726 *J. Am. Chem. Soc.* **2000,** *122,* 726−727

A Monomeric Samarium Bis(Iminophosphorano) Chelate Complex with a Sm═C Bond

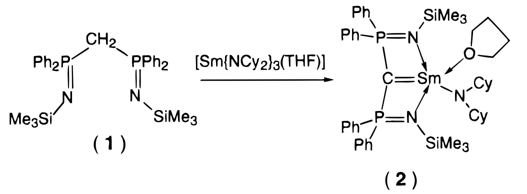
Kasani Aparna, Michael Ferguson,[†] and Ronald G. Cavell*

Contribution from the Department of Chemistry
University of Alberta, Edmonton, AB, Canada T6G 2G2

Received October 8, 1999

Lanthanide chemistry is one of the most rapidly developing areas of organometallic chemistry because of its potential relevance to catalysis.[1] Lanthanide alkyls and hydrides have recently attracted considerable interest as single-component olefin polymerization catalysts and reagents for organic synthesis.[2] Most of these complexes are stabilized by cyclopentadienyl and related ligands. The only known carbene complexes of lanthanide metals are the adducts of the neutral carbene ligands,[3−5] whereas extensive transition metal carbene chemistry is known.[6] We report herein a novel, non-Cp, samarium compound containing a metal−carbon multiple bond that was obtained by the facile deprotonation of the methylene backbone of the bis(iminophosphorano)methane ligand. This extension to the lanthanide group continues our study[7−12] of metal bis(iminophosphorano)methane complexes. The new samarium complex represents the first example of a lanthanide metal bound to the dianionic methandiide ligand environment provided by the bis(iminophosphorano)methane system.

Scheme 1



Complex **2**, [Sm{C(Ph_2P═$NSiMe_3$)$_2$-κ^3*C,N,N′*}(NCy_2)(THF)], a yellow air-sensitive crystalline solid, was obtained when 1 equiv of H_2C(Ph_2P═$NSiMe_3$)$_2$ **1**[13] was added to a toluene solution of samarium tris(dicyclohexylamide)[14] under an argon atmosphere (Scheme 1). Both of the methylene protons are removed and dicyclohexylamine is eliminated,[15] in parallel to our results with the Group 4 metals.[8] A few examples of the double deprotonation of the P−CH_2−P backbone have been structurally established in related P−C−P systems;[16−20] with the group 10 and 13 metals, however, these complexes are bi- and trimetallic bridged complexes in contrast to the present monomeric samarium complex.

The complex is paramagnetic, so the NMR resonances are broad as expected; the ^{31}P NMR spectrum for **2** consisted of one broad singlet at 43.3 ppm which is downfield shifted by 48.7 ppm with respect to the free ligand value. The proton NMR for complex **2** did not show a methylene resonance for the P−CH_2−P backbone, indicating that the ligand has been doubly deprotonated. No ^{13}C{^{1}H} NMR signal was observed for the quaternary P−C−P carbon atom despite trials with long acquisition periods, possibly because the signal is broadened due to the presence of paramagnetic samarium nuclei. Complex **2** is stable under an argon atmosphere at room temperature in aromatic solvents for extended periods of time; however, it decomposes upon thermolysis (toluene solvent at 120 °C) to give intractable compounds.

The molecular structure of [Sm{C(Ph_2P═$NSiMe_3$)$_2$-κ^3*C,N,N′*}(NCy_2)(THF)] **2**[21] was confirmed by X-ray crystallography. Two

---

[†] X-ray Structure Determination Laboratory.

* To whom correspondence should be addressed. Telephone 780-492-5310. FAX 780-492-8231. E-mail: Ron.Cavell@Ualberta.ca.

(1) (a) Gun'ko, Y. K.; Edelmann, F. T. *Comments Inorg. Chem.* **1997**, *19*, 153−184. (b) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193−2242. (c) Anwander, R.; Herrmann, W. A. *Top. Curr. Chem.* **1996**, *179*, 1−32. (d) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 247−276. (e) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865−986. (f) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466−2488. (g) Edelmann, F. T., Scandium, Yttrium, and the Lanthanide and Actinide elements, Excluding their Zero Oxidation State Complexes. In *Comprehensive Organometallic Chemistry (II)*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 4, Chapter 2, p 155. (h) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283−363.

(2) (a) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227−230. (b) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. (c) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606−7607. (d) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869. (e) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908−4910. (f) Schaverien, C. J. *Organometallics* **1994**, *13*, 69−82. (g) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103. (h) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. (i) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111−8118. (j) Arredondo, V. M.; Tian, S.; McDonald, F. T.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633−3639. (k) Arredondo, V. M.; McDonald, F. T.; Marks, T. J. *Organometallics* **1999**, *18*, 1949−1960.

(3) Herrmann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R. *Organometallics* **1997**, *16*, 682−688.

(4) Schumann, H.; Glanz, M.; Winterfeld, J.; Hemling, H.; Kuhn, N.; Kratz, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1733−1734.

(5) Arduengo, A. J., III; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 7927−7928.

(6) See for example: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 475 (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911−935. (c) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428−1438. (d) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293−1326. (e) Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397−412. (f) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1−74. (g) Wulff, W. D. *Organometallics* **1998**, *17*, 3116−3134. (h) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411−432.

(7) Cavell, R. G.; Kamalesh Babu, R. P.; Kasani, A.; McDonald, R. *J. Am. Chem. Soc.* **1999**, *121*, 5805−5806.

(8) Kamalesh Babu, R. P.; McDonald, R.; Decker, S. A.; Klobukowski, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4226−4229.

(9) Kasani, A.; McDonald, R.; Cavell, R. G. *Organometallics* **1999**, *18*, 3775−3777.

(10) Kasani, A.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1483−1484.

(11) Aparna, K.; Ferguson, M.; McDonald, R.; Cavell, R. G. *Organometallics* **1999**, *18*, 4241−4243.

(12) Kasani, A.; McDonald, R.; Cavell, R. G. *J. Chem. Soc., Chem. Commun.* **1999**, 1993−1994.

(13) Appel, R.; Ruppert, I. *Z. Anorg. Allg. Chem.* **1974**, *406*, 131−144.

(14) Minhas, R. K.; Ma, Y.; Song, J.-I.; Gambarotta, S. *Inorg. Chem.* **1996**, *35*, 1866−1873.

(15) Preparation of [Sm{C(Ph_2P═$NSiMe_3$)$_2$-κ^3*C,N,N′* }(NCy_2)(THF)] **2**: All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox. To a toluene (4 mL) solution of [Sm(NCy_2)$_3$(THF)][14] (0.205 g, 0.268 mmol), was added H_2C(Ph_2P═$NSiMe_3$)$_2$ (0.15 g, 0.268 mmol) with stirring at room temperature. The reaction mixture was stirred at room temperature for a day and heated at 80 °C for 20min. Bright yellow crystals were obtained upon allowing the flask to stand at room temperature for 2 days. The product was filtered and dried under vacuum. Yield 0.14 g, 54.4%. IR data (Nujol mull): 1435s, 1341w, 1243s, 1177w, 1146m, 1107s, 1086s, 1065s, 1026s, 948m, 917w, 886m, 834s, 763s, 749s, 729m, 713s, 699s, 678w, 659m, 648m, 608s, 548s, 521s, 511s, 480s. ^{1}H NMR (C_6D_6): δ 9.80 (br s, phenyl), 7.78 (br s, phenyl), 6.65 (br s, phenyl), 6.40 (br s, phenyl), 5.78 (br s, phenyl), 2.80 (br s, THF), 1.95 (br s, Cy), 1.34 (br s, Cy), 1.10 (s, CH_3Si), 0.94 (m, Cy), 0.36 (m, THF), −1.54 (br s, Cy), −1.85 (br s, Cy), −2.21 (br s, Cy). ^{13}C {^{1}H} NMR (C_6D_6): 133.1 (br s, phenyl), 130.0 (br s, phenyl), 129.3 (br s, phenyl), 126.8 (br s, phenyl), 69.3 (s, CH−Cy), 62.7 (s, CH_2−THF), 36.2 (s, CH_2−Cy), 26.6 (s, CH_2−Cy), 26.4 (s, CH_2−THF), 20.4 (s, CH_2−Cy), 5.5 (s, CH_3Si), ^{31}P{^{1}H} NMR (C_6D_6): δ 43.3 (br s). Anal. Calcd for desolvated crystals of $C_{47}H_{68}N_3OP_2Si_2Sm$.: C, 58.83; H, 7.14; N, 4.38. Found: C, 59.39; H, 7.25; N, 4.40.

(16) Al-Resayes, S. I.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1986**, 1710−1711.

(17) Browning, J.; Dixon, K. R.; Hilts, R. W. *Organometallics* **1989**, *8*, 552−554.

(18) Robinson, G. H.; Lee, B.; Pennington, W. T.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 6260−6261.

(19) Lee, B.; Sangokoya, S. A.; Pennington, W. T.; Robinson, G. H. *J. Coord. Chem.* **1990**, *21*, 99−105.

(20) Robinson, G. H.; Self, M. F.; Pennington, W. T.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 2424−2426.

10.1021/ja9936114 CCC: $19.00

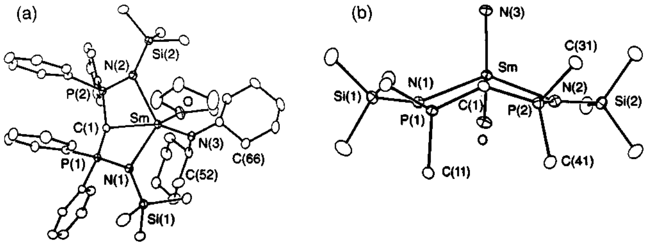


Figure 1. (a) An ORTEP[22] view of [Sm{C($Ph_2P{=}NSiMe_3)_2$-κ^3C,N,N'}-(NCy_2)(THF)] **2** showing the atom labeling scheme. The hydrogen atoms have been removed for clarity and the remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic distances [Å] and angles [deg] are as follows: Sm−C(1) = 2.467(4), Sm−N(1) = 2.409(4), Sm−N(2) = 2.449(4), Sm−N(3) = 2.216(4), Sm−O = 2.479(3), N(1)−P(1) = 1.632(4), P(1)−C(1) = 1.671(4), P(2)−C(1) = 1.666(4), P(2)−N(2) = 1.626(4), N(1)−Sm−N(2) = 120.6(1), N(1)−Sm−C(1) = 66.2(1), N(2)−Sm−C(1) = 65.8(1), P(1)−C(1)−P(2) = 138.0(3), N(1)−P(1)−C(1) = 107.5(2). (b) A side view of the central plane of **2**.

ORTEP[22] views of complex **2** along with selected bond lengths and bond angles are shown in Figure 1. The core structure consists of two nearly planar, fused four-membered rings with a Sm−C(1) shared edge. The two four-membered rings form an open book with a dihedral angle of 37.7(1)°. Intramolecular chelation of two trimethylsilyliminophosphorane units completes the coordination around the samarium. The samarium to carbon bond distance {Sm−C(1) = 2.467(4) Å} is considerably shorter (10%) than the average Sm−carbon distances[23] {average 2.743 Å, median 2.738 Å}, which indicates multiple bond character between the samarium and carbon atom and hence this species could be formulated as a carbene. This Sm−carbene distance is also shorter than the related distances in neutral carbene ligand complexes[3−5] of samarium[5] (Sm−C = 2.837(7), 2.845(7) Å) as well as other lanthanides. The Sm−N bond distances to the phosphinimine nitrogen atoms are longer than the Sm−N bond distance to the nitrogen atom of the dicyclohexylamido group indicating that the imine groups are best described as neutral donor substituents.

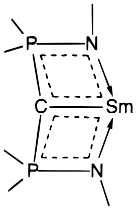


Figure 2.

The bond distances within the ligand framework in complex **2** are considerably altered in comparison with the related values in free bis(iminophosphorano)methane ligands;[24,25] the P═N bond distances are elongated and the endocyclic P−C bond distances are significantly shorter; however, the exocyclic P−C distances are unaffected. The P−C−P bond angle 138.0(3)° is considerably widened compared to the corresponding values in $CH_3CH\{Ph_2P{=}N(p\text{-tolyl})\}_2$ (112.39(19°))[24] as well as in $H_2C\{Cy_2P{=}NSiMe_3\}_2$ (117.41(12)°).[25] These factors suggest that there is a delocalization of π electron density within each four-membered metallocylic ring, arising from conjugation of Sm═C and P═N bonds which can be represented as shown in Figure 2.

The bis(iminophosphorano)methandiide ligand generated in situ by amine elimination yields a stable complex with samarium with a carbene structure. This complex represents the first example of a lanthanide bound to a dianionic carbene ligand system. Further study of this complex is underway.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, NOVA Chemicals Corp, and the University of Alberta for financial support.

Supporting Information Available: Tables of crystallographic experimental details, atomic coordinates, selected interatomic distances and angles, torsion angles, anisotropic displacement parameters, and derived atomic coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

JA9936114

---

[21] Crystal Data for [Sm{C($Ph_2P{=}NSiMe_3)_2$-κ^3C,N,N'}(NCy_2)(THF)]·0.5 toluene **2** : Triclinic, $P\bar{1}$ (No. 2), $a = 10.7169(6)$ Å, $b = 11.3464(6)$ Å, $c = 21.699(1)$ Å, $\alpha = 81.095(1)°$, $\beta = 82.152(1)°$, $\gamma = 84.774(1)°$, $V = 2575.7(2)$ Å^3, $Z = 2$. The structure was solved by direct methods and refined by full-matrix least-squares procedures: $R_1 = 0.0457$ ($wR_2 = 0.1220$) for 8085 reflections with $F_o^2 \geq 2\sigma(F_o^2)$.

[22] Johnson, C. K.; ORTEP, Report ORNL No. 5138, Oak Ridge National Labs, Oak Ridge, TN, 1976.

[23] Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187−204. The values were calculated from the data retrieved from the Cambridge Crystallographic Data Base.

[24] Avis, M. W.; Elsevier: C. J.; Veldman, N.; Kooijman, H.; Spek, A. L. *Inorg. Chem.* **1996**, *35*, 1518−1528.

[25] Crystal Structure of $CH_2\{PCy_2{=}NSiMe_3\}_2$: Kamalesh Babu, R. P.; Cavell, R. G.; McDonald, R., University of Alberta Structure Determination Laboratory, Report RGC 9802.