Electronic modification of an aminotroponiminate zinc complex leading to an increased reactivity in the hydroamination of alkenes†

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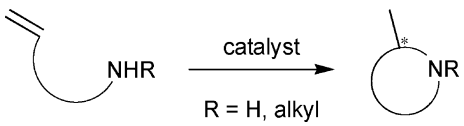
The electronically modified zinc complex 5-phenylsulfanyl-*N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl, [{PhS-ATI(*i*Pr)$_2$}ZnMe], was synthesized. It showed an increased reactivity in the intramolecular hydroamination reaction of non-activated alkenes compared to a previously-reported, non-substituted complex.

Introduction

Organozinc compounds were the first organometallic compounds having a metal to carbon σ-bond.[1] Nevertheless, for a long time organolithium and Grignard reagents were the dominating organometallic reagents in organic synthesis because they show a higher nucleophilic reactivity compared to zinc reagents.[2] About 30 years ago it was realized that the low nucleophilic reactivity of organozinc compounds can be used to prepare functionalized organozinc reagents. Today, numerous catalytic and stoichiometric zinc mediated organic reactions such as the Negishi cross coupling, the Simmons–Smith cyclopropanation, the Reformatsky reaction, the CO_2 epoxide copolymerisation and a number of nucleophlic addition and substitution reactions are known.[3] Recently we introduced organozinc complexes as catalysts for the intramolecular hydroamination reaction, which is the direct addition of N–H bonds to C–C multiple bonds (Scheme 1).[4]

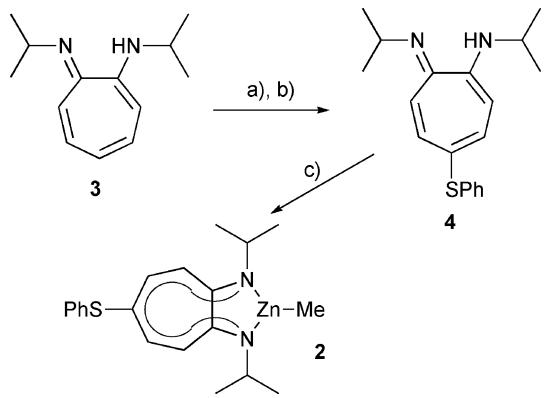


Scheme 1 Intramolecular hydroamination of aminoolefins.

A multitude of metals and catalysts has been employed for this transformation, especially the lanthanides,[4b,c,5] group 4 metals,[5,6] the platinum metals[7] and also calcium[8] and very recently gold.[4a,9] However, most of these catalysts have disadvantages like high prices, toxicity and/or little tolerance towards polar functional groups. As alternative we recently introduced the zinc complex, *N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl (**1**), as a catalyst for the intramolecular hydroamination.[10] This complex possesses interesting advantages compared to other systems: (i) it shows a very high tolerance towards polar functional groups and (ii) it is remarkably stable towards air and moisture. Zinc is also one of the least expensive and non-toxic metals which makes its use in catalysis highly desirable.

Results

In our ongoing research on zinc-catalyzed hydroamination, we first investigated the influence of steric modifications of the alkyl groups at the aminotroponimine ligand.[11] We were able to show the major influence of the steric environment around the zinc atom on both reactivity and stability of the corresponding complexes. In a second project we aimed to increase the activity of aminotroponiminate zinc complexes by changing the electronic properties of the ligand. Thus, we synthesized a series of aminotroponimines with electron donating and withdrawing groups. A series of test reactions revealed that catalyst **2**, bearing a thioether moiety in the 4-position, was superior to all other investigated catalysts. The corresponding ligand **4** was prepared in a two-step procedure from the known ligand **3** (Scheme 2).[12] Following the literature procedure, bromination occurred selectively in the 5-position giving the bromoarene in high yield.[13] Nucleophilic displacement



Scheme 2 Reagents and conditions: (a) Br_2, CH_2Cl_2, 0 °C to RT, 1 h, 90%; (b) PhSH, K_2CO_3, DMF, 70 °C, 16 h, 99%; (c) $ZnMe_2$ (1.7 eq.), toluene, RT, 3 h, 88%.

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† CCDC reference numbers 653787. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719120k Electronic supplementary information (ESI) available: Complete spectral data of the complex and its precursors, complete spectral data of the obtained products and experimental procedure of the hydroamination. See DOI: 10.1039/b719120k

proceeded smoothly and delivered the desired ligand **4** in an overall yield of 89% from **3**. The synthesis of the zinc complex **2** was equally high yielding when the ligand was reacted with $ZnMe_2$ in toluene. Compound **2** was also characterized by single crystal X-ray diffraction analysis (Fig. 1). It is a monomer in the solid state with two molecules in the unit cell, and hence, the zinc atom displays a trigonal planar geometry. Bond lengths and angles are in the expected range. Comparison with **1** shows that there are no major structural differences.

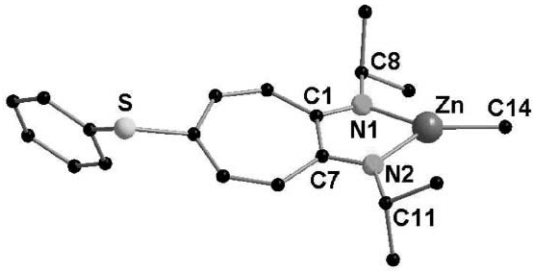


Fig. 1 Perspective view of the molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected distances [pm] and angles [°]: Zn–N1 198.79(14), Zn–N2 199.04(14), Zn–C14 194.8(2); Zn–N1–C1 113.69(10), Zn–N1–C8 124.97(10), Zn–N2–C7 114.42(11), Zn–N2–C11 124.42(11), N2–Zn–C14 139.64(8), N1–Zn1–C14 137.18(8), N1–Zn–N2 81.52(5).

The new catalyst **2** was then compared with the first generation catalyst **1** in a series of test reactions in the hydroamination of non-activated olefins bearing different functional groups (Table 1).

The reactions were carried out at 80 °C in benzene-d_6 with a catalyst loading of 2.5 mol% and 2.5 mol% of $[PhNMe_2H][B(C_6F_5)_4]$.[14] The isolated yields were around 90% or more in all the investigated cases. Entries 1–3 show the tremendous effect of incorporating donating groups in the substrates. The cyclization of **5a** was accomplished within 40 min instead of 95 min when the new catalyst **2** was used. Oxygenated furan derivative **6a** took 4 h to reach complete conversion with complex **2** and 6 h with catalyst **1**. Finally, the reaction time for the tosylated pyrrole **7a** was reduced from 4 d to 24 h by applying the new catalyst **2**. An acceleration of the reaction rate was also observed in the case of substrate **8a**, bearing a geminal disubstituted double bond. In this case, the reaction time could be reduced to about one third with catalyst **2**. The strained norbornene derivatives **9a** and **10a** selectively reacted at the terminal double bond. In the case of **9a**, cyclisation took place within 2 h with the new catalyst **2**, instead of 30 h with catalyst **1**. The time for the cyclisation of indole derivative **10a** was nearly halved with the new catalyst. Using **2**, cyclohexane derivative **11a** completely cyclised within 2 h, whereas the same compound needed 4.5 h with catalyst **1**. The reaction time for the 1,3-dithiane **12a** was reduced from 20 d with complex **1** to seven days with catalyst **2**.

Conclusions

In conclusion, we have reported the synthesis of a novel, substituted aminotroponimine ligand **4**, its complexation to zinc and the catalytic activity of the corresponding zinc complex **2**. We have demonstrated that electronic modifications of the ligand can have a high, positive impact on the catalytic activity of the zinc complex. We suppose that the thioether moiety at the backbone of the ligand acts as a donor substituent and therefore increases the electron density at the nitrogen and the zinc atoms. This effect seems to increase the stability of the chelate and also renders the zinc atom more reactive. The new catalyst **2** is easily prepared in high yields from a well-known aminotroponimine and showed higher reactivity and stability in solution. These findings make the new catalyst **2** superior to the first generation catalyst **1** and will potentially enhance the use of zinc complexes for the catalytic hydroamination.

Experimental

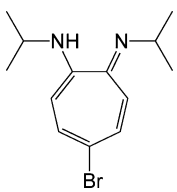
I General

^1H and ^{13}C-NMR spectra were recorded on a Bruker DRX 500 spectrometer at 353 or 298 K using the deuterated solvent as a lock and residual solvent peak as the internal reference. MS and HRMS were recorded on a Finnigan MAT 95 SQ spectrometer. IR spectra were measured on a Nicolet FT-IR 750 spectrometer. Elemental analyses were carried out with an Elementar vario EL or EL III. All reactions were, unless otherwise stated, carried out using standard Schlenk and glovebox techniques under an atmosphere of nitrogen. $[PhNMe_2H][B(C_6F_5)_4]$ was purchased from Strem. $ZnMe_2$ was obtained from Aldrich. Benzene-d_6 was dried over 4 Å molecular sieves. Aminoalkenes were prepared using modified literature procedures from commercially available starting materials from Aldrich, Acros Organics and Fluka. Prior to use, all substrates were purified either by distillation or recrystallization.

II General procedure for NMR-tube scale intramolecular aminoalkynes hydroamination

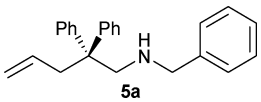
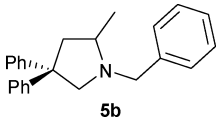
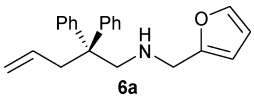
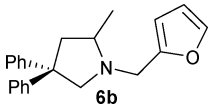
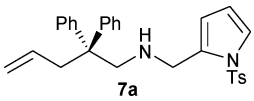
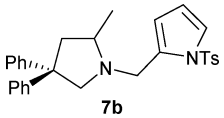
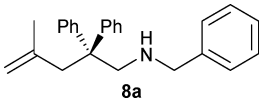
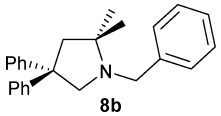
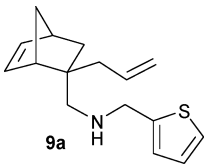
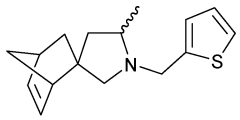
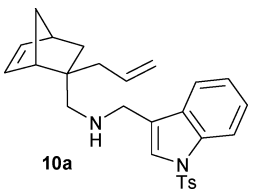
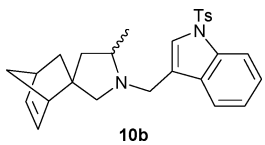
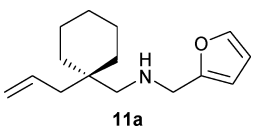
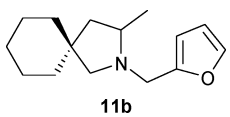
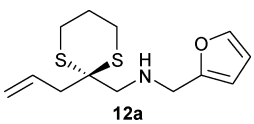
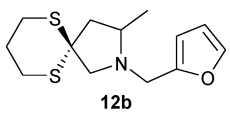
A predried NMR-tube was charged with the aminoalkene (430 μmol). A solution of **2** (5 mg, 11 μmol, 2.5 mol%) and $[PhNMe_2H][B(C_6F_5)_4]$ (9 mg, 11 μmol, 2.5 mol%) in 0.5 mL C_6D_6 was added under a nitrogen athmosphere. The NMR-tube was flame sealed under vacuum. The reaction mixture was then heated to 80 °C for the stated duration of time. The reaction progress was monitored by ^1H NMR. When the reaction was judged to be completed, the crude reaction mixture was directly subjected to column chromatography on silica. All products were analysed by ^1H, ^{13}C, ^{13}C-DEPT, IR, MS, HRMS. The NMR yields were determined by comparing the integration of a well-resolved signal for the starting material with a well-resolved signal for the heterocyclic product.

III Characterisation of new ligands and the catalysts



(4-Bromo-7-isopropyliminocyclohepta-1,3,5-trienyl)isopropylamine. A 250 mL flask was charged with H-ATI(iPr)$_2$H[15] (7.01 g, 34.4 mmol). 50 mL of CH_2Cl_2 were added and the solution was cooled to 0 °C. A solution of bromine (1.8 mL, 35.1 mmol) in

Table 1 Comparison of the reactivity of the new catalyst **2** with the first generation catalyst **1**[a]

		[{ATI(*i*Pr)$_2$}ZnMe] (**1**)		[{PhS-ATI(*i*Pr)$_2$}ZnMe] (**2**)		
Entry	Substrate	Time	Conversion	Time	Conversion	Product
1	 **5a**	95 min	Quant.[b]	40 min	Quant.[b] 93%[c]	 **5b**
2	 **6a**	6 h	Quant.[b]	4 h	Quant.[b] 96%[c]	 **6b**
3	 **7a**	96 h	95%[b]	24 h	96%[b] 87%[c]	 **7b**
4	 **8a**	20 d	86%[b]	7 d	Quant.%[b] 90%[c]	 **8b**
5	 **9a**	30 h	93%[b]	2 h	98%[b] 96%[c]	 **9b**
6	 **10a**	20 h	Quant.[b]	12 h	Quant.[b] 94%[c]	 **10b**
7	 **11a**	4.5 h	Quant.[b]	2 h	Quant.[b] 92%[c]	 **11b**
8	 **12a**	20 d	88%	7 d	96%[b] 89%[c]	 **12b**

[a] Reagents and conditions: substrate (430 μmol), catalyst (2.5 mol%), [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (2.5 mol%), C$_6$D$_6$, 80 °C. [b] Determined by ^{1}H NMR. [c] Isolated yield

20 mL of CH_2Cl_2 was added over 15 minutes. In the meantime the colour changed from bright yellow to brown. The solution was stirred for another 30 minutes at 0 °C and then warmed to rt and stirred for further 15 minutes. Then 20 mL of a 2 N NaOH solution were added and the biphasic solution was transferred into a seperatory funnel. The aqueous phase was

extracted with CH_2Cl_2 (2 × 15 mL). The combined organic phases were then washed with brine (20 mL) and dried over $MgSO_4$. The crude product could either be purified by recrystallization from ethanol or by column chromatography on silica (hexanes–TBME 2 : 1). The product was obtained as yellow, fluffy crystals (8.75 g, 30.9 mmol, 90%).

^{1}H-NMR. ($CDCl_3$, 400 MHz): δ (ppm) = 1.23 (d, J = 6.3 Hz, 12 H); 3.77 (sept., J = 6.3 Hz, 2 H); 6.03 (d, J = 12.2 Hz, 2 H); 6.92 (d, J = 12.2 Hz, 2 H); 7.63 (bs, 1 H, NH).

^{13}C-NMR. ($CDCl_3$, 100 MHz): δ (ppm) = 22.8; 46.1; 108.7; 109.7 134.8; 150.5 (C_q).

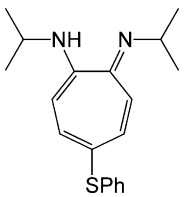
IR. (ATR): ν (cm^{-1}) = 3498 (br w); 3126 (w); 2967 (vs); 2925 (m); 2887 (w); 2865 (m); 2655 (w); 1943 (w); 1902 (w); 1853 (w); 1708 (m); 1581 (s); 1535 (s); 1512 (vs); 1467 (s); 1438 (s); 1383 (s); 1375 (s); 1364 (s); 1353 (s); 1322 (w); 1298 (m); 1260 (m); 1230 (m); 1171 (s); 1133 (m); 1124 (m); 1093 (w); 1075 (m); 1004 (w); 947 (w); 879 (w); 849 (w); 810 (s); 747 (m); 719 (m); 679 (m); 673 (m).

MS. (EI, 70 eV): m/z (%) = 284 [M^+; ^{81}Br] (56); 282 [M^+; ^{79}Br] (56); 269 (74); 267 (74); 241 (96); 239 (100); 227 (20); 226 (24); 225 (33); 224 (31); 212 (23); 211 (43); 210 (29); 209 (45); 184 (17); 182 (17); 146 (18); 145 (34); 144 (17); 131 (23); 130 (22); 119 (17); 118 (33); 103 (21); 92 (17); 91 (25); 90 (33); 98 (15); 78 (15); 77 (17); 76 (17); 63 (19).

HRMS. $C_{13}H_{19}BrN_2$ calc.: 282.0732 found: 282.0732

Elemental analysis. Calc.: C: 55.13% H: 6.76% N: 9.89% found: C: 54.89% H: 6.67% N: 9.67%

Melting point. 94 °C (EtOH)



Isopropyl-(7-isopropylimino-4-phenylsulfanylcyclohepta-1,3,5-trienyl)amine (4). A 10 mL flask was charged (4-bromo-7-isopropyliminocyclohepta-1,3,5-trienyl)isopropylamine (282 mg, 1.00 mmol), K_2CO_3 (701 mg, 5.07 mmol) and 3 mL of DMF. Thiophenol (115 µl, 1.12 mmol) was added in one portion and the solution was stirred at 70 °C overnight. The suspension was then cooled to rt and poured on a biphasic mixture of water and TBME (1 : 1, 40 mL). The aqueous phase was extracted with TBME (2 × 20 mL). The combined organic phases were washed with water and brine (30 mL). After evaporating the solvents, the crude product could either be purified by recrystallization from ethanol or by column chromatography on silica (hexanes–TBME 2 : 1). The product was obtained as yellow needles (315 mg, 998 µmol, 99%).

^{1}H-NMR. ($CDCl_3$, 400 MHz): δ (ppm) = 1.25 (d, J = 6.0 Hz, 12 H); 3.82 (sept., J = 6.0 Hz, 2 H); 6.20 (d, J = 12.4 Hz, 2 H); 6.99 (d, J = 12.0 Hz, 2 H); 7.07–7.12 (m, 1 H); 7.15–7.27 (m, 4 H); 7.70–7.95 (br s, 1 H, NH).

^{13}C-NMR. ($CDCl_3$, 100 MHz): δ (ppm) = 22.9; 46.1, 109.0, 118.1 (C_q); 125.1; 127.0; 128.8; 139.4; 140.1 (C_q); 151.4 (C_q).

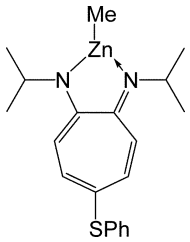
IR. (ATR): ν (cm^{-1}) = 3195 (w); 3070 (w); 3056 (w); 2966 (m); 2928 (w); 2867 (w); 1578 (s); 1536 (s); 1511 (s); 1478 (s); 1453 (m); 1437 (s); 1386 (s); 1366 (m); 1351 (m); 1326 (w); 1301 (w); 1263 (m); 1235 (m); 1174 (s); 1121 (w); 1077 (w); 1042 (w); 1024 (m); 998 (w); 962 (w); 949 (w); 891 (w); 847 (w); 813 (m); 738 (m); 690 (m).

MS. (EI, 70 eV): m/z (%) = 312 [M^+] (41); 298 (5); 297 (23); 271 (6); 270 (18); 269 (100); 253 (5); 240 (5); 239 (21); 212 (5).

HRMS. $C_{19}H_{24}N_2S$ calc.: 312.1660 found: 312.1662

Elemental analysis. calc.: C: 73.03% H: 7.74% N: 8.97% found: C: 72.84% H: 7.76% N: 9.32%

Melting point. 99 °C (EtOH)



5-Phenylsulfanyl-*N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl (2). A solution of **4** (0.20 g, 0.64 mmol) in 15 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene; 1 mL, 1.2 mmol) in 15 mL of toluene. The solution was stirred at rt for 3 h. The reaction was completed when the gas evolution had stopped. All volatiles were removed under reduced pressure and the yellow residue was washed twice with pentane (5 mL). Recrystallisation from toluene at −30 °C gave the product as yellow crystals (0.22 g, 0.56 mmol, 88%)

^{1}H-NMR. ($CDCl_3$, 500 MHz): δ (ppm) = −0.03 (s, 3 H); 1.08 (d, J = 6.3 Hz, 12 H); 3.63 (sept., J = 6.3 Hz, 2 H); 6.34 (d, J = 12.1 Hz, 2 H); 6.89 (t, J = 7.3 Hz, 1 H), 7.01 (m, J = 7.9 Hz, 2 H); 7.32 (d, J = 7.3 Hz, 2 H); 7.42 (d, J = 12.1, 2 H).

^{13}C-NMR. ($CDCl_3$, 125 MHz): δ (ppm) = −10.1, 24.0, 48.2, 110.6, 119.0, 125.2, 126.5, 128.2, 129.0, 142.1, 159.7;

MS. (EI, 70 eV): m/z (%) = 390 [M^+] (89); 375 (62); 312 (21); 295 (100); 281 (25); 269 (56); 253(44); 239 (26).

Elemental analysis. calc.: C : 61.30% H : 6.69% N : 7.15% S : 8.18% found: C : 60.78% H : 7.08% N : 7.05% S: 21%

X-Ray crystallographic studies of 2†

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −73 °C cold stream of STOE IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium Core2Duo PC.

Crystal data for 2. $C_{20}H_{26}N_2SZn$, M = 391.86, triclinic, space group P-1, a = 978.20(8) pm, b = 1028.33(9) pm, c = 1125.87(9) pm, α = 106.262(7), β = 97.856(7), γ = 112.659(7)°, V = 964.31(14) pm^3, T = 200(2) K, Z = 2, μ = 1.385 mm^{-1}, 6896 reflections collected, 3364 unique, $R1$ = 0.0235 ($I > 2\sigma(I)$), $wR2$ = 0.0599 for all 3364 data, 222 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 and SHELXL-97.[16]

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