Cyclooctatetraenyl complexes of the early transition metals and lanthanides
IX. [1] (Cyclooctatetraenyl) lanthanide diazadiene complexes

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Abstract

Complexes of the type $(COT^*)Ln(DAD)(THF)$ [Ln = Sm, Yb; $COT^* = 1,4-(Me_3Si)_2C_8H_6$; DAD = 1,4-diazadienes] have been prepared in a 'one-pot' reaction by treatment of elemental samarium or ytterbium with equimolar amounts of 1,4-bis(trimethyl-silyl)cyclooctatriene and 1,4-diazadiene ligands. ^1H and ^{171}Yb NMR data show that the Sm derivatives contain Sm^{3+} ions and coordinated DAD radical anions, while in the case of Yb the neutral DAD ligand is coordinated to divalent ytterbium. © 1997 Elsevier Science S.A.

Keywords: Organolanthanide complexes; Cyclooctatetraenyl ligands; Diazadiene ligands; Samarium; Ytterbium

1. Introduction

1,4-Diazadienes are highly versatile, structurally flexible ligands for which complexes are known with various metals throughout the Periodic Table. The diazadiene (DAD) ligands can be coordinated to a metal ion either as neutral ligands [2–6], as radical anions [7–12], or as dianions [13–18]. The latter coordination mode is preferred in the case of early transition metals in their high oxidation states as well as alkali metals. In recent years, DAD ligands have been frequently employed in lanthanide chemistry as well. It has been shown by NMR studies and crystallographic investigations that diazadienes are coordinated to lanthanides preferably as the radical anions. Among the first examples was the homoleptic neodymium(III) complex $(tBuN=CHCH=NtBu)_3Nd$, which was prepared by co-condensation of the ligand with neodymium vapor [19,20]. Later, other homoleptic complexes of the type $(DAD)_3Ln$ (Ln = Y, Sm, Yb) [20] and $(DAD)_2Ln$ (Ln = Yb) [21] have also been reported. $(C_5Me_5)_2Sm(THF)_2$ readily adds diazadienes to yield the dark brown samarium(III) complexes

$(C_5Me_5)_2Sm(DAD)$ [22]. More recently it has been shown by Scholz et al. that [(DAD)Li] units may act as Cp-like ligands in organolanthanide complexes [15,16,23]. We report here the preparation and characterization of the first (cyclooctatetraenyl)lanthanide diazadiene complexes. For solubility reasons the experiments have been carried out using the 1,4-bis(trimethyl-silyl)cyclooctatetraenyl ligand, $1,4-(Me_3Si)_2C_8H_6^{2-}$ (COT^*).

2. Results and discussion

The 1,4-bis(trimethylsilyl)cyclooctatetraenyl ligand has been introduced into organolanthanide chemistry by Cloke et al. [24–26]. This very bulky cyclooctatetraenyl dianion often provides higher solubility and better crystallinity to organolanthanide derivatives as compared to the parent COT complexes. The preparation of organolanthanide half-sandwich complexes containing one COT^* ligands is, however, not always straightforward, as the products are often contaminated with the anionic sandwich complexes $[Ln(COT^*)_2]^-$ [1]. Therefore, a salt-free route to the title compounds was developed, which involves the simultaneous reaction of lanthanide metal powders with equimolar amounts of 1,4-

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bis(trimethylsilyl)-2,5,7-cyclooctatriene and diazadienes in THF solution according to Scheme 1. The reactivity of the lanthanides was enhanced by addition of a small amount of $HgCl_2$ which is known to activate the metal surface [27]. Only in the case of ytterbium and glyoxal-bis(t-butylimine), tBuN=CHCH=NtBu, no reaction was observed. In the course of the reaction, the starting material 1,4-bis(trimethylsilyl)-2,5,7-cyclooctatriene is deprotonated to the 1,4-bis(trimethyl-silyl)cyclooctatetraenyl dianion $(COT^{''})^{2-}$. It is known from the literature that $(C_5Me_5)_2Sm(II)$ reacts with various reagents such as cyclopentadiene, terminal acetylenes, or hydrazines under deprotonation and formation of the corresponding anionic ligands [28,29]. Thus, it is plausible to assume the formation of a $(COT^{''})Ln(II)$ intermediate, which then adds the diazadiene ligand. The latter step has once again a precedent in $(C_5Me_5)_2Sm(II)$ chemistry [22]. The proposed reaction pathway is supported by the fact, that the reaction was successful only with samarium and ytterbium, which are known to have a rich organolanthanide(II) chemistry [30]. The preparation fails in the case of other lanthanide elements such as praseodymium or neodymium, which are much more difficult to reduce.

All three diazadiene complexes are isolated as deeply colored, thermally stable though highly air-sensitive crystalline solids. The dark brown color of the samarium derivatives in solution closely resembles the brown coloration of the related $(C_5Me_5)_2Sm(DAD)$ complexes [22]. All three compounds have been characterized by spectroscopic methods. The NMR spectra (^1H and ^{171}Yb) revealed interesting differences in the bonding modes of the coordinated diazadiene ligands. In the case

of the samarium derivatives 1 and 2, most of the proton NMR resonances originating from the coordinated di-azadiene ligands exhibit very strong paramagnetic shifts. For example, broad peaks at δ -182 and -226 ppm are observed for the methine protons of the tBuN=CHCH=NtBu ligand in 1. These unusual chemical shifts are typical for a combined effect of the paramagnetism of the metal ion and the radical anion of the ligand [19,20,22]. Thus, the ^1H NMR results clearly show, that the samarium derivatives 1 and 2 should be formulated as Sm^{3+} complexes of the DAD radical anions.

In marked contrast, all ^1H NMR resonances of the ytterbium complex 3 appear in the 'normal' range and show no significant paramagnetic shifts. This behavior is compatible only with the presence of divalent ytterbium, as Yb^{2+} is diamagnetic. The formulation of 3 as an organoytterbium(II) complex is further confirmed by the fact that a $^{171}Yb\{^1H\}$ NMR spectrum could be recorded. ^{171}Yb NMR spectroscopy is restricted to diamagnetic ytterbium(II) compounds [31,32]. In this case, a single resonance at 224.3 ppm with a line width at half intensity of 55 Hz is observed. Thus, the chemical shift is somewhere between the range typical for Yb^{2+} complexes with carbocyclic π ligands (e.g., 0 ppm for $(C_5Me_5)_2Yb(THF)_2$ which is used as the internal standard [31]) and complexes containing only N-donor ligands (ca. 700–800 ppm [33]). In this sense, the ^{171}Yb chemical shift further confirms the formulation of 3 as $(COT^{''})Yb^{II}[PhN=C(Me)C(Me)=NPh]$. The observed differences in the bonding modes of the diazadiene ligands can be explained by the different electronic properties of the Ln^{2+} ions. Sm^{2+} is a much stronger

1: R = tBu, R' = H
2: R = Ph, R' = Me

3: R = Ph, R' = Me
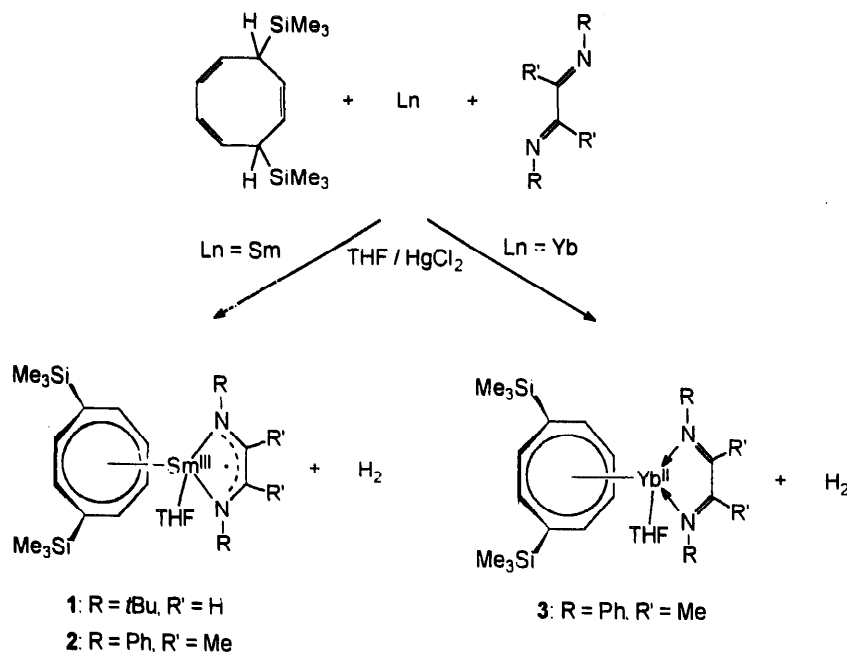
Scheme 1. Preparation of the (cyclooctatetraenyl)lanthanide diazadiene complexes 1–3.

reducing agent than Yb^{2+} [34]. Thus, an electron transfer from the central lanthanide ion to the coordinated DAD is expected to occur much more readily in the samarium derivatives.

3. Experimental

All reactions were carried out under rigorous exclusion of air and moisture using standard Schlenk line and dry-box techniques. Solvents were carefully dried over Na/benzophenone and freshly distilled under N_2 prior to use. IR spectra: Perkin–Elmer spectrometer 180 and Bio-Rad FTS 7, Nujol mulls between KBr disks. ^1H NMR spectra: Bruker WP 80 SY and Bruker AM-250 (250 MHz, TMS ext., 32°C). ^{29}Si NMR spectra: Bruker AM-250 (79.460 MHz, TMS, 32°C). ^{171}Yb NMR: Bruker AM-250 (43.765 MHz, $(C_5Me_5)_2Yb(THF)_2$, 32°C). Elemental analyses: Analytical laboratory of the Department of Inorganic Chemistry, University of Göttingen. Sm and Yb powders were purchased from Aldrich and used as received. The starting materials $1,4-(Me_3Si)_2C_8H_8$ [25], tBuN=CHCH=NtBu [5] and PhN=C(Me)C(Me)=NPh [5] were prepared according to literature procedures.

3.1. [1,4-Bis(trimethylsilyl)cyclooctatetraenyl][glyoxal-bis(t-butylimine)](tetrahydrofuran) samarium(III) (1)

A mixture of 0.67 g (4.0 mmol) tBuN=CHCH=NtBu, 1.00 g (4.0 mmol) 1,4-$(Me_3Si)_2C_8H_8$, 0.68 g (4.5 mmol) Sm powder, and 10 mg $HgCl_2$ in 100 ml THF is stirred for 3 days at room temperature. During this time, an intense dark brown coloration develops and the major part of the suspended metal dissolves. The reaction mixture is filtered through a thin layer of Celite filter aid and the filtrate is evaporated to dryness. The residue is washed twice with toluene (10 ml) and twice with hexane (20 ml) and dried under vacuum to afford 1.32 g (47%) of 1 as a dark blue-green solid. M.p. 163°C. Found: C, 53.7; H, 9.2; N, 4.1. $C_{28}H_{44}N_2OSi_2Sm$ (639.3) Calcd.: C, 53.7; H, 8.2; N, 4.4%. IR (Nujol) (cm^{-1}): 1410 (w), 1303 (w), 1261 (s), 1249 (vs), 1168 (w sh), 1153 (m sh), 1092 (vs br), 1034 (m), 1020 (vs br), 931 (m), 902 (s sh), 838 (vs br), 801 (s), 781 (s), 748 (w), 720 (m), 690 (w sh), 640 (m), 552 (m), 465 (w), 375 (s). EI-MS (70 eV): m / z (rel. int. %): 314 [Sm(tBuN=CHCH=NtBu)$^+$, 1], 169 [tBuN=CHCH=NtBu$^+$, 16], 97 [tBuN=CHCH$^+$, 18], 73 [SiMe$_3^+$, 18], 57 [$C_4H_9^+$, 100]. ^1H NMR (THF-d_8): δ 7.83 (s, 2 H, COT*-H), 1.21 (s, 18 H, tBu), 0.02 (s, 18 H, SiMe$_3$), -4.33 (br, $\nu_{1/2}$ = 5 Hz, 2 H, COT*-H), -6.94 (br, $\nu_{1/2}$ = 12 Hz, 2 H, COT*-H), -182.0 (br, $\nu_{1/2}$ = 1185 Hz, 1 H, tBuN=CHCH=NtBu), -226.0

(br, $\nu_{1/2}$ = 480 Hz, 1 H, tBuN=CHCH=NtBu) ppm. ^{29}Si NMR (THF/C_6D_6): δ 4.7 (s) ppm.

3.2. [1,4-Bis(trimethylsilyl)cyclooctatetraenyl][diacetyl-bis(phenylimine)](tetrahydrofuran)-samarium(III) (2)

In a similar manner, the reaction of 0.95 g (4.0 mmol) PhN=C(Me)C(Me)=NPh, 1.00 g (4.0 mmol) 1,4-$(Me_3Si)_2C_8H_8$, 0.68 g (4.5 mmol) Sm powder, and 10 mg $HgCl_2$ afforded 1.21 g (43%) 2 as dark brown crystals. M.p. 108°C. Found: C, 56.3; H, 7.1; N, 4.3. $C_{34}H_{48}N_2OSi_2Sm$ (707.3) Calcd.: C, 57.7; H, 6.8; N, 4.0%. IR (Nujol) (cm^{-1}): 1587 (m), 1506 (w), 1489 (s sh), 1300 (w), 1261 (vs), 1247 (vs), 1169 (w), 1152 (m), 1095 (vs br), 1078 (s sh), 1021 (s br), 1005 (m sh), 863 (m), 836 (s), 800 (vs), 745 (m), 721 (m), 696 (w), 389 (s). EI-MS (70 eV): m / z (rel. int. %): 468 [M$^+$–THF–Ph–PhN, 2], 248 [(COT*)$^+$, 12], 238 [PhNC(Me)C(Me)NPh$^+$, 22], 207 [(COT*)$^+$-C_3H_5, 78], 146 [Si$_2$Me$_6^+$, 18], 118 [PhNCMe$^+$, 100], 77 [$C_6H_5^+$, 96], 73 [SiMe$_3^+$, 24]. ^1H NMR (THF-d_8): δ 47.88 (br, $\nu_{1/2}$ = 264 Hz, 4 H, o-C_6H_5), 37.10 (br, $\nu_{1/2}$ = 120 Hz, 4 H, m-C_6H_5), 4.92 (s br, $\nu_{1/2}$ = 33 Hz, 2 H, p-C_6H_5), 0.01 (s, 6 H, Me), -0.03 (s, 18 H, SiMe$_3$), -8.62 (s, 2 H, COT*-H), -24.05 (br, $\nu_{1/2}$ = 180 Hz, 2 H, COT*-H), -45.48 (br, $\nu_{1/2}$ = 138 Hz, 2 H, COT*–H) ppm. ^{29}Si NMR (THF/C_6D_6): δ -2.6 (s) ppm.

3.3. [1,4-Bis(trimethylsilyl)cyclooctatetraenyl][diacetyl-bis(phenylimine)](tetrahydrofuran)-ytterbium(III) (3)

This compound was made analogously starting from 0.95 g (4.0 mmol) PhN=C(Me)C(Me)=NPh, 1.00 g (4.0 mmol) 1,4-$(Me_3Si)_2C_8H_8$, 0.78 g (4.5 mmol) Yb powder, and 10 mg $HgCl_2$ to yield 0.77 g as a highly air-sensitive, green-brown solid, which can be recrystallized from THF/hexane. M.p. 188°C. Found: C, 55.4; H, 7.0; N, 4.0. $C_{34}H_{48}N_2OSi_2Yb$ (730.0) Calcd.: C, 55.9; H, 6.6; N, 3.8%. IR (Nujol) (cm^{-1}): 1951 (w), 1569 (w), 1305 (w), 1262 (s), 1254 (m sh), 1169 (m sh), 1154 (s), 1097 (m br), 993 (s sh), 984 (vs), 971 (s sh), 934 (m sh), 912 (m), 825 (m), 801 (m), 739 (vs), 723 (vs), 659 (s), 633 (w), 541 (w), 492 (m), 450 (w). EI-MS (70 eV). m / z (rel. int. %): 238 [PhNC(Me)C(Me)NPh$^+$, 5], 222 [(COT*)$^+$-C_2H_2, 2], 207 [(COT*)$^+$-C_3H_5, 6], 146 [Si$_2$Me$_6^+$, 20], 118 [PhNCMe$^+$, 100], 93 [PhNH$_2^+$, 72], 77 [$C_6H_5^+$, 96], 73 [SiMe$_3^+$, 68]. ^1H NMR (THF-d_8): δ 7.39-7.19 (m, 4 H, o- or m-C_6H_5), 7.19-6.93 (m, 2 H, p-C_6H_5), 6.93-6.49 (m, 4 H, o- or m-C_6H_5), 6.05-5.50 (m, 6 H, COT*-H), 0.12 (s, 18 H, SiMe$_3$), 0.02 (s, 6 H, CH$_3$) ppm. ^{29}Si NMR (THF/C_6D_6): δ -4.2 (s) ppm. ^{171}Yb NMR (THF/C_6D_6): δ 224.3 (s, $\nu_{1/2}$ = 55 Hz) ppm.

Acknowledgements

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