Diene Complexes of Calcium and Strontium: First Crystal Structures of Calcium- and Strontium–Diene Complexes, M(2,3-dimethyl-1,4-diphenyl-1,3-butadiene)(THF)$_4$ (M = Ca and Sr)

Kazushi Mashima,*,†,‡ Hiroyasu Sugiyama,†
Nobuko Kanehisa,§ Yasushi Kai,§ Hajime Yasuda,⊥ and
Akira Nakamura*,†

Department of Macromolecular Science
Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan
Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan
Department of Applied Chemistry
Faculty of Engineering, Hiroshima University
Higashi-Hiroshima 724, Japan

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Although the chemistry of transition metal–diene complexes is well established,[1] few diene complexes of the highly electropositive metals of groups 1–3 have been synthesized.[2–11] In the case of magnesium, only one diene complex has been characterized crystallographically;[5] the diene complexes of the heavier group 2 elements are probably oligomeric, and their poor solubility has hampered structural characterization. Recent developments in the coordination chemistry of these elements have been marked by the introduction of hydrocarbon and alkoxo ligands bearing sterically bulky substituents, which allow control of the solubility and kinetic stability of the complexes.[12] While studying diene complexes of other elements,[5,11,13–15] we found that 2,3-dimethyl-1,4-diphenyl-1,3-butadiene (MPBD) forms complexes M(MPBD)(THF)$_4$ with the heavier group 2 elements whose structures have been determined for the first time by X-ray diffraction.

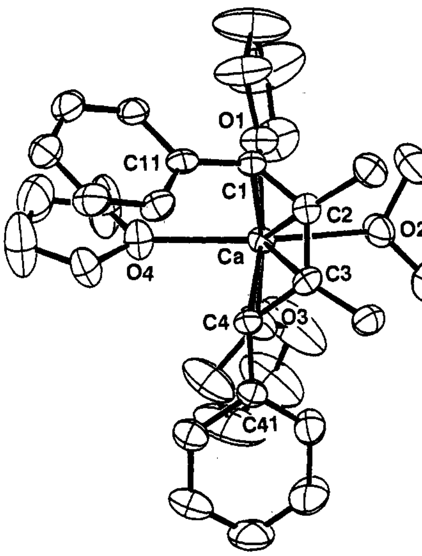

Figure 1. *ORTEP* drawing of complex **1** with the numbering scheme. Selected bond lengths (Å): Ca–C1 2.574(7), Ca–C2 2.746(7), Ca–C3 2.777(7), Ca–C4 2.588(7), C1–C2 1.448(9), C2–C3 1.375(8), C3–C4 1.472(9).

Treatment of an excess of metallic calcium with MPBD in THF under argon gives a deep red solution. After removal of unchanged metal, recrystallization from the saturated solution produces highly air-sensitive red crystals of Ca(MPBD)(THF)$_4$ (**1**) in 67% yield.[16] In sharp contrast to the oligomeric nature of the calcium complex of 1,4-diphenyl-1,3-butadiene,[8,17] **1** was monomeric. Presumably, the steric and electronic effects of introducing two methyl groups on the diene ligand prevent the formation of an oligomeric structure and make the complex soluble in THF. Similarly, reaction of metallic strontium with MPBD in THF followed by recrystallization from THF affords Sr(MPBD)(THF)$_4$ (**2**) as deep red crystals in 61% yield.[18] These complexes were characterized spectroscopically and by X-ray structural analysis.

The X-ray structure of **1**[19] (Figure 1) shows that the calcium atom is coordinated in a pseudooctahedral geometry by two carbon

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† Faculty of Science, Osaka University.

‡ Present address: Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan.

§ Faculty of Engineering, Osaka University.

⊥ Faculty of Engineering, Hiroshima University.

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(16) **1**: 67% yield, mp 110 °C dec; ^{1}H NMR (THF-d_8) δ 1.96 (s, 6H, CH_3), 2.9–3.4 (brs, 2H, PhCH), 5.59 (t, 2H, p-H, $J_{p,m}$ = 7.0 Hz), 6.11 (d, 4H, o-H, $J_{o,m}$ = 7.9 Hz), 6.49 (dd, 4H, m-H); ^{13}C NMR (THF-d_8) δ 25.7 (CH$_3$), 72.9 (PhCH, J_{C-H} = 142 Hz), 106.7 (p-Ph), 117.8 (o-Ph), 128.5 (m-Ph), 141.5 and 150.1 for C_{ipso} and C(CH$_3$)=; UV (THF) λ_{max} = 453 nm ($\epsilon = 3.9 \times 10^3$ cm^{-1} M^{-1}).

(17) Mashima, K.; Yasuda, H.; Nakamura, A., unpublished result.

(18) **2**: 61% yield, mp 100 °C dec; ^{1}H NMR (THF-d_8) δ 1.86 (s, 6H, CH_3), 3.6 (s, 2H, PhCH), 5.44 (t, 2H, p-H, $J_{p,m}$ = 7.0 Hz), 5.95 (d, 4H, o-H, $J_{o,m}$ = 7.7 Hz), 6.43 (dd, 4H, m-H); ^{13}C NMR (THF-d_8) δ 26.4 (CH$_3$), 77.9 (PhCH, J_{C-H} = 147 Hz), 105.1 (p-Ph), 115.1 (o-Ph), 129.3 (m-Ph), 141.5 and 147.3 for C_{ipso} and C(CH$_3$)=; UV (THF) λ_{max} = 472 nm ($\epsilon = 2.2 \times 10^4$ cm^{-1} M^{-1}).

(19) Crystal data of **1**: FW = 562.85, monoclinic space group $P2_1/n$, a = 10.67(2), b = 17.29(1), and c = 17.53(1) Å, β = 92.54(9)°, V = 3231(6) Å^3, Z = 4, d_{calcd} =1.157, μ (Mo Kα) = 2.20 cm^{-1}, no. of parameters = 352, no. of reflection data with $I > 3\sigma(I)$ = 2146, goodness of fit = 1.96, R = 0.062, R_w = 0.065.

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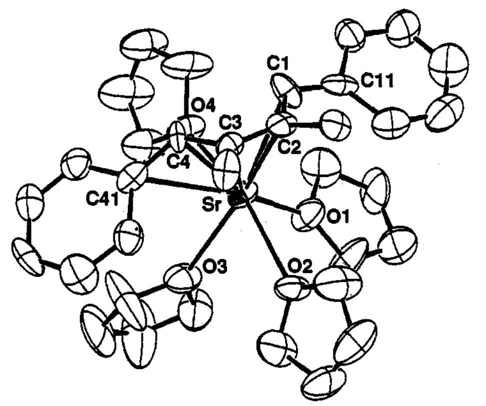

Figure 2. *ORTEP* drawing of molecule I of complex **2** with the numbering scheme.[22] Selected bond lengths (Å), molecule I/molecule II: Sr–C1 2.73(2)/2.76(2), Sr–C2 2.91(1)/2.87(2), Sr–C3 2.95(2)/2.81(1), Sr–C4 2.71(1)/2.76(1), Sr–C41 3.16(2)/3.09(2), C1–C2 1.48(2)/1.46(2), C2–C3 1.38(2)/1.38(2), C3–C4 1.47(2)/1.51(2).

atoms of the diene and four oxygen atoms of the THF ligands. The bond distances Ca–C1 [2.574(7) Å] and Ca–C4 [2.588(7) Å] are less than the distances between Ca and the internal carbon atoms of the diene [2.746(7) and 2.777(7) Å]. The bond lengths C1–C2 [1.448(9) Å] and C3–C4 [1.472(9) Å] are greater than C2–C3 [1.375(8) Å]. This trend has already been observed in diene complexes of magnesium and lithium.[3–5] In the calcium complex, the diene is coordinated in a highly dissymmetric manner.[20] One phenyl group is displaced from the normal syn position with a torsion angle C3-C2-C1-C11 of 60(1)°, while the other phenyl group occupies the syn position with a torsion angle C2-C3-C4-C41 of 158.6(7)°.

Figure 2 shows one of the two crystallographically independent but essentially identical structures of complex **2**.[21,22] The strontium atom also assumes a pseudooctahedral geometry, being surrounded by the diene and four THF ligands. In complex **2**, both phenyl groups assume a syn orientation. The most interesting feature is that the two phenyl groups bend toward the metal center, the torsion angles C3-C2-C1-C11 and C2-C3-C4-C41 being –159(1)° for molecule I [170(1)° for molecule II] and 149(1)° for molecule I [–146(1)° for molecule II], respectively. The distance Sr–C41 [3.16(2) Å for molecule I, 3.09(2) Å for molecule II] is greater than Sr–C2 [2.91(1) Å for molecule I and 2.87(2) Å for molecule II] and Sr–C3 [2.95(2) Å for molecule I, 2.81(1) Å for molecule II] and can be regarded as representing a weak σ-type interaction in complex **2**. This is consistent with the tendency for aromatic hydrocarbons to interact with the larger and polarizable heavier group 1 and 2 metals in a multihapto fashion.[23]

We also prepared a magnesium–diene complex, Mg(MPBD)(dme)$_2$ (**3**),[24] in order to elucidate the structural features of **1** and **2** in solution. The structures of calcium- and strontium–diene complexes are between η^4-diene and metallacyclo-3-pentene, while the structure of **3** is metallacyclo-3-pentene. The resonances due to $H_{1,4}$ in **1** (δ 2.9–3.4 ppm) and **2** (δ 3.6 ppm) are observed at lower field than those of **3** (δ 2.55 ppm), and also ^{13}C chemical shifts of $C_{1,4}$ in **1** (δ 72.9 ppm) and **2** (δ 77.9 ppm) appear at lower field than that in **1** (δ 48.0 ppm). For complexes **1** and **2**, the C–H coupling constants [142 Hz (**1**); 147 Hz (**2**)] correspond to $sp^{2.6}$ and $sp^{2.5}$ hybridization, respectively, whereas the coupling constant of 127 Hz for **3** corresponds to approximately $sp^{2.9}$ tetrahedral hybridization. These data are in accord with the electronic spectra of the diene complexes of magnesium (**3**), calcium (**1**), and strontium (**2**), which exhibit λ_{max} values at 248, 453, and 472 nm, respectively, and indicate increasing carbanionic character for the diene in bonding with heavier group 2 metals.

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Supplementary Material Available: Experimental details for the preparation of **1**, **2**, and **3**; X-ray data and figures giving additional atom labeling for **1** and **2** (59 pages); listing of observed and calculated structure factors for **1** and **2** (40 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS: see any current masthead page for ordering information.

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(20) The dissymmetric coordination of the diene in **1** is detectable in solution. At 30 °C, the NMR peaks of the two olefinic protons of the diene are observed as a broad singlet at δ 2.9–3.4 ppm; below 0 °C, this signal separates into two singlets at δ 2.81 and 3.28 ppm. The intensity of the signal assignable to the syn protons decreases at lower temperature. Finally, at –60 °C, only one singlet due to the anti protons at δ 3.28 ppm is observed. The observed fluxionality is explicable on the basis of an equilibrium between a coordinated (*E,E*)-diene (the most stable form in solution at low temperature) and a coordinated (*E,Z*)-diene, which corresponds to the crystal structure of **1**.

(21) Crystal data of **2**: FW = 610.39, monoclinic space group $P2_1/c$, a = 9.127(3), b = 27.68(1), and c = 26.261(5) Å, β = 97.91(3)°, V = 6570(3) Å^3, Z = 8, d_{calcd} = 1.234, μ (Cu Kα) = 25.27 cm^{-1}, no. of parameters = 730, no. of reflection data with $I > 3\sigma(I)$ = 3711, goodness of fit = 2.61, R = 0.071, R_w = 0.063.

(22) Two molecules of **2** in the crystal are related as an enantiomorphic pair. Further information, including the crystal structure of the other molecule of **2** (molecule II), is available as supplementary material.

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(24) Complex **3** was prepared by the reaction of MPBD with an excess of magnesium in THF and subsequent crystallization from DME. **3**: pale yellow solid, 47% yield, mp 147–149 °C dec; ^{1}H NMR (THF-d_8) δ 1.84 (s, 6H, CH_3), 2.55 (s, 2H, PhCH), 3.24 (s, 12H, OCH_3), 3.40 (s, 8H, OCH_2), 6.11 (t, 2H, *p*-H, $J_{p,m}$ = 7.1 Hz), 6.43 (d, 4H, *o*-H, $J_{o,m}$ = 7.6 Hz), 6.70 (dd, 4H, *m*-H); ^{13}C NMR (THF-d_8) δ 20.6 (CH$_3$), 48.0 (PhCH, J_{C-H} = 127 Hz), 58.9 (OCH$_3$), 72.7 (OCH$_2$), 113.4 (*p*-Ph), 121.6 (*o*-Ph), 130.1 (*m*-Ph), 134.1 and 157.5 for C_{ipso} and C(CH$_3$)=.