

Mini review

$[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})]_2$: a fecund precursor to a host of divalent, hydrotris(pyrazolyl)borate supported f-element complexes

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Dedicated to Professor Gary M. Ferrence on the occasion of his retirement¹

Abstract

We present an overview of recent work from our laboratories on the chemistry of the divalent lanthanide hydride $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})]_2$ (**1**). The first section deals with the hydrotris(3-*tert*-butyl, 5-methyl-pyrazolyl)borate, $(\text{Tp}^{t\text{-Bu,Me}})$, ligated divalent lanthanide complexes leading up to the discovery of **1**. The remaining sections are centered on the divalent ytterbium hydride $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})]_2$ (**1**), its preparation, molecular structure, NMR characteristics and reactivity. Three broad reactivity classes will be described, namely reactions with Lewis bases and Lewis acids, such as the perfluoroaryl boranes, σ -bond metathesis reactions generally involving acidic H–X bonds, but also an example of C–Si bond cleavage, and insertion chemistry, primarily involving alkynes. The molecular structures of several representative complexes have been determined by X-ray crystallography. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanides; Ytterbium(II); Hydrotris(pyrazolyl)borate; Hydride; Heteroleptic complexes

1. Introduction

As a result of the large ionic radius, and predominant ionic bonding, f-element complexes are prone to the formation of high coordination number complexes, exhibiting variable coordination geometries. The design of ligands to control the coordination number and geometry of these metal ions is a challenging undertaking [1–5]. Much of the early successes with divalent lanthanides came from the discovery of $\text{Ln}(\text{C}_5\text{Me}_5)_2$ [1], but the presence of two bulky pentamethylcyclopentadienyl ligands limited the incorporation of additional ligands to neutral donors. Investigation of a variety of homoleptic ‘ LnL_2 ’-type systems has expanded the possibilities of supporting environment, but still limits ligand incorporation [5]. Some of these ancillary ligands have

challenged the steric saturation limits around the metal. In extreme instances, such as $\text{Sm}(\text{Tp}^{t\text{-Bu,Me}})_2$ and $\text{Yb}(\text{Tp}^{t\text{-Bu,Me}})_2$ [6], steric saturation allows coordination of only five of the six pyrazolyl arms of the two commonly tridentate tris(pyrazolyl)borate ligands, cf. $\text{Ln}(\text{Tp}^{\text{Me}_2})_2$ [7]. In view of the sterically demanding nature of the hydrotris(3-*tert*-butyl, 5-methyl-pyrazolyl)borate ligand, $(\text{Tp}^{t\text{-Bu,Me}})$ [8,9], it was naturally of interest to explore its ability to allow the synthesis of low coordinate, low valent lanthanide complexes. Herein we discuss the chemistry leading up to the discovery of $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})]_2$ (**1**) and subsequent reactivity.

2. Hydrotris(3-*tert*-butyl, 5-methyl-pyrazolyl)borate ligation of divalent lanthanides

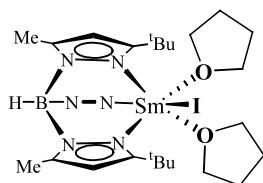
Prior to the discovery of the $\text{Ln}(\text{Tp}^{t\text{-Bu,Me}})_2$ complexes, we and Sella reported that the $\text{Tp}^{t\text{-Bu,Me}}$ ligand does indeed provide a unique coordination environment which allows the isolation of soluble, monomeric $(\text{Tp}^{t\text{-Bu,Me}})\text{YbI}(\text{thf})$ (**2**) [10]. Treatment of a tetrahydro-

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furan (thf) solution of YbI_2 with one equivalent of $\text{KTp}^{t\text{-Bu},\text{Me}}$ affords yellow **2** in high yield. Compound **2** is stable in solution and has no tendency to disproportionate to $\text{Yb}(\text{Tp}^{t\text{-Bu},\text{Me}})_2$ and YbI_2 . Such ligand redistributions are a common impediment to the isolation of mixed ligand lanthanide complexes. Soon after, the analogous samarium complex, $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{SmI}(\text{thf})_2$ (**3**), was prepared [11–13]. Interestingly, while the thf solvent molecules coordinating **3** can be easily removed by repeated toluene dissolution and removal of solvent in vacuo, the thf solvate molecule persists in the ytterbium analog, **2** [12,13]. In fact, the presence of a coordinated solvent molecule is pervasive in the derivative chemistry of **2**.

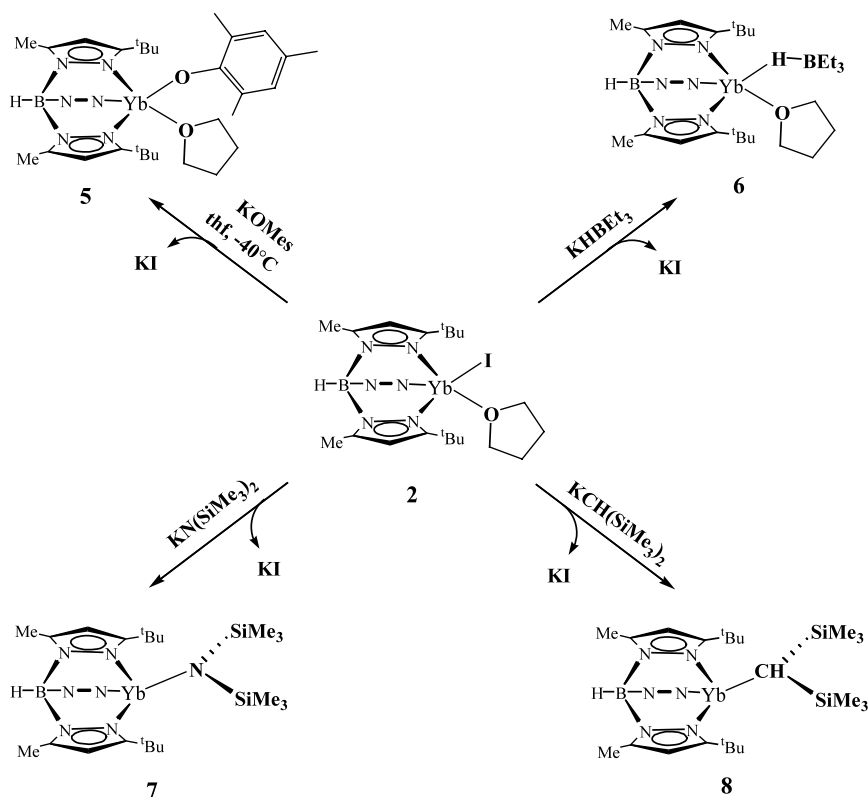
**3**

Metathesis reactions (Scheme 1) between potassium salts and **2** readily generate a variety of $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{YbER}(\text{sol})_n$ ($\text{sol} = \text{coordinated solvent}$, $n = 0, 1$) derivatives. Reaction with one equivalent of the potassium salts of the relatively bulky hydrocarbyl or

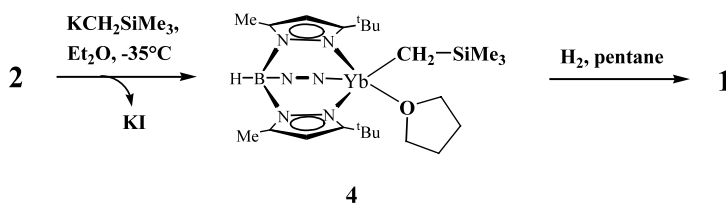
aryloxy ligands, $\text{KCH}_2\text{SiMe}_3$ and KOMes ($\text{Mes} = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$) both result in the formation of solvent ligated complexes, namely $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{Yb}(\text{CH}_2\text{SiMe}_3)(\text{thf})$ (**4**) [10a], and $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{Yb}(\text{OMes})(\text{thf})$ (**5**) [14]. Similar solvent ligation was observed in the formation of $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{Yb}(\mu\text{-HBEt}_3)(\text{thf})$ (**6**). A particular challenge of this chemistry has been the isolation of solvent free complexes. Only in the cases where the very bulky bis(trimethylsilyl)amido and bis(trimethylsilyl)methyl ligands are incorporated is there sufficient steric hindrance to prevent solvent ligation. Metathesis between **2** and appropriate alkali metal salts affords the solvent free complexes $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{Yb}(\text{N}\{\text{SiMe}_3\}_2)$ (**7**) and $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{Yb}(\text{CH}\{\text{SiMe}_3\}_2)$ (**8**) [10a]. A key goal has thus been to prepare related solvent complexes containing less bulky substituents. The presence of an effectively open coordination site is likely to yield more reactive lanthanide complexes.

3. The divalent lanthanide hydride, $(\text{Tp}^{t\text{-Bu},\text{Me}})\text{Yb}(\mu\text{-H})_2$

Given the rich chemistry of the Ln(III) hydride complexes [15] and their importance in various catalytic processes [4], we targeted the preparation of a discrete Ln(II) hydride. Prior to our utilization of the scorp-



Scheme 1.



Scheme 2.

onate ligand, divalent lanthanide hydrides were limited to the borohydride complexes $[\text{Ln}\{\{\mu\text{-H}\}_3\text{BH}\}_2(\text{CH}_3\text{CN})_n]$ ($\text{Ln} = \text{Yb}$, $n = 4$; $\text{Ln} = \text{Eu}$, $n = 2$) [16], the hydride bridged Yb(II)-transition metal compounds $[\{(\text{PMe}_3)_3\text{WH}_5\}_2\text{YbL}_3]$ and $[\{(\text{C}_5\text{H}_5)_2\text{NbH}_2\}_2\text{YbL}_3]$ ($\text{L}_3 = (\text{MeOCH}_2\text{CH}_2)_2\text{O}$) [17], $[\{\text{YbH}_2(\text{thf})\}_n]$ of unknown structure [18], and the not fully characterized $[(\text{C}_5\text{Me}_5)\text{SmH}(\text{thf})_2]$ and $[\{\text{Yb}(\text{C}\equiv\text{CC}_4\text{H}_9)_{1.5}\text{H}_{0.5}\}_n]$, obtained by cocondensation of the substrate and appropriate lanthanide metal vapors [19,20]. Our initial approach to prepare hydrides involved reaction of $(\text{Tp}^{t\text{-Bu,Me}})\text{LnI}(\text{thf})_n$ ($\text{Ln} = \text{Yb}$, $n = 1$; $\text{Ln} = \text{Sm}$, $n = 0$) with stoichiometric amounts of KHBET_3 . Instead of simple hydrides, the trialkylborane-stabilized hydrides, $(\text{Tp}^{t\text{-Bu,Me}})\text{Ln}(\text{HBET}_3(\text{thf})_n)$ ($\text{Ln} = \text{Yb}$, $n = 1$; $\text{Ln} = \text{Sm}$, $n = 0$) were obtained [10,11,21]. To our knowledge, no more recent reports of divalent lanthanide hydrides exist.

With the facile conversion of $(\text{Tp}^{t\text{-Bu,Me}})\text{YbI}(\text{thf})$ (**2**) to $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\text{CH}_2\text{SiMe}_3)(\text{thf})$ (**4**), hydrogenolysis of alkyl compounds, the by far most common route to lanthanide hydrides [15], was attempted. Exposure of an orange pentane solution of the aforementioned **4** to a hydrogen atmosphere yielded red crystalline $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})_2]$ (**1**) (Scheme 2). Over a period of hours, milligram quantities of the hydride form under 1 atm of hydrogen. However, gram quantities of **1** are best obtained by high pressure (1000 psi H_2) synthesis in an autoclave [22]. Noteworthy is the fact that the solubility of **1** in pentane is poor. Consequently, the product precipitates as a crystalline solid. Carrying out the procedure in solvents such as thf, benzene, or toluene yields other, uncharacterized, products. Similarly, reaction times greater than 12 h lead to marked decreases in yield.

The NMR spectroscopic signatures of **1** are interesting and informative. In the ^{171}Yb -NMR spectrum, Fig. 1(a), the presence of a triplet at $\delta = 772$ ($^1J_{\text{Yb,H}} = 368$ Hz) indicates that each Yb is coupled to two equivalent hydrido ligands. The ^{171}Yb -NMR signal collapses to a singlet upon ^1H decoupling, Fig. 1(b). Correspondingly, the hydride resonance at $\delta = 10.5$ in the ^1H -NMR spectrum exhibits ^{171}Yb satellites with the appropriate coupling constant ($^1J_{\text{Yb,H}} = 368$ Hz). The five peaks are in the 0.5:12.2:74.5:12.2:0.5 integration ratios, the result of a superposition of a 2.0% triplet, 24.5% doublet and a 73.4% singlet, Fig. 1(c). This is the expected result

given the 14.3% natural abundance of $I = 1/2$ ^{171}Yb and the presence of two equivalent Yb centers in the molecule. In other words the NMR data indicate a dimeric structure for **1**, $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})_2]$.

The deuterium analog of **1**, $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-D})_2]$, **1D**, exhibits a ^2H signal at $\delta = 10.5$, confirming the ^1H -NMR hydride assignment. The $^1J_{\text{Yb,D}}$ coupling of 56.8 Hz is consistent with the expected decrease for the change in nuclear gyromagnetic ratio.

Single crystal X-ray diffraction corroborated the dimeric structure for **1**. It is remarkable that a single $\text{Tp}^{t\text{-Bu,Me}}$ ligand per Yb(II) center is sufficient to allow the isolation of dimeric, solvent-free **1**. In contrast, complexes such as $[\{(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-H})\}_2]$ and related Ln(III) hydrido complexes require two bulky C_5Me_5 ligands. As the space-filling model of **1**, Fig. 2, depicts, substantial steric crowding by the pyrazolyl *tert*-butyl groups protects the cavity in which the hydrides lie. This further demonstrates the ability of the bulky $\text{Tp}^{t\text{-Bu,Me}}$ ligand to stabilize low coordinate, low valent lanthanide complexes. The steric protection afforded **1** may have suggested limited reactivity. Satisfyingly, quite the contrary is true.

4. Reactions with Lewis bases and Lewis acids

To date, a limited number of investigations have been made to this end. Solutions of **1** in benzene are stable for hours; although, substantial decomposition occurs within 2 days. In fact, **1D** undergoes H/D exchange in benzene when stirred under an atmosphere of H_2 at room temperature to give **1** [22]. While **1** is detected by ^1H -NMR spectroscopy within minutes of exposure of **1D** to H_2 , 12 h is required for 50% conversion. Qualitatively, H/D exchange is more facile than solvent metalation, the probable mechanism of the slow decomposition of **1** in benzene. Interestingly, addition of tetrahydrofuran (thf) (up to 40 equivalents/Yb) to a benzene solution of **1** has no effect. The ^1H -NMR spectrum exhibits no significant shift in the hydride or pyrazolyl borate resonances indicating the absence of thf coordination. In contrast, dissolution of **1** in thf results in rapid ligand redistribution to give $\text{Yb}(\text{Tp}^{t\text{-Bu,Me}})_2$ and presumably $[\{\text{YbH}_2(\text{thf})\}_n]$.

In an effort to abstract the hydride from **1**, the compound was treated with one equivalent of the

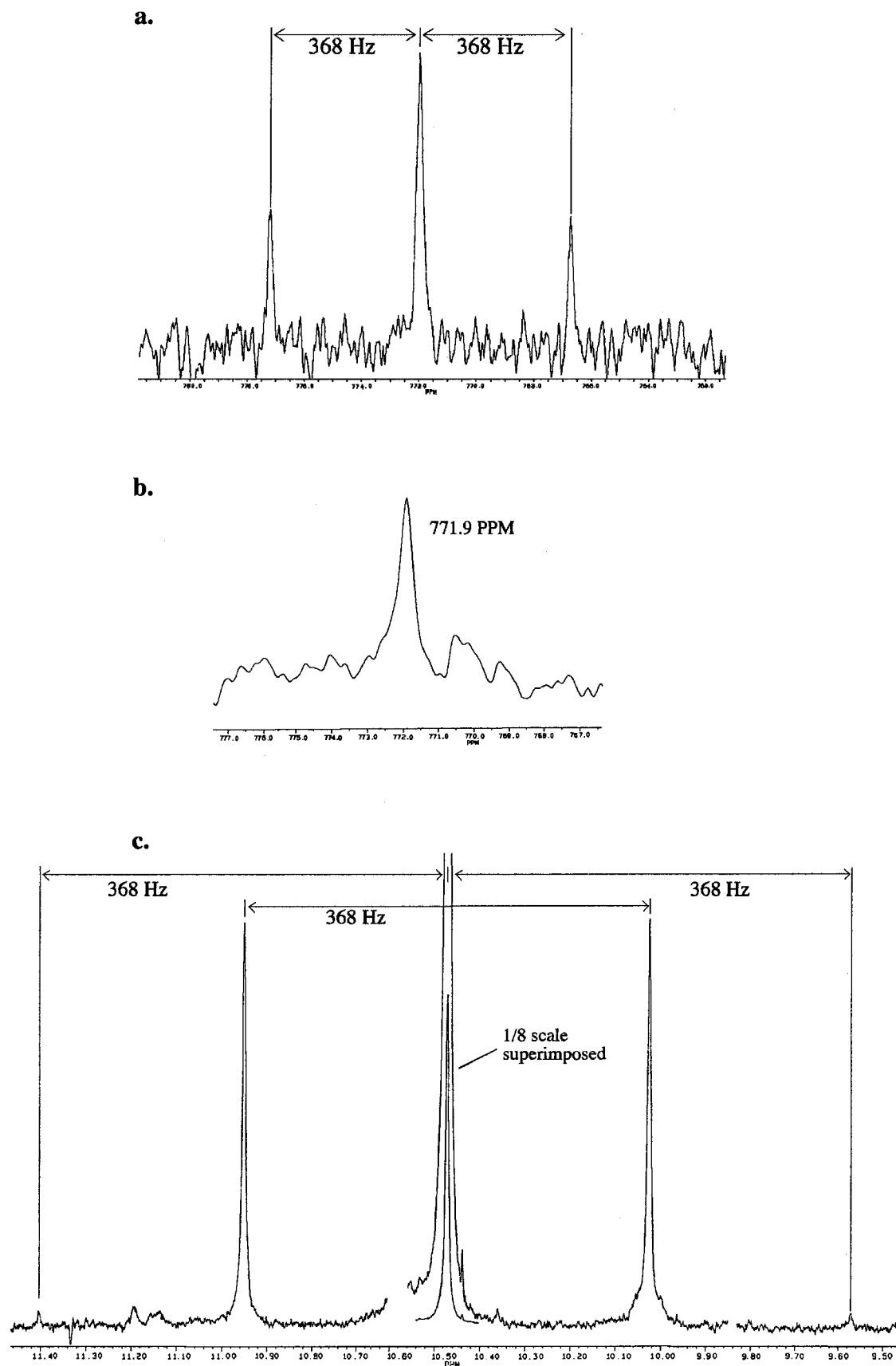


Fig. 1. (a) ^{171}Yb -NMR of $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})_2]$ (**1**). (b) $^{171}\text{Yb}\{^1\text{H}\}$ -NMR of **1**. (c) Blow up of the Yb-H hydride signal of **1**.

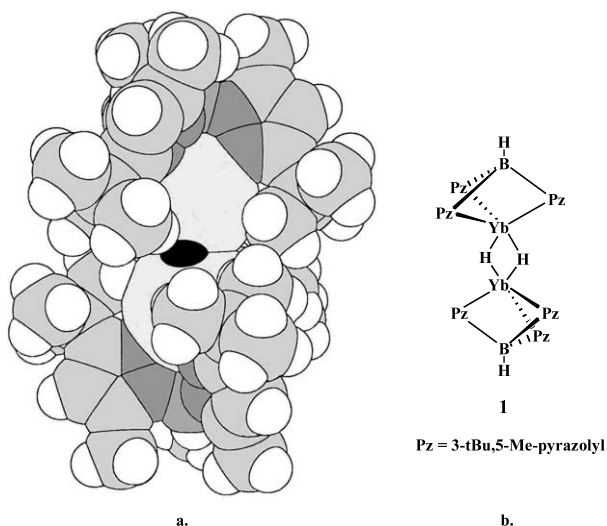
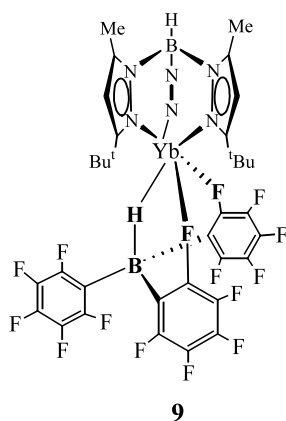


Fig. 2. (a) Space filling view of $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})]_2$ (**1**) molecule structure. \blacksquare , Yb; \blacksquare , hydride H; \blacksquare , C; \blacksquare , B; \blacksquare , N. Note the second bridging hydride is not depicted as it is located at the back. All other hydrogen atoms are unshaded. (b) Cartoon accentuating core structure of **1**.

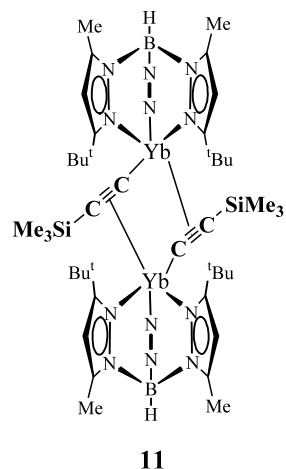
strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. Instead of hydride abstraction, cleavage of **1** and coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to Yb–H yielding $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ (**9**) was observed. Single crystal X-ray crystallography confirms this assignment and indicates the presence of two Yb–F interactions [23]. Similarly $\text{HB}(\text{C}_6\text{F}_5)_2$ coordinates to the Yb–hydride to yield $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\text{H})_2\text{B}(\text{C}_6\text{F}_5)_2$ (**10**). While confident of the composition, the exact bonding mode remains to be determined [23]. We anticipate two bridging Yb–H–B functions along with one Yb–F interaction. Bonding features similar to **9** have been established by Evans in reaction of $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ with $\text{B}(\text{C}_6\text{F}_5)_3$ [24].



5. σ -bond metathesis reactions

Akin to the established Ln(III) hydride reactivity, $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})]_2$ (**1**) rapidly undergoes σ -bond

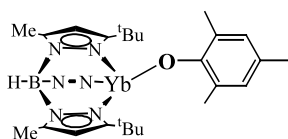
metathesis reactions with protic substrates, H–L, quantitatively yielding $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}\text{-L}$ derivatives and H_2 . Reactions of **1** with $\text{HN}(\text{SiMe}_3)_2$ and with terminal alkynes $\text{HC}\equiv\text{CR}$ afford the previously fully characterized complexes $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\text{N}\{\text{SiMe}_3\}_2)$ (**7**) [10] and $[(\text{Tp}^{t\text{-Bu,Me}})\text{YbC}\equiv\text{CR}]_2$ (**11**) [25], respectively. The alkynide complex is far from static in solution as illustrated by the 1:1 comproportionation of benzene solutions of $[(\text{Tp}^{t\text{-Bu,Me}})\text{YbC}\equiv\text{CSiMe}_3]_2$ (**11a**) and $[(\text{Tp}^{t\text{-Bu,Me}})\text{YbC}\equiv\text{C}(\text{tert-C}_4\text{H}_9)]_2$ (**11b**) to yield a 1:2:1 statistical mixture of **11a**, $[(\text{Tp}^{t\text{-Bu,Me}})_2\text{Yb}_2\text{-}(\text{C}\equiv\text{CSiMe}_3)(\text{C}\equiv\text{C}^t\text{-Bu})]$ (**11c**) and **11b**.



With the solvent free precursor, **1**, at hand, a simple entry into the preparation of coordinatively unsaturated ytterbium complexes is possible. Isolation of the yellow–orange lanthanide aryloxide complex $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\text{OMes})(\text{thf})$ (**5**) from $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\text{I})(\text{thf})$ involves reaction in thf at -45°C (Scheme 1). Reaction of **1**, on the other hand, with HOMes in benzene at ambient temperature afforded the monomeric solvent free lanthanide aryloxide complex $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\text{OMes})$ (**12**) as an orange solid [14]. The monomeric nature of **12** was corroborated by X-ray crystallography and is in contrast to the dimeric structure observed for the related divalent samarium complex, $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{OAr})]_2$ [26]. The large cone angle of $\text{Tp}^{t\text{-Bu,Me}}$, 184° , as compared to the C_5Me_5 ligand, 146° , preserves the monomeric structure. The most striking feature in a comparison between **5** and **12** is that the solvent free aryloxide complex appears structurally very similar to **5**, only with a vacant coordination site. Instead of adopting a tetrahedral coordination environment or undergoing dimerization, $(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\text{OMes})$ prefers to maintain a geometry analogous to the solvated **5** through formation of two agostic interactions with *tert*-Bu protons. Dissolution of **12** in tetrahydrofuran at ambient temperature resulted in clean transformation to the solvated complex **5**. The coordinated thf ligand in **5** is persistent even in non-etheral solvents [12].

Table 1
Colors of $(\text{Tp}^{t\text{-Bu,Me}}\text{YbL}(\text{sol})_n)$ complexes

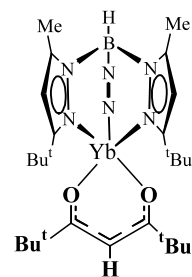
L	Sol _{1,0}	Complex	Color
H	–	1	Red
I	thf	2	Yellow
CH ₂ SiMe ₃	Et ₂ O	4	Orange
OMes	thf	5	Yellow/orange
HBEt ₃	thf	6	Orange
N(SiMe ₃) ₂	–	7	Orange
CH(SiMe ₃) ₂	–	8	Orange
HB(C ₆ F ₅) ₃	–	9	Pale yellow
H ₂ B(C ₆ F ₅) ₂	–	10	Pale yellow
C≡CSiMe ₃	–	11	Orange
OMes	–	12	Orange
dpm	–	13	Dark green
Cp/Cp ^{TMS}	–	14	Orange–red
η ³ -propargyl	–	15	Purple–red
cis-alkenyl	–	16	Red–orange
OCH(C ₆ H ₅) ₂	–	17	Orange–red
OCH=	–	18	Yellow



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Room temperature reaction of $[(\text{Tp}^{t\text{-Bu,Me}}\text{YbH})_2]$ with two equivalents of dipivaloylmethane in benzene yielded the Yb(II) β-diketonate, $(\text{Tp}^{t\text{-Bu,Me}}\text{Yb}(\text{dpm}))$ (**13**), as a dark green solid in quantitative yield [14]. Complex **13** is very soluble in a range of solvents including aliphatic (hexane), aromatic (benzene) and ethereal (thf) as well as methylenechloride, yet it does

not appear to react with any of these solvents and the dark green color persists. The $^{171}\text{Yb}\{^1\text{H}\}$ -NMR resonance was observed as a singlet with an unusually large chemical shift of 1046 ppm. Observation of the various NMR nuclei at their usual positions confirms divalent ytterbium has been preserved, a particularly important point in light of the unusual green color of complex **13**. The vast majority of Yb(II) complexes, including all $(\text{Tp}^{t\text{-Bu,Me}}\text{YbL})_n$ compounds reported to date, have colors ranging from red to yellow (Table 1). Single crystal X-ray diffraction analysis confirmed the assignment of β-diketonate complex as $(\text{Tp}^{t\text{-Bu,Me}}\text{Yb}(\text{dpm}))$.



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$[(\text{Tp}^{t\text{-Bu,Me}}\text{YbH})_2]$ reacts with cyclopentadiene and trimethylsilylcyclopentadiene yielding the corresponding complexes, of $(\text{Tp}^{t\text{-Bu,Me}}\text{Yb}(\text{C}_5\text{H}_5\text{R}))$ (R = H, **14a**; SiMe₃, **14b**) [27]. The X-ray structure of the red–orange **14b** identified the molecular structure as containing an η⁵-C₅H₄SiMe₃ complimented by a distorted Tp^{t-Bu,Me} ligand with a side-on bound η²-pyrazolyl ring; see ORTEP (Fig. 3(a)) and corresponding cartoon (Fig. 3(b)). It is instructive to compare the molecular structure of **14b** with other Yb(II) complexes containing the

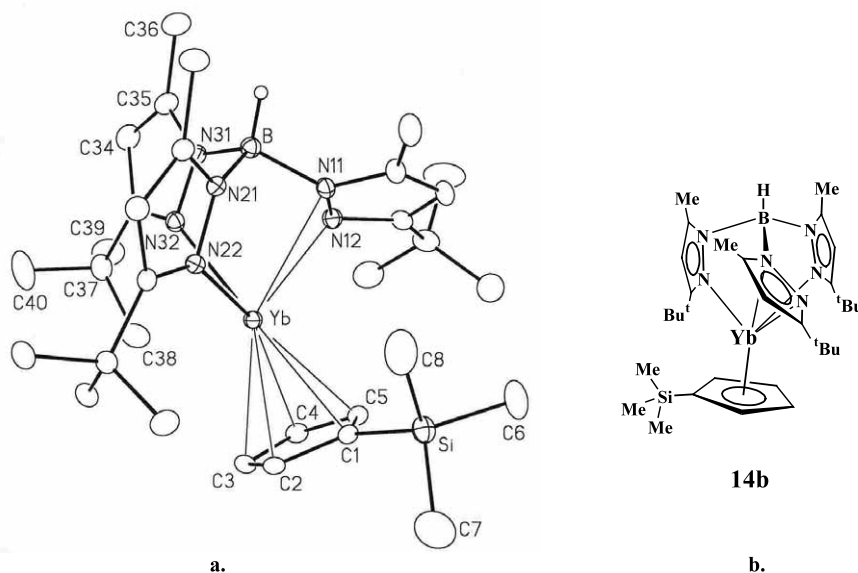
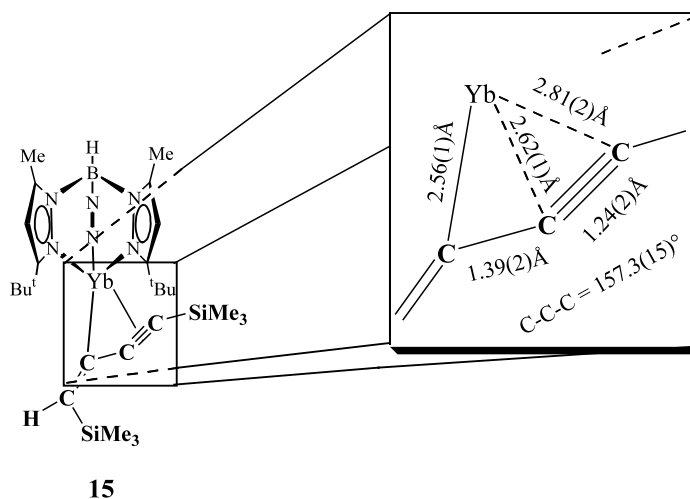


Fig. 3. (a) Perspective view of $(\text{Tp}^{t\text{-Bu,Me}}\text{Yb}\{\text{C}_5\text{H}_4(\text{SiMe}_3)\})$ (**14b**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level; hydrogen atom attached to boron is shown with an arbitrarily small thermal parameter, all other hydrogen atoms are not depicted. (b) Cartoon accentuating η²-pyrazolyl bonding mode in **14b**.



Scheme 3.

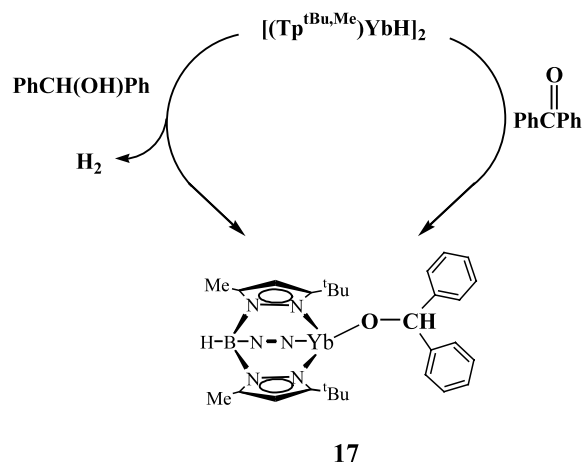
$\text{Tp}^{t\text{-Bu,Me}}$ ligand. In the series of $(\text{Tp}^{t\text{-Bu,Me}}\text{YbER}(\text{sol}))_n$ complexes, **1**, **2**, **4–9** and **11–13**, the $\text{Tp}^{t\text{-Bu,Me}}$ ligand adopts its usual tridentate bonding mode and coordinates to Yb by the lone pairs of the pyrazolyl rings' 2-N donor atoms [10,11,22,23,25,27]. In the present case, distortion of the $\text{Tp}^{t\text{-Bu,Me}}$ ligand from the symmetric η^3 -bonding is due to the strong steric repulsion between the $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ group and the pyrazolyl ligand, exacerbated in the present case by the presence of the *tert*-Bu substituent at the 3-position [27].

6. Insertion reactions

Complex **1** readily undergoes insertion of unsaturated functional groups. Analogous to $[(\text{C}_5\text{H}_4\text{R})_2\text{YH}(\text{thf})_2]$ [28], **1** forms the *cis*-alkenyl unit upon addition to diphenylacetylene [25]. But, in marked contrast, **1** cleaves the Si–C bond of bis(trimethylsilyl)acetylene [22] rather than insert the C=C bond. This stoichiometric reaction proceeds nearly quantitatively, yielding $[(\text{Tp}^{t\text{-Bu,Me}}\text{YbC}\equiv\text{CSiMe}_3)_2]$, **11a** and HSiMe_3 . Only rarely has lanthanide mediated Si–C bond cleavage been observed [29–32]. Indeed, with **1**, metathesis of the Si–C σ -bond appears to be limited to $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$. Already the diyne, bis(trimethylsilyl)diacetylene, undergoes the usual C=C insertion. Addition of a stoichiometric amount of $\text{Me}_3\text{SiC}\equiv\text{C}\equiv\text{CSiMe}_3$ to $[(\text{Tp}^{t\text{-Bu,Me}}\text{YbH})_2]$ gave the red–purple η^3 -propargyl containing complex $[(\text{Tp}^{t\text{-Bu,Me}}\text{Yb}\{\eta^3\text{-(Me}_3\text{Si)CCC=CH(SiMe}_3)\})]$ (**15**) in high yield and establishes that η^3 -propargyl bonding is viable for the lanthanides (Scheme 3) [22]. This monomeric complex is the result of addition of the hydrido group to the terminal carbon atom of one of the C–C triple bonds accompanied by coordination of the remaining C–C

triple bond. The Yb(II)-cumulene bonding in **15** is best compared with that in the d^0 transition metal complex $[(\text{C}_5\text{H}_5)_2\text{Zr}(\text{Me})(\eta^3\text{-CH}_2\text{CCPh})]$ [33]; however, structural characteristic of **15** supports a greater contribution from the η^3 -propargyl resonance form as opposed to the alternative η^3 -allenyl form in the Zr complex. The distended M–C and M–CR bond distance in **15** compared to the Zr complex are attributed to the larger size of the Yb(II) metal center and the weaker interaction between the Yb^{2+} and the η^3 -propargyl ligand.

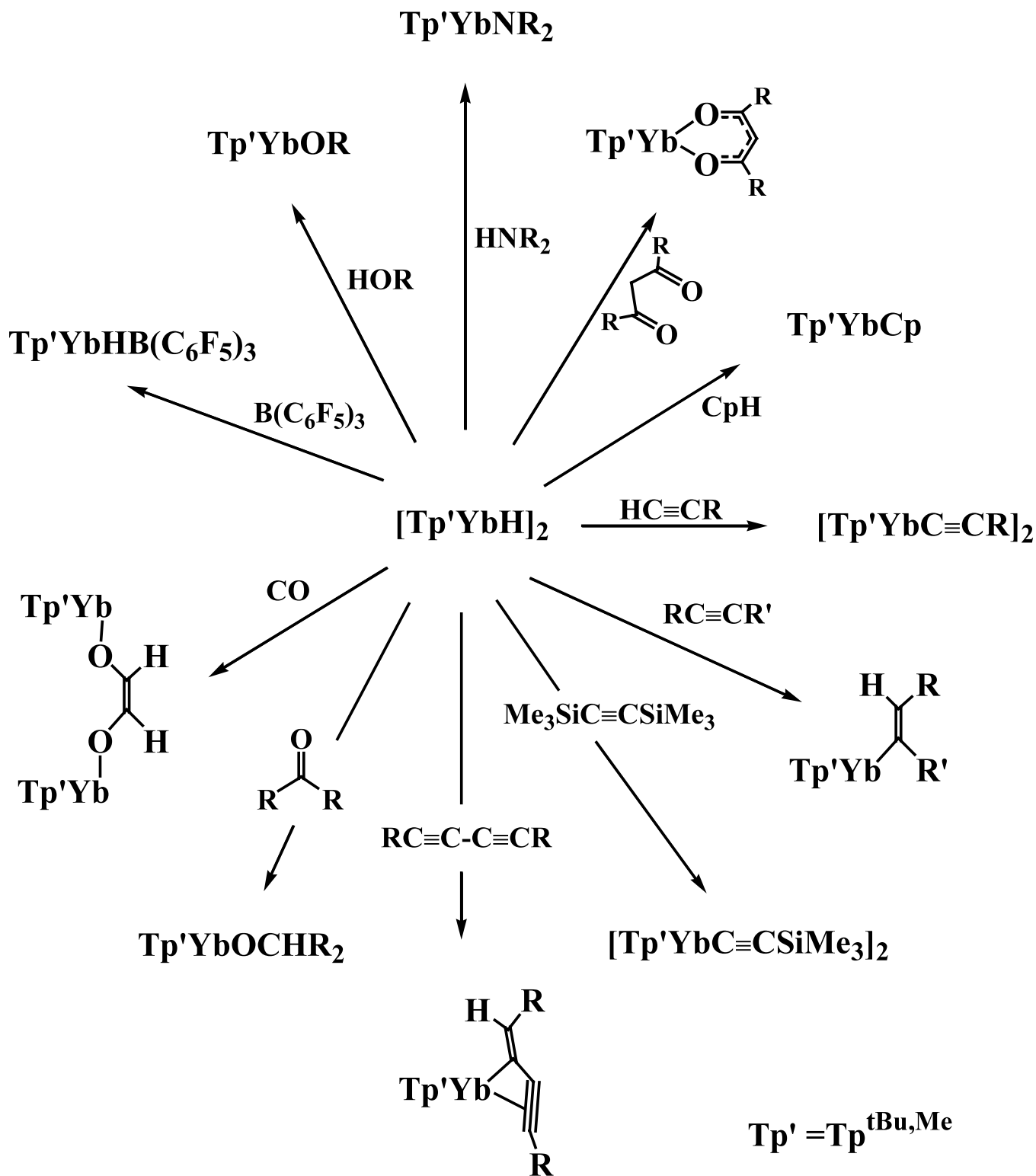
Several other substrates have been examined for reactivity with **1**. With the exception of the aforementioned bis(trimethylsilyl)acetylene, internal alkynes undergo insertion to apparently yield the *cis*-alkenyl species as illustrated by the formation of $[(\text{Tp}^{t\text{-Bu,Me}}\text{YbC}(\text{Ph})=\text{CHPh})]$ (**16**) from the reaction of **1** with diphenylacetylene. Perhaps not surprisingly, in view of the weaker Lewis acidity of Yb(II) compared to Ln(III) ions, reaction of **1** with ethylene is sluggish. Ketones

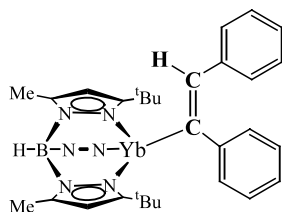


Scheme 4.

react with $[(\text{Tp}'^{\text{tBu,Me}}\text{YbH})_2]$ by inserting into the Yb–H bond to yield the corresponding Yb-alkoxide. For example, reaction between benzophenone and **1** produces $(\text{Tp}'^{\text{tBu,Me}}\text{YbOCH}(\text{C}_6\text{H}_5)_2)$ (**17**). The identity of **17** has

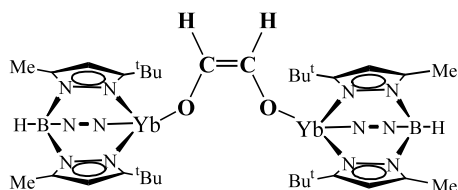
been spectroscopically confirmed by comparison to the identical product produced from the σ -bond metathesis between **1** and $\text{HOCH}(\text{C}_6\text{H}_5)_2$ (Scheme 4) [25].





16

Particularly noteworthy is that reductive coupling of CO readily occurs with **1**. Exposure of a suspension of $[(\text{Tp}^{t\text{-Bu,Me}})\text{YbH}]_2$ in pentane to a CO atmosphere leads to a color change from red to yellow–orange with formation of a compound formulated as $(\text{Tp}^{t\text{-Bu,Me}})\text{YbOCH}=\text{CHOYb}(\text{Tp}^{t\text{-Bu,Me}})$ (**18**). Coupling constant data obtained from NMR analysis of the ^{13}C analog, $(\text{Tp}^{t\text{-Bu,Me}})\text{YbO}^{13}\text{CH}=\text{CHOYb}(\text{Tp}^{t\text{-Bu,Me}})$ established **18** as containing the *cis*-ene-diolate moiety, consistent with the Zr complex *cis*- $[(\text{tert-Bu}_3\text{SiHN})_3\text{-ZrOCH}=\text{CHOZr}(\text{NHSitert-Bu}_3)_3]$ [34]. The only precedent for such lanthanide mediated CO coupling reaction is the report by Evans et al. [35]. The reaction of $\{(\text{C}_5\text{Me}_5)_2\text{SmH}\}_2$ with CO also resulted in formation of *cis*-ene-diolate.



18

7. Conclusions

The divalent lanthanide hydride, $[(\text{Tp}^{t\text{-Bu,Me}})\text{Yb}(\mu\text{-H})_2]$, is proving to be a versatile precursor to a wide range of divalent ytterbium complexes (Scheme 5). The presence of the bulky $\text{Tp}^{t\text{-Bu,Me}}$ ligand is an essential prerequisite. It provides the necessary steric protection to produce low coordination and facilitates the formation of isolable, clean and high yield products.

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