Bridged Aminotroponiminate Complexes of Zinc

Michael T. Gamer[a] **and Peter W. Roesky***[a]

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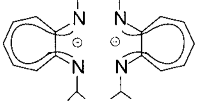
Reactions of the *n*-propyl-bridged diaminotroponimine $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ with dialkylzinc compounds in toluene lead, depending on the stoichiometric ratio, either to dimetallic singly bridged products of composition $[(\mathrm{RZn})_2\{(i\mathrm{Pr})\mathrm{TP}\}]$ [R = Me (**1**), Et (**2**)] or to dimetallic doubly bridged helical products of composition $[\mathrm{Zn}\{(i\mathrm{Pr})\mathrm{TP}\}]_2$ (**3**). Compound **3**, which was characterised by single-crystal diffraction methods, is the first bridged aminotroponiminate complex in which a helical structure is observed.

Introduction

Aminotroponiminates ($\{\mathrm{ATI}\}^-$) are bidentate, monoanionic ligands containing a 10π-electron backbone. Like 1,4-diazabutadiene, $\{\mathrm{ATI}\}^-$ forms five-membered metallacycles upon coordination to a metal atom. In contrast to 1,4-diazabutadiene, however, $\{\mathrm{ATI}\}^-$ is believed to be much more resistant to electrophiles and nucleophiles. The ligand system was introduced into the coordination chemistry in the 1960s mostly by researchers at DuPont. Between 1961 and 1970 a large number of $\mathrm{Mn^{II}}$, $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, and $\mathrm{Ni^{II}}$ complexes were prepared in order to study the magnetic moments and NMR contact shifts; only one Mn complex was characterised by single-crystal X-ray methods. This early work was reviewed by Holm in 1971.[1]

Recent reports from us and other research groups have described the preparation and characterisation of aminotroponiminates as cyclopentadienyl alternatives for main group and transition elements.[2] We have shown that bis(aminotroponiminate)yttrium amides are active as catalysts for hydroamination/cyclisation catalysis.[3] Recently we started to prepare singly bridged aminotroponiminates.[4] It was shown that the trimethylene-bridged ligand 1,3-bis[2-(isopropylamino)troponiminate]propane ($\{(i\mathrm{Pr})\mathrm{TP}\}^{2-}$) (**A**) ($[H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ = trimethylenedinitrilobis[2-(isopropylamino)cyclohepta-2,4,6-triene]) is able to coordinate in a chelating or a metal-bridging mode to various metals of group 13 and the lanthanides.[4,5,6] Up to now $\{(i\mathrm{Pr})\mathrm{TP}\}^{2-}$ has only been treated with trivalent metals. In most cases a chelating coordination mode was observed with these metal centres. A metal−metal bridging mode has only been observed in those cases in which a chelating coordination mode is prevented due to steric reasons, for example $[(\mathrm{R_2Al})_2\{(i\mathrm{Pr})\mathrm{TP}\}]$ (R = Me, Et, *i*Bu).[6] We are interested in extending our research to the divalent metal zinc. To the best of our knowledge no zinc complexes of singly bridged aminotroponiminates are known. In contrast, two zinc complexes with non-bridged aminotroponiminate, which were structurally not characterised, have been reported by Holm[7] and Lippard;[8] some tropocoronand complexes are also known.[9]

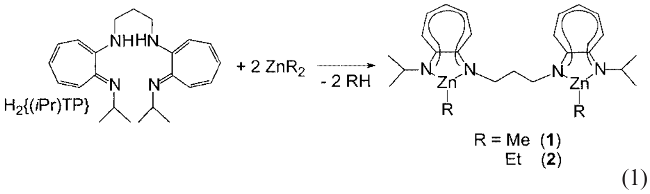
Herein we report on the reaction of $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ with dialkylzinc compounds which lead exclusively to metal-bridging products. Depending on the stoichiometry either singly or doubly bridged helical products were obtained.



A

Results and Discussion

The dimetallic zinc complexes $[(\mathrm{RZn})_2\{(i\mathrm{Pr})\mathrm{TP}\}]$ [R = Me (**1**), Et (**2**)] were synthesised by reaction of the neutral ligand $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$[4] with the corresponding dialkylzinc compounds $\mathrm{R_2Zn}$ in *n*-pentane [Equation (1)]. Upon cooling, **1**−**2** were obtained as yellow crystalline solids with a fairly high sensitivity towards air and moisture.



(1)

The reactivity of $\mathrm{ZnMe_2}$ towards $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ is much higher than that of $\mathrm{ZnEt_2}$. Compound **2** was synthesised by addition of $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ to a solution of $\mathrm{ZnEt_2}$ in toluene

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[a] Institut für Chemie, Freie Universität Berlin,
Fabeckstraße 34−36, 14195 Berlin, Germany

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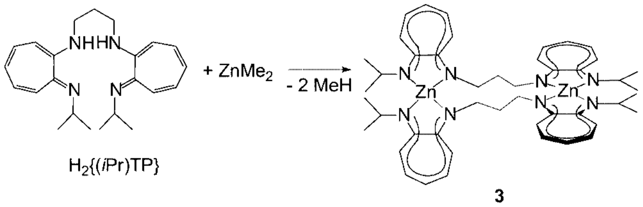
at room temperature. In contrast, compound **1** was only obtained in high yields when performing the reaction at −50 °C. At room temperature the same reaction sequence leads to a mixture of **1** and higher substituted products such as $[Zn\{(i\text{Pr})TP\}]_2$ (**3**) (see below). The new complexes were characterised by standard analytical/spectroscopic techniques. The ^1H and ^{13}C NMR spectra also point to a symmetrical coordination of the $\{(i\text{Pr})TP\}^{2-}$ anion in solution. The signals of the isopropyl C*H* proton of **1** and **2** are well-resolved into a septuplet and show only a slight downfield shift [δ = 3.74 (**1**), 3.74 (**2**) ppm] compared to that of the free ligand $H_2\{(i\text{Pr})TP\}$ (δ = 3.55 ppm).[4] This is in agreement with comparable alkyllanthanide compounds of composition $[\{(i\text{Pr})TP\}LnR]$ [Ln = La, Lu; R = $CH(SiMe_3)_2$, CH_2SiMe_3] in which the isopropyl C*H* signal is also shifted downfield {δ = 3.67 ppm $[\{(i\text{Pr})TP\}_2LaCH(SiMe_3)_2]$,[4] δ = 3.93 ppm $[\{(i\text{Pr})TP\}_2LuCH_2SiMe_3]$}.[10] In contrast, the signals of the isopropyl C*H* in the comparable aluminium complexes $[(R_2Al)_2\{(i\text{Pr})TP\}]$ (R = Me, Et, *i*Bu) are shifted to higher field (δ = 3.50−3.54 ppm). For **1** and **2** sharp signals for the Zn−Me and Zn−Et groups, respectively, are observed in the ^1H NMR spectra (δ = −0.07 (**1**); 0.74, 1.58 (**2**) ppm] and in the $^{13}C\{^1H\}$ NMR spectra [δ = −10.8 (**1**); 3.0, 13.8 (**2**) ppm]. The signals of the $Zn-CH_3$ and $Zn-CH_2$ groups, respectively, are in general shifted to higher field than those of the starting material $ZnMe_2$ (^1H: δ = 0.51 ppm; $^{13}C\{^1H\}$: δ = −4.2 ppm)[11] and $ZnEt_2$ (^1H: δ = 0.08, 1.05 ppm;[12] $^{13}C\{^1H\}$: δ = 6.82, 10.35 ppm).[13]

The formation of **1** and **2** is in contrast to our previous observation of the coordination behaviour of the $\{(i\text{Pr})TP\}^{2-}$ anion. In group-3, group-13 and lanthanide chemistry the ligand always adopts a chelating coordination mode, if this is possible, for steric reasons. Since non-bridged diaminotroponiminate complexes of zinc are known,[7] we initially expected a chelating coordination of the ligand. To study the reactivity of the $\{(i\text{Pr})TP\}^{2-}$ ligand, $H_2\{(i\text{Pr})TP\}$ was treated in a 1:1 stoichiometric ratio with $ZnMe_2$ in toluene [Equation (2)]. After recrystallisation, the dimetallic zinc complex $[Zn\{(i\text{Pr})TP\}]_2$ (**3**) was obtained as yellow crystals. The new complex was characterised by standard spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction.



(2)

Compound **3** crystallises in the monoclinic space group *C*2/*c* having four molecules in the unit cell (Figure 1). The dimetallic complex adopts a helical structure with a crystallographic inversion centre. Both of these helical enantiomers are observed in the unit cell. The zinc atoms have a distorted tetrahedral coordination sphere. The N−Zn−N angles inside the aminotroponiminate moiety are 81.3(2) and 81.0(2)°. The other N−Zn−N angles range from 119.3(2) to 134.5(2)°. The Zn−N bond lengths are in the expected range of 198.3(5)−199.9(5) pm. In comparable tropocoronand complexes the Zn−N distances vary from 197.2(5) to 209.6(4) pm.[9b]

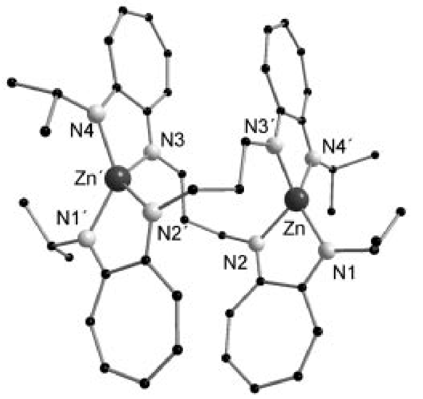


Figure 1. Perspective view of the molecular structure of **3**; selected distances [pm] and angles [°]: Zn−N1 198.5(5), Zn−N2 198.7(5), Zn−N3′ 199.9(5), Zn−N4′ 198.3(5); N1−Zn−N2 81.3(2), N1−Zn−N3′ 125.2(2), N1−Zn−N4′ 134.5(2), N2−Zn−N3′ 119.3(2), N2−Zn−N4′ 120.6(2), N3′−Zn−N4′ 81.0(2)

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** show a diastereotopic splitting of the isopropyl CH_3 signals. Based on these observations we suggest that the helical structure observed in the solid state may be retained in solution. A similar diastereotopic splitting has been observed by other chiral (isopropylamino)troponiminate complexes such as $[\{(i\text{Pr})_2ATI\}_3Ln]$ (Ln = Y, La) [$\{(i\text{Pr})_2ATI\}$ = *N*-isopropyl-2-(isopropylamino)troponiminate]. The signal of the isopropyl C*H* proton of **3** is well resolved into a septuplet but shows a slight downfield shift (δ = 3.76 ppm) compared to that of the free ligand $H_2\{(i\text{Pr})TP\}$ (δ = 3.55 ppm).[4] This is in agreement with **1** and **2**. Compound **3** is the first bridged aminotroponiminate complex in which a helical structure is observed.

Conclusions

Reactions of $H_2\{(i\text{Pr})TP\}$ with dialkylzinc compounds in toluene led, in a 1:2 stoichiometric ratio, to the dimetallic singly bridged products of composition $[(RZn)_2\{(i\text{Pr})TP\}]$ [R = Me (**1**), Et (**2**)]. The reactivity of $ZnMe_2$ towards $H_2\{(i\text{Pr})TP\}$ is much higher than that of $ZnEt_2$. When $H_2\{(i\text{Pr})TP\}$ was treated in a 1:1 stoichiometric ratio with $ZnMe_2$ in toluene the dimetallic doubly bridged helical zinc complex $[Zn\{(i\text{Pr})TP\}]_2$ (**3**) was obtained. Due to the helical structure of **3** the ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound show a diastereotopic splitting of the isopropyl CH_3 signals confirming that the helical structure observed in the solid state is retained in solution.

Experimental Section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glove box. Ether solvents (tetrahydrofuran and diethyl ether) were predried with Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum-line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom% D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded with a Jeol 400 MHz FT NMR spectrometer or with a Bruker AC 250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Elemental analyses were carried out with an Elementar vario EL. $ZnMe_2$ and $ZnEt_2$ were purchased from Aldrich Inc. $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ was prepared according to a literature procedure.[4]

[(MeZn)$_2${(*i*Pr)TP}] (1): A 2 M $ZnMe_2$ solution in toluene (5 mL, 10 mmol) was diluted with 25 mL of toluene. At −70 °C a solution of $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ (1.82 g, 5 mmol) in toluene (30 mL) was added. The reaction mixture was warmed up to −50 °C, followed by gas evolution. After the gas evolution had stopped (about 3 h), the mixture was warmed up to room temperature, filtered, and the solvent was removed. The resulting yellow solid was washed twice with *n*-pentane (5 mL) and dried in vacuo. Yield 2.17 g (83%). $C_{25}H_{36}N_4Zn_2$ (523.34): calcd. C 57.38, H 6.93, N 10.71; found C 56.94, H 6.80, N 10.32. ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = -0.07$ (s, 6 H, $ZnCH_3$), 1.13 [d, 12 H, $CH(CH_3)_2$, $^3J_{H,H} = 6.2$ Hz), 2.26 (quint, 2 H, $CH_2CH_2CH_2$, $^3J_{H,H} = 7.0$ Hz), 3.33 (t, 4 H, NCH_2, $^3J_{H,H} = 7.0$ Hz), 3.74 [sept, 2 H, $CH(CH_3)_2$, $^3J_{H,H} = 6.2$ Hz], 6.36 (t, 2 H, H_{ring}, $^3J_{H,H} = 9.2$ Hz), 6.52 (d, 2 H, H_{ring}, $^3J_{H,H} = 11.2$ Hz), 6.52 (d, 2 H, H_{ring}, $^3J_{H,H} = 11.4$ Hz), 6.92−7.01 (m, 4 H, H_{ring}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100.40 MHz, 25 °C): $\delta = -10.8$, 24.5, 33.5, 48.3, 48.7, 111.9, 112.0, 117.9, 134.6, 134.7, 160.2, 161.4 ppm.

[(EtZn)$_2${(*i*Pr)TP}] (2): A 1 M $ZnEt_2$ solution (4 mL, 4 mmol) in toluene was diluted with 25 mL of toluene. At ambient temperature a solution of $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ (0.73 g, 2 mmol) in toluene (30 mL) was added, immediately followed by gas evolution. The mixture was stirred for 6 h at room temperature, filtered, and the solvent was removed. The remaining yellow solid was washed twice with *n*-pentane (5 mL) and dried in vacuo. Yield 0.99 g (89%). $C_{27}H_{40}N_4Zn_2$ (551.37): calcd. C 58.81, H 7.31, N 10.16; found C 58.57, H 7.35, N 9.88. ^1H NMR (C_6D_6, 250 MHz, 25 °C): $\delta = 0.74$ (q, 4 H, $ZnCH_2CH_3$, $^3J_{H,H} = 8.1$ Hz), 1.15 [d, 12 H, $CH(CH_3)_2$, $^3J_{H,H} = 6.2$ Hz], 1.58 (t, 6 H, $ZnCH_2CH_3$, $^3J_{H,H} = 8.1$ Hz), 2.21 (quint, 2 H, $CH_2CH_2CH_2$, $^3J_{H,H} = 7.0$ Hz), 3.38 (t, 4 H, NCH_2, $^3J_{H,H} = 7.0$ Hz), 3.75 [sept, 2 H, $CH(CH_3)_2$, $^3J_{H,H} = 6.2$ Hz], 6.36 (t, 2 H, H_{ring}, $^3J_{H,H} = 9.1$ Hz), 6.55 (d, 2 H, H_{ring}, $^3J_{H,H} = 11.1$ Hz), 6.59 (d, 2 H, H_{ring}, $^3J_{H,H} = 11.2$ Hz), 6.91−7.05 (m, 4 H, H_{ring}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25 °C): $\delta = 3.0$, 13.8, 25.3, 34.0, 48.8, 49.3, 112.7, 112.8, 118.7, 135.3, 135.5, 161.0, 162.1 ppm.

[Zn{(*i*Pr)TP}]$_2$ (3): At ambient temperature, 1 mL of a 2 M solution of $ZnMe_2$ in toluene (2 mmol) was added to a solution of $H_2\{(i\mathrm{Pr})\mathrm{TP}\}$ (0.79 g, 2 mmol) in 25 mL of toluene. The mixture was stirred for 3 h at room temperature. After the gas evolution had stopped, the solution was heated briefly under reflux. The mixture was then filtered, and the solvent was removed. The remaining yellow solid was washed twice with *n*-pentane (5 mL) and dried in vacuo. Single crystals were obtained from toluene at −40 °C. Yield 1.45 g (85%). $C_{40}H_{60}N_8Zn_2$ (855.80): calcd. C 64.56, H 7.07, N 13.09; found C 64.33, H 6.98, N 12.77. ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 1.05$ [d, 12 H, $CH(CH_3)_2$, $^3J_{H,H} = 6.2$ Hz], 1.06 [d, 12 H, $CH(CH_3)_2$, $^3J_{H,H} = 6.2$ Hz], 1.98 (quint, 4 H, $CH_2CH_2CH_2$, $^3J_{H,H} = 7.4$ Hz), 3.24−3.31 (m, 4 H, NCH_2), 3.37−3.45 (m, 4 H, NCH_2), 3.76 [sept, 4 H, $CH(CH_3)_2$, $^3J_{H,H} = 6.2$ Hz], 6.19 (t, 4 H, H_{ring}, $^3J_{H,H} = 9.1$ Hz), 6.35 (d, 4 H, H_{ring}, $^3J_{H,H} = 11.5$ Hz), 6.40 (d, 4 H, H_{ring}, $^3J_{H,H} = 11.7$ Hz), 6.81−6.88 (m, 8 H, H_{ring}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100.40 MHz, 25 °C): $\delta = 23.7$, 24.0, 32.1, 47.4, 48.4, 111.3, 111.8, 115.8, 134.5, 134.7, 160.0, 161.3 ppm.

X-ray Crystallographic Studies of 3: Crystals of $C_{23}H_{30}N_4Zn$ were grown from a toluene solution. A suitable crystal was covered with mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the −70 °C cold stream of an STOE IPDS diffractometer (Ag-K_α radiation). Subsequent computations were carried out with an Intel PIII PC. Data collection and refinement: SHELXS-97,[14] SHELXL-97;[15] monoclinic, space group $C2/c$ (no. 15); lattice constants $a = 1279.76(7)$, $b = 1542.66(8)$, $c = 2170.34(13)$ pm, $\beta = 97.635(7)°$, $V = 4246.8(4)\ 10^6\ \mathrm{pm}^3$, $Z = 8$; $\mu(\text{Ag-}K_\alpha) = 0.623\ \mathrm{mm}^{-1}$; $2\theta_{max.} = 38.00°$; 3475 ($R_{int} = 0.1560$) independent reflections measured, 2660 of which were considered observed with $I > 2\sigma(I)$; max. residual electron density 1.718 and -0.721 e/A^{-3}; 262 parameters (all non-hydrogen atoms were calculated anisotropic; the positions of the H atoms were calculated for idealised positions) $R1 = 0.0881$; $wR2 = 0.2182$. CCDC-194178 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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