Cyclopentadienyl Complexes of Yttrium Aminotroponiminates: An Example for an Improved Alternative Ligand System

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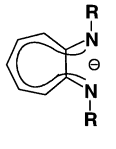
Mixed aminotroponiminate ($[ATI]^-$) cyclopentadienyl complexes were prepared using two different synthetic routes. Reaction of $[[(iPr)_2ATI]YCl_2(THF)_2]_2$ (**1**) with KCp* (Cp* = C_5Me_5) or $Li[C_5H_3(SiMe_3)_2]$ affords $[(iPr)_2ATI]YCp_2$* (**2a**) and $[(iPr)_2ATI]Y[C_5H_3(SiMe_3)_2]_2$ (**2b**), respectively. Moreover, $[(iPr)_2ATI]YCp_2$* has also been obtained from the reaction of Cp_2*$Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**3**) and $[(iPr)_2ATI]K$. The single crystal X-ray structure of $[(iPr)_2ATI]YCp_2$* shows that the steric demand of the $[(iPr)_2ATI]^-$ ligand is somewhat similar to that of the well-known cyclopentadienyl group and diazadiene ligand. $[(iPr)_2ATI]Y[C_5H_3(SiMe_3)_2]_2$ shows a dynamic behavior in solution (^{1}H NMR), which is essentially caused by rotation of the cyclopentadienyl group rather than by migration of the $[(iPr)_2ATI]^-$ ligand.

Introduction

Recently, there has been significant interest in early transition metal chemistry for the replacement cyclopentadienyl (or related systems) by other ligands in order to generate a similar steric and electronic environment.[1] For example, a number of metal complexes of the lanthanides and group 3 elements have been synthesized in which cyclopentadienyl is replaced by anionic bidentate nitrogen ligands such as amides,[2] benzamidinates,[3] and diazadienes.[4]

The aminotroponiminates ($[ATI]^-$) **A**, have been introduced as cyclopentadienyl alternatives for group 3,[5] group 4,[6] and the lanthanide elements.[5] $[ATI]^-$ is a bidentate mono-anionic ligand that features a 10 π electron backbone.[7] Upon coordination to a metal atom, $[ATI]^-$ forms a five-membered metallacycle adjacent to the seven-membered carbon ring. Recently, it was shown that the heteroleptic yttrium amides $[ATI]Y[N(SiMe_3)_2]_2$ and $[ATI]_2Y[N(SiMe_3)_2]$ are active catalysts for the hydroamination/cyclization reaction of aminoalkynes.[8] The new catalysts were obtained by transmetallation of the corresponding chloro precusors $[[ATI]YCl_2(THF)_2]_2$ and $[ATI]_2YCl$ using $K[N(SiMe_3)_2]$.



A

In order to compare the coordination behavior and the steric demands of both $[ATI]^-$ and cyclopentadienyl groups, our main interest is now focused on mixed cyclopentadienyl-$[ATI]^-$ complexes. In this paper, the synthesis of new cyclopentadienyl-$[ATI]^-$ yttrium complexes starting from the isopropyl derivative $[[(iPr)_2ATI]YCl_2(THF)_2]_2$ (**1**)[5] is reported. These reactions lead to complexes of the general formula $[(iPr)_2ATI]YCp_2$ [Cp = C_5Me_5, $C_5H_3(SiMe_3)_2$]. **1** can be obtained from $[(iPr)_2ATI]K$ and YCl_3 (Scheme 1).

Results and Discussion

Transmetallation of **1** with a slight excess of potassium pentamethylcyclopentadienyl (KCp*) in THF (Scheme 1), followed by workup in pentane, yields the corresponding dicyclopentadienyl complex $[(iPr)_2ATI]YCp_2$* (**2a**) as a pure yellow solid in fairly good yield. **2a** can also be obtained by the "classical" route using Cp_2*$Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**3**)[9] as the starting material. Reaction of **3** with 1 equivalent of $[(iPr)_2ATI]K$ in toluene, followed by extraction with pentane, also affords **2a** (Scheme 1). **2a** is an air and moisture sensitive compound and has been characterized by MS, ^{1}H- and ^{13}C-NMR spectroscopy, and elemental analysis. The ^{1}H-NMR spectrum shows a sharp singlet for the protons of the Cp* unit, and this signal is shifted slightly downfield ($\delta = 1.94$) compared with that of **3** ($\delta = 1.83$).[9] The room temperature ^{1}H- and ^{13}C-NMR spectra point to a symmetrical coordination of the $[(iPr)_2ATI]^-$ ligand in solution, which is in agreement with the coordination observed in the solid state (see below). The signal of the isopropyl C*H* of **2a** is well resolved into a septet, but shows a marked upfield shift ($\delta = 3.82$) compared to the starting material **1** ($\delta = 4.04$).[5] In contrast to the anionic dicyclopentadienyl diazadiene complex of lanthanum, $[Cp_2$*$La(DAD)]^-$ {DAD = (Ph)N=C(Ph)C(Ph)=N(Ph)},[10] and the dicyclopentadienyl diazadiene complexes of group 4 metals, Cp_2*M(DAD) (M = Zr, Hf),[11] **2a** does not show a rapid dynamic exchange of the chelating ligand in solution at room temperature. Whereas DAD

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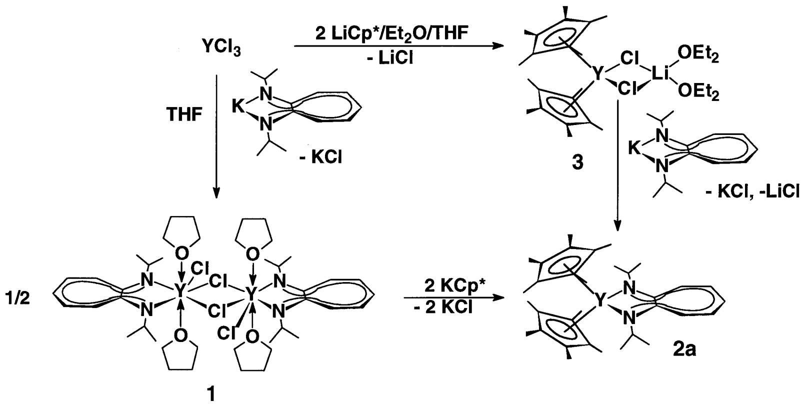
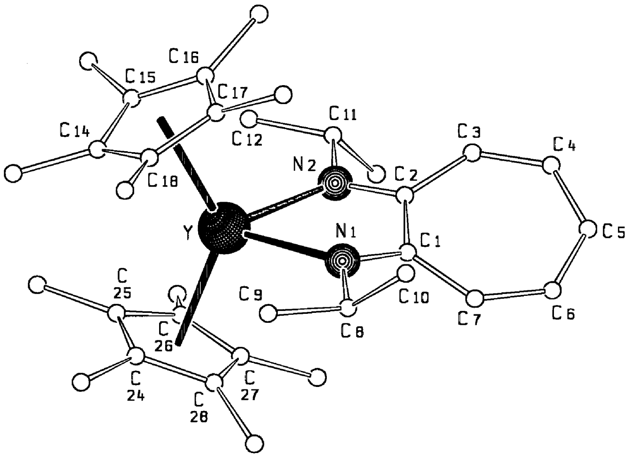
Scheme 1



complexes show a rapid migration of the Cp*M unit from one side of the reduced DAD ligand to the other, the rigid geometry of the $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ ligand (also seen in the single crystal X-ray structure of **2a**) prevents such a strong movement of the $\mathrm{Cp_2^*Y}$ moiety.

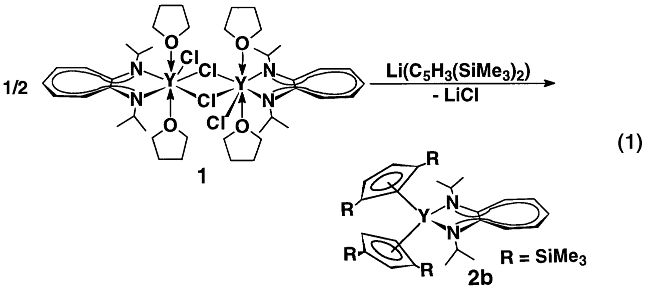
Figure 1. Solid-state structure of **2a** showing the atom labeling scheme, omitting hydrogen atoms (SCHAKAL drawing)[a]



[a] Selected distances [pm] and angles [°]: C1−N1 132.7(4), C2−N2 132.9(4), C14−Y 277.5(3), C15−Y 275.4(3), C16−Y 270.8(3), C17−Y 271.8(3), C18−Y 276.4(3), C24−Y 269.0(4), C25−Y 271.1(3), C26−Y 275.5(3), C27−Y 273.3(3), C28−Y 271.1(4), N1−Y 239.8(2), N2−Y 239.0(3), $\mathrm{C_g}$1−Y 244.6, $\mathrm{C_g}$2−Y 244.2; N2−Y−N1 69.38(9), N1−Y−C14 127.52(10), N2−Y−C14 131.12(10), N1−Y−C15 132.13(10), N2−Y−C15 102.46(10), N1−Y−C16 103.40(9), N2−Y−C16 84.06(10), N1−Y−C17 84.22(9), N2−Y−C17 98.73(10), N1−Y−C18 97.93(10), N2−Y−C18 128.48(10), $\mathrm{C_g}$1−Y−$\mathrm{C_g}$2 133.95 ($\mathrm{C_g}$ = ring centroid).

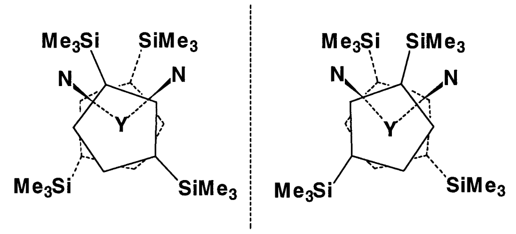
The solid-state structure of **2a** was investigated by single-crystal X-ray diffraction (Figure 1). Suitable crystals were obtained by slow evaporation of a saturated heptane solution of **2a**. The structure reveals a pseudo-tetrahedral arrangement of the ligands around the yttrium atom. The $\mathrm{C_g}$−Y ($\mathrm{C_g}$ = Cp*-ring centroids) distances ($\mathrm{C_g}$1−Y 244.6 pm and $\mathrm{C_g}$2−Y 244.2 pm) are in the expected range of other $\mathrm{Cp_2^*Y^{III}}$ compounds [e.g. 240.8(4) pm in $\mathrm{Cp_2^*}$Y(DAD)[10] and 266(2) pm in $\mathrm{Cp_2^*Y(\mu\text{-}Cl)_2Li(THF)_2}$[12]]. The angle $\mathrm{C_g}$1−Y−$\mathrm{C_g}$2 (133.95°) is approximately five degrees smaller than that in $\mathrm{Cp_2^*}$Y(DAD) [138.6(2)°]. Similar bonding modes are observed for $\mathrm{Cp_2^*Sm[N(}t\mathrm{Bu){=}CHCH{=}N(}t\mathrm{Bu)]}$.[13] Both Cp* rings in **2a** are located in a staggered position with respect to each other. A C_2-symmetric coordination of the $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ ligand along the Y−C5 axis with symmetric N−Y distances [N1−Y 239.8(2) and N2−Y 239.0(3) pm] is observed. The whole $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ framework is twisted, i.e. the atom C1 (C2) is located about 40 pm above (below) the least-squares mean plane defined by the seven membered ring (C1−C7). This observation is in sharp contrast to the comparable group 4 complexes, $[(i\mathrm{Pr})_2\mathrm{ATI}]_2\mathrm{MCl_2}$ (M = Zr, Hf),[6] which show a planar coordination of the ligand. The N1−Y1−N2 angle [69.38(9)°] is in the range of comparable compounds such as **1** [67.4(2)°][5] and also of $\mathrm{Cp_2^*}$Y(DAD) [70.1(1)°], suggesting a similar steric demand for $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ and DAD.

$[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{Y[C_5H_3(SiMe_3)_2]_2}$ (**2b**) is prepared in a similar way to **2a**. Transmetallation of **1** with lithium bis[1,3-(trimethylsilyl)cyclopentadienyl], $\mathrm{Li[C_5H_3(SiMe_3)_2]}$ in toluene in a 2:1 molar ratio (equation 1), followed by workup in pentane, leads to **2b** as a yellow solid in very high yields. **2b** has been characterized by MS, IR, ^{1}H-NMR spectroscopy, and elemental analysis. In contrast to **2a** the ^{1}H-NMR spectrum of **2b** shows a dynamic behavior in solution. At low temperature (213 K) two doublets for the methyl protons of the isopropyl groups of the $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ ligand are observed along with two singlets for the $\mathrm{Me_3Si}$ groups. These signals start to coalesce with increasing temperature and have a coalescence temperature of about T_c = 273 K. At higher temperatures (313 K and above) the signals due to the methyl protons of the isopropyl groups appear as one doublet and the signal of the $\mathrm{Me_3Si}$ groups as a singlet. Since the $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ ligand does not show a fluctionality in **2a**, these results were interpreted as evidence that the two diastereotopic isopropyl groups exist in different chiral environments and, due to the reciprocal nature of this effect, so do the $\mathrm{Me_3Si}$ groups. It was shown earlier that $\mathrm{[C_5H_3(SiMe_3)_2]_2ZrX_2}$ (X = F, Br, I) complexes crystallize in a staggered conformation.[14] These conformations are chiral in the absence of rotation of the cyclopentadienyl groups. In accordance with these results, two enantiomeric conformations are depicted in Figure 2 by considering a stronger repulsion of the $\mathrm{Me_3Si}$ groups in the back of the bent metallocene than in the front. At high temperature both enantiomers interconvert rapidly, thus showing only one set of signals. A similar diastereotopic splitting of the isopropyl signals of the $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ ligand was observed earlier for the chiral homoleptic compounds $[(i\mathrm{Pr})_2\mathrm{ATI}]_3\mathrm{Ln}$ (Ln = Y, La, Sm).[5]



(1)

Figure 2. Schematic representation of both enantiomers of **2b** observed at low temperature in the ^{1}H NMR (considering the absence of a suitable scrambling mechanism at these temperatures)



From the coalescence temperature (T_c = 273) and the separation ($\Delta\nu$ = 33.21 s^{-1}, 250 MHz NMR) of the two coalescing doublets of the isopropyl groups in the absence of any exchange, the free energy for the rotation about the Y−C$_g$ axis was calculated to be $\Delta G_{Tc}^{\geq}$ = 56.95 kJ/mol, according to equation 2.[15]

$$\Delta G_{Tc}^{\ddagger} = -RT_c \ln(\pi\Delta\nu\, h/\sqrt{2}\, k_b T_c) \qquad (2)$$

In summary, new mixed cyclopentadienyl−$[\mathrm{ATI}]^-$ complexes of yttrium have been prepared. It has been demonstrated that the steric demand of the $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ ligand is comparable to that of the well-known cyclopentadienyl groups and diazadiene ligands. The fluctional behavior of $[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{Y}[\mathrm{C_5H_3(SiMe_3)_2}]_2$ (**2b**) is essentially caused by rotation of the cyclopentadienyl groups and not by migration of the $[(i\mathrm{Pr})_2\mathrm{ATI}]^-$ ligand.

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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, or interfaced to a high vacuum (10^{-4} Torr) line, or in an argon-filled Braun Atmospheres glove box. Ether solvents (tetrahydrofuran and diethyl ether) were pre-dried over Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl. Hydrocarbon solvents (toluene and pentane) were distilled under nitrogen from Na wire. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy 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 on a Bruker AC 250 spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were performed on a Bruker IFS 28, mass spectra were recorded at 70 eV on Varian MAT 711. Elemental analyses were performed in the micro analytical laboratory of the Institut für Anorganische Chemie der Universität Karlsruhe (S. Ariman). KCp*[16], $\mathrm{Li[C_5H_3(SiMe_3)_2]}$,[13] $\mathrm{Cp_2{*}Y(\mu\text{-}Cl)_2Li(OEt_2)_2}$,[9] $[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{K}$,[5] and $[[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{YCl_2(THF)}]_2$,[5] were prepared by literature procedures.

Preparation of $[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{YCp}^*_2$ (**2a**) − *Route A:* THF was condensed at −196°C onto a mixture of 189 mg (0.21 mmol) of $\{[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{YCl_2(THF)_2}\}_2$ and 174 mg (1.0 mmol) of KCp*, and the mixture was stirred for 18 h at room temperature. The solvent was evaporated in vacuum, and pentane was condensed onto the mixture. The solution was then filtered, and the solvent removed. This procedure was repeated twice. The remaining solid was recrystallized from pentane. − Yield 130 mg (56%).

Route B: THF was condensed at −196°C onto a mixture of 390 mg (0.21 mmol) of $\mathrm{Cp_2{*}Y(\mu\text{-}Cl)_2Li(OEt_2)_2}$, and 161 mg (1.0 mmol) of $[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{K}$ and the mixture was stirred for 18 h at room temperature. The solvent was evaporated in vacuum, and pentane was condensed onto the mixture. The solution was then filtered, and the solvent removed. The remaining solid was recrystallized from pentane. − Yield 180 mg (49%). − ^{1}H NMR (C_6D_6, 250 MHz, 25°C): δ = 1.17 [d, 12 H, $(CH_3)_2CH$, J(H,H) = 6.3 Hz], 1.94 (s, 30 H, CH_3Cp), 3.82 [sept, 2 H, $(CH_3)_2CH$, J(H,H) = 6.4 Hz], 6.09−6.24 (m, 3 H, $H^{3,5,7}$), 6.84 (dd, 2 H, $H^{4,6}$). − $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz, 25°C): δ = 13.4 (CH_3Cp), 22.9 [$(CH_3)_2CH$], 49.4 [$(CH_3)_2CH$], 115.1 (C^5), 115.3 (Cp), 119.6 ($C^{3,7}$), 133.4 ($C^{4,6}$), 164.2 ($C^{1,2}$). − EI/MS (70 eV) *m/z* (%): 562 ([*M*]$^+$, rel. int. 11), 427 ([*M* − Cp*]$^+$, 100), 223 ([Cp*Y − H]$^+$, 64), 204 ([$C_{13}H_{20}N_2$]$^+$, 87). − $C_{33}H_{49}N_2Y$ (562.67): calcd. C 70.44, H 8.78, N 4.98; found C 70.03, H 8.57, N 5.31.

Preparation of $[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{Y(C_5H_3(SiMe_3)_2)_2}$ (**2b**): THF was condensed at −196°C onto a mixture of 217 mg (0.25 mmol) of $\{[(i\mathrm{Pr})_2\mathrm{ATI}]\mathrm{YCl_2(THF)_2}\}_2$ and 216 mg (1.0 mmol) of $\mathrm{Li[C_5H_3(SiMe_3)_2]}$, and the mixture was stirred for 18 h at room temperature. The solvent was evaporated in vacuum, and pentane was condensed onto the mixture. The solution was then filtered, and the solvent removed. This procedure was repeated twice. −Yield 335 mg (94%). − IR (KBr) ṽ = 1592 cm^{-1} (st), 1506 (vs), 1470 (st), 1249 (st), 833 (vs). − ^{1}H NMR ([D$_8$]toluene, 250 MHz, 70°C): δ = 0.20 (s, 36 H, CH_3Si), 1.38 [d, 12 H, $(CH_3)_2CH$, J(H,H) = 6.6 Hz], 3.56 [sept, 2 H, $(CH_3)_2CH$], 6.09−6. 20 (m, 3 H, $H^{3,5,7}$), 6.16 (d, 2 H, Cp), 6.35 (d, 2 H, Cp), 6.64 (dd, 2 H, $H^{4,6}$), 6.71 (s, 1 H, Cp). − $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 62.9 MHz, 25°C): δ = 1.4 (CH_3Si), 20.7 [$(CH_3)_2CH$], 46.3 [$(CH_3)_2CH$], 110.6 (Cp), 115.3 (C^5), 117.9 (Cp), 119.5 ($C^{3,7}$), 133.4 ($C^{4,6}$), 164.2 ($C^{1,2}$). − ^{29}Si NMR ([D$_8$]toluene, 49.7 MHz, 25°C): δ = −9.5. − EI/MS (70 eV) *m/z* (%): 710 ([*M*]$^+$, rel. int. 11), 637 ([*M* − $C_3H_{15}Si$]$^+$, 8), 501 [*M* − ($C_9H_{11}N_2$)]$^+$, 100), 297 ([$C_{11}H_{21}YSi_2$)]$^+$ 37). − $C_{35}H_{61}N_2Si_4Y$ (711.23): calcd. C 59.12, H 8.65, N 3.94; found C 58.75, H 8.71, N 4.50.

Crystal Structure Analysis of **2a**: Stoe-IPDS diffractometer (Mo-K_α radiation); T = 203(3) K; data collection and refinement: SHELXS-86[17], SHELXL-93[18]; monoclinic, space group *P*-1; lattice constants a = 9.694(2), b = 10.284(2), c = 15.730(3) Å, α = 88.39(2), β = 89.57(2), γ = 75.18(2)°, V = 1515.6(5) Å^3, Z = 2;

μ(Mo-K_α) = 2.666 mm^{-1}; $2\theta_{max.}$ = 26.00; 5511 independent reflections measured, of which 4539 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.526 and −0.367 e/A^{-3}; 339 parameters (all non hydrogen atoms were calculated anisotropically; the positions of the H atoms were calculated for idealized positions) R_1 = 0.0427. − Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-407970, the name of the author, and the journal citation.

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