1100 *Organometallics* **2007,** *26,* 1100−1103

Lanthanide Complexes of Amino−Carbenes: On the Samarium−Carbene Bond from DFT Calculations

Laurent Maron*,† and Didier Bourissou*,‡

LNMO (Laboratoire de Nanophysique, Magnétisme et Optoélectronique) INSA, Université Paul Sabatier, 135, avenue de Rangueil, F-31077 Toulouse Cedex, France, and Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS (UMR 5069), Université Paul Sabatier, 118, route de Narbonne, F-31062 Toulouse Cedex 09, France

Received October 9, 2006

Summary: The coordination of the four model amino−carbene ligands ***A−D*** *to SmCl$_3$ has been theoretically investigated. Strong coordination energies were predicted for all carbenes (ΔG(25 °C) < -35 kcal mol^{-1} for the monoadducts). The nature of the Sm−carbene bonds was studied by molecular orbital and natural bond orbital (NBO) analyses. No evidence for significant carbene-to-Sm π-donation or Cl-to-carbene back-donation was observed. The strong Sm−carbene bonds, culminating in the abnormal NHC species* ***D****, can thus be essentially attributed to carbene-to-Sm σ-donation.*

Introduction

Over the last 15 years, N-heterocyclic carbenes (NHCs)[1] have been widely used as ligands for transition-metal catalysts.[2] The stronger donating properties of NHCs relative to those of phosphines were recognized early on, and on the basis of theoretical as well as experimental investigations, NHCs have long been considered as pure σ-donor ligands,[3] the high energy of the vacant carbene orbital presumably preventing efficient π-back-donation. However, this description now appears somewhat oversimplified, since more detailed studies on the precise nature of transition-metal−NHC bonds support the existence of significant π-back-bonding (up to 15−30% of the overall orbital interaction energies for electron-rich metal centers).[4] The electronic flexibility of NHC ligands has been further substantiated with the recent observation of "secondary" interactions such as π-donation from the carbene to the metal[5] and "peripheral" back-donation from neighboring chlorine ligands to the carbene center.[6,7] From these results, it is clear that a detailed description of the bonding in transition-metal NHC complexes must take into account these weak interactions, especially since a broad range of situations can be expected with the variety of aminocarbene complexes now available (cyclic vs acyclic,[8] monoamino vs diamino,[9] abnormal NHCs,[10] remote NHCs, ...[11]).

Although they have been comparatively much less developed than their late-transition-metal counterparts, NHC complexes of early transition and f-block metals are attracting increasing interest,[12−16] NHCs apparently being effective ligands for practically any metal center. With these electron-poor metal fragments, the metal−NHC bonds can be expected to result essentially from the carbene-to-metal σ-donation, especially for

---

* To whom correspondence should be addressed. L.M.: fax, +33 (0)5 61 55 96 97; tel, +33 (0)5 61 55 96 64; e-mail, laurent.maron@irsamc.ups-tlse.fr.

† LNMO (Laboratoire de Nanophysique, Magnétisme et Optoélectronique) INSA.

‡ Laboratoire Hétérochimie Fondamentale et Appliquée du CNRS.

(1) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162−2187. (b) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913−921. (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−92.

(2) (a) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181−222. (b) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617−618*, 70−80. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309. (d) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951−961. (e) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239−2246. (f) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247−2273. (g) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619−636. (h) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815−1828.

(3) (a) Green, J. C.; Scurr, R. G.; Arnold, P. L.; Cloke, F. G. N. *J. Chem. Soc., Chem. Commun.* **1997**, 1963−1964. (b) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801−5809.

(4) (a) Termaten, A. T.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem. Eur. J.* **2003**, *9*, 3577−3582. (b) Hu, X.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755−764.

(5) (a) Hu, X.; Tang, Y.; Gantzel, P.; Meyer, K. *Organometallics* **2003**, *22*, 612−614. (b) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516−3526.

(6) This peculiar situation has been evidenced for a few NHC adducts of high-valent metal chlorides: (a) Abernethy, C. D.; Codd, G. M.; Spicer, M. D.; Taylor, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 1128−1129. (b) Braband, H.; Abram, U. *Chem. Commun.* **2003**, 2436−2437. (c) Shukla, P.; Johnson, J. A.; Vidovic, D.; Cowley, A. H.; Abernethy, C. D. *Chem. Commun.* **2004**, 360−361.

(7) Such Cl−C$_{carbene}$ interactions were also predicted to be quite accessible in energy for rhodium(I) complexes of phosphino−carbenes: Miqueu, K.; Despagnet-Ayoub, E.; Dyer, P. W.; Bourissou, D.; Bertrand, G. *Chem. Eur. J.* **2003**, *9*, 5858−5864.

(8) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219−224.

(9) (a) Solé, S.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2001**, *292*, 1901−1903. (b) Cattoën, X.; Gornitzka, H.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 1342. (c) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 8670−8671. (d) Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705−5709.

(10) (a) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 10473−10481. (b) Kovacevic, A.; Gründemann, S.; Miecznikowski, J. R.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *Chem. Commun.* **2002**, 2580−2581. (c) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461−2468. (d) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5046−5047. (e) Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernández, R.; Brown, J. M.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3290−3291. (f) Bacciu, D.; Cavell, K. J.; Fallis, I. A.; Ooi, L.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5282−5284. (g) Arnold, P. L.; Pearson, S. *Coord. Chem. Rev.*, in press.

(11) (a) Schneider, S. K.; Roembke, P.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A. *Eur. J. Inorg. Chem.* **2005**, 2973−2977. (b) Schneider, S. K.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A. *Dalton Trans.* **2006**, 1226−1233. (c) Schuster, O.; Raubenheimer, H. G. *Inorg. Chem.* **2006**, *45*, 7997−7999.

(12) For group 4 metal complexes, see: (a) Herrmann, W. A.; Öfele, K.; Elison, M.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1994**, *480*, C7−C9. (b) Kuhn, N.; Kratz, T.; Bläser, D.; Boese, R. *Inorg. Chim. Acta* **1995**, *238*, 179−181. (c) Niehues, M.; Erker, G.; Kehr, G.; Schwab, P.; Fröhlich, R. *Organometallics* **2002**, *21*, 2905−2911. (d) Niehues, M.; Kehr, G.; Erker, G.; Wibbeling, B.; Fröhlich, R.; Blacque, O.; Berke, H. *J. Organomet. Chem.* **2002**, *663*, 192−203.

10.1021/om060924g CCC: $37.00

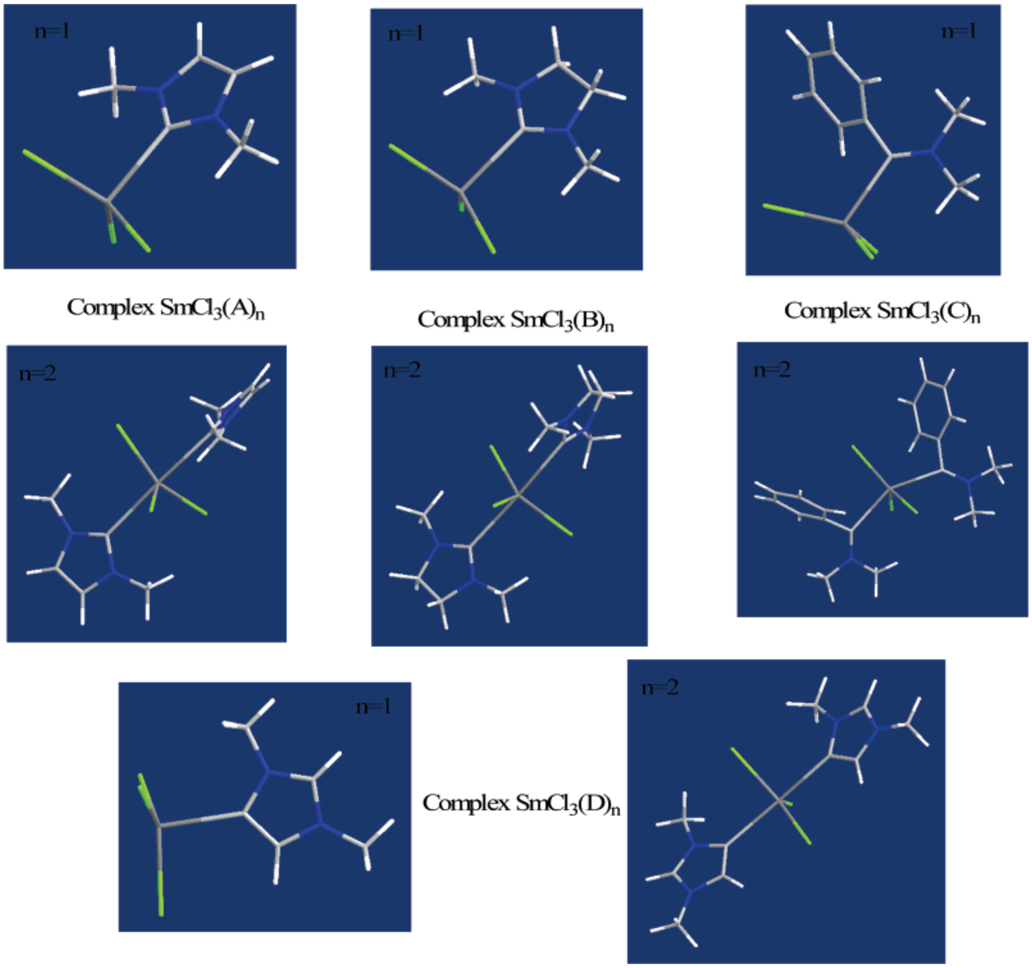
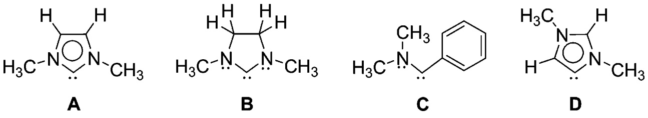


Figure 1. Optimized structures for the mono- and bis-adducts of $SmCl_3$.

d^0 fragments that are not capable of π-back-donation. Such a situation has been recently substantiated both experimentally and theoretically for MCl_4 (M = Zr, Hf) and Cp_2TiMe^+ fragments.[12c,d] The increasing number of structurally characterized NHC complexes involving f-block metals[16b] prompted us to investigate the bonding situation in lanthanide amino−carbene complexes. The $SmCl_3$ fragment was chosen as a representative example, and the influence of the carbene structure was studied using the model NHCs **A** and **B**, amino−aryl−carbene **C**, and abnormal NHC **D** (Chart 1). The geometry of the resulting mono- and bis(carbene) complexes will be discussed, as well as their bonding energies. Special attention has been devoted to the nature of the Sm−carbene bonds. Accordingly, “secondary” interactions were found to have only negligible contributions, and the influence of the σ-donating properties of the carbene ligand was emphasized.

Chart 1. Structure of the Model Carbene Ligands A−D



Results and Discussion

The mono- and bis-adducts between $SmCl_3$ and carbenes **A**−**D** have been investigated at the DFT (B3PW91) level. The optimized complexes are represented in Figure 1, and the main geometrical parameters are listed in Table 1. The geometry of the $SmCl_3$ fragment deviates from planarity within the mono-adducts, as deduced from the sums of the Cl−Sm−Cl bond angles from 350.3° (**B** and **C**) up to 355.1° (**D**). For comparison, coordination of the imidazol-2-ylidene **A** to the $Y[N(SiHMe_2)_3]$ fragment was found experimentally to induce significant pyramidalization around the yttrium center (sum of N−Y−N bond angles of 345.7°).[14] All of the bis-adducts derived from NHCs **A**, **B**, and **D** adopt the expected trigonal-bipyramidal geometry,

---

[13] For Sm and Yb complexes, see: (a) 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. (b) Schumann, H.; Glanz, M.; Winterfeld, J.; Hemling, H.; Kuhn, N.; Kratz, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1733−1734. (c) Schumann, H.; Glanz, M.; Winterfeld, J.; Hemling, H.; Kuhn, N.; Kratz, T. *Chem. Ber.* **1994**, *127*, 2369−2372. (d) Desmurs, P.; Dormond, A.; Nief, F.; Baudray, D. *Bull. Soc. Chim. Fr.* **1997**, *134*, 683−688. (e) Baudry-Barbier, D.; Andre, N.; Dormond, A.; Pardes, C.; Richard, P.; Visseaux, M.; Zhu, C. J. *Eur. J. Inorg. Chem.* **1998**, 1721−1727. (f) Glanz, M.; Dechert, S.; Schumann, H.; Wolff, D.; Springer, J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2467−2477. (g) Ferrence, G. M.; Arduengo, A. J., III; Jockisch, A.; Kim, H.-J.; McDonald, R.; Takats, J. *J. Alloys Compd.* **2006**, *418*, 184−188.

[14] For Y, La and Er complexes, see: Herrmann, W. A.; Munck, F. C.; Artus, G. R. J.; Runte, O.; Anwander, R. *Organometallics* **1997**, *16*, 682−688.

[15] For U and Ce complexes, see: (a) Oldham, W. J., Jr.; Oldham, S. M.; Scott, B. L.; Abney, K. D.; Smith, W. H.; Costa, D. A. *Chem. Commun.* **2001**, 1348−1349. (b) Nakai, H.; Hu, X.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Inorg. Chem.* **2004**, *43*, 855−857. (c) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Polyhedron* **2004**, *23*, 2689−2694. (d) Mehdoui, T.; Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. *Chem. Commun.* **2005**, 2860−2862.

[16] For reviews on f-block N-heterocyclic carbene complexes, see: (a) Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2165−2168. (b) Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2006**, 3959−3971.

Table 1. Selected Geometrical and Energetic Data for the Mono- and Bis-Adducts between SmCl$_3$ and Carbenes A−D[a]

complex	Sm−Cl[b]	Sm−C$_{carbene}$	Cl−C$_{carbene}$[c]	Cl−Sm−C$_{carbene}$[d]	ΔG_{coord}
SmCl$_3$(**A**)	2.57	2.58	3.85	96.9	−40.3
SmCl$_3$(**A**)$_2$	2.62	2.70/2.71	3.71	88.5	−18.6
SmCl$_3$(**B**)	2.57	2.60	3.82	95.3	−37.4
SmCl$_3$(**B**)$_2$	2.62	2.74/2.74	3.54	82.7	−16.0
SmCl$_3$(**C**)	2.57	2.60	3.69	91.1	−35.9
SmCl$_3$(**C**)$_2$	2.62	2.69/2.69	3.38	80.2	−15.8
SmCl$_3$(**D**)	2.58	2.51	3.83	97.6	−50.8
SmCl$_3$(**D**)$_2$	2.64	2.63/2.63	3.58	85.4	−26.2

[a] Bond lengths are given in Å, bond angles in deg, and Gibbs free energies of coordination (ΔG_{coord}) in kcal/mol, at 25 °C. [b] Average value (discrepancies <0.05 Å). [c] Shortest Cl−C$_{carbene}$ distance. [d] Associated with the shortest Cl−C$_{carbene}$ distance.

the two carbene ligands occupying the apical positions. The only noticeable difference concerns the relative orientation of the two NHC planes, which are perpendicular for **A** and **B** but coplanar with the abnormal NHC **D**, the two N−CH$_3$ groups being in syn positions. These conformational preferences are most probably due to subtle steric effects, by analogy with those observed for the related square-bipyramidal (NHC)$_2$MCl$_4$ (M = Zr, Hf) adducts.[12d] The reduced symmetry of the amino−phenyl−carbene **C** results in a significantly distorted trigonal bipyramid, with a C$_{carbene}$−Sm−C$_{carbene}$ bond angle of 145.2°. The Sm−Cl bond length slightly and gradually increases from SmCl$_3$ (2.53 Å) to the mono-adducts (2.57−2.58 Å) and to the bis-adducts (2.62−2.64 Å). Although not rigorously indicative of the bond strength, the Sm−C$_{carbene}$ bond lengths (2.51−2.60 Å in the mono-adducts and 2.63−2.70 Å in the bis-adducts) fall in the same range as the Sm−Cl bond lengths and correlate fairly well with those determined experimentally for the few structurally authenticated NHC complexes of f-block metals.[16b]

At this stage, a more accurate evaluation of the Sm−carbene bond strength was provided by the Gibbs free energies of coordination. Accordingly, the formation of the mono-adduct was found to be strongly thermodynamically favored for all carbenes **A**−**D** (Table 1). For comparison, mono-adducts of dimethyl ether (DME) and tetrahydrofuran (THF) as model coordinating solvents were calculated and the corresponding Gibbs free energies of coordination were estimated to be −21.8 and −23.7 kcal mol^{-1}, respectively. These values are about half of those predicted for carbenes **A**−**D** and suggest that lanthanide carbene complexes should be quite stable in solution. The much higher bonding energies of NHCs relative to that of THF also give quantitative insight into the synthetic route used to prepare the first NHC lanthanide complexes: that is, displacement of a THF by a carbene ligand.[13a−c]

The nature of the Sm−carbene bond in SmCl$_3$ mono-adducts was then studied by both molecular orbital and natural bond orbital (NBO) analyses. In addition to the expected carbene-to-metal σ-donation, particular attention was paid to the possible contribution of weak "secondary" interactions such as carbene-to-metal π-donation[5] and chlorine-to-carbene "peripheral" back-donation.[6,7] Although the Cl−C$_{carbene}$ distances in the various adducts remain rather long (more than 3.38 Å, compared to 3.45 Å for the sum of the van der Waals radii), rather acute Cl−Sm−C$_{carbene}$ bond angles (down to 80°) were found in some cases (Table 1), raising the question of the possible involvement of a bonding interaction between the chlorine lone pairs and the carbene vacant orbital.[17] At first glance, the presence of occupied orbitals of adequate symmetry, even for adducts featuring long Cl−C$_{carbene}$ distances, may argue in favor of such Cl−C$_{carbene}$ interactions. HOMO-3 for the SmCl$_3$(**A**) adduct and HOMO-6 for the SmCl$_3$(**B**)$_2$ bis-adduct are given in Figure 2 as representative examples. However, the magnitude of the Cl−C$_{carbene}$ bonding interaction could hardly be estimated from these MO considerations and was therefore more accurately assessed by NBO analyses.

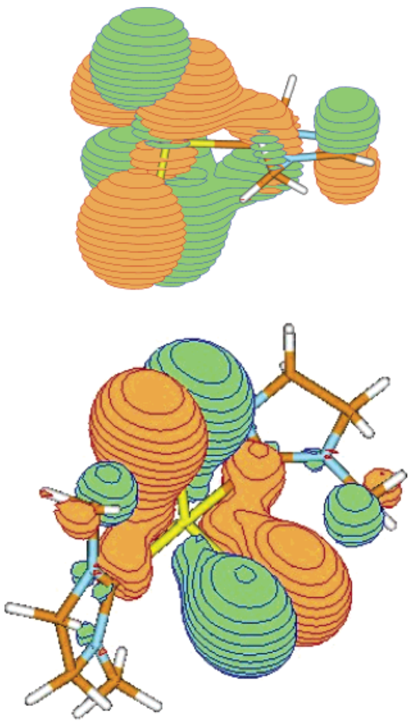


Figure 2. HOMO-3 of the adduct SmCl$_3$(**A**) (top) and HOMO-6 of the adduct SmCl$_3$(**B**)$_2$ (bottom), suggesting the possible involvement of a Cl−C$_{carbene}$ interaction.

As expected for an NHC complex of a d^0 metal fragment, a strong carbene-to-samarium σ-donation (54.0 kcal mol^{-1}) but no samarium-to-carbene π-back-donation was found at the second-order donor−acceptor interaction level for both SmCl$_3$(**A**) and SmCl$_3$(**B**)$_2$ adducts. In addition, only marginal carbene-to-samarium π donation (around 1.0 kcal mol^{-1}) and chlorine-to-carbene "peripheral" back-donation (around 0.5 kcal mol^{-1}) were observed. Accordingly, the strength of the coordination of **A** and **B** to SmCl$_3$ essentially results from the strong σ-donating properties of the NHC. At this stage, it is interesting to compare the bonding situation encountered with the various models of amino−carbenes. The free energy of the first coordination was predicted to increase gradually from the imidazol-2-ylidene to the imidazolidin-2-ylidene and to the amino−phenyl−carbene. Although fairly small in magnitude, these variations nicely correlate with those of the carbene-to-samarium σ-donation, as estimated from the NBO analyses. In all cases, the contribution of the "secondary" interactions remains negligible. Interestingly, coordination of the abnormal NHC **D** to SmCl$_3$ was predicted to be favored by about 10 kcal mol^{-1} in comparison to that of the related imidazol-2-ylidene **A**. Accordingly, the energetic separation between **A** and its wrong isomer **D** (18.2 kcal mol^{-1} in favor of **A)** is reduced down to 7.7 kcal mol^{-1} for the corresponding SmCl$_3$ mono-adducts. Here also, the strengthening of the Sm−C$_{carbene}$ bond,

---

(17) In a similar way, Arnold et al. recently observed marked bending in Ti(NHC)(O-*i*-Pr)$_n$(Br)$_{3-n}$ complexes without specific pseudo-back-bonding between the adjacent ligands and the carbene center: Mungur, S. A.; Blake, A. J.; Wilson, C.; McMaster, J.; Arnold, P. L. *Organometallics* **2006**, *25*, 1861−1867.

which is also apparent from the noticeable shortening of the bond length (from 2.58 Å in $SmCl_3$(**A**) to 2.51 Å in $SmCl_3$(**D**)), is directly related to a stronger carbene-to-samarium σ-donation (65.0 kcal mol^{-1}), as estimated from the NBO analysis. The stronger donating properties of abnormal NHCs have already been demonstrated by Crabtree et al. from the average ν(CO) stretching frequencies within $Ir(CO)_2Cl(NHC)$ complexes, which reflect the superposition of σ-donation and π-back-donation.[10c] Similar variations are observed here for the coordination of **A** and **D** to a d^0 metal partner such as $SmCl_3$, which emphasizes the different σ-donating properties of the two NHC ligands. As observed for carbenes **A**−**C**, only negligible contributions of carbene-to-samarium π-donation and chlorine-to-carbene back-donation were observed for **D**, so that the coordination of amino−carbenes to $SmCl_3$ definitely seems to be driven by the carbene-to-metal σ-donation. Notably, the trend observed in terms of σ-donation within the four $SmCl_3$ mono-adducts, that is, $\mathbf{D} > \mathbf{A} \geq \mathbf{B} \geq \mathbf{C}$, also holds true for the second coordination, as deduced from the corresponding Gibbs free energies (Table 1). In all cases, the values for the second coordination were about half of those of the first coordination.

Conclusion

The coordination of four model amino−carbene ligands to $SmCl_3$ has been investigated at the DFT level of theory. The formation of the mono-adducts was predicted to be strongly thermodynamically favored for all carbenes, and the Sm−carbene bonds were found to essentially result from carbene-to-metal σ-donation with negligible, if any, “secondary” interactions such as carbene-to-samarium π-donation and chlorine-to-carbene back-donation. Accordingly, the coordination of amino−carbenes to a lanthanide center appears to be almost exclusively driven by their σ-donating properties, which can thereby be estimated and compared to each other. Noticeable variation has been observed between the four model amino−carbene ligands **A**−**D**. Even larger differences may be expected for f-block metals more covalent than samarium, and work is in progress in that direction.

Experimental Section

Computational Details. Sm was treated with a Stuttgart−Dresden pseudopotential in combination with their adapted basis set.[18,19] In all cases, the basis set has been augmented by a set of f polarization functions.[20] Carbon, nitrogen, oxygen, and hydrogen atoms have been described with a 6-31G(d,p) double-ζ basis set.[21] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[22,23] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the extrema (minima) was verified with analytical frequency calculations. All of these calculations were performed with the Gaussian 98[24] suite of programs. The electronic density has been analyzed using the natural bond orbital (NBO) technique.[25]

Acknowledgment. We are grateful to the CNRS, UPS, and French Ministry of Research for financial support of this work. CalMip (CNRS, Toulouse, France) is acknowledged for calculation facilities.

Supporting Information Available: A table giving geometries and energies for the optimized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060924G

---

(18) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123−141.

(19) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431−1441.

(20) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111−114.

(21) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222.

(22) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(23) Burke, K.; Perdew, J. P.; Yang, W. *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum Press: New York, 1998.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

(25) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.