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A samarium cyclooctatetraene complex as catalyst for hydroamination/cyclisation catalysis

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Received (in Cambridge, UK) 16th July 2004, Accepted 31st August 2004
First published as an Advance Article on the web 30th September 2004

DOI: 10.1039/b410918j

The cyclooctatetraene-bis(phosphinimino)methanide complex [{CH(PPh$_2$NSiMe$_3$)$_2$}Sm(η^8-C$_8$H$_8$)] has been prepared; although this compound has no alkyl or amide ligand it shows moderate activity as a catalyst for the hydroamination/cyclisation reaction.

The catalytic addition of an amine R_2N–H bond to alkenes or alkynes (hydroamination) to give nitrogen containing molecules is of great interest for academic and industrial research since most amines are made today in multi-step syntheses. In lanthanide chemistry amido and alkyl metallocene complexes are proved to be efficient catalysts for the hydroamination/cyclisation of primary aminoolefins, allenes and alkynes.[1] Besides the well established metallocenes today a number of non-cyclopentadienyl lanthanide complexes, which are based on amido and alkoxide ligands are known to be active in the hydroamination/cyclisation catalysis.[2–4] The first non-cyclopentadienyl organolanthanide catalyst for the hydroamination/cyclisation reaction was developed by us.[2] In all metallocenes and non-cyclopentadienyl lanthanide catalysts the cyclopentadienyl, amido or alkoxide ligand acts as spectator ligand (L) whereas an alkyl or another amido group (R) plays the role of a leaving group. Thus, all these catalysts have the general formula L_2LnR or $LLnR_2$.[1–4] It was shown that the leaving group R is replaced by the substrate in the initial step of the catalytic reaction. Recently Collin and Trifonov reported that an anionic bis(binaphthyldiamino) ytterbium complex can act as catalyst for the hydroamination/cyclisation reaction.[5] Unfortunately no detailed studies on the mechanism were presented but it seems reasonable that either one of the binaphthyldiamino ligands detaches during the reaction or an ionic mechanism takes place. Based on these observations we were curious to investigate if an uncharged lanthanide complex with no obvious leaving group, which can dissociate from the metal centre, may also act as catalyst for the hydroamination/cyclisation reaction. Therefore, we desired to synthesise a lanthanide complex in which the metal centre is completely shielded by ligands, which could stay attached under catalytic conditions.

Herein we report on a cyclooctatetraene bis(phosphinimino)-methanide complex of samarium, [{CH(PPh$_2$NSiMe$_3$)$_2$}Sm(η^8-C$_8$H$_8$)] (**1**). Compound **1** is obtained by reaction of bis(phosphinimino)methanide samarium dichloride [{CH(PPh$_2$-NSiMe$_3$)$_2$}SmCl$_2$]$_2$[6] with $K_2C_8H_8$ in THF. Compound **1** can also be obtained by reaction of [(η^8-C$_8$H$_8$)SmI(THF)$_3$] with K{CH(PPh$_2$NSiMe$_3$)$_2$}[7] in THF (equation 1).† The solid state structure of complex **1** was established by single crystal X-ray diffraction (Fig. 1). The co-ordination polyhedron is formed by the η^8-co-ordinated cyclooctatetraene ring and the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand. As a result of the steric crowding on the metal centre the Sm–C bond lengths to the eight-membered ring vary over the wide range of 259.4(7) pm–267.5(5) pm (av. 264.8(5) pm).[8] The geometry of the very bulky {CH(PPh$_2$-NSiMe$_3$)$_2$}$^-$ ligand is as expected.[6,7] A six-membered metallacycle (N1–P1–C1–P2–N2–Sm) is formed by chelation of the two trimethylsilylimine groups to the lanthanide atom. The ring adopts a twist boat conformation, in which the central carbon atom and the lanthanide atom are displaced from the N_2P_2 least-square-plane. The distance between the central carbon atom (C9) and the samarium atom (272.4(5) pm) is longer than average Sm–C distances, however a resultant tridentate coordination of the ligand is observed as before.[6,7] Because of the steric crowding on the metal centre the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand is asymmetrically bonded. Thus, the Sm–N2 distance (245.8(7) pm) is significantly shorter than the Sm–N1 distance (253.3(2) pm). As a result of the two sterically demanding ligands the metal centre is completely shielded and no vacant co-ordination site is left for any solvent molecule.

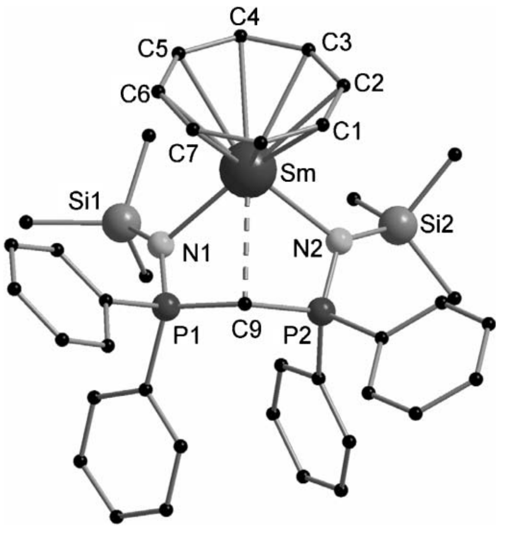
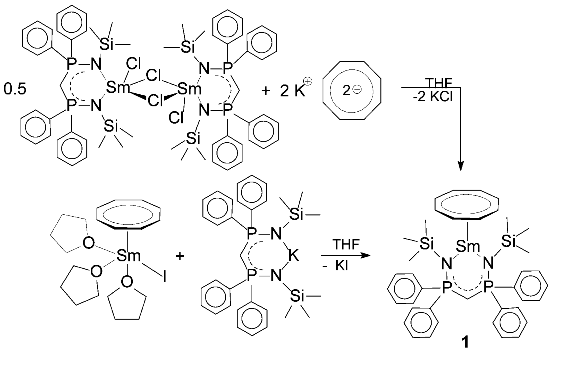


Fig. 1 Solid-state structure of **1**, omitting hydrogen atoms.

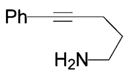
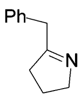
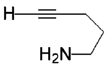
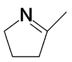
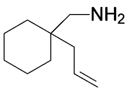
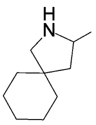
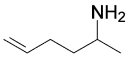
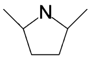


1

(1)

The observed signals in the NMR spectra of **1** are in good agreement with the solid state structure. Due to the paramagnetic samarium centre the NMR signals are shifted over a wide range. Thus, in the ^{1}H NMR spectrum the signal of the cyclooctatetraene ring shows a characteristic broad singlet at δ 10.73 ppm.[8] Compared to diamagnetic {CH(PPh$_2$NSiMe$_3$)$_2$}Ln-compounds the characteristic signal of the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand in the ^{31}P{^{1}H} NMR spectrum (δ 56.1 ppm) shows a significant

Table 1 Hydroamination/cyclisation reaction of terminal aminoolefins and alkynes[a]

Entry	Substrate	Prod.	Cat.	T/°C	Yield (%)[b]	N_t/h^{-1}
1			**1**	20	—	—
2			**1**	120	quant.	0.60
3			**1**[c]	120	quant.	0.33
4			**2**	20	quant.	3.3[d]
5			**1**	120	quant.	1.54
6			**1**	120	44	0.13
7			**1**	120	—	—

[a] 0.6 mmol substrate; 2 mol% of **1**, solvent: C_6D_6 in a *sealed* NMR tube. [b] Determined by ^{1}H NMR. [c] 6 mol% of **1**. [d] Ref. 2*a*.

downfield shift.[6] As a result of these paramagnetic shifts it is easy to judge if the ligand stays attached on to the metal centre during the catalytic reaction.

We have tested compound **1** in the intramolecular hydroamination/cyclisation reaction of terminal aminoolefins and alkynes (Table 1)‡. Since compound **1** has no leaving group it should not be an active catalyst in this reaction. It turned out that one aminoolefin and some aminoalkynes (entries 1–3, 5 and 6) are converted to the cyclic product at elevated temperature. The rigorously anaerobic reaction of the catalysts with dry, degassed aminoolefin and aminoalkyne proceeds regiospecifically. Kinetic studies indicate zero-order behaviour in substrate over a ten-fold concentration range.[1] Running the reaction with high catalyst concentrations in NMR scale shows that neither the bis(phosphinimino)methanide ligand nor the cyclooctatetraene ring is cleaved off from the catalyst. To support these results compound **1** was heated in toluene in the presence of dry *n*-butylamine for seven days. Under these conditions only a slight decomposition of **1** was observed.

Compound **1** cannot compete with the well established metallocene catalysts such as $[(\eta^5\text{-}C_5Me_5)_2YCH(SiMe_3)_2]$ (**2**)[1] (entry 4), but it shows a new mechanistic pathway of the hydroamination/cyclisation reaction. Even a good leaving group seems to increase the rate of the catalysis significantly, the reaction obviously also works in some cases in the absence of such a leaving group. Although we cannot absolutely exclude that a vacant coordination site, which causes the catalytic activity, is generated by some decomposition or some dynamic process within the coordination sphere of **1**, we suggest that compound **1** just weakly polarises the substrate and thus offers a moderate activity.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Notes and references

† *Preparation of 1*: Route A: A solution of 381 mg (0.25 mmol) $[\{CH(PPh_2NSiMe_3)_2\}SmCl_2]_2$ in 10 mL of THF was added to a freshly prepared solution of 0.49 mmol $K_2C_8H_8$ in THF and the mixture was stirred for 18 h at room temperature. The solvent was then evaporated in vacuo and 20 mL of toluene condensed onto the mixture. The mixture was filtered, and the solvent taken off in vacuo. The product was recrystallized from THF/n-pentane (1 : 2). Yield 316 mg (78%), red crystals. Route B: 20 mL of THF was condensed at −196 °C onto a mixture of 200 mg (0.34 mmol) of $K\{CH(PPh_2NSiMe_3)_2\}$ and 185 mg (0.31 mmol) $[(C_8H_8)SmI(THF)_3]$. The mixture was stirred for 18 h at room temperature and filtered. The solvent was then evaporated in vacuo and toluene condensed onto the mixture. The mixture was refluxed for a short period, filtered, and the solvent taken off in vacuo. The product was recrystallized from THF/n-pentane (1 : 2). Yield 211 mg (84%), red crystals. IR (KBr [cm^{-1}]): 3017 (m), 1436 (s), 1260 (s), 1240 (s), 1155 (m), 1107 (m), 985 (s), 919 (s), 843 (m), 748 (m), 690 (m), 616 (s), 589 (s), 559 (s), 515 (s), 505 (m). ^{1}H-NMR (C_6D_6, 250 MHz, 25 °C): δ −0.06 (s, 18H, $SiMe_3$), 3.87 (br, 1H, CH), 6.37–6.43 (m, 4H, Ph), 6.51 (br, 4H, Ph), 6.60–6.66 (m, 2H, Ph), 7.38–7.44 (m, 2H, Ph), 7.62–7.68 (m, 4H, Ph), 9.74 (br, 4H, Ph), 10.73 (br, 8H, C_8H_8) ppm. ^{29}Si-NMR (C_6D_6, 49.7 MHz, 25 °C): δ 4.4 ppm. $^{31}P\{^1H\}$-NMR (C_6D_6, 101.3 MHz, 25 °C): δ 56.1 ppm. EI-MS (70 eV) m/z (%): 813 ([M]$^+$, rel. int. 5), 709 ([M − C_8H_8]$^+$, 100), 543 ($[C_{30}H_{36}N_2P_2Si_2]^+$, 18), 354.5 ([M − C_8H_8]$^{2+}$, 15). $C_{39}H_{47}N_2P_2Si_2Sm$ (812.29): calcd. C 57.67, H 5.83, N 3.45; found C 57.42, H 5.93, N 3.43%.

‡ *General procedure for the hydroamination reaction (NMR scale reaction)*: Compound **1** was weighed under argon gas into an NMR tube. C_6D_6 (~0.7 mL) was condensed into the NMR tube, and the mixture was frozen to −196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before the insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was exactly calculated by comparison of the integrations of the corresponding signals. *Crystal data for 1*: $C_{39}H_{47}N_2P_2Si_2Sm$, M = 812.26, monoclinic, space group $P2_1/n$, a = 1230.50(8) pm, b = 1962.30(13) pm, c = 1565.00(10) pm, β = 99.364(8)°, V = 3728.5(4)10^6 pm^3, T = 203(2) K, Z = 4, μ = 0.938 mm^{-1}, 24303 reflections collected, R1 = 0.0585 for 3378, F > 2 (F), wR2 = 0.1811 for all 7714 data, 421 parameters, all non hydrogen atoms calculated anisotropic; the positions of the H atoms were calculated for idealised positions. The structure was solved and refined using SHELXS-97[9a] and SHELXL-97.[9b] CCDC 242557. See http://www.rsc.org/suppdata/cc/b4/b410918j/ for crystallographic data in .cif or other electronic format.

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