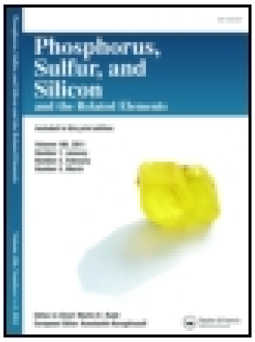

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An investigation of the binding of (*S*)-monothioBINOLate to rare earth metal cations

Grace B. Panetti, Elena J. Varela, Michael R. Gau, Eric J. Schelter, and Patrick J. Walsh

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA, United States

ABSTRACT

Two novel rare earth compounds have been synthesized using the previously reported (*S*)-MonoThioBINOL [(*S*)-H_2-MTB], (*S*)-2-hydroxy-2′-mercapto-1,1′-binaphthyl). We have shown here that while the H-bonded complex containing TMG-H^+ (tetramethyl guanidium cation) maintains the structure that the analogous BINOLate complex adopts, the complex with lithium cations in the secondary coordination sphere crystallizes as an '–ate' complex with an outer sphere lithium counter cation solvated by DME.

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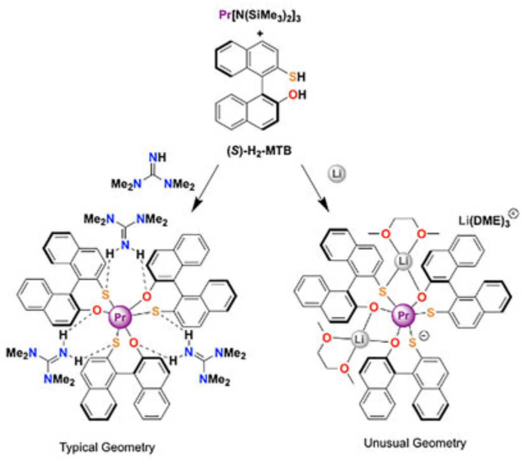
Rare earth; monothioBINOL; hydrogen bonding; anionic

GRAPHICAL ABSTRACT



Introduction

Asymmetric catalysis remains the most efficient method of producing optically active compounds from achiral or meso substrates.[1,2] Among known catalytic systems, chiral rare earth complexes demonstrate high, tunable Lewis-acidity, high coordination numbers, and labile coordination, which make them useful for otherwise difficult asymmetric transformations.[3–7] A class of rare earth complexes of particular interest is Shibasaki's rare earth alkali metal BINOLate (REMB) framework $[M_3(THF)_n][(BINOLate)_3RE]$ (REMB; RE = Sc, Y, La-Lu; M = Li, Na, K; B = 1,1′-bi-2-naptholate; RE/M/B/= 1/3/3; Scheme 1a).[8,9] These complexes have bifunctional Lewis acidic/Brønsted basic capabilities and a modular secondary coordination sphere allowing cooperative activation of one or more substrates.[10,11] As a result, Shibasaki's catalysts are among the most efficient and effective known and exhibit high enantioselectivity across a broad range of reactions. Our team found the catalytic success and robust structures of the REMB framework to be an inspiration for investigating the primary and secondary coordination spheres. We have modulated the central atom to contain Ce(IV) or U(IV) and the secondary coordination sphere to contain cationic H-bond donors, $ZnEt^+$ cations, and Cu^I cations (Scheme 1a, b).[12–17] With this knowledge in hand, we were interested to further probe the binding of BINOL derived ligands by employing (*S*)-MonoThioBINOL [**(*S*)-H_2-MTB,** (*S*)-2-hydroxy-2′-mercapto-1,1′-binaphthyl]. **(*S*)-H_2-MTB** (and the deprotonated variant (*S*)-MonoThioBINOLate (S)-MTB) was previously investigated by the Woodward group to probe catalysis with other Lewis

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CONTACT Eric J. Schelter schelter@sas.upenn.edu; Patrick J. Walsh pwalsh@sas.upenn.edu P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA, 19104, United States.

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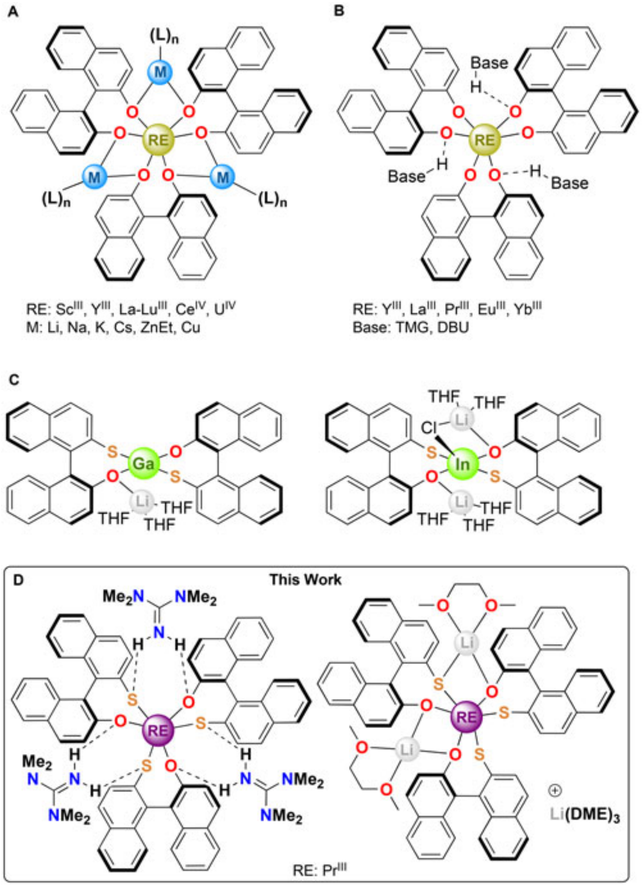


Scheme 1. (a) Previously synthesized structures of the REMB structural motif; (b) Previously isolated rare earth BINOLate hydrogen-bonded networks; (c) Group 13 MTB compounds previously isolated by the Woodward group; (D) **(*S*)-MTB** rare earth compounds in this study.

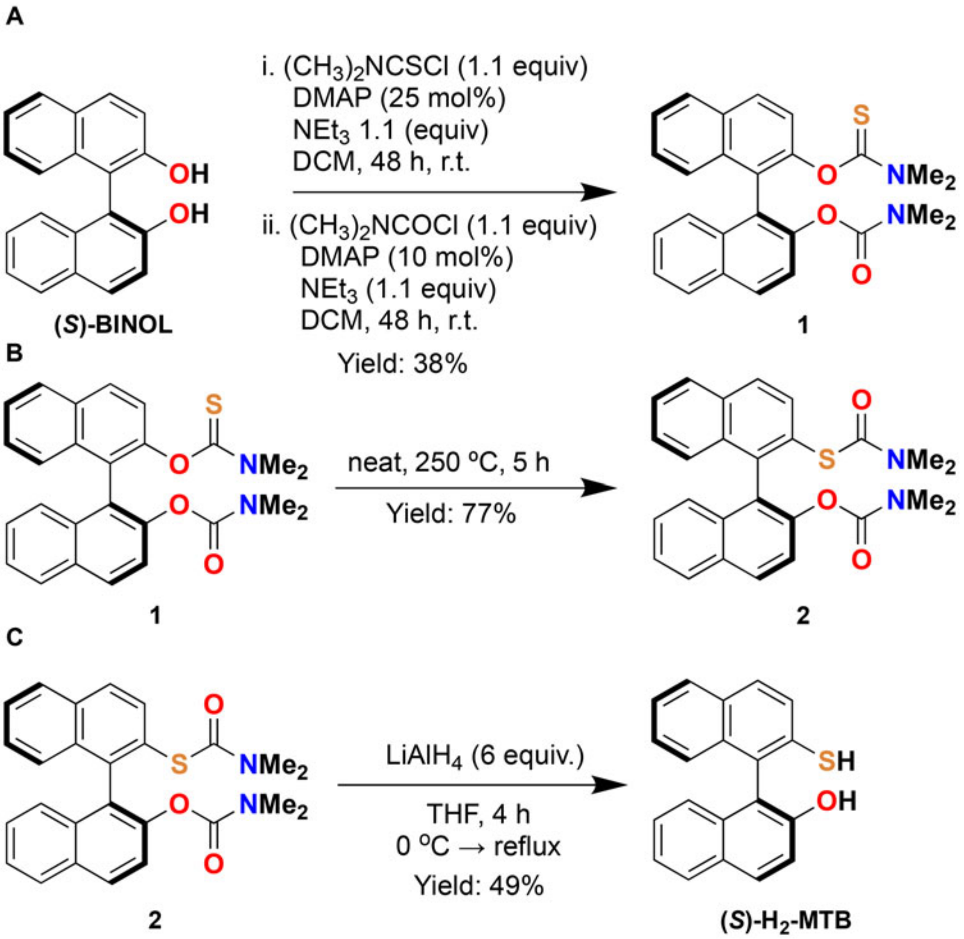
acids.[18,19] Their investigations produced crystal structures with gallium (III) or indium (III) as the central cations and lithium as the secondary cation, which were isostructural to known group 13, lithium bis-BINOLate structures (Scheme 1c).[20] Due to the lack of information of f-element bonding to this ligand, we decided to investigate the bonding with robust secondary cations, tetramethyl guanidium (TMG-H$^+$) and lithium (Scheme 1d).

Results and discussion

The desired proligand **(*S*)-H$_2$-MTB** was synthesized according to a modified procedure published by the Woodward laboratories.[18] The acylation began with **(*S*)-BINOL** and *N*,*N*-dimethylthiocarbamoyl chloride using triethylamine (NEt_3) as the base and catalytic amounts of 4-*N*,*N*-dimethylaminopyridine (DMAP) (Scheme 2a). This reaction was complete after 48 hours at room temperature. Next, into the same reaction vessel was added additional NEt_3 and DMAP followed by *N*,*N*-dimethylcarbamoyl chloride. After another 48 hours of stirring, the reaction was complete yielding **1**. In our hands, the product isolated after aqueous workup was often contaminated with a C_2-symmetric product identified as 2,2′-bis(*N*,*N*-dimethylcarbamoyloxy)-1,1′-binapthyl and an unidentified yellow oil.[21] These byproducts were conveniently separated by flash chromatography and recrystallization respectively. The subsequent Newman-Kwart rearrangement was conducted in a similar method to the reported procedure; however, in our hands the heat source was found to be important for the rearrangement (Scheme 2b). Microwave irradiation and sand baths provided inconsistent results and low conversions, while using a molten mixture of 1:1 $NaNO_3/KNO_3$ as a heating bath reliably converted all of intermediate **1** into the rearrangement product **2** (Figure S1 Supplemental Materials). Lastly, in our hands, the reported base hydrolysis yielded a complex mixture of products by ^1H NMR, which was unsuitable for coordination chemistry. Instead, we found that treatment with an excess of lithium aluminum hydride (LAH) in THF produced clean **(*S*)-H$_2$-MTB** following work up (Scheme 2c). With pure proligand in hand, we turned our focus to its coordination chemistry.

Complex **3** was synthesized from a yellow solution of **(*S*)-H$_2$-MTB**, TMG (tetramethyl guanidine), and $Pr[N(SiMe_3)_2]_3$ in THF (Scheme 3a). The complex was isolated using crystallization in moderate yield (62%) as yellow hexagonal plates. Crystals suitable for X-ray diffraction were grown from solutions of **3** in THF subjected to pentane vapor diffusion. The structure of **3** (Figure 1) was determined to have a similar structure to other isolated $[TMG\text{-}H]^+$ containing rare earth BINOLate structures. It contained a 6-coordinate rare earth cation at a C_3 axis of symmetry. The $[TMG\text{-}H]^+$ protons participated in hydrogen bonding with all six heteroatoms bound to the rare earth cation, each $[TMG\text{-}H]^+$ bonding to one oxygen and one sulfur atom. The primary difference between the parent BINOLate complexes (Scheme 1b) and **3** is the large increase of the Pr–S bonds' distance relative to their Pr–O bonds, which is reflected in the ligand torsion angles (Scheme S1) and the Pr–S–C bond angle. The Pr–S bond distance in structure **3** is 2.9145(10) Å, which is nearly 0.6 Å longer than the Pr–O bond length (2.325(3) Å). In contrast to the parent system, where the largest deviation between the RE–O bonds is 0.024 Å. To accommodate this large change in the bond distances, the ligand increases its dihedral angle about the binapthyl C1-C1′ bond by 8° compared to the parent BINOLate system with the lanthanum cation (dihedral: 64.10°). The Pr–S–C bond angle is also much more acute (92.57(14)°) than the Pr–O–C bond angle (128.0(3)°).

To further probe the coordination chemistry of **(*S*)-MTB** we next focused our efforts on structures with lithium in the secondary coordination sphere. Compound **4** was synthesized by adding $LiN(SiMe_3)_2$ to a solution of $Pr[N(SiMe_3)_2]_3$ and **(*S*)-H$_2$-MTB** in DME. X-ray quality crystals were grown from the reaction mixture by layering with pentane and were isolated in 56% yield (Scheme 3b). The ^1H NMR in THF-d_8 indicated a complete lack of symmetry, which was consistent with the ^7Li NMR spectrum containing 3 different signals at δ 41.97, 22.23, and −31.45 ppm. The absence of symmetry was consistent with the crystal structure, whereby the complex crystalized as a monoanionic species with an external DME solvated lithium counter cation (Figure 2). This is, to our knowledge, the first structurally characterized



Scheme 2. (a) Asymmetric carbamoylation of (*S*)-**BINOL** yielding intermediate **1** (b) thermal Newman-Kwart rearrangement of intermediate **1** to yield **2** (C) LAH deprotection of synthetic intermediate **2** to produce (*S*)-H_2-**MTB**.

charge separated tris-BINOLate structure reported. Another notable aspect was one of the **(*S*)-MTB** ligands rotated and broken the typical C_3 symmetry to enable a lithium cation to engage in binding to two **(*S*)-MTB** oxygen atoms. We expect this is due to the high oxophilicity of lithium cations. Similarly to complex **3**, the Pr–S distances are on average 0.506 Å longer than the Pr–O bonds, and the ligands' dihedral angles range from 73.6° to 74.8°.

Conclusions and future directions

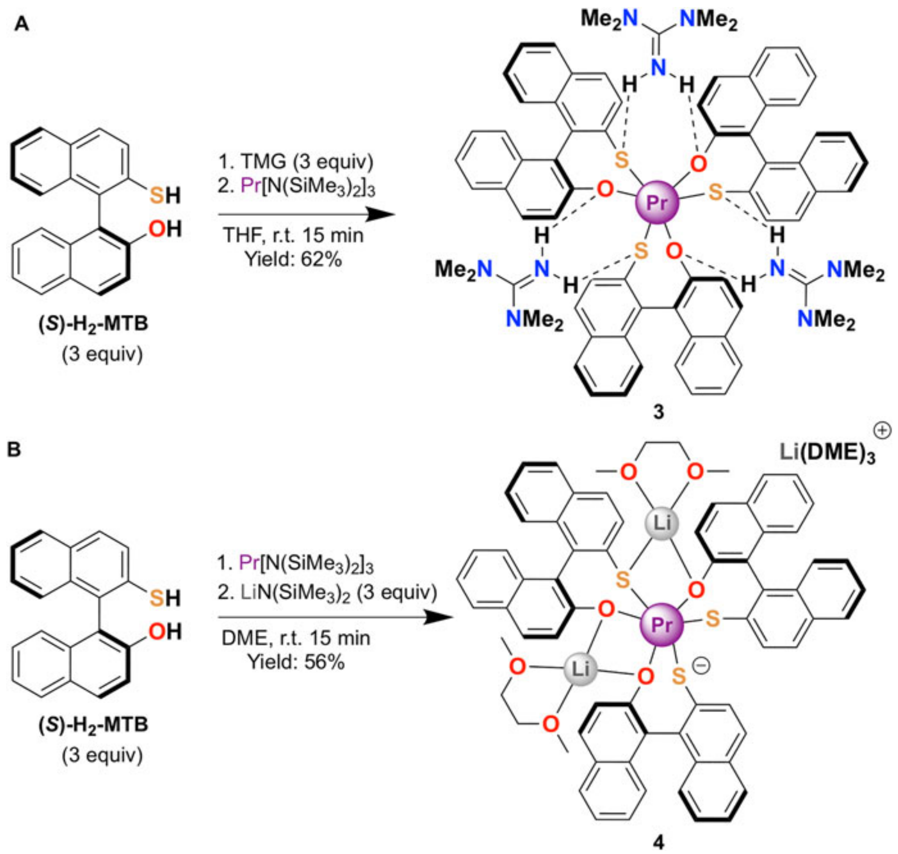
In summary, we have synthesized the first two complexes containing three **(*S*)-MTB** ligands. This study expands the chemistry of **(*S*)-MTB** from group 13 metals to the rare earth metal praseodymium. Using **(*S*)-MTB** we showed the importance of oxygen ligation for lithium in the secondary coordination sphere by isolating the first charge-separated BINOLate complex. Future work will include the exploration of the utility of these compounds in asymmetric catalysis.

Experimental

General methods, materials and measurements

For all reactions and manipulations performed under an inert atmosphere (N_2), standard Schlenk techniques or a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X/Q5 Cu–0226S catalyst purifier system were used. Glassware was oven-dried for at least 12 h at 150 °C prior to use. ^{1}H NMR spectra were obtained on a Brüker AM-500 or a Brüker UNI-400 Fourier transform NMR spectrometer at 500 or 400 MHz, respectively. ^{13}C{^{1}H} NMR spectra were recorded on a Brüker AM-500 Fourier transform NMR spectrometer at 126 MHz. All spectra were measured at 300 K unless otherwise specified. Chemical shifts were recorded in units of parts per million (ppm) downfield from residual proteo solvent peaks (^{1}H) or characteristic solvent peaks (^{13}C{^{1}H}).

Tetrahydrofuran, dichloromethane, toluene, dimethoxymethane, and pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising of columns packed with Q5 reactant and neutral alumina respectively (for hexanes and pentane), or two columns of neutral alumina (for THF). Chlorobenzene, heptane, and hexanes were purchased from Fisher Scientific. Deuterated tetrahydrofuran, chloroform and dichloromethane were purchased from Cambridge Isotope Laboratories, Inc. Deuterated tetrahydrofuran was stored for at least 12 h over potassium mirror prior to use. (*S*)-BINOL was purchased from AKScientific and dried at 25 °C and 50 mtorr overnight. $LaCl_3$, $PrCl_3$, $EuCl_3$ (>99.9%



Scheme 3. (a) Synthesis of complex **3** from **(*S*)-H$_2$-MTB**, TMG, and $Pr[N(SiMe_3)_2]_3$ (b) Synthesis of unusual complex **4** from **(*S*)-H$_2$-MTB**, $LiN(SiMe_3)_2$, and $Pr[N(SiMe_3)_2]_3$.

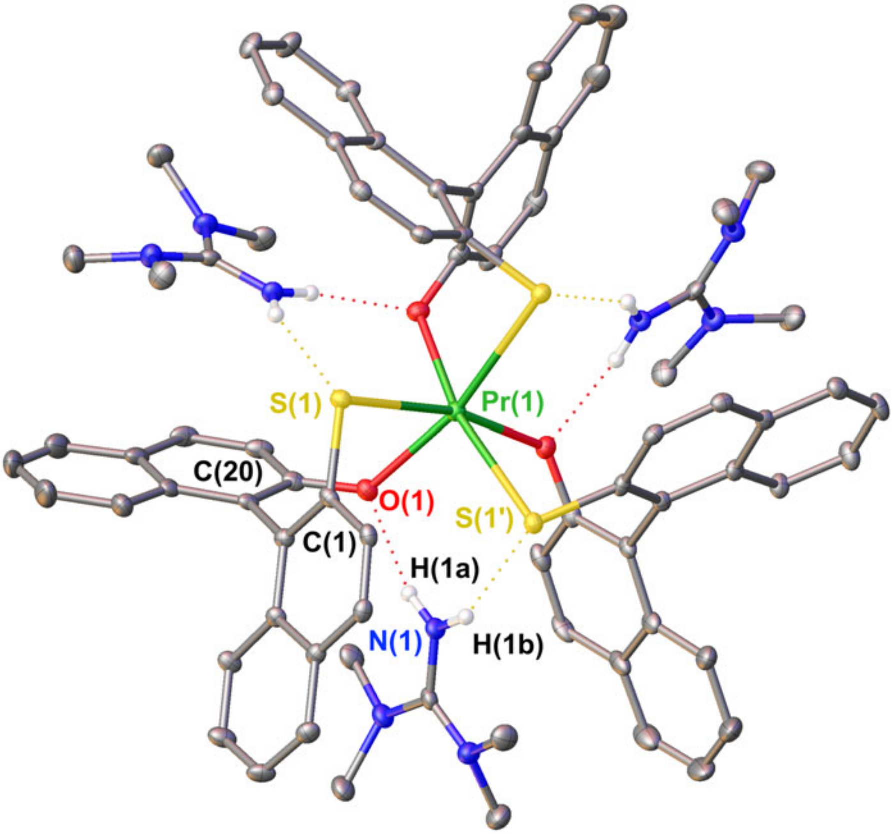


Figure 1. Thermal ellipsoids of complex **3,** $[TMG\text{-}H^+]_3[((S)\text{-}MTB)_3Pr^{3-}]\bullet 1.33(THF)$, at the 30% probability level. C–H hydrogen atoms and interstitial solvent removed for clarity. S(1) and S(1′) are at a position related by symmetry. Selected bond distances (Å): Pr(1)–O(1) 2.325(3), Pr(1)–S(1) 2.9145(10), O(1)–H(1a) 2.008, S(1′)–H(1b) 2.468. Selected bond angles (deg): O(1)–Pr(1)–S(1) 81.46(7), O(1)–Pr(1)–S(1′) 98.057, Pr(1)–S(1)–C(1) 92.57(14), Pr(1)–O(1)–C(20) 128.0(3). Ligand torsion angle (deg): 72.2 (Scheme S1 Supplemental Materials).

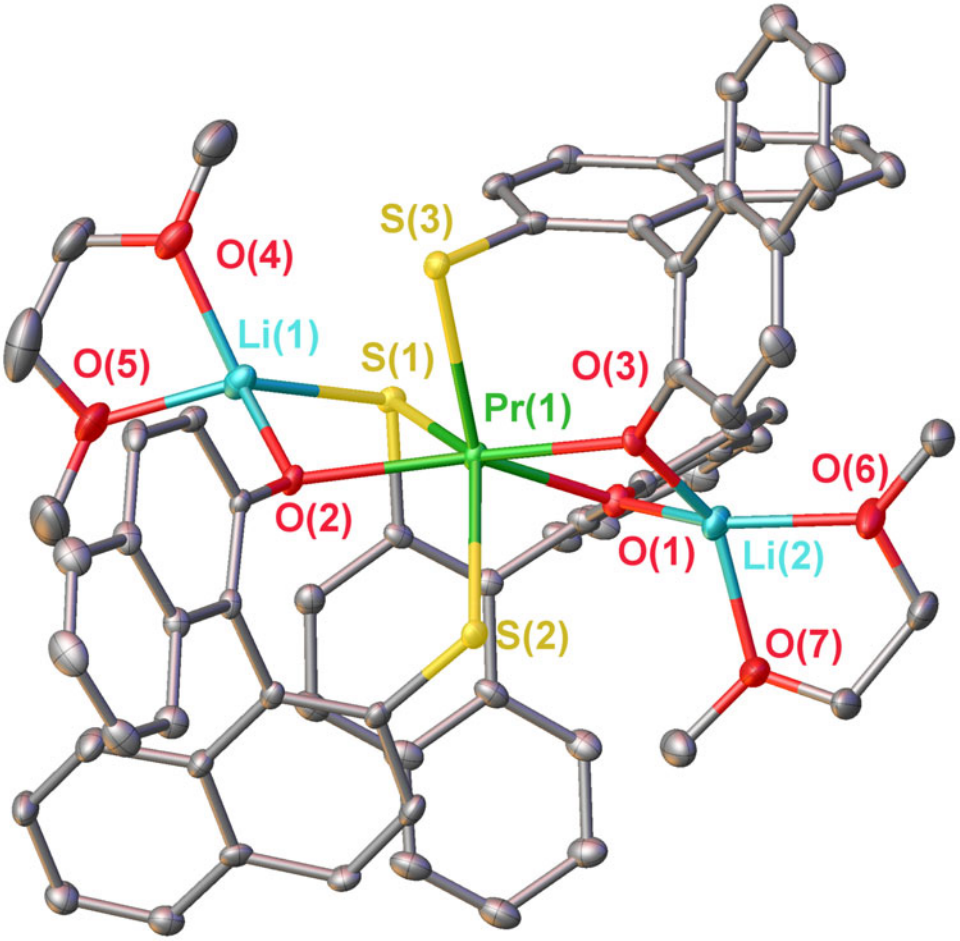


Figure 2. Thermal ellipsoid plot of complex **4,** $[Li(DME_3)^+][(Li(DME))_2Pr((S)\text{-}MTB)_3^-]\cdot$ (DME) at the 30% probability level. C–H hydrogen atoms, lithium counter cation, and interstitial solvent removed for clarity. Selected bond distances (Å): Pr(1)–O(1) 2.355(4), Pr(1)–O(2) 2.382(5), Pr(1)–O(3) 2.358(5), Pr(1)–S(1) 2.9340(19), Pr(1)–S(2) 2.848(2), Pr(1)–S(3) 2.8321(17), Li(1)–O(2) 1.917(16), Li(1)–S(1) 2.520(15), Li(2)–O(1) 1.937(17), Li(2)–O(3) 1.886(16). Selected bond angles (deg): O(1)–Pr(1)–O(3) 69.8(2), O(2)–Pr(1)–S(1) 75.83(14), O(1)–Li(2)–O(3) 89.7(6), O(2)–Li(1)–S(1) 95.0(6). Ligand torsion angle (deg): 73.600-74.759 (Scheme S1).

purity) were purchased from Strem and used after drying at 140 °C at 50 mtorr overnight. Thiocarbamoyl chloride was recrystallized from pentane prior to use.[18] $Pr[N(SiMe_3)_2]_3$ was prepared according to literature procedures.[22] The Supplemental Materials contains synthetic information on (*S*)-H_2-MTB, ^1H NMR (Figures S2 and S3), ^7Li NMR (Figure S4), and details regarding X-ray data collection (Table S1).

Synthetic details and characterization

Synthesis of $[TMG\text{-}H^+]_3[((S)\text{-}MTB)_3Pr^{3-}]\bullet 1.33(THF)$ 3

In an inert atmosphere glovebox, a 20 mL glass scintillation vial was charged with a Teflon-coated stirbar, (*S*)-2-hydroxy-2′-mercapto-1,1′-binaphthyl [**(*S*)-H_2-MTB**] (0.035 g, 0.1162 mmol, 3.1 equiv.; FW: 302.39 g·mol^{-1}), and THF (4 mL). Tetramethylguanidine (0.0134 g, 0.1162 mmol, 3.1 equiv.; FW: 115.19 g·mol^{-1}) was then added, resulting in a bright yellow solution. $Pr[N(SiMe_3)_2]_3$ (0.025 g, 0.0375 mmol, 1 equiv.; FW: 668.13 g·mol^{-1}) was then added as a solid to the stirred solution. The solution was stirred for 1 h, filtered through a Celite padded coarse porosity filter and layered with pentane. $[TMG\text{-}H^+]_3[((S)\text{-}MTB)_3Pr^{3-}]\bullet 1.33(THF)$ was isolated as a yellow crystalline solid by decanting the solution and drying under vacuum. Yield: 0.334 g (1.10 mmol, 49%; 302.39 g·mol^{-1}). ^1H NMR (500 MHz, CD_2Cl_2) δ 24.59, 20.13, 16.78, 15.50, 14.38, 13.70, 12.18, 12.14, 10.56, 9.94, 9.60, 8.62, 8.12, 7.55, 7.54, 7.32, 7.30, 7.30, 7.21, 7.00, 6.97, 6.54, 6.44, 6.25, 6.10, 5.66, 5.48, 5.40, 5.36, 4.65, 3.75, 3.01, 1.89, 1.49, 1.35, 0.98, 0.16, −0.16, −0.75, −5.60, −6.01, −8.08, −12.88, −14.40.

Synthesis of $[Li(DME_3)][Li(DME))_2Pr(MTB)_3]\cdot(DME)$ 4

In an inert atmosphere glovebox, a 20 mL glass scintillation vial was charged with a Teflon-coated stirbar, (*S*)-2-hydroxy-2′-mercapto-1,1′-binaphthyl ((*S*)-H_2-MTB) (0.045 g, 0.148 mmol, 3 equiv.; FW: 302.39 g·mol^{-1}), and DME (4 mL). A solution of $Pr(N(SiMe_3)_2)_3$ (0.025 g, 0.0375 mmol, 1 equiv.; FW: 668.13 g·mol^{-1}) in 2 mL of DME was added to the stirring solution. After 5 min of stirring, a solution of $LiN(SiMe_3)_2$ in 2 mL of DME was added. The resulting yellow green solution was stirred for 1 h. The solution was then filtered through a pad of Celite over a coarse porosity fritted filter and layered with pentane. The crystals formed were collected by filtration over a medium porosity fritted filter and washed with 3 × 2 mL of pentane. The solid was dried under high vacuum for 3 h. Yield: 0.042 g (0.028 mmol, 74%; 1513.46 g·mol^{-1}). ^{1}H NMR (500 MHz, THF-d_8) δ 23.48, 18.58, 17.48, 17.24, 14.62, 12.60, 12.01, 10.21, 9.88, 9.70, 9.57, 9.41, 9.21, 8.38, 8.09, 8.08, 7.98, 7.70, 7.66, 7.57, 7.35, 7.31, 7.23, 7.18, 7.13, 6.81, 6.66, 6.59, 6.57, 6.56, 6.55, 6.33, 6.27, 6.18, 5.72, 5.42, 5.30, 5.09, 4.60, 4.52, 4.03, 3.76, 3.19, 3.17, 2.35, 1.35, 0.94, 0.16, 0.12, 0.10, 0.06, −0.07, −0.75, −1.08, −5.24, −7.71, −12.85.

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ORCID

Grace B. Panetti http://orcid.org/0000-0001-7833-5706
Elena J. Varela http://orcid.org/0000-0002-8143-6206
Patrick J. Walsh http://orcid.org/0000-0001-8392-4150

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