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Journal of Organometallic Chemistry 647 (2002) 123–127

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Cyclopentadienyl complexes of yttrium and the lanthanides with bis(phosphinimino)methanides

Michael T. Gamer, Peter W. Roesky *

Institut für Anorganische Chemie der Universität Karlsruhe (TH), Engesserstraße 15, D-76128 Karlsruhe, Germany

Received 4 September 2001; received in revised form 8 October 2001

Abstract

Metallocenes of yttrium and the lanthanides with bis(phosphinimino)methanides in the coordination sphere are reported. Reaction of $[\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}LnCl_2]_2$ (Ln = Y, Sm, Er) with $Na(C_5H_5)$ in a 1:4 molar ratio in THF afforded the corresponding metallocenes $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}]$. The structures of these new compounds were investigated in solution and in the solid state. Single crystal X-ray structures show that both imine groups and the methine carbon are bound to the lanthanide atom. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bis(phosphinimino)methanides; Cyclopentadienyl; Lanthanides; N ligands; Yttrium

1. Introduction

In the last 15 years, enormous progress has been observed in the design and application of amido-metal chemistry of the early transition metals. Whereas, in the early stages of this area cyclopentadienyl-analogous amido ligands were studied for comparison with and for further investigations of the well-known cyclopentadienyl moiety. Today, the stable amido metal bond is utilized in amido-metal chemistry to produce well-defined reaction centers in transition metal complexes. In this way, the reactivity of the resulting early transition metal compounds can be specifically tailored to allow applications in areas such as, the activation of small poorly reactive molecules, homogeneous catalysis, or organic synthesis [1,2]. One synthetic approach among others is the use of P–N ligands such as phosphoraneiminate, phosphinimines, and phosphinimides in main group and transition metal chemistry [3–8]. Lately, our attention was drawn to the phosphinimine $\{CH(PPh_2NSiMe_3)_2\}^-$, which has been previously used in main group and transition metal chemistry [9–17] as a potential precursor to stable yttrium and lanthanide complexes. We have previously reported the synthesis of a series of lanthanide bis(phosphinimino)methanide dichloride complexes including yttrium, $[\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}LnCl_2]_2$ (Ln = Y, Sm, Dy, Er, Yb, Lu) [18]. These compounds were obtained by the reaction of $K\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}$ [19], with the corresponding yttrium or lanthanide trichlorides. Moreover, a further reaction of the yttrium and the samarium compound to the amido complexes $[\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}Ln(NPh_2)_2]$ (Ln = Y, Sm) was also reported by us [18].

In order to compare the coordination behavior and the steric demands of $\{CH(PPh_2NSiMe_3)_2\}^-$ and cyclopentadienyl groups, our interest is now mainly focused on mixed cyclopentadienyl–bis(phosphinimino)methanides complexes. In this paper we report on the synthesis of a series of biscyclopentadienyl yttrium and lanthanide bis(phosphinimino)methanide complexes $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}]$ (Ln = Y, Sm, Er), which were obtained from $[\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}LnCl_2]_2$ and $Na(C_5H_5)$. The structures of these new compounds were investigated in solution and in the solid state.

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* Corresponding author. Tel.: +49-721-608-2855; fax: +49-721-608-8440.

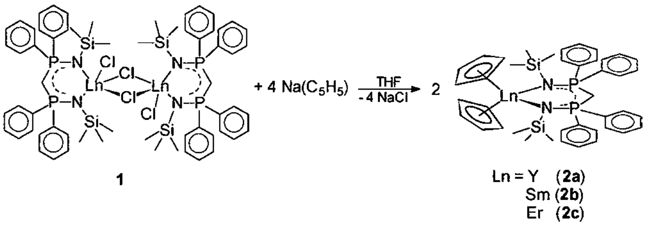
E-mail address: roesky@achibm6.chemie.uni-karlsruhe.de (P.W. Roesky).

PII: S0022-328X(01)01358-4

2. Results and discussion

2.1. Synthesis

Reaction of $[\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}LnCl_2]_2$ (Ln = Y (**1a**), Sm (**1b**), Er (**1c**)) with $Na(C_5H_5)$ in a 1:4 molar ratio in THF afforded the corresponding metallocenes $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}]$, (Ln = Y (**2a**), Sm (**2b**), Er (**2c**)) as crystals in good yields (Eq.(1)) [20]. Complex **2a**–**c** can also be obtained in a one-pot reaction starting from $LnCl_3$, $K\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}$ [19], and $Na(C_5H_5)$.



(1)

The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures of all three compounds were established by single crystal X-ray diffraction. The ^{1}H-NMR spectrum of the diamagnetic compound **2a** shows a significant downfield shift of the methine proton (δ 2.75) compared to **1a** (δ 1.9). Furthermore, the ^2J(H,P) coupling constant of the methine proton of **2a** (13.0 Hz) is significantly larger than that of **1a** (1.9 Hz). On the other hand, in the protonated ligand $CH_2(PPh_2NSiMe_3)_2$, the ^2J(H,P) coupling constant is in a similar range (13.9 Hz) [21]. In contrast to **1a** no ^2J(H,Y) coupling is seen even at low temperatures (−70 °C). This effect might be caused by a non-rigid structure of **2a** in solution. The ^{1}H-NMR spectrum of **2a** shows the expected sharp singlet (δ 6.18) of the protons on the $\eta^5\text{-}C_5H_5^-$ ligands. In the $^{31}P\{^1H\}$-NMR spectrum a doublet (δ 15.7) is observed which is shifted upfield by almost 5 ppm relative to **1a** (δ 20.4), showing that the phosphorous atoms are chemically equivalent in solution. The splitting of $^{31}P\{^1H\}$ signal is caused by a ^2J(P,Y) coupling of 5.5 Hz.

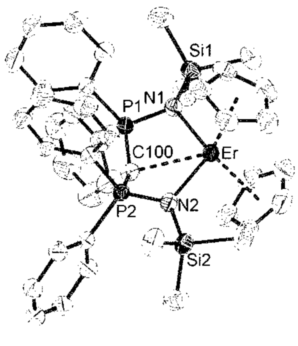


Fig. 1. Perspective ORTEP view of the molecular structure of **2c**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles (°): compound **2a**: N1–Y 253.7(2), N2–Y 252.0(2), N1–P1 159.7(2), N2–P2 160.2(2), C100–Y1 263.8(3), C100–P1 172.0(3), C100–P2 170.9(3), Cg1–Y 246.2(12), Cg2-Y 241.2(13); N1–Y–N2 121.23(7), N1–Y–C100 61.19(8), N2–Y–C100 61.89(8), Cg1–Y–Cg2 123.44(1), P1–N1–Y 97.67(10), P2–N2–Y 98.43(10), P1–C100–P2 143.0(2) (Cg, ring centroid). Compound **2b**: N1–Sm 255.5(2), N2–Sm 254.0(2), N1–P1 159.1(2), N2–P2 159.4(2), C100–Sm 269.7(2), C100–P1 171.7(2), C100–P2 171.0(2), Cg1–Sm 248(2), Cg2–Sm 247(2); N1–Sm–N2 119.39(6), N1–Sm–C100 60.32(6), N2–Sm–C100 61.02(6), Cg1–Sm–Cg2 122.86(0), P1–N1–Sm 98.37(8), P2–N2–Sm 99.23(8), P1–C100–P2 142.11(13). Compound **2c**: N1–Er 251.7(3), N2–Er 250.1(3), N1–P1 160.3(3), N2–P2 160.3(3), C100–Er 262.1(3), C100–P1 172.0(3), C100–P2 171.8(3), Cg1–Er 247.0(15), Cg2–Er 240(1); N1–Er–N2 121.94(9), N1–Er–C100 61.52(9), N2–Er–C100 62.33(10), Cg1–Er–Cg2 123.41(0), P1–N1–Er 97.70(14), P2–N2–Er 98.52(14), P1–C100–P2 142.2(2).

In the EI mass spectra of **2a**–**c** the molecular ions as well as their characteristic fragmentation pattern were observed. The molecular ions usually have a very small intensity, whereas for the fragment $[(\eta^5\text{-}C_5H_5)Ln\{CH(PPh_2NSiMe_3)_2\}]^+$ the highest intensities are observed.

2.2. Molecular structures of $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2N,N',\kappa C\}]$ (2a–c)

By recrystallizing **2** from toluene or THF–*n*-pentane (1:2) single crystals were obtained. The solid state structure of **2a**–**c** were established by single crystal X-ray diffraction. Due to the similar ion radii of the lanthanides, the single crystal X-ray structures of **2a**–**c** are isostructural. As an representative example, the structure of **2c** is shown in Fig. 1. Compounds **2a**–**c** crystallize in the triclinic space group $P\bar{1}$ having two molecules in the unit cell. The structure shows the expected η^5-coordination of the cyclopentadienyl ligands, with the planar η^5-rings exhibiting no significant distortion within the carbon framework (average C–C bond distances 139.9(5) pm (**2a**), 139.9(5) pm (**2b**), 140.6(7) pm (**2c**)). The Ln–C_{ring} distances are in the range between 269.4(3) and 271.8(3) pm (av. 270.2(3) pm) (**2a**), 273.0(2) and 277.2(3) pm (av. 275.0(2) pm) (**2b**), and 269.2(4) pm and 270.2(4) pm (av. 269.0(4) pm) (**2c**) with a Ln-ring centroid distance of 241.2(13) and 246.2(12) pm (**2a**), 247(2) and 248(2) pm (**2b**), and 240(1) pm and 247.0(15) pm (**2c**). The data is in agreement with other biscyclopentadienyl complexes of the lanthanides [22] such as $[(\eta^5\text{-}C_5H_5)_2Ln\{N(SPPh_2)_2\}]$ (Y-ring centroid 239.4 and 237.7 pm [23]; Er-ring centroid 236.2 and 237.8 pm [24]).

The geometry of the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand is as expected. The P–N and P–C bond distances as well as the P1–C100–P2 angles vary only slightly within the series **2a**–**c**. A six membered metallacycle (N1–P1–C100–P2–N2–Ln) is formed by chelation of the two trimethlysilylimine groups to the lanthanide atom. The Ln–N distances are 252.0(2) and 253.7(2) pm

(**2a**), 254.0(2) and 255.5(2) pm (**2b**), and 250.1(3) and 251.7(3) pm (**2c**). 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 (C100) and the lanthanide atom (263.8(3) pm (**2a**), 269.7(2) pm (**2b**), and 262.1(3) pm) is longer than usual Ln–C distances [22], however resultant tridentate coordination of the ligand was observed earlier in **1** [18], $[\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}Ln(NPh_2)_2]$ [18], $K\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}$ [19], $[Li(THF)][CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C]$ [19], $[Al(CH_3)_2\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}]$ [14], $[GaCl_2\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}]$ [14], and in $[Ir\{CH(PPh_2N(p\text{tolyl}))_2\text{-}\kappa^2 N,N',\kappa C\}(COD)]$ [9].

3. Conclusions

A series of lanthanide metallocene complexes, $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}]$, having the mono anionic $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand in the coordination sphere were synthesized. The crystal structures of these complexes show that the methine carbon atom is bound to the lanthanide atom. In contrast, no interaction between the lanthanide atom and the methine group is observed in solution. This effect might be caused by a non-rigid structure of **2** in solution. The data obtained from the crystal structures suggests that the steric demand of the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand is much higher than that of cyclopentadienyl groups. Therefore, by using the bulky $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand in lanthanide chemistry the synthesis of new complexes, which are significantly different from well-known cyclopentadienyl compounds should be possible.

4. Experimental

4.1. 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 ethyl ether) were predried over 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 on Bruker AC 250. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P-NMR), respectively. Mass spectra were recorded at 70 eV on Varian MAT 711. Elemental analyses were performed at the microanalytical laboratory of the Institute of Inorganic Chemistry at Karlsruhe. $LnCl_3$ [25], $[\{CH(PPh_2NSiMe_3)_2\}LnCl_2]_2$ [18] and $K\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}$ [19] were prepared according to literature procedures.

5. $[(\eta^5\text{-}C_5H_5)_2Ln\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}]$ (Ln = Y (2a), Sm (2b), Er (2c))

5.1. Route A

THF (20 ml) was condensed at − 196 °C onto a mixture of 0.25 mmol **1** and 95 mg (1.07 mmol) of $Na(C_5H_5)$ and the mixture was stirred for 18 h at room temperature (r.t.). 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) or toluene.

5.2. Route B

THF (20 ml) was condensed at − 196 °C onto a mixture of 0.51 mmol $LnCl_3$ and 360 mg (0.54 mmol) of $K\{CH(PPh_2NSiMe_3)_2\text{-}\kappa^2 N,N',\kappa C\}$ and the mixture was stirred for 18 h at r.t. The solvent was then evaporated in vacuo and 95 mg (1.07 mmol) of $Na(C_5H_5)$ was added to the remaining solid. Again, 15 ml of THF was condensed at − 196 °C onto the mixture and the suspension was stirred for 6 h at r.t. The mixture was then filtered and the solvent taken off in vacuo. The product was recrystallized from THF–*n*-pentane (1:2) or toluene.

Compound **2a** (Ln = Y): Yield: 213 mg (55%). — ^{1}H-NMR (d_8-THF, 250 MHz, 25 °C): δ-0.02 (s, 18H, $SiMe_3$), 2.75 (t, 1H, CH, ^2J(H,P) = 13.0 Hz), 6.18 (s, 10H, C_5H_5), 7.11–7.38 (br, 12H, Ph), 7.42–7.54 (br, 8H, Ph). — ^{13}C{^{1}H}-NMR (d_8-THF, 62.9 MHz, 25 °C): δ 4.1 ($SiMe_3$), 9.5 (t, CH, ^1J(C,P) = 129 Hz), 111.0 (C_5H_5), 128.5 (Ph), 131.4 (Ph), 131.5 (d, Ph), 133.0 (br, Ph). — ^{29}Si-NMR (d_8-THF, 49.7 MHz, 25 °C): $\delta = -5.9$. — ^{31}P{^{1}H}-NMR (d_8-THF, 101.3 MHz, 25 °C): δ 15.7 (d, ^2J(P,Y) = 5.5 Hz). — EI–MS (70 eV) *m*/*z* (%): 776 ($[M]^+$, relative intensity 0.5), 711 ($[M-C_5H_5]^+$, 100), 543 ($[C_{30}H_{36}N_2P_2Si_2]^+$, 74), 335.5 ($[M-C_5H_5]^+/2$, 5). — $C_{41}H_{49}N_2P_2Si_2Y$ (776.88): Calc.: C, 63.39; H, 6.36; N, 3.61. Found: C, 63.10; H, 6.01; N, 3.41%.

Compound **2b** (Ln = Sm): Yield: 188 mg (45%). — EI–MS (70 eV) *m*/*z* (%): 839 ($[M]^+$, relative intensity

0.1), 774 ($[M-C_5H_5]^+$, 100), 709 ($[M-(C_5H_5)_2]^+$, 8). — $C_{41}H_{49}N_2P_2Si_2Sm$ (838.33): Calc.: C, 58.74; H, 5.89; N, 3.34. Found: C, 58.20; H, 5.47; N, 3.12%.

Compound **2c** (Ln = Er): Yield: 175 mg (41%). — EI–MS (70 eV) m/z (%): 855 ($[M]^+$, relative intensity 1), 790 ($[M-C_5H_5]^+$, 100), 543 ($[C_{30}H_{36}N_2P_2Si_2]^+$, 74). — $C_{41}H_{49}ErN_2P_2Si_2$ (855.32): Calc.: C, 57.58; H, 5.77; N, 3.28. Found: C, 57.30; H, 5.34; N, 3.52%.

5.3. X-ray crystallographic studies of 2a–c

Crystals of **2a**–**c** were grown from a THF–*n*-pentane (1:2) or a toluene solution. Suitable crystals were coated in mineral oil (Aldrich) and mounted on glass fibers. The crystal was transferred directly to the −73 °C cold stream of a STOE IPDS diffractometer with Ag–K_α radiation (**2a**, **2b**) or a STOE-IPDS II diffractometer with Mo–K_α radiation (**2c**). Structures were solved using SHELXS-97 [26] and refined against F^2 using SHELXL-97 [27].

Compound **2a**: $C_{41}H_{49}N_2P_2Si_2Y$, Triclinic, $P\bar{1}$ (no. 2); lattice constants $a = 1031.67(7)$, $b = 1187.31(8)$, $c = 1760.02(11)$ pm, $\alpha = 74.058(8)$, $\beta = 77.750(8)$, $\gamma = 77.835(8)°$, $V = 1998.9(2)$ 10^6 pm^3, $Z = 2$; $\mu(\text{Ag–K}_\alpha) = 0.889$ mm^{-1}; $\theta_{max} = 21.0$; 8143 [$R_{int} = 0.047$] independent reflections measured, of which 6062 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.361 and −0.375 e Å^{-3}; 439 parameters, R_1 $(I > 2\sigma(I)) = 0.0376$; wR_2 (all data) = 0.0826.

Compound **2b**: $C_{41}H_{49}N_2P_2Si_2Sm$ Triclinic, $P\bar{1}$ (no. 2); lattice constants $a = 1030.92(8)$, $b = 1178.52(11)$, $c = 1761.91(15)$ pm, $\alpha = 73.937(10)$, $\beta = 77.129(10)$, $\gamma = 77.313(10)°$, $V = 1976.7(3)$ 10^6 pm^3, $Z = 2$; $\mu(\text{Ag–K}_\alpha) = 0.887$ mm^{-1}; $\theta_{max} = 22.25$; 9645 [$R_{int} = 0.0249$] independent reflections measured, of which 8610 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.835 and −0.758 e Å^{-3}; 434 parameters, R_1 $(I > 2\sigma(I)) = 0.0250$; wR_2 (all data) = 0.0698.

Compound **2c**: $C_{41}H_{49}ErN_2P_2Si_2$, Triclinic, $P\bar{1}$ (no. 2); lattice constants $a = 1031.59(8)$, $b = 1185.13(11)$, $c = 1754.22(15)$ pm, $\alpha = 74.052(10)$, $\beta = 78.014(10)$, $\gamma = 78.086(10)°$, $V = 1991.5(3)$ 10^6 pm^3, $Z = 2$; $\mu(\text{Mo–K}_\alpha) = 2.278$ mm^{-1}; $\theta_{max} = 27.0$; 7626 [$R_{int} = 0.0644$] independent reflections measured, of which 7454 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.863 and −1.998 e Å^{-3}; 434 parameters, R_1 $(I > 2\sigma(I)) = 0.0385$; wR_2 (all data) = 0.1022.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 169514 for compound **2a**, 169515 for compound **2b**, and 169516 for compound **2c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (Heisenberg fellowship), the Karl-Winnacker-Stiftung, and the Fonds der Chemischen Industrie. Additionally, generous support from Professor Dr. D. Fenske is gratefully acknowledged.

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