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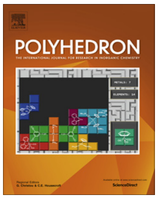

1,3,5-Triazapentadienyltin(II) complexes and the additional reaction of phenylamine with *N,N'*-diisopropylcarbodiimide

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ABSTRACT

A series of tin(II) complexes **2**–**5** bearing 1,3,5-triazapentadienyl ligands are reported: $Sn[N(Ph)C(R')NC(R')N(SiMe_3)]_2$ [R' = 1-piperidino, **2**; NMe_2, **3**], $[N(Ph)C(NMe_2)NC(NMe_2)N(H)]SnCl$ (**4**) and $[\{N(SiMe_3)C(R')NC(R')N\}_2Sn_2]_2$ (R' = 1-piperidino) (**5**). Their single-crystal X-ray diffraction studies are presented. Compounds **3** and **4** are efficient catalysts for the catalytic addition of phenylamine to *N,N'*-diisopropylcarbodiimide giving guanidine.

1. Introduction

As the counterparts of β-diketimate anions, 1, 3, 5-triazapentadienyl anions, as ancillary ligands in organometallic chemistry, also own similar attractive features [1–6]. Their transition metal complexes [7–15], some main group lithium, thallium [16–18] metal complexes and silicon fluoride $\mathbf{L}SiF_2$ ($\mathbf{L} = NC(NMe_2)NC(NMe_2)NAr$, Ar = 2,6-$^iPr_2C_6H_3$) [19] have been reported.

Tin(II) complexes with nitrogen ligands have been prepared, e.g. β-*N*-functionalized tin(II) alkyls SnRX (R = $C(SiMe_3)_2C_5H_4N$-2, and X = R, Cl or $N(SiMe_3)_2$ [20], the tin(II) primary amido derivatives $Sn_2\{N(H)Dipp\}_4$ and $Sn_2\{N(H)Dipp\}_3Cl$ [21], chloro- and azido-tin(II) 1,5-diazapentadienyls [22,23], tin(II) 1-azaallyls [24], and tin(II) benzamidinates [25–27]. The tin(II) poly(pyrazolyl)borates $[H_2B(pz)_2]SnCl$ and $[B(pz)_4]_2Sn$ have also been reported [28]. However, tin(II) 1, 3, 5-triazapentadienyl complexes have not been involved.

Our group presented the synthesis and characterization of magnesium(II) and aluminum complexes supported by 1,3,5-triazapentadienyl ligands [29,30], and their zinc complexes could be used as catalyst in the ring-opening polymerization of *rac*-lactide [30]. As a continuation, exploitation of other metal complexes including tin(II) complexes of these ligands and their application is certainly required.

Construction of C—N bonds and formation of guanidines by catalytic addition of amines and carbodiimides have been paid a great attention for the straightforward and atom-economic preparation of substituted guanidines, which represent an essential functionality in many biologically and pharmaceutically relevant compounds [31,32]. Some divalent lanthanide complexes and half-sandwich yttrium complex were proved to be excellent catalysts for this transformation [33,34]. The lanthanide aryloxides supported by a bridged-amidinate [35], or by a β-diketimate ligand [36], as well as the phenylene-bridged β-ketoiminate dilanthanide aryloxides [32] are also efficient catalysts for this purposes. Herein we describe the isolation of a novel group of tin(II) 1,3,5-triazapentadienyl complexes: $Sn[N(Ph)C(R')NC(R')N(SiMe_3)]_2$ [R' = 1-piperidino, **2**; NMe_2, **3**], $[N(Ph)C(NMe_2)NC(NMe_2)N(H)]SnCl$ (**4**), and $[\{N(SiMe_3)C(R')NC(R')N\}_2Sn_2]_2$ (R' = 1-piperidino) (**5**). The catalytic activity of **3** and **4** as catalysts in the addition reaction of phenylamine to *N,N'*-diisopropylcarbodiimide has been evaluated.

2. Experimental

2.1. General procedures

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were purchased from commercial sources. Deuterated solvent $CDCl_3$ was dried over activated molecular sieves (4 Å) and vacuum transferred before use. Diethyl ether was dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. Glassware was

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oven-dried at 150 °C overnight. The NMR spectra were recorded on Bruker DRX-300 spectrometer and recorded in $CDCl_3$. The chemical shifts are reported in δ values in ppm relative to external $SiMe_4$ for ^1H and ^{13}C and $SnMe_4$ for ^{119}Sn. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were carried out using a Vario EL-III analyzer (Germany).

2.2. Synthesis and characterization

2.2.1. $Sn[N(Ph)C(R')NC(R')N(SiMe_3)]_2$ (R′ = 1-piperidino) (2)

1-Piperidinocarbonitrile (0.57 mL, 4.9 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.42 g, 2.45 mmol) in Et_2O (30 mL) at –78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $SnCl_2$ (0.23 g, 1.22 mmol) was added at –78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred for 24 h and filtered. The filtrate was concentrated *in vacuo* to *ca.* 20 mL and cooled at −25 °C for 1 d, yielding colorless crystals of **2** (0.52 g, 48%). MP:126–128 °C. *Anal.* Calc. for $C_{42}H_{68}N_{10}Si_2Sn$: C, 56.81; H, 7.72; N, 15.77. Found: C, 57.03; H, 7.80; N, 15.61%. ^1H NMR ($CDCl_3$): δ −0.06, −0.01, 0.09 (3s, 18H, $SiMe_3$), 1.16–1.58 (m, 24H, CH_2), 2.75–3.48 (m, 16H, CH_2), 6.82–7.30 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 1.09, 2.66, 3.34 ($SiMe_3$), 25.2, 26.2, 26.6 (CH_2), 46.8, 49.3 (NCH_2), 120.6 (*p*-*C*Ph), 123.1, 123.7 (*m*-*C*Ph), 128.6, 129.0 (*o*-*C*Ph), 151.9 (*C*ipso-Ph), 156.4, 158.0 (N*C*N). ^{119}Sn NMR ($CDCl_3$): δ −593.5.

2.2.2. $Sn[N(Ph)C(NMe_2)NC(NMe_2)N(SiMe_3)]_2$ (3)

$(CH_3)_2NCN$ (0.44 mL, 5.48 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.47 g, 2.74 mmol) in Et_2O (30 mL) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $SnCl_2$ (0.26 g, 1.37 mmol) was added at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred for 24 h and filtered. The filtrate was concentrated *in vacuo* to *ca.* 15 mL and cooled at −25 °C for 1 d, yielding colorless crystals of **3** (0.52 g, 52%). Mp:100–102 °C. *Anal.* Calc. for $C_{30}H_{52}N_{10}Si_2Sn$: C, 49.52; H, 7.20; N, 19.25. Found: C, 49.88; H, 7.65; N, 19.02%. ^1H NMR ($CDCl_3$): δ 0.26, 0.41, 0.45 (3s, 18H, $SiMe_3$), 2.68, 2.99, 3.25, 3.41 (4s, 24H, $N(CH_3)_2$), 6.98–7.54 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ −0.69, 1.48, 3.03 ($SiMe_3$), 39.0, 39.8, 40.5, 41.1 (NMe), 122.4 (*p*-*C*Ph), 124.7, 124.9 (*m*-*C*Ph), 129.8, 130.6 (*o*-*C*Ph), 151.4 (*C*ipso-Ph), 160.7, 164.3 (N*C*N). ^{119}Sn NMR ($CDCl_3$): δ −561.1.

2.2.3. $[N(Ph)C(NMe_2)NC(NMe_2)N(H)]SnCl$ (4)

$(CH_3)_2NCN$ (0.38 mL, 4.67 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.40 g, 2.34 mmol) in Et_2O (30 mL) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $SnCl_2.2H_2O$ (0.53 g, 2.34 mmol) was added at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred for 12 h. The pale yellow mixture was filtered. The filtrate was concentrated *in vacuo* to *ca.* 10 mL and left at room temperature for several days to give colorless block crystals of **4** (0.89 g, 79%). Mp: 136–138 °C. *Anal.* Calc. for $C_{12}H_{18}ClN_5Sn$: C, 37.29; H, 4.69; N, 18.12. Found: C, 37.01; H, 4.65; N, 17.98%. ^1H NMR ($CDCl_3$): δ 2.77, 3.04 (d, 12H, $N(CH_3)_2$), 5.3 (s, ^1H, NH), 6.87–7.22 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 38.9, 40.2 (d, $N(CH_3)_2$), 122.1 (*p*-*C*Ph, *m*-*C*Ph), 130.3 (*o*-*C*Ph), 149.3 (C_{ipso}), 159.1, 161.2 (N*C*N). ^{119}Sn NMR ($CDCl_3$): δ −258.6.

2.2.4. $[N(Ph)C(NMe_2)NC(NMe_2)N(H)]SnCl$ (4′)

$(CH_3)_2NCN$ (0.45 mL, 5.60 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.49 g, 2.80 mmol) in Et_2O (30 mL) at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred overnight. $SnCl_2$ (0.53 g, 2.80 mmol) was added at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred for 12 h, and then filtered. The filtrate was concentrated *in vacuo* and left at room temperature for four days to give colorless block crystals of **4′** (0.36 g, 33%). Mp: 132–134 °C.

2.2.5. $[\{N(SiMe_3)C(R')NC(R')NH\}_2Sn_2]_2$ (R′ = 1-piperidino) (5)

1-Piperidinecarbonitrile (0.46 mL, 4.00 mmol) was added to a solution of $LiN(SiMe_3)_2$ (0.334 g, 2.00 mmol) in Et_2O(30 mL) at −78 °C. The resulting mixture was warmed to *ca.*25 °C and stirred overnight. $SnCl_2$ (0.20 g, 1.06 mmol) was added at −78 °C. The resulting mixture was warmed to *ca.* 25 °C and stirred for 24 h, then filtered. The filtrate was concentrated to give colorless crystals of **5** (0.19 g, 42%). Mp:113–115 °C. *Anal.* Calc. for $C_{60}H_{116}N_{20}Si_4Sn_4$: C, 42.27; H, 6.86; N, 16.43. Found: C, 41.97; H, 6.65; N, 16.22%. ^1H NMR ($CDCl_3$): δ 0.02–0.25 (m, 36H, $SiMe_3$), 1.16–1.56 (m, 48H, $(CH_2)_3$), 3.13–3.67 (t, 32H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 1.97–3.49 ($SiMe_3$), 25.13 ($(CH_3)_2$), 27.61 ($(CH_3)_2$), 46.26 (NCH_2), 49.29 (NCH_2), 159.48 (N*C*N), 164.19 (N*C*N).

2.2.6. X-ray crystallography

Data collection of **2**–**5** was performed with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer using the omega scan mode yielding a total of *N* reflections. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. Corrections were applied for Lorentz and polarization effects as well as absorption using multi-scans (SADABS) [37]. The structure was solved by the direct method (SHELXS-97) [38]. The remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites, using riding modes (SHELXTL) [39]. Crystal data and details of data collection and refinements for **2**–**5** are summarized in Table 1. Selected bond distances and bond angles are listed in Tables 2–4. CCDC (reference numbers 791258-**2**, 791257-**3**, 816129-**4**, 1059848-**4′**, 816128-**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

3. Results and discussion

The 1,3,5-triazapentadienyl ligands were prepared according to the literature procedures [14,29]. The reactions of corresponding ligands and anhydrous $SnCl_2$ at the ratio of 2:1 at low temperature led to the formation of **2** and **3**. Compound **4** was obtained by treatment of the ligand with $SnCl_2{\bullet}2H_2O$ at the ratio of 1:1 in diethyl ether. Small amount of crystals of **4′**, a polymorph of **4** were isolated in the related 1: 1 reaction of ligand: $SnCl_2$ carried out in Et_2O. **4′** was identified solely by its X-ray structure. Reaction of a 1:1 ratio of the ligand with $SnCl_2$ in diethyl ether solution yielded **5**, with the elimination of LiCl and Me_3SiCl. It is noteworthy that the 1,3,5-triazapentadienate ligand in **5** is dianionic; because of the absence of one $SiMe_3$ group, the ligands formed aggregates leading to the tetramer **5**. The dianionic feature of the 1,3,5-triazapentadienate ligand was also found in its silicon fluorides [29] (Scheme 1).

The ^1H NMR spectrum of **3** in $CDCl_3$ at ambient temperature shows the methyl protons of the $N(CH_3)_2$ as four singlets at δ = 2.68, 2.99, 3.25, 3.41, and the corresponding carbon atoms caused the appearance of four signals at δ = 39.0, 39.8, 40.5, 41.1. The phenyl carbon atoms showed six signals at δ = 122.4, 124.7, 124.9, 129.8, 130.6 and 151.4. The methylsilyl protons gave rise to three distinct signals at δ = 0.26, 0.41 and 0.45, corresponding to the three $^{13}C\{^1H\}$ NMR signals of the methylsilyl carbon atoms at −0.69, 1.48, 3.03. The ^1H NMR and ^{13}C NMR spectra of **2** were essentially similar to those of **3**, suggesting very similar solution structures. The shielding of $Si(CH_3)$ groups may have been caused by restricted rotation of $Si(CH_3)_3$ due to the neighboring NMe_2 or