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## Chelating Bis(thiophosphinic amidate)s as Versatile Supporting Ligands for the Group 3 Metals. An Application to the Synthesis of Highly Active Catalysts for Intramolecular Alkene Hydroamination

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Permethylmetallocene and related derivatives of the group 3 metals have been shown to be effective catalysts for alkene polymerization,<sup>1</sup> hydrosilylation,<sup>2</sup> hydroboration,<sup>3</sup> hydrogenation,<sup>4</sup> as well as intramolecular hydroamination.5 By virtue of the importance of these and related reactions that are catalyzed by group 4 metallocenes, we were interested in evaluating chelating thiophosphinic amidates as an alternative ligand class for the complexation of early metals. The attractive features of this ligand motif include pseudotetrahedral bonding geometry at phosphorus for increased steric shielding of the complexed metal relative to the planar central carbon present in the more familiar amidinato<sup>6</sup> group and diminished predisposition toward aggregate formation with oxophilic metals by virtue of terminal sulfur (vs oxygen) substitution. Surprisingly, thiophosphinic amides have thus far only been employed as simple additives to influence the outcome of selected reactions involving the addition of organometallic reagents to aldehydes.<sup>7</sup> In this Communication, we report the structure of the first low-coordinate yttrium-bis(thiophosphinic amidate) complex. The utilization of this complex as well as related chelates of representative group 3 and lanthanide metals (e.g., Y, Nd, and Dy) for the efficient catalysis of intramolecular alkene hydroaminations is then described.

The thiophosphinic amides **1a**,**c**,**d** and **f**-**i** employed in this study were prepared by the reaction of the diamine with the appropriate dialkyl- or diarylchlorophosphine (2.1 equiv) followed by the addition of sulfur (2.2 equiv) or selenium in the case of **1b** (Figure 1).<sup>8</sup> Attachment of the proligands **1a**-**i** to group 3 metals could be quantitatively achieved by direct metalation with 1 equiv of the appropriate amide Ln[N(TMS)<sub>2</sub>]<sub>3</sub> **3a**-**c** (Ln = Y, Nd, or Dy) in C<sub>6</sub>D<sub>6</sub> or toluene to deliver complexes **4a**-**i** (Scheme 1).

Crystals of complex  $4h_{(Y)}$  suitable for X-ray diffraction were obtained directly from the reaction mixture (toluene as solvent). The molecular structure is shown in Figure 2. The complex has a distorted square-pyramidal geometry, with the bis(trimethylsilyl)amido ligand at the apex. The structure confirms the bidentate nature of the thiophosphinic amidate (NPS) ligand, with S-Y-N angles of 67.94(7)° and 69.88(7)° and the apical amido possessing N-Y-N and S-Y-N deflections of 120.86(11)°, 115.71(11)° and  $105.53(8)^\circ$ ,  $107.88(8)^\circ$ , respectively. The bond length of Y-N(3) [2.234(3) Å] is considerably shorter than Y–N(1) [2.314(3) Å] or Y-N(2) [2.309(3) Å] in consonance with the greater ability of N(3) to engage in  $\pi$ -dative bonding to Y. It is also of interest that the bond length of Y-N(3) [2.234(3) Å] in  $4h_{(Y)}$  is shorter than those of the 16 e<sup>-</sup> complex  $Cp*_2Y-N(TMS)_2$  [Y-N: 2.274(5) Å and 2.253(5) Å] (which has two independent molecules in the asymmetric unit)9 or that of the 14 e<sup>-</sup> complex [Cp\*Si(Me)<sub>2</sub>N-(t-C<sub>4</sub>H<sub>9</sub>)Y-N(TMS)<sub>2</sub> [Y-N(TMS)<sub>2</sub>: 2.255(8) Å].<sup>10</sup> In light of these structural features, complexes belonging to the NPS class differ considerably from the majority of those (i.e., metallocenes and amido complexes) that possess activity as catalysts for small molecule synthesis.11



Figure 1. Proligands used in amine elimination reactions with 3a-c.



 $\textit{Figure 2.}\$  Chem 3D perspective view of  $4h_{(Y)}$  from the ORTEP diagram program.

Scheme 1



The catalyzed intramolecular hydroamination of alkenes,<sup>5a-f</sup> allenes,<sup>5g</sup> and alkynes<sup>12</sup> has attracted considerable attention as a valuable method for the synthesis of nitrogenous heterocycles.<sup>13</sup> Whereas various transition metal complexes are capable of mediating addition reactions involving alkynes, those involving the less reactive alkene linkage are less common. A limited number of group 3 metal complexes appear very well suited for effecting this process chemoselectively and under mild reaction conditions.<sup>5a-d</sup> Our recent interest in this area led us to its exploration as an initial venue for catalysis by group 3 NPZ complexes.

The cyclization of 2-aminohex-5-ene (**5**) was selected for initial examination.<sup>5a,d</sup> Successful implementation of the desired reaction proved remarkably straightforward as the requisite catalytic species could, in all cases, be generated quantitatively and in situ. Accord-





<sup>a</sup> Reaction was conducted at 120 °C. <sup>b</sup> Ratio based on <sup>1</sup>H NMR integration: 6a/6b = 3.14 (septet)/2.93 (m) (NCH peaks). <sup>c</sup> Based on <sup>1</sup>H NMR integration relative to p-xylene as the internal standard. <sup>d</sup> Reaction not run to completion.

ingly, incubation of the appropriate bis(thiophosphinic amide) [or bis(selenophosphinic amide)] 1 (5 mol %) with Ln[N(TMS)<sub>2</sub>]<sub>3</sub> 3 (Ln = Y, Nd, and Dy) (5 mol %) in C<sub>6</sub>D<sub>6</sub> at 120 °C led to smooth "amine elimination"<sup>10</sup> with concomitant formation of the active NPZ catalyst 4. Subsequent addition of 5 followed by heating at 60 °C then provided the pyrrolidines 6a,b, typically in >95% yield. Alternatively, cyclization of 5 on a 3 mmol scale followed by separation of the products from the catalyst by vacuum transfer and protonation (HCl-MeOH) furnished 6a,b as the hydrochloride salts in quantitative yield. A compilation of reaction times and diastereoselectivities observed for the cyclization of aminoalkene 5 in the presence of the NPS and related chelates 4 appears in Table 1.

Several of the trends that emerge from the foregoing examples are worthy of comment. Yttrium bis(thiophosphinic amidate)s  $4a_{(Y)}$ and  $4c_{(Y)}$  that possess comparatively hindered and electron-rich alkyl substituents have high catalytic activity, with  $4a_{(Y)}$  being comparable to the best metallocene or nonmetallocene group 3 hydroamination reported to date.<sup>5e</sup> As a means of perspective, the cyclization of 5 to the pyrrolidines 6a,b in the presence of 5 mol % of the simple amide 3a at 60 °C serves as a benchmark and was extremely lethargic, requiring 31 days to reach 95% conversion.<sup>5e</sup> Excessive shielding of the active metal center results in decreased activity (e.g.,  $4d_{(Y)}$  vs  $4c_{(Y)}$ ), consistent with the observed trend in lanthanocenes.5a Replacement of sulfur with selenium as the chalcogen substituent of phosphorus (cf.,  $4b_{(Y)}$ ) leads to a reduction of catalytic activity, albeit not dramatic. Significantly, replacement of the chalcogen with oxygen (complex  $4e_{(Y)}$ ) results in complete suppression of catalysis. In consonance with this result, it is significant that the yttrium chelate that is derived from the corresponding tethered bis(enamide) 2a is of low catalytic activity. In this case (5 mol % cat.), cyclization of 5 to 6a,b (6a:b = 4:1) proceeded only to 92% conversion at 120 °C over 6 days. By way of contrast, the yttrium complex analogously generated from the bis(thioenamide) 2b is of considerably higher activity. For this complex, the cyclization of 5 to 6a,b required only 5 h at 30 °C to reach >95% conversion and proceeded with remarkably high diastereoselectivity (6a:b = 33:1). The relative activity of complexes derived from 1a and alternative group 3 metals was subsequently explored using an early lanthanide (e.g., Nd) and one comparable in size to yttrium (e.g., Dy). In variance with the activity dependence expected for group 3 metallocenes, the neodymium



complex  $4a_{(Nd)}$  proved less reactive than  $4a_{(Y)}$ . As would be expected, however, cyclization diastereoselectivity using the Nd chelate was also diminished.<sup>5a</sup> Interestingly, the dysprosium complex  $4a_{(Dv)}$  was found to have considerably lower activity than the corresponding yttrium chelate. To the best of our knowledge, this is the first instance where the catalytic activity of complexes derived from Y and a lanthanide of similar covalent radius (Dy) has been directly compared in alkene hydroamination.

Complexes  $4a_{(Y)}$ ,  $4a_{(Nd)}$ , and  $4a_{(Dy)}$  were then evaluated in terms of relative catalytic activity in intramolecular hydroaminations involving aminoalkenes 7 and 9 (Scheme 2). Although these reactions were slower and in the case of 7 less stereoselective than those involving aminoalkene 5, similar trends in catalytic activity were observed, with  $4a_{(Y)}$  showing the highest activity. It is of interest in a preparative context that all of the complexes  $4a_{(Ln)}$ show high activity toward the cyclization of substrates containing 1,2-disubstituted alkenes (i.e., 9), as these are known to be reluctant participants in the hydroamination reaction.<sup>5c</sup>

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Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds and crystallographic data for complex  $4h_{(Y)}$  (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

## References

- (1) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. J. (1) Jeske, G., Schock, E. L., Swepsiol, T. Y., Schulmann, H., Harris, T. S. A. M., Chem. Soc. **1985**, 107, 8103.
   (2) Molander, G. A.; Retsch, W. H. J. Am. Chem. Soc. **1997**, 119, 8817.
   (3) Harrison, K. N.; Marks, T. J. J. Am. Chem. Soc. **1992**, 114, 9221.
   (4) Conticello, V. P.; Brard, L.; Gairdello, M. A.; Tsuji, Y.; Sabat, M.; Stern, C. M. Marks, T. J. J. Chem. Soc. **1992**, 114, 9221.

- C. L.; Marks, T. J. J. Am. Chem. Soc. 1992, 114, 2761.
- (5) (a) Gagné, M. R.; Stern, C. L.; Marks, T. J. J. Am. Chem. Soc. 1992, 114, 275.
  (b) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. Organometallics 1999, 18, 4421.
  (c) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. Org. Lett. 2001, 3, 3091.
  (d) Molander, G. A.; Dowdy, E. D.; Pack, S. C. S. Starks, T. S. Starks, T. J. Starks, T. J. Starks, T. J. Starks, T. Sta S. K. J. Org. Chem. 2001, 66, 4344 and references therein. (e) Kim, Y. K.; Livinghouse, T. Angew. Chem., Int. Ed. 2002, 41, 3645. (f) Kim, Y K.; Livinghouse, T.; Bercaw, J. E. Tetrahedron Lett. 2001, 42, 2933. (g) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. J. Am. Chem. Soc. 1999, 121, 3633 and references therein.
- (6) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teubin, J. H. J. Am. Chem. Soc. 1993, 115, 4931.
- (a) Shi, M.; Sui, W.-S. Tetrahedron: Asymmetry 2000, 773. (b) Shi, M.; (7)Sui, W.-S. Tetrahedron: Asymmetry 1999, 3319. (c) Shi, M.; Sui, W.-S. Tetrahedron: Asymmetry 2000, 835.
- (8) Bochmann, M.; Bwembya, G. C.; Whilton, N.; Song, X.; Hursthouse, M. B.; Coles, S. J.; Karaulov, A. J. Chem. Soc., Dalton Trans. 1995, 1887.
   (9) Hann, K. H.; Boer, J. L.; Teubin, J. H.; Spek, A. L.; Kojić-Prodić, B.;
- Hays, G. R.; Huis, R. Organometallics 1986, 5, 1726
- Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. Can. J. Chem. 1995, 73, 2233. (11) Molander, G. A.; Romero, J. A. C. Chem. Rev. 2002, 102, 2161 and
- references therein. (12) McGrane, P. L.; Jensen, M. D.; Livinghouse, T. J. Am. Chem. Soc. 1992,
- (13) Muller, T. E.; Beller, M. Chem. Rev. 1998, 98, 675.

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