nonbonding electron pair. The calculation of the partial charges according Mullikan at the MP2 level for the central nitrogen atom gives the value of −0.36, in spite of the total change +1 of the $OCNCO^+$ ion. According to the analysis of the natural bond orbitals this is a result of the existence of two nonbonding electron pairs at nitrogen with an occupation of 1.6 and 1.5 e^-; the former has 23% s character and is responsible for the bending.

Finally it should be noted that the isoelectronic N_5^+ ion has recently been prepared in the form of the highly explosive $N_5^+AsF_6^-$, which is also strongly bent at the central nitrogen atom.[7]

Experimental Section

F−CO−NCO was prepared in 70% yield from Cl−CO−NCO by halogen exchange with an excess of $SF_3/SbCl_5$ at 75 °C. The product must be removed immediately from the reaction vessel in order to avoid decomposition into COF_2 and $OC(NCO)_2$. The latter polymerizes under these conditions. Further physical data see ref. [5].

$OCNCO^+Sb_3F_{16}^-$: By using a glass vacuum line under liquid nitrogen cooling, F−CO−NCO (60 mg, 0.67 mol), SbF_5 (600 mg, 7.76 mmol), and $CF_3{-}CH_2{-}CF_3$ (2–3 mL) were condensed into an 8 mL glass ampule, which was then sealed. At room temperature colorless crystals appeared which largely dissolved after brief heating to 60 °C, and the undissolved part melted. Slow cooling to 10 °C gave colorless needles, which decompose slowly at room temperature, and turn brown. Raman (Spex Industries 1403, 1064 nm excitation light, 300 mW, solid −90 °C): 2359(20), 2320(5), 1512(1), 1126(1), 1076(1), 914(40), 697(100), 674(60), 656(80), 610(15), 588(8), 560(1), 514(3), 350(5), 323(2), 298(30), 288(20), 271(5), 271(5), 232(10), 217(12), 190(30), 146(10), 130(5) cm^{-1}; ^{13}C NMR ($CF_3CH_2CF_3$): $\delta = 122.4$. Crystal structure analysis: A suitable crystal was adjusted under nitrogen and cooling on an Enraf Nonius CAD4 diffractometer (MoK_α, graphite monochromator). Lattice constants were obtained by fine adjustment of 25 reflections with $20° < \theta < 25°$. Intensities were measured with the ω scan method allowing a maximum of 60 s per reflection, of which 25% were used for the background measurement, psi scan absorption correction. Solution and refinement of the structure was done with the shelx programs.[8] $a = 954.8(1)$, $b = 735.8(1)$, $c = 2093.2(3)$ pm, $\beta = 94.65(1)°$, $V = 1465 \times 10^6$ pm^3, $P2_1/c$, 4688 measured, 4264 independent reflections, 218 parameters, $R_1 = 0.021$, $Rw^2 = 0.055$.

$OCN{-}FCO \cdot SbF_5$: The preparation was similar to that for $OCNCO^+Sb_3F_{16}^-$, only a 1:1 stoichiometry of F−CO−NCO and SbF_5 in the solvent $CF_3CH_2CF_3$ or $(CF_2Cl)_2$ was used. Colorless needles were obtained upon cooling to −40 °C which melt at 5–18 °C to give a viscous liquid. Raman (solid, −90 °C): 2271(5), 1662(10), 1509(1), 1490(2), 1273(5), 950(15), 754(2), 708(15), 679(45), 649(100), 594(20), 527(25), 299(15), 284(5), 265(5), 234(8), 196(4), 163(4), 125(70), 114(30) cm^{-1}. Crystal structure analysis: $a = 875.36(8)$, $b = 543.21(5)$, $c = 1503.1(1)$ pm, $\beta = 100.96(1)°$, $V = 701.7(1) \times 10^6$ pm^3, $P2_1/c$, 2125 measured, 1948 independent reflections, 110 parameters, $R_1 = 0.024$, $Rw^2 = 0.073$.

$OCNCO^+AsF_6^-$: Reaction of F−CO−NCO and AsF_5 in the stoichiometry 1:1 in $(CF_2Cl)_2$, as described above, crystallization, as described above, crystallization at −40 °C, colorless cubes that melt under gas evolution above O °C. Raman spectrum: 2366(10), 2287(1), 930(20), 915(15), 701(10), 685(100), 632(5), 613(2), 586(8), 573(4 =), 559(3), 518(4), 372(40), 205(50), 192(30), 124(80) cm^{-1}. Crystal structure analysis: $a = 1096.0(2)$, $b = 1118.3(3)$, $c = 1118.3(3)$ pm, $V = 1449.5 \times 1O^6$ pm^3, probably *Pnma*, pseudo-etragonal twinned with −1 0 0, 0 0 1, 0 1 0.

$OCNCO^+As_2F_{11}^-$: Reaction of F−CO−NCO and AsF_5 in 1:3 stoichiometry in $CF_3CH_2CF_3$, as described above, colorless platelets that melt above O °C under gas evolution, crystallization at −70 °C. Crystal structure analysis: $a = 566.5(2)$, $b = 1173.3(4)$, $c = 1612.9(7)$ pm, $\alpha = 110.60(3)$, $\beta = 90.74(3)$, $\gamma = 89.96(3)°$, $V = 1003.4 \times 10^6$ pm^3, $P\bar{1}$, pseudo-monoclinic twinned.

$OCN{-}FCO \cdot AsF_5$: Reaction of F−CO−NCO and AsF_5 in 1:1 stoichiometry in $CF_3{-}CH_2{-}CF_3$, as described above, colorless needles after cooling to −70 °C. Crystal structure analysis: $a = 855.2(1)$, $b = 525.42(6)$, $c = 1481.5(1)$, $\beta = 100.26(1)°$, $V = 655.1(1) \times 10^6$ pm^3, $P2_1/c$, 3296 measured, 2872 independent reflections, 110 parameters, $R_1 = 0.027$, $R_w{}^2 = 0.076$.

Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410736, CSD-410737, and CSD-410738.

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[1] P. Pyykkö, N. Runeberg, *J. Mol. Struct. (Theochem.)* **1991**, *234*, 279–290.

[2] D. Sülzle, P. E. L'Bannon, H. Schwarz, *Chem. Ber.* **1992**, *125*, 279–283.

[3] S. S. Yong, G. Chen, S. Ma, R. G. Cooks, F. C. Gozzo, M. N. Eberlin, *J. Mass. Spectr.* **1995**, *30*, 807–816.

[4] H. Hagemann, *Angew. Chem.* **1977**, *89*, 789–796; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 743.

[5] O. Glemser, U. Biermann, M. Fild, *Chem. Ber.* **1967**, *100*, 1082–1087.

[6] Gaussian 94, Revision E.2: M. J. Risch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Peterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, N. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Brinkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, USA, **1995**.

[7] K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112–2118; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004–2010.

[8] G. M. Sheldrick, Program for crystal structure solution, Universität Göttingen, **1986**; Program for crystal structure refinement, Universität Göttingen, **1997**.

Stabilization of a Discrete Lanthanide(II) Hydrido Complex by a Bulky Hydrotris(pyrazolyl)borate Ligand[**]

Gregory M. Ferrence, Robert McDonald, and Josef Takats[*]

Organo f-element chemistry has witnessed spectacular growth in the past twenty years and, parallel with this development, hydrido complexes were synthesized for most of the lanthanides.[1] However, in spite of the importance of such species in various catalytic processes, often with activities

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[*] Prof. Dr. J. Takats, Dr. G. M. Ferrence, Dr. R. McDonald[+]
Department of Chemistry
University of Alberta
Edmonton, Alberta, T6G 2G2 (Canada)
Fax: (+1) 780-492-8231
E-mail: joe.takats@ualberta.ca

[+] X-ray structure analysis.

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much higher than those of transition metal hydrides, most of these compounds are $\mathrm{Ln^{III}}$ derivatives and contain the cyclopentadienyl ligand or its substituted analogues. Divalent lanthanide hydrides are limited to the borohydride complexes $[\mathrm{Ln}\{(\mu\text{-H})_3\mathrm{BH}\}_2(\mathrm{CH_3CN})_n]$ (Ln = Yb, $n = 4$; Ln = Eu, $n = 2$),[2] the trialkylborane-stabilized hydrides $[\mathrm{Ln}(\mathrm{Tp}^{t\mathrm{Bu,Me}})(\mathrm{H\text{-}BEt_3})(\mathrm{thf})_n]$ (Ln = Sm, $n = 0$; Ln = Yb, $n = 1$),[3] the hydride-bridged $\mathrm{Yb^{II}}$–transition metal compounds $[\{(\mathrm{PMe_3})_3\mathrm{WH_5}\}_2\mathrm{YbL_3}]$ and $[\{(\mathrm{C_5H_5})_2\mathrm{NbH_2}\}_2\mathrm{YbL_3}]$ ($\mathrm{L_3} = (\mathrm{MeOCH_2CH_2})_2\mathrm{O}$),[4] $[\{\mathrm{YbH_2(thf)}\}_n]$[5] of unknown structure, and the not fully characterized $[(\mathrm{C_5Me_5})\mathrm{SmH(thf)_2}]$[6a] and $[\{\mathrm{Yb(C{\equiv}CC_4H_9)_{1.5}H_{0.5}}\}_n]$,[6b] which were obtained by cocondensation of samarium and ytterbium metal vapors with $\mathrm{C_5Me_5H}$ and 1-hexyne, respectively. To our knowledge, well-defined, discrete $\mathrm{Ln^{II}}$ complexes with hydrido ligands that are bound exclusively to the f-block element have not been previously reported.

Given the availability of lanthanide complexes with bulky $\mathrm{Tp}^{\mathrm{R,R'}}$ ligands ($\mathrm{Tp}^{\mathrm{R,R'}}$ = hydrotris(3-R-5-R′pyrazolyl)borate), specifically $\mathrm{Tp}^{t\mathrm{Bu,Me}}$,[3, 7] it was of interest to investigate how the steric bulk of $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ might be utilized to obtain a stable $\mathrm{Ln^{II}}$ hydride and how the structure and reactivity thereof would be affected. Here we report the synthesis and structure of a well-defined divalent ytterbium hydrido complex and preliminary reactivity studies.

Hydrogenolysis of lanthanide–hydrocarbyl bonds has emerged as the method of choice for the synthesis of lanthanide hydrides. It was first introduced to this area by Evans et al.[8] and has been widely exploited by others.[9] The complex $[(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Yb(CH_2SiMe_3)(thf)}]$ [3] appeared to be a convenient potential precursor for related $\mathrm{Yb^{II}}$ hydrido derivatives. Indeed, exposure of a solution of orange $[(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Yb(CH_2SiMe_3)(thf)}]$ in pentane to a hydrogen atmosphere resulted in precipitation of a red solid. Washing with pentane gave $[\{(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{YbH}\}_2]$ (**1**) as red crystals in 69% yield [Eq. (1)].

$$2[(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Yb(CH_2SiMe_3)(thf)}] + \mathrm{H_2} \xrightarrow[-\mathrm{THF},\ -\mathrm{SiMe_4}]{\text{pentane}} [\{(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Yb}(\mu\text{-H})\}_2] \quad \mathbf{1} \tag{1}$$

The formulation of the compound is based on elemental analysis and IR and multinuclear NMR spectroscopy. The ^{1}H NMR spectrum shows the presence of a $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand and the absence of the $\mathrm{CH_2SiMe_3}$ group and, remarkably, of THF. A signal at $\delta = 10.5$, which integrates as 1 H per $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand and exhibits ^{171}Yb satellites, was assigned to the hydrido ligand. The presence of a triplet at $\delta = 772$ ($^1J_{\mathrm{Yb,H}} = 369$ Hz) in the ^{171}Yb NMR spectrum indicates that each Yb is coupled to two equivalent hydrido ligands. The ^{171}Yb NMR signal collapses to a singlet on ^{1}H decoupling. Hence, the structure of **1** can be formulated as a dimer, namely, $[\{(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Yb}(\mu\text{-H})\}_2]$. The deuterium analogue of **1** $[(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Yb}(\mu\text{-D})]_2$ (**1D**) was prepared, and its ^{2}H NMR spectrum showed a signal at $\delta = 10.5$, which confirmed the assignment of the corresponding ^{1}H NMR signal. The deuterido complex exhibits ^{171}Yb coupling ($^1J_{\mathrm{Yb,D}} = 56.8$ Hz) that is consistent with the decrease in coupling constant expected for the change in nuclear gyromagnetic ratio.[10] Although these data left no doubt as to the elemental composition, they did not distinguish between dimeric or higher oligomeric structures. Therefore the structure of **1** was determined by single-crystal X-ray diffraction (Figure 1), which revealed the dimeric nature of the compound. The $\mathrm{Yb^{2+}}$ center is five-coordinate with one κ^3-$\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand and two bridging hydrido ligands. The molecule lies on a center of inversion, and the asymmetric unit contains two independent half-dimers. The average Yb–N bond length of 2.50(2) Å is typical for $(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{YbL_2}$ complexes. The bridging hydrido ligands were located, and their thermal parameters were refined isotropically and independent of each other. However, their positions were constrained to be symmetrically bridging and of equal distance in each independent molecule. The Yb–H distance thus obtained was 2.26(3) Å. This value is comparable to the average Y–H bond length of 2.16 Å in $[\{(\mathrm{CH_3C_5H_4})_2\mathrm{Y(thf)}(\mu\text{-H})\}_2]$,[8] after correcting for the difference in ionic radii, but somewhat shorter than the Yb–H distance of 2.32–2.33 Å in $[\{(\mathrm{C_5H_5})_2\mathrm{NbH_2}\}_2\mathrm{Yb}\{(\mathrm{MeOCH_2CH_2})_2\mathrm{O}\}]$.[4] The Yb ⋯ Yb′ distances of 3.659(1) and 3.641(1) Å in the two independent dimers of **1** are shorter than the metal–metal distances of the related $\mathrm{Ln^{III}}$ complexes[11] $[\{(\mathrm{CH_3C_5H_4})_2\mathrm{Ln(thf)}(\mu\text{-H})\}_2]$ (Ln = Y: 3.664(1) Å, Er: 3.616(5) Å),[8] $[\{(\mathrm{C_5H_3}t\mathrm{Bu_2})_2\mathrm{Sm}(\mu\text{-H})\}_2]$ (3.771(2) Å),[12] and $[\{(\mathrm{C_5Me_5})_2\mathrm{Sm}(\mu\text{-H})\}_2]$ (3.905(3) Å).[13] The large distance in the last-named complex probably reflects steric constraints imposed by the bulky $\mathrm{C_5Me_5}$ ligands. Although the metal–metal distance in **1** is somewhat short, direct Yb–Yb covalent bonding is unlikely, and the short separation reflects strong Yb-(μ-H)-Yb bonding.[14]

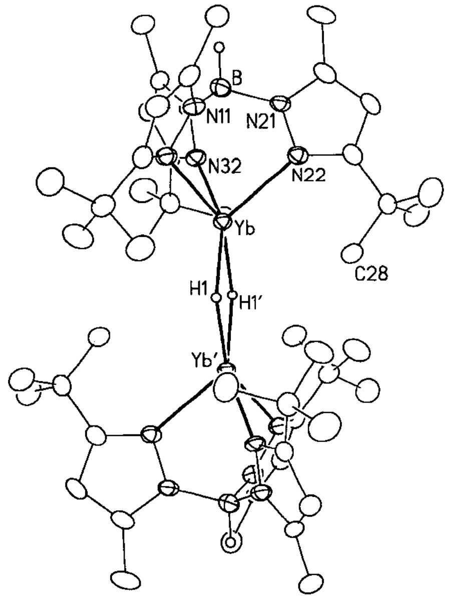
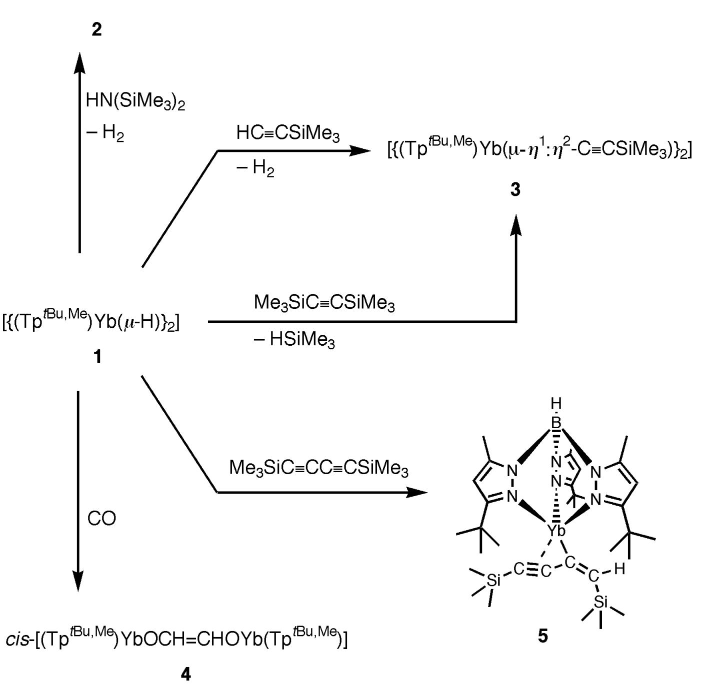


Figure 1. ORTEP plot of **1**. Primed atoms are related to unprimed atoms by a crystallographic inversion center. Only one of the two independent molecules is shown (see Experimental Section for details). Selected bond lengths [Å]: Yb–N (av) 2.50, Yb–Yb′ 3.6593(10), Yb–H 2.26(3).

It is remarkable that a single $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand per $\mathrm{Yb^{II}}$ center is sufficient to allow the isolation of dimeric, solvent-free **1**, whereas two $\mathrm{C_5Me_5}$ ligands are required for $\mathrm{Sm^{III}}$ and related dimeric $\mathrm{Ln^{III}}$ hydrido complexes. This demonstrates the ability of the bulky $\mathrm{Tp}^{t\mathrm{Bu,Me}}$ ligand to provide steric protection and stabilize reactive lanthanide complexes. The $Tp^{tBu,Me}$ ligands effectively encompass the metal and hydrido ligands. However, despite the apparent limitations caused by such steric shielding, preliminary reactivity studies indicate a rich chemistry of **1** (Scheme 1).



Scheme 1. Reactivity studies on **1**.

Complex **1** readily undergoes acid–base reactions with proton donors L–H with elimination of H_2 and formation of the corresponding [$(Tp^{tBu,Me})Yb{-}L$] derivatives. The reactions in benzene with $HN(SiMe_3)_2$ and with the terminal alkyne $HC{\equiv}CSiMe_3$ give the previously fully characterized complexes [$(Tp^{tBu,Me})YbN(SiMe_3)_2$] (**2**) and [$\{(Tp^{tBu,Me})YbC{\equiv}CSiMe_3\}_2$] (**3**) respectively.[3, 15] Analagous to trivalent rare earth hydrido complexes,[1] **1** undergoes insertion of unsaturated functional groups. For example, exposure of a suspension of **1** in pentane to a CO atmosphere leads to a color change of the solid from red to yellow-orange. The NMR spectroscopic data showed the product to be the ene–diolate **4**. Calculation of the coupling constants from the NMR data of the ^{13}C analogue of **4** [$(Tp^{tBu,Me})YbO^{13}CH{=}^{13}CHOYb(Tp^{tBu,Me})$] gave values in close agreement with those of *cis*-[$(tBu_3SiHN)_3ZrOCH{=}CHOZr(NHSitBu_3)_3$];[16a] hence, **4** was assigned as the *cis* isomer. The related [$\{(C_5Me_5)_2SmH\}_2$] was also reported to react with CO to form the *cis* ene–diolate.[16b] It is noteworthy that reductive coupling of CO also occurs readily with the Yb^{II} hydrido complex.

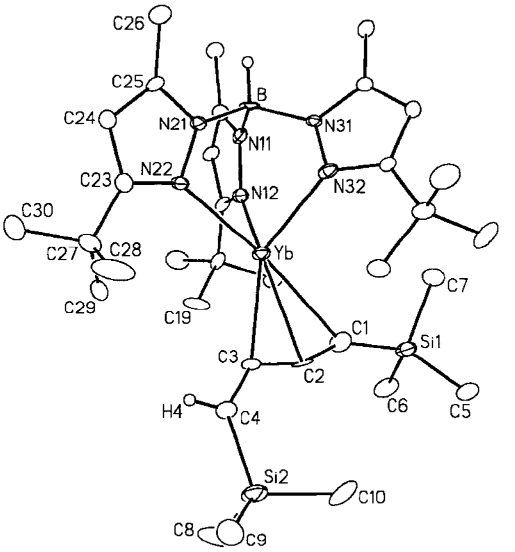


Figure 2. ORTEP plot of **5**. Selected bond lengths [Å] and angles [°]: Yb–N (av) 2.44, Yb–C1 2.81(2), Yb–C2 2.623(13), Yb–C3 2.556(14), C1–C2 1.24(2), C2–C3 1.39(2), C3–C4 1.31(2); Si1-C1-C2 150.9(14), C1-C2-C3 157.3(15).

The facile insertion reactions of **1** can be used to generate complexes whose structures were previously unprecedented in rare-earth chemistry. Thus, reaction with the diyne $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ gave the red-purple complex **5** in high yield. The absence of the hydride signal at $\delta = 10.5$ in the ^1H NMR spectrum indicated consumption of **1**. In addition to the characteristic $Tp^{tBu,Me}$ signal, a 1H signal at $\delta = 7.65$ and the presence of two $SiMe_3$ signals indicate an olefinic bond that arose from addition of Yb–H across one of the triple bonds. Since the data did not distinguish between addition of the hydride to the terminal or internal carbon atom, the structure of **5** was determined by single-crystal X-ray diffraction (Figure 2), which revealed a monomeric complex and addition of the hydrido group to the terminal carbon atom of one of the C–C triple bonds. The Yb^{2+} center is bonded to a κ^3-$Tp^{tBu,Me}$ ligand and to three carbon atoms (C1–C3) of the four-carbon cumulene unit. Since there is no interaction with C4, C3–C4 remains a free double bond (C–C 1.31(2) Å). The remaining C–C bond lengths (C2–C3 1.39(2) Å, C1–C2 1.24(2) Å) and the Yb–C distances are suggestive of an η^3-propargyl group, as shown in Scheme 1. Such a coordination mode is becoming more common in transition metal chemistry,[17] but lanthanide propargyl complexes are rare. There is NMR spectroscopic evidence for formation of [$(C_5Me_5)_2LnCH_2C{\equiv}CMe$] (Ln = La, Ce) in the catalytic dimerization of 2-butyne, and this is supported by the synthesis and characterization of [$(C_5Me_5)_2YCH_2C{\equiv}CMe$],[18] but its structure is not known. The Yb^{II}–cumulene bonding in **5** is best compared with that in the d^0 transition metal complex [$(C_5H_5)_2Zr(Me)(\eta^3\text{-}CH_2CCPh)$].[19] The $R_2C{-}C$ (1.39(2) Å) and $C{\equiv}C$ (1.24(2) Å) bond lengths and the $C{-}C{\equiv}C$ bond angle (157.3(15)°) of **5** are similar to those of the Zr complex (1.344(5) Å, 1.259(4) Å, and 155.4(3)°, respectively). The trend in C-C distances and the C2-C3-C4 bond angle (130.9(15)°), however, support a greater contribution from the η^3-propargyl resonance form in **5** as opposed to the alternative η^3-allenyl form in the Zr complex. Although the M–C and M–CR distances o^3-f **5** (2.62(1), 2.81(2) Å, respectively) are significantly longer than the corresponding distances in the Zr complex (2.438(4) and 2.361(3) Å, respectively), this is due to the larger size of Yb^{2+} and the weaker interaction between Yb^{2+} and the η^3-propargyl ligand. The structure of **5** provides the first indication that the η^3-propargyl bonding is also viable for the lanthanides.

It is noteworthy that the stoichiometric reaction of **1** in benzene with the silylalkyne $Me_3SiC{\equiv}CSiMe_3$ (1 equiv alkyne/Yb) did not proceed by insertion into the Yb–H bond, but led to C–Si cleavage to give **3** and $HSiMe_3$ in nearly quantitative yield. Since no cleavage was observed in the formation of **5**, we do not anticipate this C–Si metathesis to be general. We are, nonetheless, currently investigating other silane substrates and internal alkynes.

Other well-known properties of Ln^{III} hydrido complexes that were briefly examined for **1** include polymerization of alkenes[1] and metalation of aromatic solvents.[20] Perhaps not surprisingly, in view of the weaker Lewis acidity of Yb^{II} compared to Ln^{III} ions, reaction of **1** with ethylene produced polyethylene, but slowly; no polymerization of propene was observed. Solutions of **1** in benzene are stable for hours. Slow decomposition occurs over several days, but the products are as yet unidentified.[21] Similarly, addition of THF (up to 40 equiv/Yb) to a solution of **1** in benzene has no effect; however, dissolution of **1** in THF results in rapid decomposition to $[\{Yb(Tp^{tBu,Me})\}_2]$[22] and uncharacterized products.

In conclusion, the bulky $Tp^{tBu,Me}$ ligand allowed the isolation and structural characterization of the first discrete Ln^{II} hydrido complex, $[(Tp^{tBu,Me})Yb(\mu\text{-}H)]_2$, which shows interesting and varied reactivity.

Experimental Section

All manipulations were performed under an N_2 atmosphere by glove box or Schlenk techniques. The NMR spectra were recorded in $[D_6]$benzene at 25 °C; ^{171}Yb NMR shifts are referenced to $[Cp^*_2Yb(thf)_2]$ in THF at 298 K.[23]

1: $[(Tp^{tBu,Me})Yb(CH_2SiMe_3)(thf)]$ (5.75 g, 7.61 mmol) in pentane (ca. 30 mL) was charged into a glass-lined medium-pressure autoclave. The autoclave was pressurized with H_2 to 1200 psi for 8 h. After pressure release, the autoclave contents were filtered and rinsed with pentane (3 × 10 mL) to give **1** as red crystals (3.13 g, 68.8 %). Crystals suitable for X-ray structure analysis were selected from the product without further purification. IR (benzene-cast film): $\tilde{\nu} = 2511\ cm^{-1}$ (br, ν(BH)); $^1H\{^{11}B\}$ NMR (400 MHz): $\delta = 10.50$ (s, 2H, YbH, ^{171}Yb satellites, $J_{Yb,H} = 369$ Hz), 5.82 (s, 6H, 4-pz-H), 4.85 (s, 2H, BH), 2.19 (s, 18H, pz-CH_3), 1.58 (s, 54H, pz-$C(CH_3)_3$); $^{11}B\{^1H\}$ NMR (128 MHz): $\delta = -7.6$ (s, $\Delta\nu_{1/2} = 360$ Hz); ^{171}Yb NMR (70 MHz): $\delta = 772$ (t, $^1J_{Yb,H} = 369$ Hz); $^{171}Yb\{^1H\}$ NMR: $\delta = 772$ (s, $\Delta\nu_{1/2} = 28$ Hz); $^{13}C\{^1H\}$apt NMR (100 MHz): $\delta = 13.49$ (pz-CH_3), 31.77 (pz-$C(CH_3)_3$), 32.65 (pz-$C(CH_3)_3$), 103.25 (4-pz-C), 145.50 (5-pz-C), 164.24 (3-pz-C); elemental analysis calcd for $C_{48}H_{82}B_2N_{12}Yb_2$(%): C 48.25, H 6.92, N 14.07; found: C 48.18, H 7.12, N 14.06.

1D was prepared analogously to **1** under 700 psi D_2. IR (benzene-cast film): $\tilde{\nu} = 2545\ cm^{-1}$ (br, ν(BH)); ^1H NMR: $\delta = 5.81$ (s, 6H, 4-pz-H), 4.9 (s, 2H, BH), 2.19 (s, 18H, pz-CH_3), 1.57 (s, 54H, pz-$C(CH_3)_3$); ^2H NMR (61 MHz): $\delta = 10.5$ (s, YbD, ^{171}Yb satellites, $J_{Yb,D} = 56.8$ Hz).

4: A slurry of **1** (150 mg, 0.126 mmol) in pentane (3 mL) was frozen in liquid N_2, and the vessel was evacuated and backfilled with 10 psi CO. Upon warming to room temperature, the suspension changed from red-orange to yellow-orange over 15 min. After brief evacuation to remove excess CO, the flask and contents were transferred to a glove box. Addition of pentane (3 mL) followed by centrifugation and drying the isolated solid product in vacuo yielded **4** (68 mg, 43.3 %). $^1H\{^{11}B\}$ NMR (400 MHz): $\delta = 7.03$ (s, 2H, OCH), 5.77 (s, 6H, 4-pz-H), 4.78 (s, 2H, BH), 2.17 (s, 18H, pz-CH_3), 1.43 (s, 54H, pz-$C(CH_3)_3$); $^{11}B\{^1H\}$ NMR (128 MHz): $\delta = -7.0$ (s, $\Delta\nu_{1/2} = 360$ Hz); $^{171}Yb\{^1H\}$ NMR: $\delta = 482$ (s, $\Delta\nu_{1/2} = 19$ Hz); $^{13}C\{^1H\}$apt NMR (100 MHz): $\delta = 13.4$ (pz-CH_3), 31.0 (pz-$C(CH_3)_3$), 32.2 (pz-$C(CH_3)_3$), 103.4 (4-pz-C), 145.6 (5-pz-C), 163.8 (3-pz-C); elemental analysis calcd for $C_{50}H_{82}B_2N_{12}O_2Yb_2$(%): C 48.01, H 6.61, N 13.43; found: C 47.91, H 6.60, N 13.03. Substitution of ^{13}CO for CO yielded *cis*-$[(Tp^{tBu,Me})YbO^{13}CH{=}^{13}CHOYb(Tp^{tBu,Me})]$. ^1H NMR (400 MHz): $\delta = 6.6$–7.2 (6-line AA′XX′ pattern, 2H, $O^{13}CH$), 5.77 (s, 6H, 4-pz-H), 4.78 (s, 2H, BH), 2.17 (s, 18H, pz-CH_3), 1.49 (s, 54H, pz-$C(CH_3)_3$); $^{11}B\{^1H\}$ NMR (128 MHz): $\delta = -7.0$ (s, $\Delta\nu_{1/2} = 389$ Hz); $^{171}Yb\{^1H\}$ NMR (70 MHz): $\delta = 481$ (s, $\Delta\nu_{1/2} = 20$ Hz); $^{13}C\{^1H\}$apt NMR (100 MHz): $\delta = 133.2$ (6-line AA′XX′ pattern, OCH, $^1J_{C,H} = 177.4$, $^2J_{C,H} = 19.8$, $^1J_{C,C} = 64.1$, $^3J_{H,H} = 0.0$ Hz).

5: $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (65 mg, 0.334 mmol) was added to a solution of **1** (200 mg, 0.168 mmol) in benzene (5 mL). After about 15 min, the solution had become deep red-purple. The solvent was removed in vacuo to give **5** (211 mg, 79.6 %). Crystals of **5** suitable for X-ray structure analysis were grown by cooling a saturated benzene solution to about 5 °C. ^1H NMR (400 MHz): $\delta = 7.65$ (s, 1H, C=CH), 5.67 (s, 3H, 4-pz-H), 4.8 (br s, 1H, BH), 2.16 (s, 9H, pz-CH_3), 1.40 (s, 27H, pz-$C(CH_3)_3$), 0.46 (s, 9H, $Si(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$); $^{11}B\{^1H\}$ NMR (128 MHz): $\delta = -7.9$ (s, $\Delta\nu_{1/2} = 160$ Hz); $^{171}Yb\{^1H\}$ NMR (70 MHz): $\delta = -50$ (s, $\Delta\nu_{1/2} = 45$ Hz); $^{13}C\{^1H\}$apt NMR (100 MHz): $\delta = -0.40$ ($SiCH_3$), 0.86 ($SiCH_3$), 13.3 (pz-CH_3), 31.0 (pz-$C(CH_3)_3$), 32.4 (pz-$C(CH_3)_3$), 102.7 (4-pz-C), 145.8 (5-pz-C), 163.6 (3-pz-C), 152.5 ($R_2C{=}CHR$), 136.9, 154.5, 217.1 (propargyl C); elemental analysis calcd for $C_{34}H_{59}BN_6Si_2Yb$(%): C 51.57, H 7.51, N 10.61; found: C 51.17, H 7.27, N 10.12.

Crystal data for **1**: $C_{48}H_{82}B_2N_{12}Yb_2$, $M_r = 1194.96$, triclinic, space group $P\bar{1}$, $a = 12.454(2)$, $b = 12.659(2)$, $c = 21.021(3)$ Å, $\alpha = 90.015(9)$, $\beta = 103.632(10)$, $\gamma = 119.333(8)^\circ$, $V = 2781.6(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.427\ g\,cm^{-3}$, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $T = -60\,^\circ C$, $\mu(Cu_{K\alpha}) = 6.365\ mm^{-1}$, $R_1 = 0.0495$, $wR_2 = 0.1108$ for 5571 observed reflections from 7428 independent reflections; GOF 1.070.

Crystal data for **5**: $C_{34}H_{59}BN_6Si_2Yb$, $M_r = 791.90$, monoclinic, space group $P2_1/n$, $a = 12.1188(6)$, $b = 30.4075(15)$, $c = 12.3534(8)$ Å, $\beta = 115.251(4)^\circ$, $V = 4117.3(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.278\ g\,cm^{-3}$, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $T = -60\,^\circ C$, $\mu(Cu_{K\alpha}) = 4.966\ mm^{-1}$, $R_1 = 0.0723$, $wR_2 = 0.1455$ for 3220 observed reflections from 5527 independent reflections; GOF 1.022.

The Structures were solved by direct methods (SHELXS-86 for **1**, DIRDIF-96 for **5**) and refined by full-matrix least-squares on F^2 (SHELXL-93). Semiempirical and face-indexed Gaussian integration absorption corrections were applied to the data sets of **1** and **5**, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. The asymmetric unit of compound **1** consists of two crystallographically independent, but chemically identical, molecules. Comparison of geometrical data (bond lengths, bond angles, torsion angles) between the two molecules shows no significant differences (within experimental error). Each molecule lies on an independent inversion center; consequently, the solution is based on two independent half-molecules. The bridging hydrido ligands of **1** were located by comparison of residual between the two independent molecules. Their thermal parameters were refined isotropically and independently. The solution was constrained such that all Yb–H distances were equivalent. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112689 and -125990. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] a) M. Ephritikhine, *Chem. Rev.* **1997**, *97*, 2193–2242; b) F. T. Edelmann in *Comprehensive Organometallic Chemistry II*, *Vol. 4* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson, M. F. Lappert), Elsevier, Tarrytown, NY, **1995**, pp. 11–212; c) H. Schumann, J. A. Messe-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–985.

[2] J. P. White III, H. Deng, S. G. Shore, *Inorg. Chem.* **1991**, *30*, 2337–2342.

[3] L. Hasinoff, J. Takats, X. W. Zhang, A. H. Bond, R. D. Rogers, *J. Am. Chem. Soc.* **1994**, *116*, 8833–8834.

[4] M. L. H. Green, A. K. Hughes, D. M. Michaelidou, P. Mountford, *J. Chem. Soc. Chem. Commun.* **1993**, 591–593.

[5] M. N. Bochkarev, I. M. Penyagina, L. N. Zakharov, Y. F. Rad'kov, E. A. Fedorova, S. Y. Khorshev, Y. T. Struchkov, *J. Organomet. Chem.* **1989**, *378*, 363–373.

[6] a) W. J. Evans, I. Bloom, W. E. Hunter, J. L. Atwood, *Organometallics* **1985**, *4*, 112–119; b) W. J. Evans, S. L. Engerer, K. M. Coleson, *J. Am. Chem. Soc.* **1981**, *103*, 6672–6677.

[7] J. Takats, *J. Alloys Compd.* **1997**, *249*, 52–55.

[8] W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1982**, *104*, 2008–2014.

[9] a) G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103; b) H. Schumann, G. Jeske, *Z. Naturforsch. B* **1985**, *40*, 1490–1494; c) K. H. den Haan, Y. Wielstra, J. H. Teuben, *Organometallics* **1987**, *6*, 2053–2060; d) C. J. Schaverien, *Organometallics* **1994**, *13*, 69–82.

[10] R. M. Silverstein, G. C. Bassler, T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th ed., Wiley, New York, **1981**, p. 199.

[11] After allowing for the larger size of Yb^{2+} compared to other Ln^{3+} ions. Although the coordination number does not remain constant in the series, the size variation of the lanthanide ions can be confidently predicted as $Yb^{2+} > Sm^{3+} > Y^{3+} \geq Er^{3+}$; R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.

[12] Y. K. Gun'ko, B. M. Bulychev, G. L. Soloveichik, V. K. Belsky, *J. Organomet. Chem.* **1992**, *424*, 289–300.

[13] W. J. Evans, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403.

[14] Indeed, the ${}^1J_{\mathrm{Yb,H}}$ coupling constant of 369 Hz in **1** is substantially larger than those of $[(\mathrm{Tp}^{t\mathrm{Bu,Me}})\mathrm{Yb}(\mu\text{-}\mathrm{HBEt_3})(\mathrm{thf})]$ (200 Hz)[3] and $[\{(\mathrm{C_5H_5})_2\mathrm{NbH_2}\}_2\mathrm{Yb}\{(\mathrm{MeOCH_2CH_2})_2\mathrm{O}\}]$ (170 Hz).[4]

[15] G. M. Ferrence, unpublished results.

[16] a) C. C. Cummins, G. D. Van Duyne, C. P. Schaller, P. T. Wolczanski, *Organometallics* **1991**, *10*, 164–170; b) W. J. Evans, J. W. Grate, R. J. Doedens, *J. Am. Chem. Soc.* **1985**, *107*, 1671–1679.

[17] Reviews: a) A. Wojcicki, *New. J. Chem.* **1994**, *18*, 61–68; b) S. Doherty, J. F. Corrigan, A. J. Carty, E. Sappa in *Advances in Organometallic Chemistry, Vol. 37* (Eds.: F. G. A. Stone, R. West), Academic Press, New York, **1995**, pp. 39–130.

[18] H. J. Heeres, A. Heeres, J. H. Teuben, *Organometallics* **1990**, *9*, 1508–1510.

[19] P. W. Blosser, J. C. Gallucci, A. Wojcicki, *J. Am. Chem. Soc.* **1993**, *115*, 2994–2995.

[20] a) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203–219; b) M. Booij, B. J. Deelman, R. Duchateau, D. S. Postman, A. Meetsma, J. H. Teuben *Organometallics* **1993**, *12*, 3531; c) P. L. Watson, *J. Chem. Soc. Chem. Commun.* **1983**, 276–277; d) W. J. Evans, T. A. Ulibarri, J. W. Ziller, *Organometallics* **1991**, *10*, 134–142.

[21] The deuterido complex **1D** undergoes H/D exchange in benzene when stirred under an atmosphere of H_2 at room temperature to give **1**. 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 a solution of **1** in benzene.

[22] X. Zhang, R. McDonald, J. Takats, *New. J. Chem.* **1995**, *19*, 573–585.

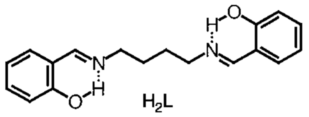
[23] A. G. Avent, M. A. Edelman, M. F. Lappert, G. A. Lawless, *J. Am. Chem. Soc.* **1989**, *111*, 3423–3425.

Self-Assembled Three-Dimensional Coordination Polymers with Unusual Ligand-Unsupported Ag–Ag Bonds: Syntheses, Structures, and Luminescent Properties[**]

Ming-Liang Tong, Xiao-Ming Chen,[*] Bao-Hui Ye, and Liang-Nian Ji

Self-assembled supramolecular architectures are currently of great interest due to their intriguing network topologies and their potential in microelectronics, nonlinear optics, porous materials, and other applications.[1–10] Since the self-assembly of these architectures is highly influenced by factors such as the solvent system,[11] templates,[12a,b] and counterion,[12c, 13] the exploration of synthetic routes is a long-term challenge.

Neutral monodentate phenol groups are notoriously poor donors for transition metal ions. To the best of our knowledge, no supramolecular coordination aggregate self-assembled by neutral bis-monodentate phenol groups has been documented, although a number of deprotonated dicatechol ligands have been successfully applied to self-assemble helicate-type coordination polymers.[14] We report here on the preparation, X-ray crystal structures, and luminescent properties of novel three-dimensional, noninterpenetrating networks in which bis-monodentate phenol groups of a Schiff base ligand serve as bridges, namely, $[Ag_2(H_2L)_3]_n(NO_3)_{2n}$ (**1**) and $[Ag_2(H_2L)_3]_n(ClO_4)_{2n}$ (**2**); H_2L = *N*,*N'*-bis(salicylidene)-1,4-diaminobutane.



H_2L

X-ray crystallography shows that **1** is made up of a three-dimensional, noninterpenetrating coordination network and nitrate ions (Figure 1). Each Ag^I atom is coordinated by three phenol groups from three H_2L ligands in an unusual, perfect trigonal arrangement (Ag–O 2.190(2) Å, O-Ag-O 119.62(2)°). Trigonal coordination arrangements have recent precedence in two Ag^I complexes with tricyanobenzene and tris(4-ethynylbenzonitrile)benzene ligands, in which the Ag^I atom is not in idealized trigonal geometry.[15] In **1** each pair of the adjacent, centrosymmetrically related Ag^I atoms are joined by a ligand-unsupported metal–metal bond (2.934(2) Å), the Ag–Ag bond lies on a crystallographic threefold axis, and all six H_2L ligands are symmetrically equivalent. The six phenol groups ligated to the pair of Ag^I atoms are in a staggered arrangement structurally similar to that of the hydrogen atoms in an ethane molecule (**I** in Scheme 1). Within the H_2L

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[*] Prof. Dr. X.-M. Chen, M.-L. Tong, Dr. B.-H. Ye, Prof. L.-N. Ji
School of Chemistry and Chemical Engineering
Zhongshan University
Guangzhou 510275 (China)
Fax: (+86) 20-8411-2245
E-mail: cedc03@zsu.edu.cn

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