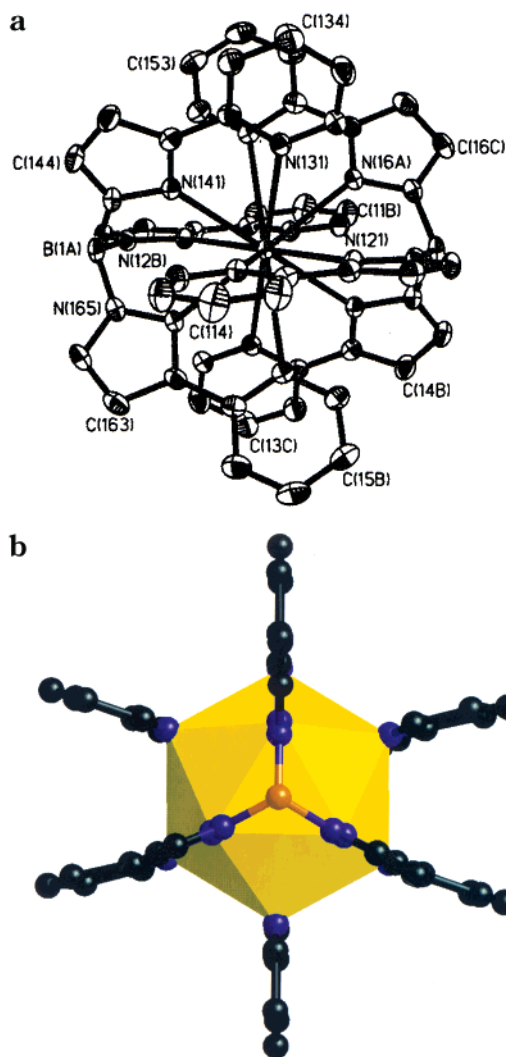


Figure 9. Two views of the molecular structure of $[\text{Ln}(\text{Tp}^{2\text{-Pyr}})_2]^+$ ($\text{Ln} = \text{Sm}, \text{Eu}$) emphasizing the icosahedral coordination polyhedron. Figure 9a reprinted with permission from ref 59. Copyright 1997 American Chemical Society. Figure 9b with permission from Prof. M. D. Ward.

$(\text{MeOH})_2]\text{PF}_6$.⁵⁶ Analogously with $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{F}]$ (see section III.A), the ligand provides a protective pocket that prevents the formation of bridges that might otherwise lead to precipitation of the extremely insoluble LnF_3 . In the absence of added PF_6^- complexes of the type $[\text{Ln}(\text{Tp}^{2\text{-Pyr}})(\text{NO}_3)_2]$ could be isolated. Ward has also reported the synthesis and structure of dibenzoylmethane and tropolonate complexes $[\text{Ln}(\text{Tp}^{2\text{-Pyr}})\text{LL}']$ ($\text{Ln} = \text{Tb}, \text{L} = \text{L}' = \text{dbm}$; $\text{Ln} = \text{Eu}, \text{L} = \text{trop}, \text{L}' = \text{NO}_3$).⁵⁷

The reaction of the LnCl_3 with $\text{KTp}^{2\text{-Pyr}}$ in a 1:2 ratio yielded the corresponding homoleptic cation $[\text{Ln}(\text{Tp}^{2\text{-Pyr}})_2]^+$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Tb}$), which could be crystallized as the BPh_4^- salt. The metal center is 12-coordinate with an unusual and startlingly satisfying icosahedral coordination polyhedron (Figure 9).^{58,59}

The photophysical properties of $[\text{Ln}(\text{Tp}^{2\text{-Pyr}})(\text{NO}_3)_2]$ and $[\text{Ln}(\text{Tp}^{2\text{-Pyr}})_2](\text{NO}_3)$ ($\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$) have been investigated in detail in a range of solvents for the former and in CH_2Cl_2 for the latter. The characteristics of the emission were quite similar in both sets of complexes. Not surprisingly, only the Eu and Tb

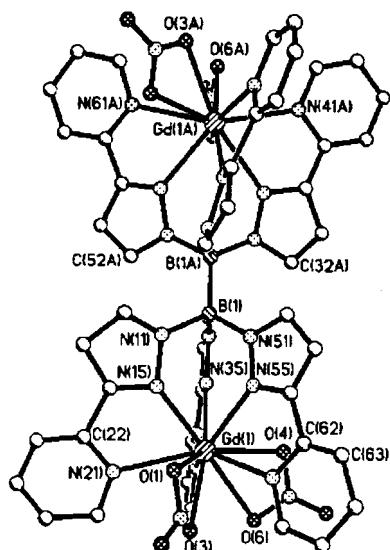


Figure 10. The molecular structure of $[(\text{NO}_3)_2\text{Gd}(2\text{-pyrpyz})_3\text{B}-\text{B}(2\text{-pyrpyz})_3\text{Gd}(\text{NO}_3)_2]$. Reprinted with permission from ref 62. Copyright 1999 American Chemical Society.

complexes show significant metal-based luminescence. The efficiency of the luminescence was considerably higher for the Tb complex since, in the case of Eu, the presence of low-lying charge transfer states allow back energy transfer to the ligand followed by rapid deactivation. As is common in such systems, emission was considerably more intense in solvents not containing OH groups.⁶⁰

A particularly intriguing ligand is hexakis(3-(2-pyridyl)pyrazolyl)diboranate, which contains two hexadentate binding sites linked back-to-back via a B–B bond.^{61,62} The La and Gd nitrate complexes have been structurally characterized and, while not showing any particularly unusual structural features, are very aesthetically pleasing (Figure 10).

The photophysics of these and the Eu and Tb complexes of all of the above ligands have been studied in some detail and show subtle variations in behavior, which have been discussed in considerable detail.⁶²

The use of the $\text{Tp}^{2-(6\text{-methyl})\text{Pyr}}$, a ligand with methyl groups *ortho* to the pyridine nitrogens, results in disruption of the ligand denticity, which is now unable to bind in hexadentate fashion and instead gives four or five coordinate binding. The nitrogen atoms of the “free” pyridine groups hydrogen bond to coordinated water molecules (Figure 11). Because of the presence of such coordinated water, the luminescence is much reduced compared with that of the hexadentate analogues.⁶³ Further variations reported recently include the $\text{Tp}^{2-(4-t\text{-Bu})\text{Pyr}}$ ligand for which the La nitrate complex has been isolated, $[\text{La}(\text{Tp}^{2-(4-t\text{-Bu})\text{Pyr}})(\text{NO}_3)_2]$.⁶⁴ A cautionary note is sounded by the unexpected isolation of a mixed Tp/Bp cation, $[\text{Nd}(\text{Tp}^{2-\text{Pyr}})(\text{Bp}^{2-\text{Pyr}})]^+$ from the crystallization of $[\text{Nd}(\text{Tp}^{2-\text{Pyr}})(\text{NO}_3)_2]$. Consistent with a fragmentation pathway, the anion contains the “missing” pyrazole group in the form of $[\text{Nd}(\text{PyrpzH})(\text{NO}_3)_4]^-$.

Very recently Ward and co-workers have reported initial attempts to generate C_3 -symmetric chiral

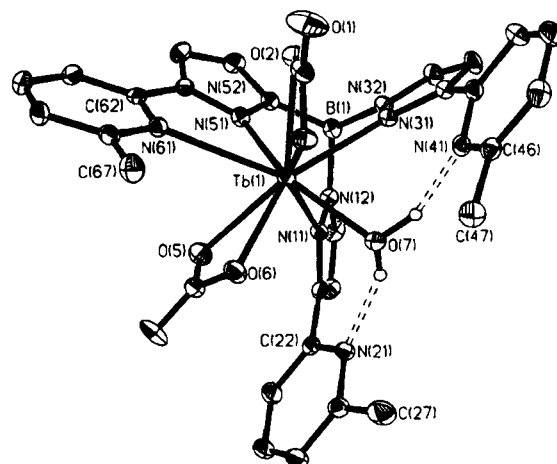


Figure 11. The molecular structure of $[\text{TbTp}^{2-(6\text{-MePyr})}(\text{NO}_3)_2(\text{OH}_2)_2]$. Reproduced from ref 63 by permission of The Royal Society of Chemistry. Copyright 1999.

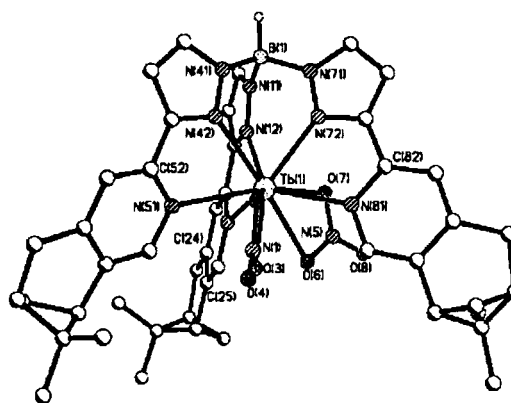


Figure 12. The molecular structure of $[\text{Tb}(\text{Tp}^{2-\text{Pyr}^*})(\text{NO}_3)_2]$. Reproduced from ref 68 by permission of The Royal Society of Chemistry. Copyright 2001.

podands (related to those originally developed by Tolman^{65–67}). The introduction of chiral pinene units onto the pyridine groups of $\text{Tp}^{2-\text{Pyr}}$ led to the synthesis of $\text{Tp}^{2-\text{Pyr}^*}$. The Tb complex $[\text{Tb}(\text{Tp}^{2-\text{Pyr}^*})(\text{NO}_3)_2]$ (Figure 12) shows the expected 10-coordination, analogous to that seen for the achiral $\text{Tp}^{2-\text{Pyr}}$ analogues.⁶⁸

Finally, in this section it is worth mentioning one additional new generation Tp ligand, the hydrotris(3-carboxypyrollidido)pyrazolylborate, Tp^{cpd} . With La, Nd, and Sm the 10-coordinate $[\text{Ln}(\text{Tp}^{\text{cpd}})_2]^+$ can be isolated in which one ligand binds in κ^4 and the other in κ^6 fashion (Figure 13). In solution, however, rapid interconversion between the bonding modes results in a single environment being observed for the pyrazolyl groups in the NMR spectra.⁶⁹

3. Dihydrobis(Pyrazolyl)borate ($\text{Bp}^{\text{R,R'}}$) Complexes

Very little work has been carried out with the $\text{Bp}^{\text{R,R'}}$ ligand system. The homoleptic $[\text{Y}(\text{Bp})_3]$ and $[\text{Ln}(\text{Bp}^{\text{Me}_2})_3]$ ($\text{Ln} = \text{Y}, \text{Ce}, \text{Sm}, \text{Yb}$) have been prepared,^{70,71} and we have noted already a few mixed Tp/Bp complexes. Recently, Ward has utilized his $\text{Bp}^{2-\text{Pyr}}$ ligand to prepare lanthanide complexes. Reaction of hydrated lanthanide nitrate or chloride with $\text{Bp}^{2-\text{Pyr}}$ in methanol yields the corresponding $[\text{Tb}(\text{Bp}^{2-\text{Pyr}})_2\text{NO}_3]$ or, after addition of sodium perchlorate and DMF, $[\text{Eu}(\text{Bp}^{2-\text{Pyr}})_2(\text{DMF})]\text{ClO}_4$. Lumi-

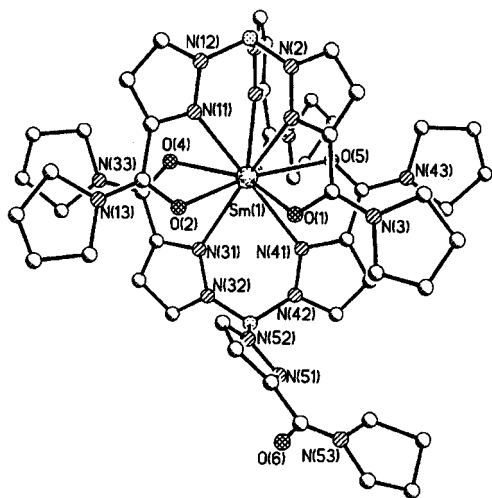


Figure 13. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{cpd}})_2]^+$. Reproduced from ref 69 by permission of The Royal Society of Chemistry. Copyright 2000.

nescence studies suggest that in aqueous solution the pendant arms dissociate from the metal center to an appreciable extent.⁷² In related work, the Eu and Gd analogues $[\text{Ln}(\text{Bp}^{2\text{-Pyr}})_2\text{NO}_3]$ ($\text{Ln} = \text{Eu}, \text{Gd}$) were also prepared along with closely related bis(3-(2-pyrazinyl)pyrazolyl)borates.⁶²

A further extension of this approach leads to the $\text{Bp}^{6\text{-(2,2'-bipy)}}$ ligand, which not only has six binding sites, but also has the potential for forming helical binuclear complexes. To the authors' chagrin, however, reaction with Gd nitrate yielded only a mononuclear complex, $[\text{Gd}(\text{Bp}^{6\text{-(2,2'-bipy)}})(\text{NO}_3)_2]$ ⁷³ in which the two arms of the Bp ligand bind in a manner analogous to terpyridine. Again, the photophysics of these complexes were described.^{62,73} The $\text{Bp}^{2\text{-Pyr,CH}_2\text{OMe}}$ ligand, with a methoxymethyl group in the 5-position of the pyrazolyl groups has been prepared and the structure of $[\text{La}(\text{Bp}^{2\text{-Pyr,CH}_2\text{OMe}})_2(\text{NO}_3)]$ determined.⁶⁴

B. Divalent Complexes

1. Bis $\text{Tp}^{\text{R,R'}}$ Complexes

The first report of divalent complexes with polypyrazolyl ligands came from Jones and Evans who prepared $[\text{LnTp}_2(\text{THF})_x]$ and $[\text{Ln}(\text{Tp}^{\text{Me}_2})_2]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) by metathesis.⁷⁴ This short report, which contained no structural data, drew attention to the insolubility of the $[\text{Ln}(\text{Tp}^{\text{Me}_2})_2]$ complexes and pointed toward the suppressed reactivity of the $[\text{LnTp}_2(\text{THF})_x]$ complexes compared to the corresponding lanthanocenes. Simultaneous work by Marques, Sella, and Takats concerning the synthesis and reactivity of these same complexes was communicated at a number of conferences.^{75–80}

Marques has shown that the THF-soluble lanthanide- Tp^{Me_2} and $\text{B}(\text{pz})_4$ ⁸¹ complexes contain two coordinated THF molecules that can easily be replaced by other donors. The solid-state structures of $[\text{EuTp}_2\text{L}_2]$ ($\text{L} = \text{diphenylsulfoxide (DPSO), pentamethyleneurea}$) have been determined and revealed that they are eight coordinate with square antiprismatic geometry (Figure 14).⁸² Related $[\text{EuTp}_2\text{L}_2]$ compounds have been studied by Fourier transform ion cyclotron resonance mass spectrometry.⁸³ Infra-

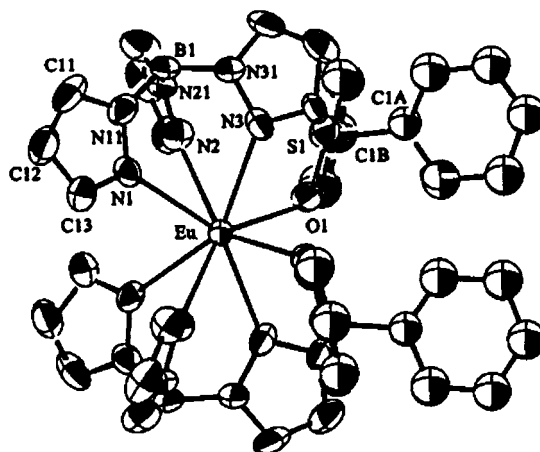
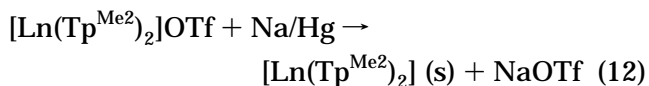
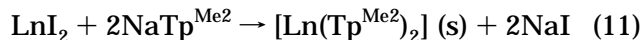


Figure 14. The molecular structure of $[\text{EuTp}_2(\text{DPSO})_2]$. Reprinted from ref 82 with permission from Elsevier Science. Copyright 2000.

red multiphoton dissociation experiments allowed evaluation of the relative bond strength of the ligand L.

The extreme insolubility of the $[\text{Ln}(\text{Tp}^{\text{Me}_2})_2]$ complexes made separation from the coprecipitated potassium halides and purification of the products a challenge. Although sublimation affords pure Eu and Yb products, the Sm complex undergoes extensive decomposition. A more convenient approach involves the use of the sodium salt of the Tp^{Me_2} ligand (eq 11).^{76–79,84} This leaves the fairly soluble NaI in the THF solution and affords pure products in high yields by simple filtration. The Yb and Eu complexes could also be prepared by reduction of $[\text{Ln}(\text{Tp}^{\text{Me}_2})_2]\text{OTf}$ (eq 12).³⁴



Two different approaches were used to crystallize these complexes. While Takats used slow diffusion,⁸⁴ Sella used sublimation in a temperature gradient.³⁴ The composition and the structures are in contrast to the corresponding lanthanocenes—the complexes are unsolvated and exhibit S_6 symmetry (i.e., they are trigonal antiprismatic, Figure 15a). The extreme insolubility of these complexes appears to be related to the efficiency of the crystal packing. The complexes crystallize in the hexagonal space group $R\bar{3}$ and therefore correspond to an essentially hcp packing of spheres.

The analogous $[\text{Ln}(\text{Tp}^{\text{Me}_2,4\text{-Et}})_2]$ complexes, which differ only in the substituent in the 4-position of the pyrazolyl ligands, are very soluble in hexanes and other hydrocarbon solvents (Figure 15b). Additionally, the thermal stability of the three complexes is in the order of their reduction potential, $\text{Eu} \gg \text{Yb} > \text{Sm}$. It was not possible therefore to collect reliable PES data for Yb and Sm due to decomposition of the complexes in the inlet system of the instrument. The europium complex, which is highly luminescent, can be seen as a vapor in the gas phase at temperatures

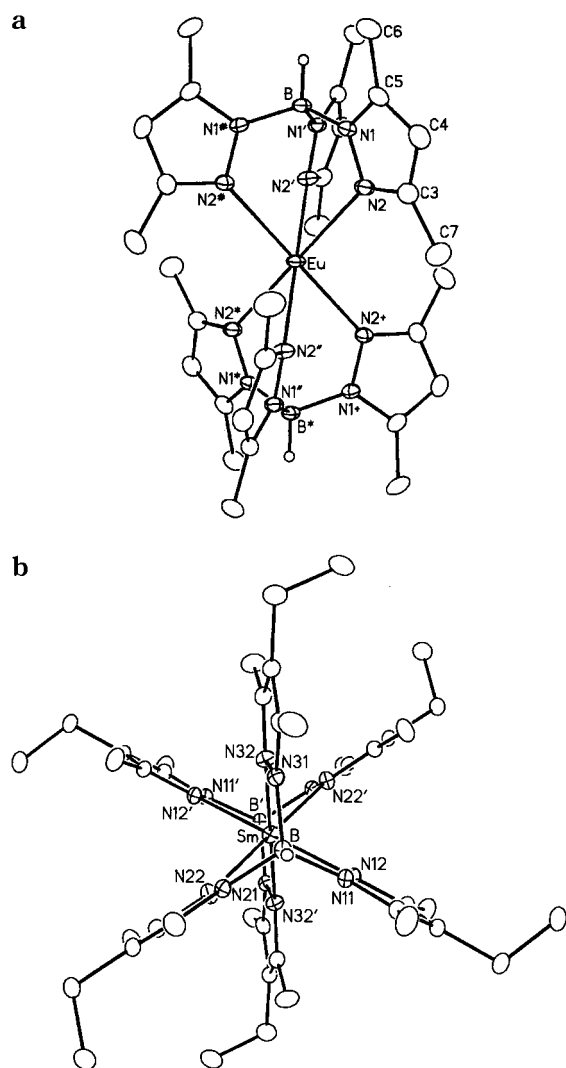


Figure 15. The molecular structures of (a) [Eu(Tp^{Me2})₂] and (b) [Sm(Tp^{Me2,4-Et})₂]. Reprinted with permission from ref 85. Copyright 2001 American Chemical Society.

in excess of 300 °C.⁸⁵ Full details of the synthesis and structural comparison of these and related [Ln(Tp^{Ph})₂] and [Ln(Tp^{Tn})₂] complexes appeared in a recent report.⁸⁵ The luminescence of the [Eu(Tp^{Me2})₂] complex has been described in detail by Christou and co-workers and shown to arise from excitation of a charge-transfer transition followed by emission from the metal orbital manifold. By preparing the corresponding Tp^{CF₃,CF₃} complex, the authors were able to obtain blue luminescence.⁸⁶ The reactivity of [Sm(Tp^{Me2})₂] will be discussed in section III.

As will be discussed in section II B2 below, the Tp^{tBu,Me} ligand has been used to prepare half-sandwich Ln(II) complexes. However, when reacted with LnI₂ in a 2:1 ratio, it is possible to isolate homoleptic complexes of formula [Ln(Tp^{tBu,Me})₂] (Ln = Sm, Yb).⁸⁷ As a result of the steric demand of the *tert*-butyl groups, only one of the Tp^{tBu,Me} ligands retains its classic tridentate bonding mode; the other is coordinated via two pyrazolyl nitrogens and an agostic B–H–Ln interaction (Figure 16). The observation of ¹⁷¹Yb–HB coupling confirms the persistence of the agostic interaction in solution. The complexes are fluxional in solution and variable temperature

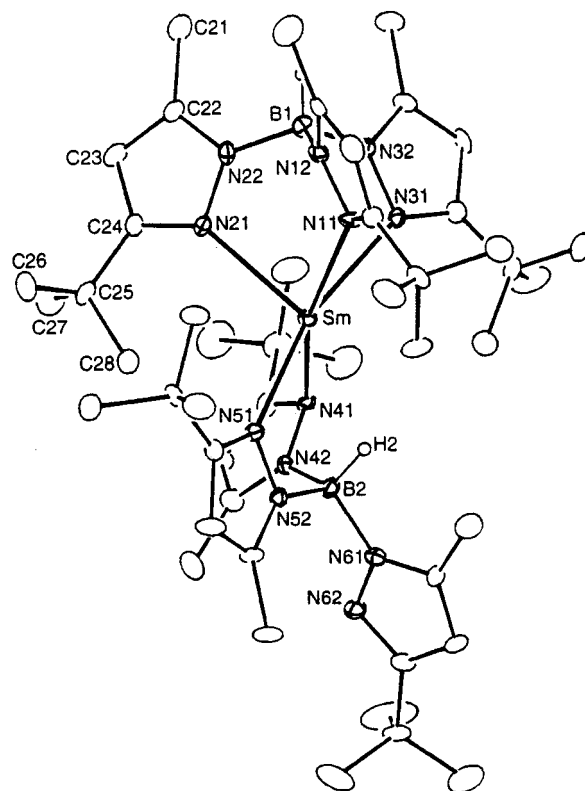
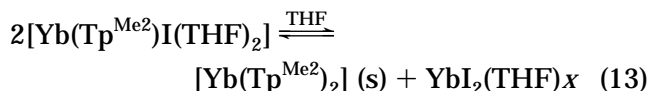


Figure 16. The molecular structure of [Sm(Tp^{tBu,Me})₂]. Reprinted from ref 87 with permission from Elsevier Science. Copyright 1995.

NMR studies revealed two distinct dynamic processes. The low-temperature process involves exchange of pyrazolyl groups within individual Tp^{tBu,Me} ligands, without bonding mode exchange. Above room temperature, the bonding modes of the two ligands also begin to slowly exchange. The activation barriers for the exchange processes are 8.5 and 16.5 kcal/mol, respectively.

2. Mono Tp^{R,R'} Complexes

Attempts to prepare divalent half sandwich complexes of Eu, Sm, or Yb containing Tp^{Me2} have proved frustrating. Zhang and Takats were able to isolate and structurally characterize the half sandwich complex [Yb(Tp^{Me2})I(THF)₂].⁸⁸ However, attempts by other groups to reproduce this result have been unsuccessful—the insolubility of [Yb(Tp^{Me2})₂] is such that the equilibrium is easily shifted to the right (eq 13).⁴⁷



Indeed, attempted derivatization of the compound proved unsuccessful and led only to the isolation of the insoluble [Yb(Tp^{Me2})₂].⁸⁸ By contrast, the use of the bulkier Tp^{tBu,Me} ligand makes the synthesis of such half-sandwich complexes relatively straightforward. Reaction of LnI₂ (Ln = Sm, Yb) with KTp^{tBu,Me} gives the air-sensitive complexes [Ln(Tp^{tBu,Me})_nI(THF)_n] (Ln = Sm, *n* = 2; Ln = Yb, *n* = 1) the crystal structures of which have been determined (Figure

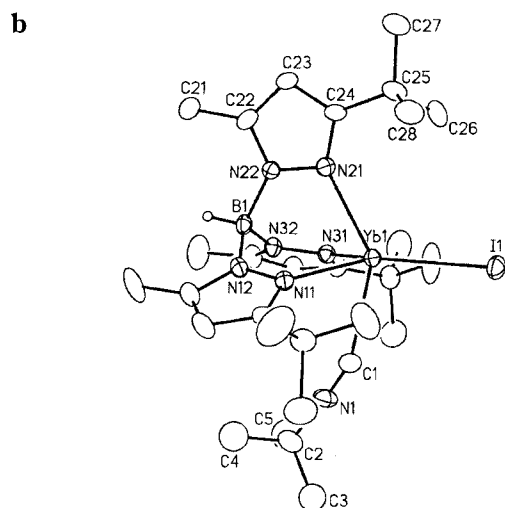
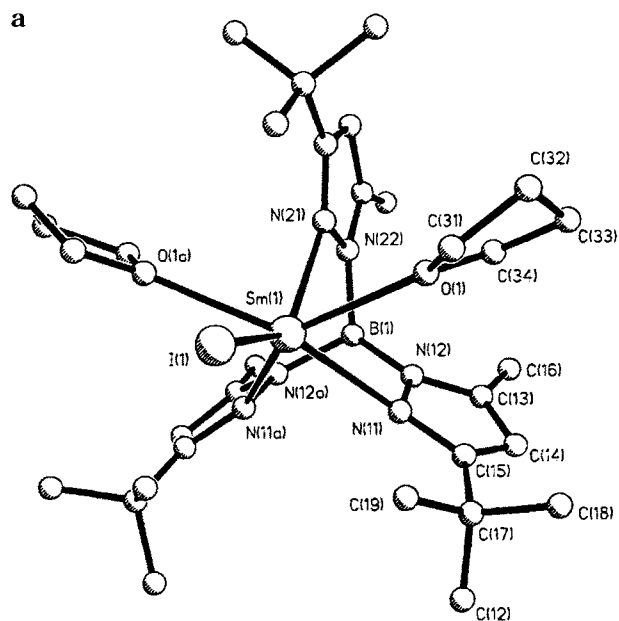


Figure 17. The molecular structures of (a) $[\text{Sm}(\text{Tp}^{\text{tBu,Me}})\text{I}(\text{THF})_2]$ and (b) $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})\text{I}(\text{CN}^{\text{tBu}})]$ (ref 47).

17a).^{47,89,90} The THF ligands can be replaced by other donors including pyridines and *tert*-butylisocyanide. The crystal structures of $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})\text{I}(3,5\text{-Me}_2\text{pyr})_2]$ and $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})\text{I}(\text{CN}^{\text{tBu}})]$ have been determined (Figure 17b).⁴⁷

Replacement of the iodide for other anionic ligands proved to be a challenge. The use of lithium and sodium reagents gave unsatisfactory results in most cases;⁴⁷ however, successful derivatization was achieved by using potassium reagents (Scheme 1, Figure 18).^{90,91} While the ytterbium complex proved to be amenable to derivatization, samarium was more temperamental. Thus, although use of the bulky "Lappert hydrocarbyl", $[\text{Sm}(\text{Tp}^{\text{tBu,Me}})(\text{CH}\{\text{SiMe}_3\}_2)]$, attempts to prepare the Sm(II) analogues of $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})(\text{OMe})(\text{THF})]$ and $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ ⁹⁰ resulted in ligand redistribution and formation of $[\text{Sm}(\text{Tp}^{\text{tBu,Me}})_2]$.⁸⁸ This is presumed to be a consequence of the larger ionic radius of samarium which results in less effective saturation of the coordination sphere by the pyrazolylborate ligand.

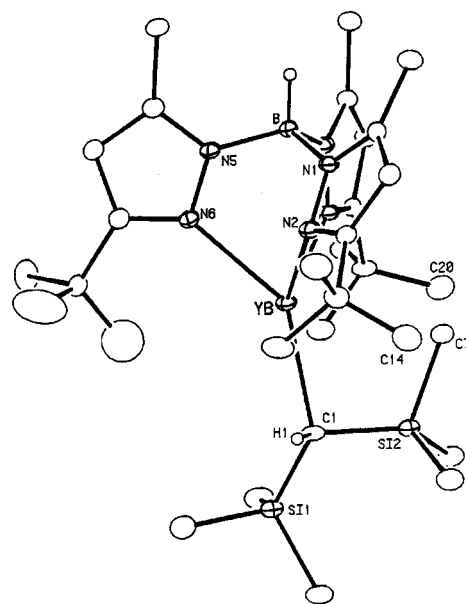


Figure 18. The molecular structure of $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})\text{CH}\{\text{SiMe}_3\}_2]$. Reprinted with permission from ref 90. Copyright 1984 American Chemical Society.

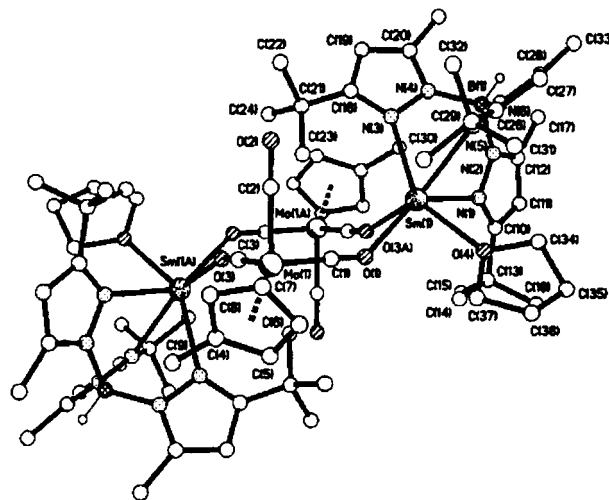


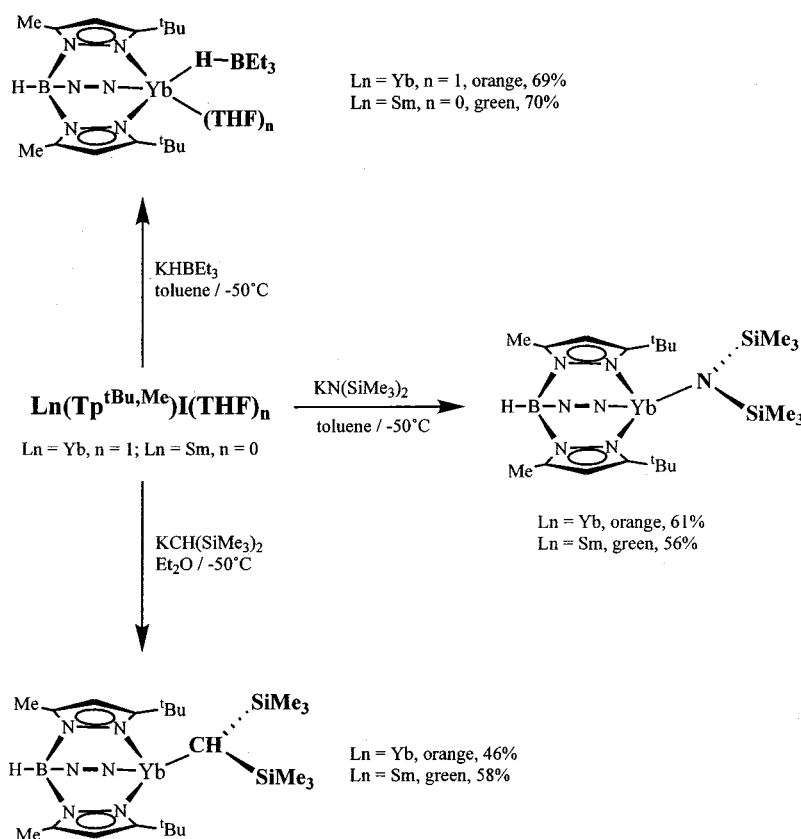
Figure 19. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{tBu,Me}})(\text{THF})(\mu\text{-CO})(\text{MeCp})\text{Mo}(\text{CO})_2)_2]$. Reproduced from ref 92 by permission of The Royal Society of Chemistry. Copyright 1998.

In line with the idea that steric saturation is important in suppressing ligand redistribution, the reaction of $[\text{Ln}(\text{Tp}^{\text{tBu,Me}})\text{I}(\text{THF})_n]$ with $\text{NaMoCp}(\text{CO})_3$ gives both Yb and Sm analogues, $[\text{Ln}(\text{Tp}^{\text{tBu,Me}})(\text{THF})(\mu\text{-CO})(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2)_2]$.⁹² The crystal structure of these highly air-sensitive tetrametallic complexes show the central core to adapt a puckered "deck-chair" conformation (Figure 19) with each lanthanide ion bonded to isocarbonyl groups from different metals giving six-coordinate lanthanide centers.

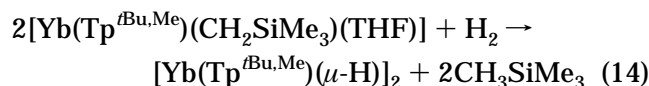
In an attempt to obtain divalent lanthanide hydrides, $[\text{Ln}(\text{Tp}^{\text{tBu,Me}})\text{I}(\text{THF})_n]$ was treated with KH-BEt_3 . However, the interesting $[\text{Ln}(\text{Tp}^{\text{tBu,Me}})(\mu\text{-H-BEt}_3)(\text{THF})_n]$ (Scheme 1) complexes were isolated instead.^{90,91} For the ytterbium complex, the detection of ¹⁷¹Yb-¹H coupling corroborates the bonding of the triethylborohydride ligand.

The long sought after Yb(II) hydride was finally synthesized by hydrogenolysis of $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})(\text{CH}_2\text{-$

Scheme 1



$\text{SiMe}_3(\text{THF})$] (eq 14) (Figure 20).⁹³ The hydride is very reactive toward acidic or unsaturated substrates (Scheme 2). CO insertion results in the formation of an ene-diolate. Reaction with terminal acetylenes gives the corresponding acetylides. In the case of the 1,4-bis(trimethylsilyl)-1,3-butadiyne, insertion occurs giving a four carbon cumulene unit reminiscent of an η^3 -propargyl complex.⁹³



Protonolysis reactions with C_5H_6 and $\text{C}_5\text{H}_5\text{SiMe}_3$ give good yields of the mixed Tp/CpR complexes (eq 15).⁹⁴ Although the NMR spectra of both compounds are temperature invariant down to -100°C , the structure of the SiMe_3 complex shows an unusual distortion of the $\text{Tp}^{\text{tBu,Me}}$ ligand (Figure 21). One of the pyrazolyl rings is twisted around the B–N bond such as to bring both nitrogens in contact with the metal center. Similar distortions have also been noted for $[\text{U}(\text{Tp}^{\text{Me}_2})_2\text{I}]$ ⁹⁵ and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{SePh-4-Bu}]$.³⁸ Further details on the reactivity of the hydride can be found in a recent mini-review.⁹⁶

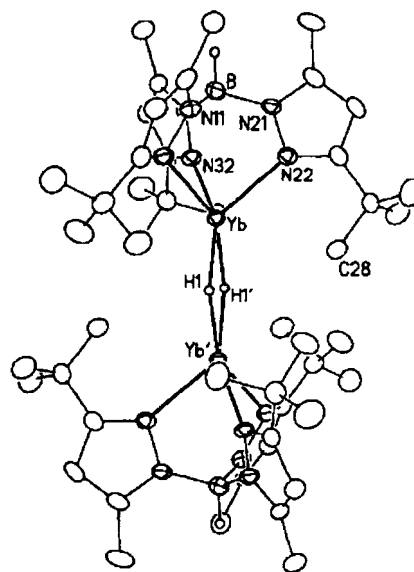
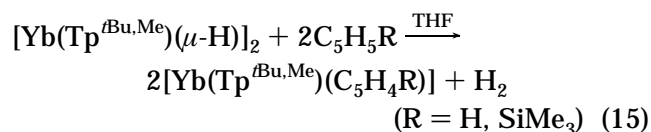


Figure 20. The molecular structure of $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})(\mu\text{-H})_2]$. Reprinted with permission from ref 93. Copyright 1999.

Half-sandwich complexes have also been prepared using the Tp^{Ms} ligand. Thus, reaction of YbI_2 with TlTp^{Ms} at low temperature (below 0°C) results in the formation of an orange solution which, intriguingly, appears to be an -ate complex containing TII. Extraction with THF followed by crystallization gives $[\text{Yb}(\text{Tp}^{\text{Ms}})\text{I}(\text{THF})_2]$ (eq 16). Carrying out the reaction at room temperature results in a rearrangement of the ligand, leading to the isolation of $[\text{Yb}(\text{Tp}^{\text{Ms}*})\text{I}(\text{THF})_2]$. The isomerization, which occurs spontaneously at room temperature, was monitored by NMR spectroscopy.

Scheme 2

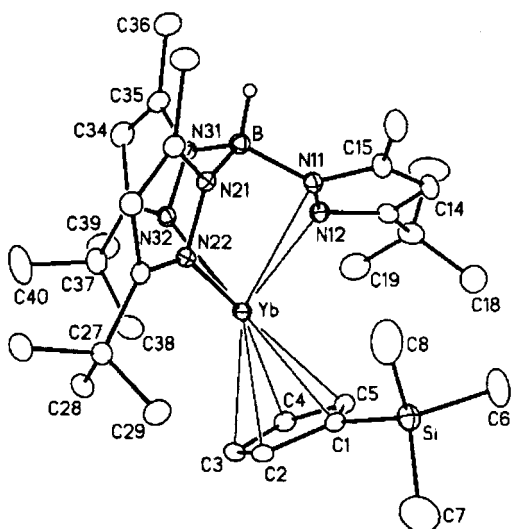
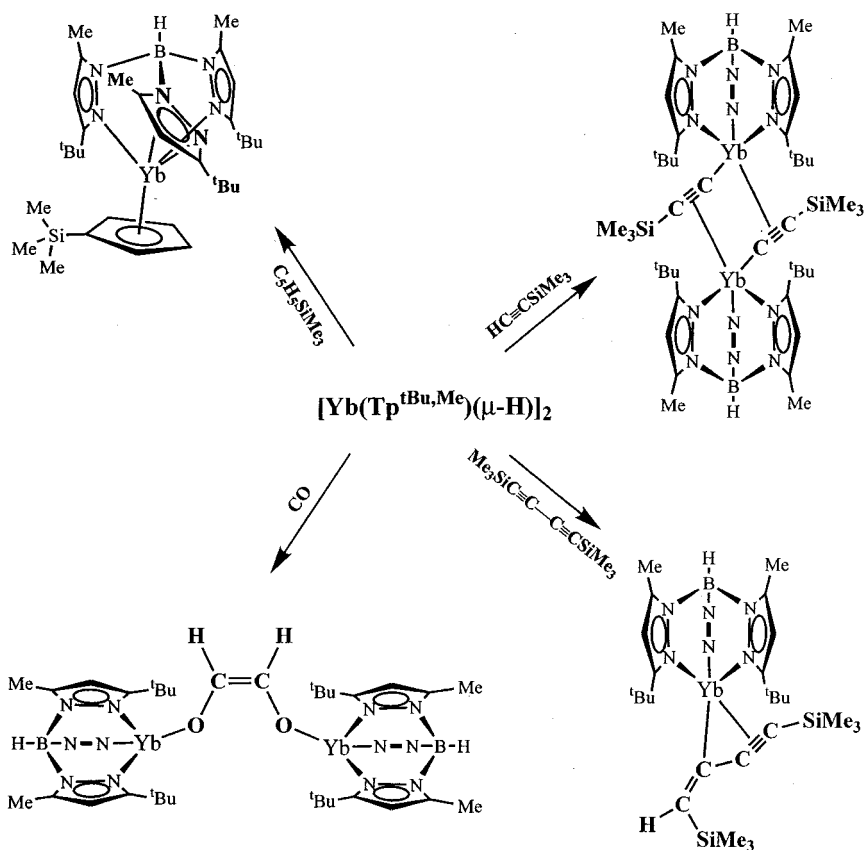
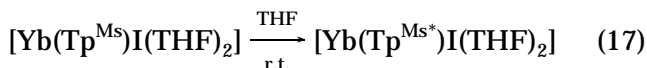
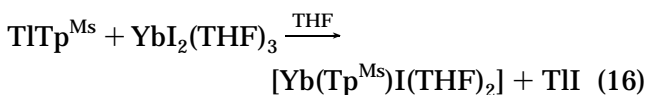


Figure 21. The molecular structure of $[\text{Yb}(\text{Tp}^{\text{tBu,Me}})(\text{C}_5\text{H}_4\text{-SiMe}_3)]$. Reprinted with permission from ref 94. Copyright 2000 Elsevier Science.

copy and was found to be both concentration and temperature dependent (eq 17).



The use of the methyl-substituted ligand $\text{Tp}^{\text{Ms,Me}}$ and $\text{Tp}^{\text{Ms,Me}*}$ gave rise to analogous complexes, which,

in contrast to their less substituted analogues, do not appear to interconvert.⁹⁷ The symmetrically bonded $\text{Tp}^{\text{Ms,Me}}$ complex appears to be kinetically more stable than the Tp^{Ms} derivative, and it may be possible to structurally characterize the complex in the future.

X-ray structural characterization of $[\text{Yb}(\text{Tp}^{\text{Ms}*})\text{I}(\text{THF})_2]$ and $[\text{Yb}(\text{Tp}^{\text{Ms,Me}*})\text{I}(\text{THF})_2]$ showed that in both complexes the metal center is six-coordinate with the three *fac*-sites being occupied by the $\text{Tp}^{\text{Ms}*}$ ligand, and the remainder of the coordination sphere occupied by the iodine and the two oxygen atoms of the THF molecules. The greater steric demand of $\text{Tp}^{\text{Ms,Me}*}$ ligand relative to $\text{Tp}^{\text{Ms}*}$ is evidenced by slightly longer Yb–I and average Yb–O distances of 3.123(2) and 2.46(1) Å, respectively, compared to the corresponding values of 3.094(1) and 2.43(1) Å in $[\text{Yb}(\text{Tp}^{\text{Ms}*})\text{I}(\text{THF})_2]$. In accord with this, the average I–Yb–O angle in the former complex, 83.3(3) Å, is some 4° less than the 87.5(3)° observed in the latter.⁹⁷

The utility of $[\text{Yb}(\text{Tp}^{\text{Ms}*})\text{I}(\text{THF})_2]$ as precursor for further derivatization has been demonstrated. Reaction with $\text{KN}(\text{SiMe}_3)_2$ gives $[\text{Yb}(\text{Tp}^{\text{Ms}*})\text{N}(\text{SiMe}_3)_2]$. The high solubility of the compound in all type of solvents so far prevented isolation of crystals suitable for characterization by X-ray diffraction. During one attempted crystallization of $[\text{Yb}(\text{Tp}^{\text{Ms}*})\text{N}(\text{SiMe}_3)_2]$ from a toluene solution, orange crystals of $[\text{Yb}(\text{Tp}^{\text{Ms}*})-(\mu\text{-Cl})_2]$ were obtained (Figure 22). In this compound, the ytterbium center is six-coordinate by the three nitrogen atoms of the $\text{Tp}^{\text{Ms}*}$ ligand and by the two chloride bridging ligands, the sixth coordination position being filled by an interaction with the carbon C(233) of the mesityl substituent of one pyrazolyl ring

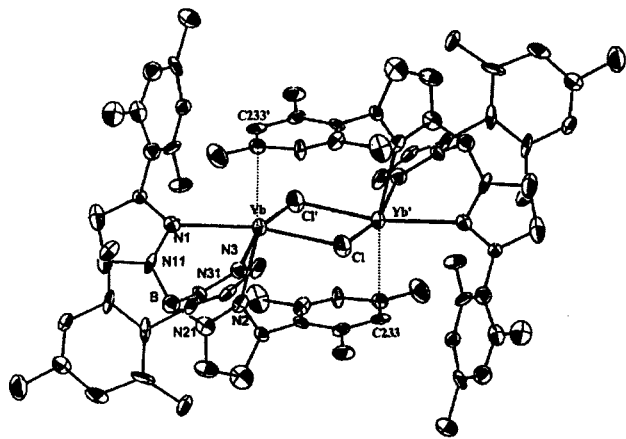


Figure 22. A view of the molecular structure $[\text{Yb}(\text{Tp}^{\text{Ms}^*})(\text{Cl})]_2$ (ref 98).

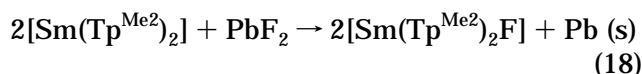
(3.08 Å). The compound could be obtained on a preparative scale by reacting $[\text{Yb}(\text{Tp}^{\text{Ms}^*})\text{N}(\text{SiMe}_3)_2]$ with HNEt_3Cl .⁹⁸

III. Reactivity of $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$: Another Route to $\text{Sm}(\text{III})$ Pyrazolylborate Complexes

Of the “sandwich” complexes, most attention has focused on $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$. The most striking observation is that its reactivity is significantly suppressed compared with other divalent samarium complexes, the samarocenes in particular. Thus, no direct reactions have been observed with simple olefins, alkynes, isonitriles, CO, and other “obvious” substrates. This is ascribed to the extraordinary steric protection afforded by the interlocking methyl groups of the two ancillary ligands. Despite this, a number of more or less unique reactions have been observed as described in the following sections.

A. Reactions with X_2 , RX and E_2R_2 Reagents

$[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ reacts with chloro- and bromocarbon compounds to yield the corresponding trivalent halide complexes, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$). However, the salt metathesis route described in section II.A.1.2 gives better yield routes of these compounds. Reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with hexafluorobut-2-yne results in C–F bond cleavage giving the corresponding fluoride, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{F}]$, but the deliberate oxidation of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with PbF_2 provides a more convenient synthesis for this compound, (eq 18)



The toluene solubility of the compounds suggested the presence of molecular compounds. This was corroborated by the X-ray structures of the chloride and fluoride derivatives (Figure 23). In solution, the complexes exhibit rapid fluxionality as evidenced by a single sharp set of Tp^{Me_2} resonances in the ^1H NMR spectrum.

Addition of iodine to a slurry of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ in THF produced $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{I}]$ as a white, THF in-

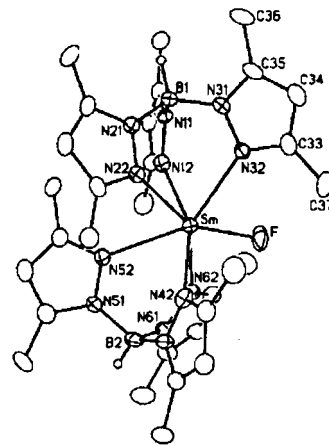
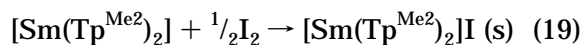


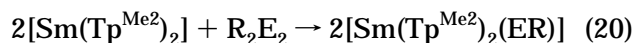
Figure 23. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{F}]$. Reprinted with permission from ref 85. Copyright 2001 American Chemical Society.

soluble precipitate, (eq 19). In this case also, a better yield was obtained by the salt metathesis route.



The insolubility of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{I}]$ suggested that the compound should be formulated as the iodide salt of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]^+$. Single X-ray diffraction analysis corroborated this formulation. Addition of further iodine results in formation of the corresponding triiodide salt $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{I}_3]$.⁹⁹ Oxidation of $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$ with TIBPh_4 results similarly in formation of the salt $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]\text{BPh}_4$.⁸⁵

Reductive cleavage of dichalcogenides by $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ was used to prepare a series of chalcogenolates of the type $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{ER}]$ ($\text{ER} = \text{SPh}, \text{SPh-4-Me}, \text{SePh}, \text{SePh-4-Bu}^t, \text{SePh-4-OMe}, \text{TePh}$)³⁸ (eq 20). The ^1H NMR spectra of all the complexes are rather structurally uninformative and are suggestive of molecular complexes with a fluxional coordination sphere. Cooling the samples results in broadening and shifting of the resonances, and by -90°C the dynamic process is sufficiently slow for $\text{E} = \text{Se}$ that six resonances assigned to the methyl and three to the methyne protons of the Tp^{Me_2} ligands are observed. This is consistent with a C_2 -symmetric coordination geometry.



The X-ray crystal structures of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SPh-4-Me})]$, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SePh})]$, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SePh-4-Bu}^t)]$, and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{TePh})]$ have been determined. The compounds $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SPh-4-Me})]$ and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{TePh})]$ are seven-coordinate with two tridentate Tp^{Me_2} ligands and the chalcogenolate ligand and display pentagonal bipyramidal geometry (Figure 24a). The $\text{Sm}-\text{N}$ bond distances are unexceptional. In $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SPh-4-Me})]$, the thiolate ligand is significantly bent with a $\text{Sm}-\text{S}-\text{C}$ angle of $114.6(1)^\circ$, and the phenyl group shows an apparent π -stacking interaction with one pyrazolyl group, the centroid-to-centroid distance being 3.444 Å. A similar type of interaction occurs between the phenyl ring and one of the pyrazolyl rings in $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{TePh})]$. The two

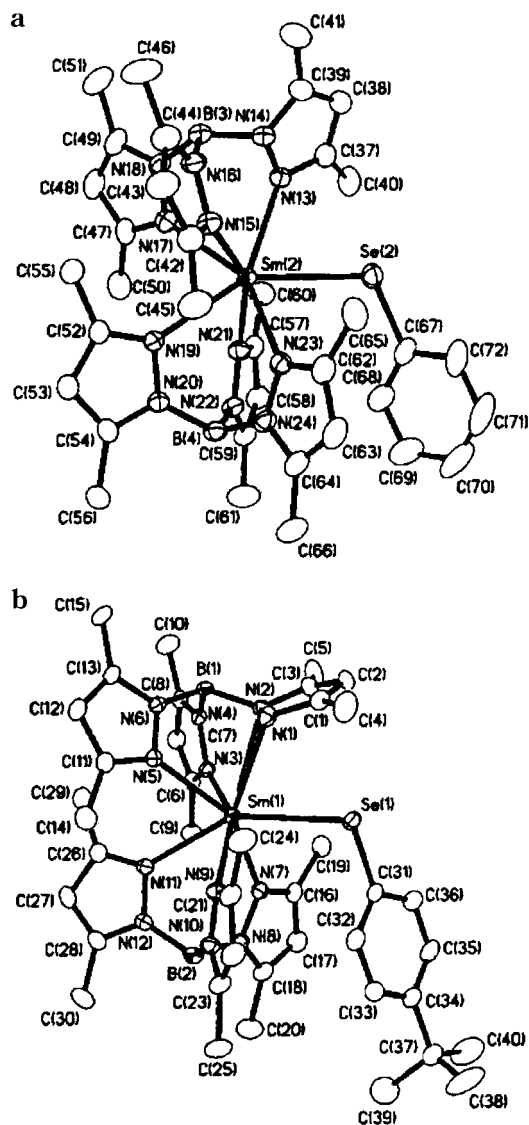


Figure 24. The molecular structures of (a) $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{-SePh}]$ and (b) $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{SePh-4-Bu}^4]$, the latter showing the severe distortion of one Tp^{Me_2} ligand. Reprinted with permission from ref 38. Copyright 2000 American Chemical Society.

Tp^{Me_2} ligands are mutually staggered and bent back from each other at angles about 150° . The boron atoms are both tetrahedral and the Tp^{Me_2} ligands show the typical twisting of the pyrazolyl rings about their B–N bonds, the maximum BNNSm torsional angles being 34.4° and 47.7° for $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SPh})]$ and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{TePh})]$, respectively.

By contrast with these complexes, which are seven-coordinate, in $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SePh-4-Bu}^4)]$ one of the Tp^{Me_2} ligands binds normally through three nitrogen atoms, while the other contains one pyrazolyl ring bonded to samarium through both of its nitrogen atoms leading to a BNNSm torsional angle of 91.3° (Figure 24b). This mode of bonding is similar to those seen in $[\text{U}(\text{Tp}^{\text{Me}_2})_2\text{I}]$ ⁹⁵ and $[\text{Yb}(\text{Tp}^{\text{Bu,Me}})(\text{C}_5\text{H}_4\text{SiMe}_3)]$.⁹⁴ For $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SePh})]$, two independent molecules, with different conformations, are found in the asymmetric unit. The molecular structure of one of them is similar to the one found in $[\text{Sm}(\text{Tp}^{\text{Me}_2})(\text{SPh-4-Me})]$ and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{TePh})]$ with maximum twists about the B–N bonds of 51.2° , and the other one adopts

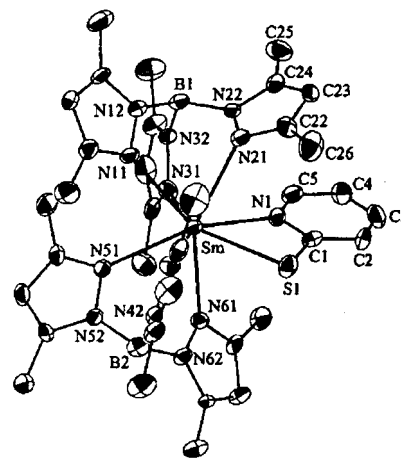
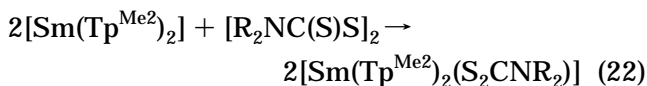
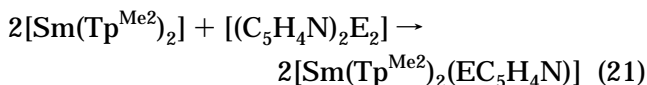


Figure 25. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{Spyr})]$. Reprinted with permission from ref 100. Copyright 2000 American Chemical Society.

the side-on coordination mode found in $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{SePh-4-Bu}^4)]$ with a BNNSm torsional angle of 83.7° .

The reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with excess of PhTePh or alternatively of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{TePh})]$ with one or more equivalents of PhTePh yielded the salt $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2](\text{TePh})_3$, which contains the unprecedented $(\text{PhTe})_3^-$ anion.⁹⁹

The reducing properties of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ have been used to prepare the eight-coordinate complexes $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{EC}_5\text{H}_4\text{N})]$ (E = S, Se), according to eq 21 and the dithiocarbamate compounds, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{S}_2\text{-CNR}_2)]$ (R = Me, Et) (eq 22).¹⁰⁰ The pyridinolate, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_5\text{H}_4\text{N})]$, has been prepared by the metathesis route from $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{Cl}]$.



The crystal structures of these compounds have been determined (Figure 25). They are all eight-coordinate with dodecahedral geometry, with the samarium atoms bound in tridentate fashion to two polypyrazolylborate ligands and in bidentate fashion by the third ligand.

The ^1H NMR spectra of the Epyr (E = S, Se) derivatives featured 12 singlets due to the methyl group protons and 6 due to the methylene H(4) hydrogen, indicating rigid solution structure with C_1 symmetry. Pairwise exchange between methyl groups gives rise to selective broadening of resonances in the ^1H NMR spectrum as the temperature is raised (Figure 26). On the other hand, the ^1H NMR spectrum of the pyridinolate complex exhibited only three resonances for the Tp^{Me_2} ligands implying fluxional solution behavior. On the basis of 2D NMR experiments, a mechanism involving metal-centered rearrangements between different coordination geometries was proposed, the rate of the mechanism being controlled by steric interactions between the ligands. Although related rearrangements have been reported before, the use of the unsymmetrical bidentate ligands

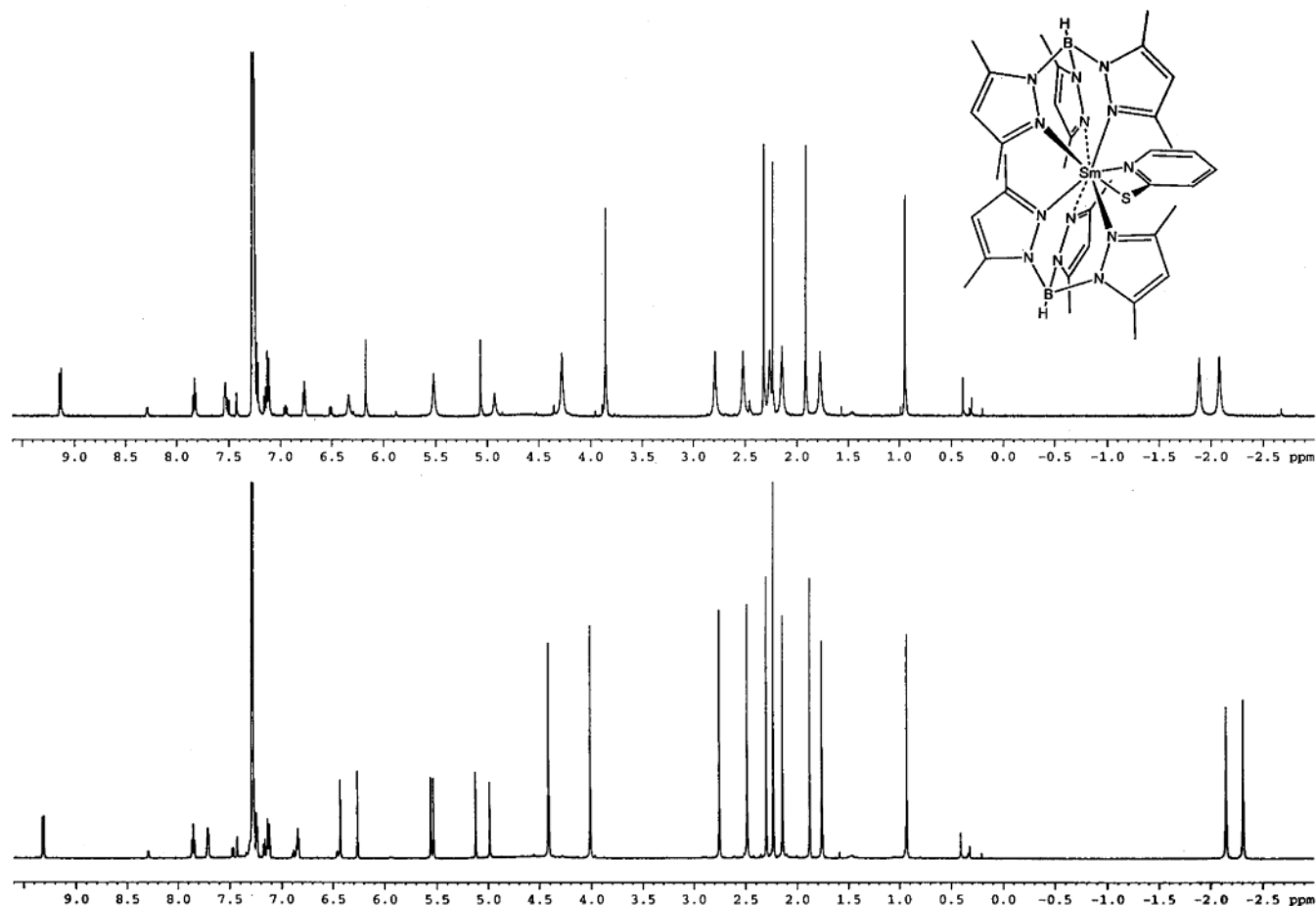


Figure 26. 400 MHz ^1H NMR spectra of $\text{Tp}^{\text{Me}_2}_2\text{Sm}(\text{Spyr})$ at 20 °C (below) and 60 °C (above) in C_6D_6 .

$\text{EC}_5\text{H}_4\text{N}$ results in much more detailed information about the dynamics. The experiments gave evidence for two distinct dynamic regimes occurring in solution.¹⁰⁰

B. Reduction of Organic Substrates

Despite its insoluble nature, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ undergoes one-electron-transfer reactions with a variety of organic substrates.

The complexes $[\text{Ln}(\text{Tp}^{\text{Me}_2})_2]$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) react smoothly with TCNE and TCNQ to give charge-transfer salts of $[\text{Ln}(\text{Tp}^{\text{Me}_2})_2]\text{Z}$ ($\text{Z} = \text{TCNE}, \text{TCNQ}$), which crystallize from THF with varying amounts of THF included in the lattice. Although the crystal structure of the Yb compound with TCNE crystallized as a simple salt, the IR spectra of the products formed with the larger lanthanide ions suggested interactions between the anion and the metal center.¹⁰¹

$[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ reacts with $\text{PhN}=\text{NPh}$ in toluene to form a deep green solution from which green crystals of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{PhNNPh})]$ could be isolated. The same complex is obtained when the reaction is carried out with 2 equiv of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ per molecule of azobenzene. The solid-state structure shows that both Tp^{Me_2} ligands retain their tridentate coordination modes and that the azobenzene is η^2 -bonded to the Sm center, with an approximate C_2 symmetry (Figure 27). The ^1H NMR spectrum displays three sets of resonances assigned to the two Tp^{Me_2} ligands, in the

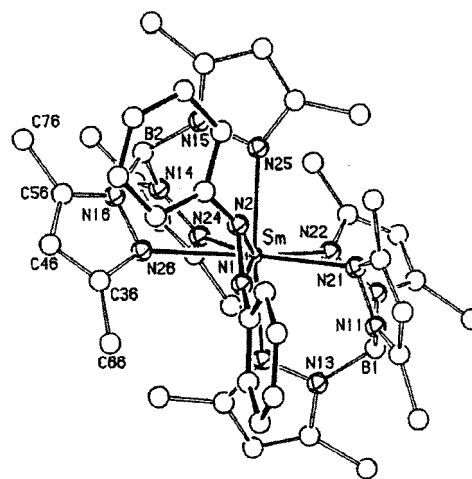


Figure 27. A view of the molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{PhNNPh})]$ highlighting the approximate C_2 symmetry of the molecule (ref 84).

ratio 1:1:1, consistent with a C_2 symmetric structure. As expected from the alternating spin delocalization in a conjugated system the *ortho*, *meta*-, and *para*-phenyl protons are found at -189 , $+73$, and -171 ppm, respectively.⁸⁴ An analogous compound was obtained from the reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with a stoichiometric amount of benzaldehyde azine. The ^1H NMR of the deep green solid is consistent with a C_2 symmetric structure. The *ortho*, *meta*-, and *para*-phenyl protons are found at -159 , $+63$, and -192

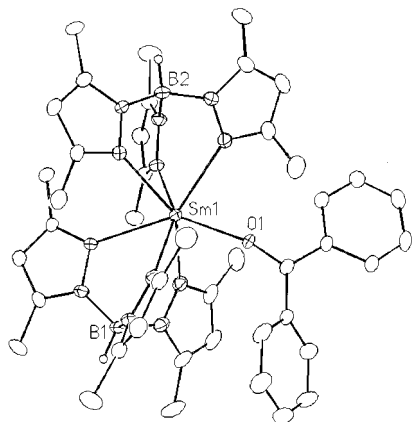


Figure 28. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OCPh}_2)]$ (ref 102).

ppm, respectively.⁹⁸

Reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with benzophenone, fluorenone, and phenanthrenequinone result in intensely colored solutions from which the compounds $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OCPh}_2)]$,⁹¹ $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_{13}\text{H}_8)]$, and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\eta^2\text{-O}_2\text{C}_{14}\text{H}_8)]$ were isolated.¹⁰² The radical anion nature of the coordinating ligands is demonstrated by the intense colors of the compounds and by their ¹H NMR spectra, which display resonances associated with the protons of the aromatic rings strongly shifted from the diamagnetic position, due to spin delocalization in the conjugated system. Otherwise, the spectra are consistent with C_2 symmetric structures. Crystallographic analysis also provides corroboration for the ketyl formulation of the compounds. The structures of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OCPh}_2)]$ and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_{13}\text{H}_8)]$ have been determined.¹⁰² As a representative example, the structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OCPh}_2)]$ is shown in Figure 28. The C–O bond distance of 1.315(6) Å is significantly longer than a C–O double bond (1.23(2) Å in free benzophenone) and compares well with the values reported for other ketyl compounds.^{103–107} The geometry of the carbonyl carbon atom is planar, as can be seen from the angles around it (359.9(5)°), implying that it is still sp^2 -hybridized. The steric protection provided by the two Tp^{Me_2} ligands allows stabilization of ketyl radical anions and is also responsible for the rigid structure observed in solution for these compounds.

In contrast to the monomeric nature of the above complexes, less bulky substrates such as benzaldehyde or pyrazine react with $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ to yield the dimetallic compounds, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2[\mu\text{-OCH}(\text{Ph})\text{-CH}(\text{Ph})\text{O}]$ and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2[\mu\text{-(C}_4\text{H}_4\text{N}_2)_2]$. In these complexes, two $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ units are bridged by dianionic ligands formed by C–C coupling of two nascent radical anions (Figure 29). In accord with the smaller size of the coordinating ligands, that also prevents formation of stable radical anions, the compounds display fluxional behavior in solution.⁹⁸

Reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with 2,6-di-*t*-Bu-1,4-benzoquinone (*para*-*Bu*'₂quinone) and 3,5-di-*t*-Bu-1,2-benzoquinone (*ortho*-*Bu*'₂quinone) affords red $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ (*para*-*Bu*'₂quinone) and green $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ (*ortho*-*Bu*'₂quinone), respectively. The compounds have been structurally characterized.^{91,108} In the absence of the bulky *t*Bu groups, both mono- and

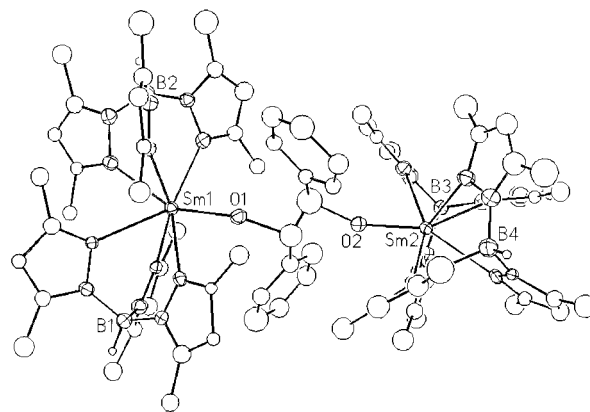


Figure 29. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2(\mu\text{-OCHPhCHPhO})$ (ref 98).

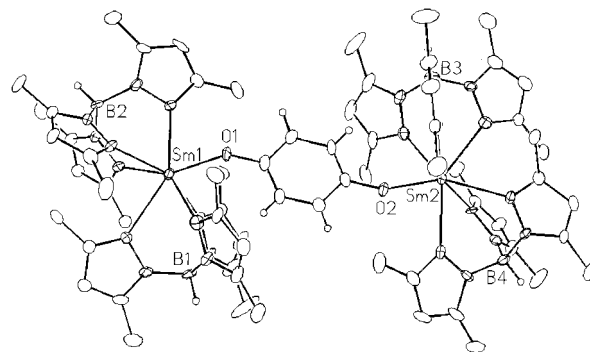
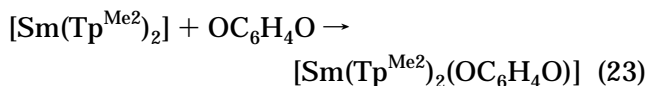


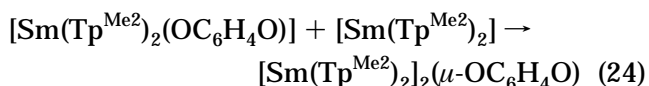
Figure 30. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2(\mu\text{-OC}_6\text{H}_4\text{O})$ (ref 102).

dimetallic complexes $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\textit{para}\text{-quinone})]$ and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2(\mu\text{-}\textit{para}\text{-quinone})]$ can be prepared.^{102,108} Thus, addition of one equivalent of 1,4-benzoquinone to a suspension of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ in THF led to rapid dissolution of the purple starting material and production of a dark blue solution, from which the blue $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_6\text{H}_4\text{O})]$ was isolated (eq 23).



Attempts to obtain crystals suitable for X-ray diffraction analysis failed as crystallization of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_6\text{H}_4\text{O})]$ from THF or toluene solutions led always to formation of yellow crystals of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2(\mu\text{-OC}_6\text{H}_4\text{O})$, a dimetallic compound in which the orthoquinone radical anion is further reduced to the dianionic form by a second molecule of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ (Figure 30).

The dimeric compound could be obtained on a preparative scale by addition of one equivalent of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ to $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OC}_6\text{H}_4\text{O})]$ (eq 24). Reaction with anthraquinone yields a similar dimetallic complex.¹⁰⁸



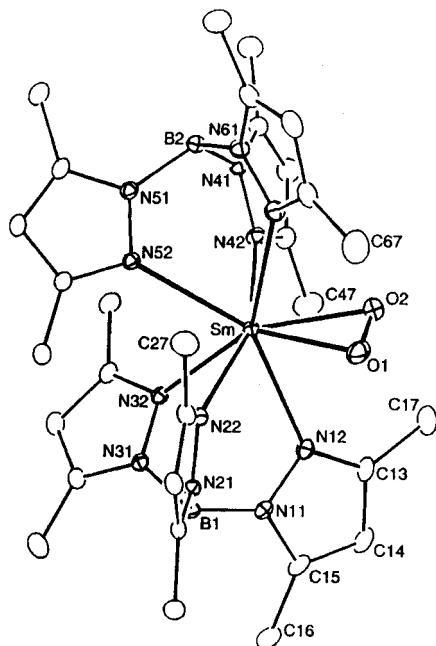


Figure 31. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{O}_2)]$. Reprinted with permission from ref 109. Copyright 1994 American Chemical Society.

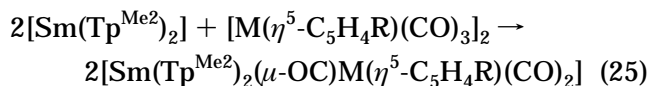
C. Reduction of Molecular Oxygen

The first example of a lanthanide superoxo complex was obtained when a slurry of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ was stirred at -78°C under an atmosphere of dioxygen. The insoluble $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ slowly dissolved leading to a red solution. As the solution was allowed to warm to room temperature, and the excess oxygen was removed, the color changed from red to pale green. The UV and the Raman spectrum of the compound, especially $^{16}\text{O}/^{18}\text{O}$ isotope substitution experiments, gave good evidence for O_2^- coordination. Final corroboration came from a single-crystal X-ray analysis which showed that the dioxygen is bonded to samarium in a symmetrical, side-on fashion (Figure 31).¹⁰⁹ Similar complexes have been postulated for Sm, Eu, and Yb with both Tp and Tp^{Me_2} ligands although no corroborating structural data were presented.¹¹⁰

D. Reduction of Transition-Metal Carbonyl Complexes

Like its samarocene analogue, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ is a sufficiently strong reducing agent to react with many transition-metal carbonyl complexes to form anions. The products however differ considerably because of the greater steric crowding afforded by the Tp^{Me_2} ligands.

The reaction of 2 equiv of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with $[\text{M}(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_3]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) gives good yields of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\mu\text{-OC})\text{M}(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_2]$ ($\text{M} = \text{Cr}, \text{R} = \text{H}; \text{M} = \text{Mo}, \text{R} = \text{Me}, \text{Bu}^t; \text{M} = \text{W}, \text{R} = \text{H}$) (eq 25).¹¹¹ The solid-state IR spectra show the B–H stretching vibration at 2555 cm^{-1} , indicative of κ^3 -coordination modes of the two Tp^{Me_2} ligands. In addition, there are three intense bands in the carbonyl region, two of them corresponding to terminal CO stretches and one, at a very low energy, ascribed to a bridging isocarbonyl group.



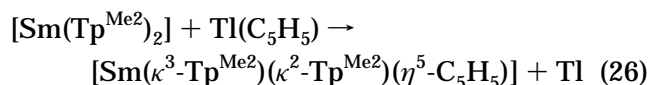
The crystal structure confirmed the proposed formulation (Figure 32). The samarium center is seven-coordinate with two tridentate Tp^{Me_2} ligands, staggered with respect to each and bent back with a B(1)–Sm–B(2) angle of 149.8° , and by the oxygen atom of the bridging isocarbonyl ligand. The ^1H NMR spectra of all compounds show only three peaks in the ratio 3:3:1 for the three pyrazolyl groups, indicating a fluxional system. The reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with $\text{Co}_2(\text{CO})_8$ results in the formation of the salt $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2][\text{Co}(\text{CO})_4]$.¹¹¹

By contrast to the above reactions which occur at room temperature, the reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with $\text{Re}_2(\text{CO})_{10}$ in toluene takes place only if the temperature is raised above room temperature. The elemental analysis of the compound isolated from the reaction mixture heated to 80°C was consistent with the formulation $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2][\text{Re}_4(\text{CO})_{17}]$. Crystallization from toluene yielded the corresponding protonated cluster $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2][\text{HRe}_4(\text{CO})_{17}]$ which has been structurally characterized.¹¹² The anion consists of a 64-electron cluster that adopts a spiked triangular structure with the hydride bridging two Re atoms in the equatorial plane of the cluster.

If the reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with $\text{Re}_2(\text{CO})_{10}$ is carried at lower temperature and for shorter periods, it was possible to isolate, in addition to $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2][\text{Re}_4(\text{CO})_{17}]$, variable amounts of a yellow compound formulated as $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2][\text{Re}(\text{CO})_5]$, based on IR data. An analogous compound, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2][\text{Mn}(\text{CO})_5]$ was also isolated from the reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with $\text{Mn}_2(\text{CO})_{10}$. In addition, a salt of $\text{Mn}(\text{CO})_5^-$ containing the formate bridged cation $\{[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]_2(\mu\text{-O}_2\text{CH})\}^+$ was also isolated as a minor side product.¹¹³

E. Reactions with TICp and $\text{Hg}(\text{CCPh})_2$: Formation of Heteroscorpionate Ligands

Oxidation of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with TICp gives good yield of the corresponding mixed ligand complex, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{C}_5\text{H}_5)]$ (eq 26). The spectroscopic data clearly indicate different coordination modes for the two Tp^{Me_2} ligands. Thus, the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows two signals at -5.23 and -6.98 ppm, and there are two B–H resonances in the ^1H NMR spectrum at -5.05 and -4.10 ppm. Similarly, the infrared spectrum exhibits two $\nu(\text{B-H})$ stretching vibrations at 2565 and 2448 cm^{-1} . The positions of these IR bands are indicative of a κ^3 - and a κ^2 -coordinated Tp^{Me_2} ligands. Finally, the single ^1H NMR resonance at 9.94 ppm, accounting for 5H, is in accord with an η^5 -Cp ligand. A single-crystal X-ray study confirmed the bonding postulate (Figure 33a).¹¹⁴



A related mixed Tp/Cp compound was obtained by oxidation of divalent samarium with a thallium reagent. Thus, reaction of SmI_2 and TlCpPPh_2 fol-

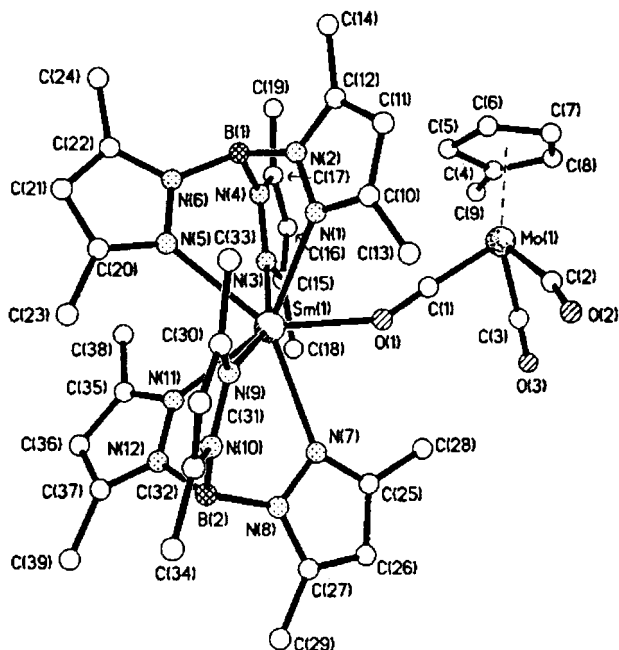


Figure 32. The molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\mu\text{-OC})\text{Mo}(\eta^5\text{-MeCp})(\text{CO})_2]$. Reprinted from ref 111 with permission from Elsevier Science. Copyright 1997.

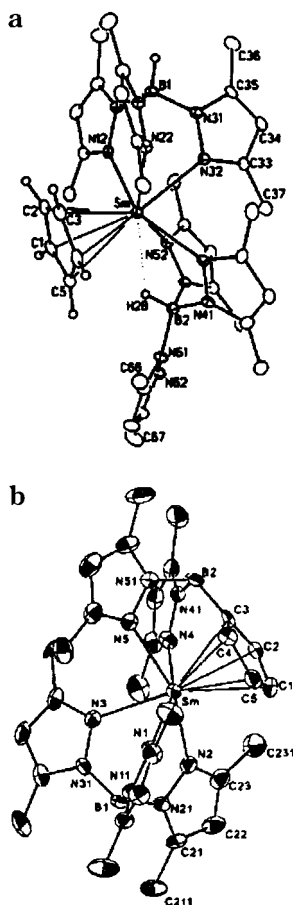
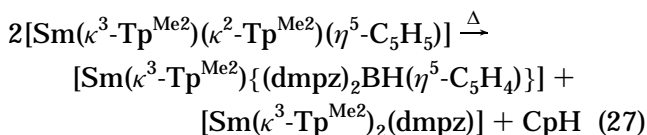


Figure 33. The molecular structures of (a) $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{Cp})]$ and (b) the rearranged complex, $[\text{Sm}(\kappa^3\text{-Tp}^{\text{Me}_2})(\text{dmpz})_2\text{-BH}(\eta^5\text{-C}_5\text{H}_4)]$. Reprinted with permission from ref 114. Copyright 1999 American Chemical Society.

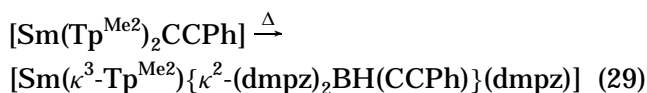
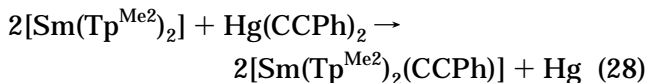
lowed by treatment with KTp^{Me_2} gave moderate yields of $[\text{Sm}(\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)(\text{Tp}^{\text{Me}_2})\text{I}(\text{THF})]$, a complex with four different ligands around the metal.¹¹⁵ The

solid state structure of the complex was determined, and it was established that, at low temperature, the asymmetric structure is maintained in solution. The absence of suitable stereochemical probe in the molecule precludes an answer to the intriguing question of whether this ostensibly labile complex is configurationally stable.

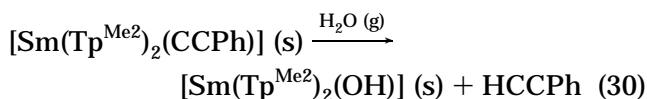
Thermolysis of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{C}_5\text{H}_5)]$ resulted in an unprecedented transformation in which the Cp displaces a dimethylpyrazole group from one of the Tp^{Me_2} ligands, and undergoes C–H activation generating an unprecedented mixed C_5H_4 -substituted Bp ligand (eq 27, Figure 33b).¹¹⁴



A similar reaction has since been observed for $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{CCPh}]$. Treatment of a THF slurry of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2]$ with mercury diphenylacetylide resulted in a colorless solution and a black precipitate (eq 28, Figure 34a).¹¹⁶ Thermolysis of the resulting $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{CCPh})]$ in benzene- d_6 solution at 105 °C for 36 h led to quantitative conversion to a new complex (eq 29). One of the Tp^{Me_2} ligands is still bonded to samarium via the classic, tridentate fashion, while in the other a pyrazolyl ring has been displaced by the phenylacetylide group. The displaced pyrazolate remains coordinated to the same samarium center (Figure 34b).



Finally, it should be noted that carefully controlled reaction of water vapor with solid $[(\text{Tp}^{\text{Me}_2})_2\text{Sm}(\text{CCPh})]$ (a solid–gas reaction) quantitatively and cleanly transforms the latter to the corresponding hydroxide (eq 30, Figure 35).¹¹⁷ The formation of a monomeric lanthanide hydroxide provides another example of the steric protection offered by the “ $\text{Sm}(\text{Tp}^{\text{Me}_2})_2$ ” fragment to a variety of substrates.



IV. Fragmentation Reactions of Trivalent Lanthanide Tp Complexes

A recurring feature of the pyrazolylborate ligands is their vulnerability to fragmentation reactions. This aspect, although mentioned in the chemical literature on a number of occasions,^{118–120} has been consistently underplayed in previous reviews of the field but cannot be ignored. Throughout this review, attention has been drawn to unexpected products isolated from reaction mixtures or from attempts to crystallize

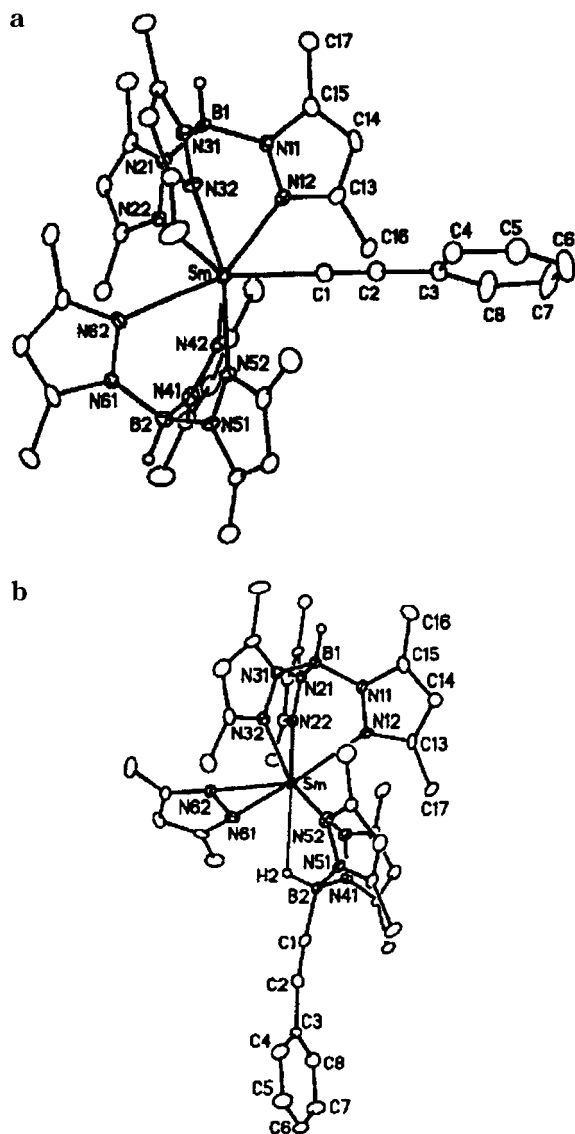


Figure 34. The molecular structures of (a) $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2\text{-(CCPh)}]$ and (b) the rearranged complex, $[\text{Sm}(\kappa^3\text{-Tp}^{\text{Me}_2})\{\kappa^2\text{-(dmpz)}_2\text{BH}(\text{CCPh})\}(\text{dmpz})]$. Reprinted with permission from ref 116. Copyright 2000 American Chemical Society.

particular compounds. A small number of reports have appeared in which the fragmentation of Tp ligands has been reported. We note particularly the work of Onishi who has reported the isolation of $[\text{NdTp}_2\text{Cl}(\text{Hpz})]$ from attempts to synthesize $[\text{NdTp}_2\text{-Cl}]$ even though steps were taken to maintain rigorously anhydrous conditions.¹⁶ Curiously, preparations of Tp complexes from aqueous or alcoholic solutions have been widely successful, although, most of the complexes are insoluble and precipitate from the preparation solutions. Similarly, Ward and co-workers' syntheses of Tp^{Pyr} complexes have for the most part been carried out in hydroxylic media, and only once has a fragmented product been reported.

By contrast, the synthesis of lanthanide complexes with Tp^{Me2} has been plagued by such problems. At least 12 structures of the binuclear complex $[\text{Ln}(\text{Tp}^{\text{Me}_2})(\text{dmpz})_2\text{BH}(\mu\text{-O})_2]$ (Ln = La, Ce, Sm)^{37,47,48,88,102,121} (Figure 36) have been determined with a generous variety of cocrystallized solvents, only one of which has so far appeared in the pub-

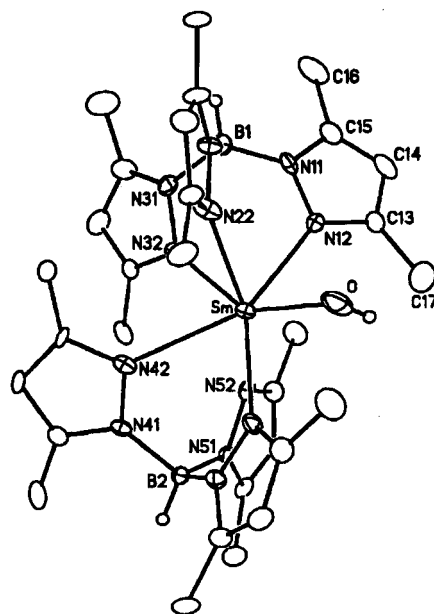


Figure 35. A view of the molecular structure of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OH})]$ (ref 117).

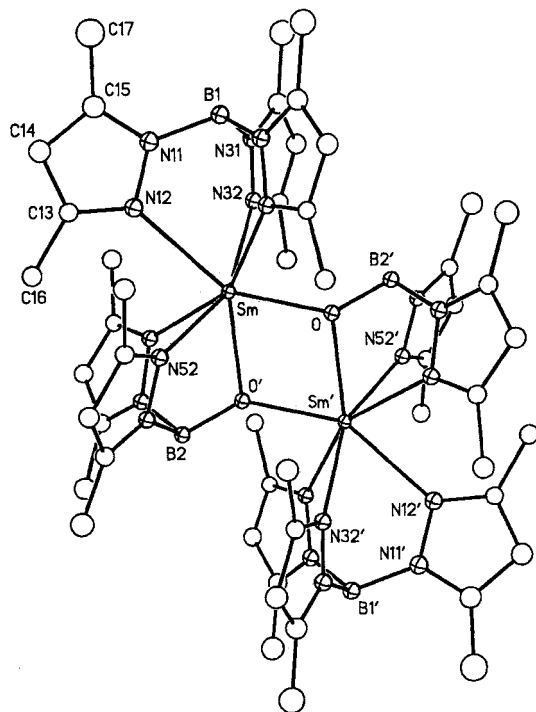


Figure 36. The molecular structure of one example of the ubiquitous dimeric complex $[\text{Sm}(\text{Tp}^{\text{Me}_2})(\mu\text{-O})\text{HB}(\text{dmpz})_2]_2$ (see section IV for references).

lished literature (Figure 36).¹¹⁰ The dimer appears to result from the displacement of a pyrazolyl group from a Tp^{Me2} ligand by adventitious water. It is noteworthy that Tp^{Me2} should appear to be more vulnerable to such decomposition than ligands that do not contain a methyl group in the 5-position.

As mentioned previously, the hydroxide $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{OH})]$ can be isolated as a solid by careful reaction of solid $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{CCPh})]$ with water vapor.¹¹⁷ The complex may also be obtained from the reaction of $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{NPh}_2)]$ with stoichiometric amount of degassed water. However, in solution the complex is

very unstable and rapidly decomposes. The major decomposition product is the dimer $[\text{Sm}(\text{Tp}^{\text{Me}_2})(\text{dmpz})_2\text{-BH}(\mu\text{-O})_2]$. Thus, it is not unreasonable to suggest that the hydroxide complex, $(\text{Tp}^{\text{Me}_2})_2\text{Ln}(\text{OH})$, is the primary product of the hydrolysis for many of the complexes described above, all of which involve fairly basic anionic ligands. A full understanding of the subsequent steps of the decomposition pathway will require extensive exploratory synthesis; however, it appears that steric crowding and transient formation of the terminal monomeric hydroxide leads to the formation of the boronate-bridged binuclear complex. By contrast, it has proved possible to prepare less congested, stable dimeric Ln(III) complexes with bridging hydroxides with $\text{HB}(3,5\text{-Me}_2\text{pz})(\text{CCPh})$ and benzotriazolylborate ligands as ancillaries.^{117,122}

V. Conclusions and Prospects for the Future

The first f-element pyrazolylborate complexes were prepared some 30 years ago; however, a resurgence of interest in these compounds is apparent from the plethora of recent contributions. Interest in the structure of these complexes stems from the extreme steric crowding and attendant protection offered by the $\text{Tp}^{\text{R,R}'}$ ligands. This has allowed the isolation of ligands not previously observed bound to a lanthanide center, including superoxide, and the first terminal fluoride and hydroxide moieties. It is intriguing to speculate therefore whether the steric protection afforded by the " $\text{Ln}(\text{Tp}^{\text{Me}_2})_2$ " unit might not permit the isolation of terminal hydride. Work by the authors in this direction is in progress. In parallel with this, it cannot be long before hydrocarbyl systems of the type $[\text{Ln}(\text{Tp}^{\text{Me,Me}})_2\text{R}]$ will be isolated at a nonreducible lanthanide metal center. The application of bulky, second generation $\text{Tp}^{\text{R,R}'}$ ligands ($\text{R} = \text{Me}$, Bu^t ; $\text{R}' = \text{Me}$) have also revealed that ligand redistribution in divalent, half-sandwich $[\text{Ln}(\text{Tp}^{\text{R,R}'})\text{X}]$ type complexes can be effectively suppressed. The use of even bulkier substituents may well permit the isolation of Sm(II) hydrides.

Although reactivity studies and practical applications of lanthanide pyrazolylborate complexes are still in their infancy, rich derivative chemistry can confidently be predicted. For instance, isolation of $[\text{Sm}(\text{Tp}^{\text{R,R}'})\text{H}]$ would provide an entry into an exciting new area involving highly reactive hydrides bound to a very reducing metal center. On the application front, already $[\text{Eu}(\text{Tp}^{\text{R,R}'})_2]$ complexes ($\text{R, R}' = \text{Me}$, CF_3) are proving to be promising candidates as volatile phosphors for thin film devices.⁸⁶

With the advent of new $\text{Tp}^{\text{R,R}'}$ ligands and the availability of various heteroscorpionate ligands, there is much room for further exploration. With serendipity as a companion, many exciting discoveries await the chemist who takes up the challenge and ventures into the world of lanthanide pyrazolylborate chemistry.

VI. Acknowledgments

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years. The authors also wish to express their gratitude to all of their co-workers mentioned in the references for their dedication and enthusiasm for lanthanide chemistry.

VII. Abbreviations

Ln = Y, La-Lu
 Cp = cyclopentadienyl
 Cp* = pentamethylcyclopentadienyl
 COT = cyclooctatetraenyl
 pzH = pyrazole
 dmpzH = 3,5-dimethylpyrazole
 β -dike = $\text{CH}(\text{CO})_2\text{R}_2$

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