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THE X-RAY STRUCTURE OF A MAGNESIUM-1,3-DIENE COMPLEX. THE UNIQUE MODE OF COORDINATION OF DIENE OBSERVED IN PENTA-COORDINATED $Mg(THF)_3$(*s-cis*-PhCH=CH-CH=CHPh)

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X-ray analysis of $Mg(THF)_3$(*s-cis*-PhCH=CH-CH=CHPh) revealed a novel magnesium-1,3-diene structure with trigonal bipyramidal coordination.

The structure of magnesium-diene complexes prepared from 1,3-diene and activated magnesium is of considerable importance in organomagnesium chemistry. Five-membered metallacyclic or cyclic oligomeric structure has been proposed for these compounds.[1,2) These classes of compounds are valuable as a reagent for organic[3,4) as well as organometallic synthesis.[5-7) This type of reagent has recently been used in the preparation of $ZrCp_2$(RCH=CH-CH=CHR)(Cp=cyclopentadienyl, R=H or Ph) which reveals the first example of *s-trans*-diene coordination to mononuclear metal species.[8,9) The chemical nature of the Mg-C bond is interesting since the diene ligand behaves as η^4-coordinated diene when oxidized by air or I_2 releasing the coordinated diene while it behaves as 2-buten-diylmagnesium toward alkylene dihalides, dienes and protic agents.[1,2) We present here the first X-ray structure analysis of a magnesium-diene complex, 1,4-diphenyl-2-buten-1,4-diylmagnesium crystallized from the THF solution.

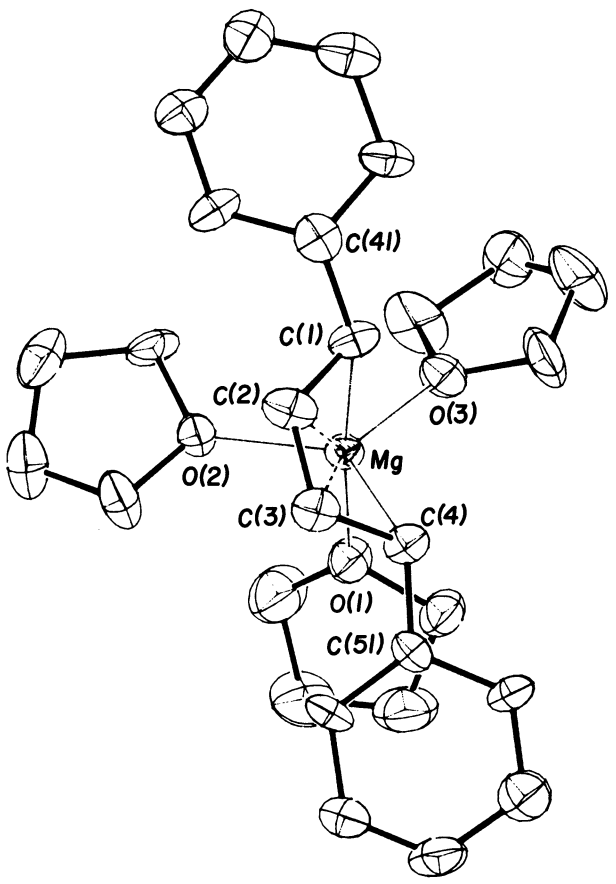
Crystal Data: $C_{28}H_{38}O_3Mg$, M=446.9, monoclinic, $P2_1/c$, a=14.529(2), b=15.929(2), c=11.440(2) Å, β=102.03(1)°, U=2589.4(6) Å^3, Z=4, Dc=1.146 g cm^{-3}, μ(Mo-$K\alpha$)=1.73 cm^{-1}. The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer with Zr-filtered Mo-$K\alpha$ radiation. The crystal was sealed in a thin-walled glass capillary tube in argon. 1850 reflections were collected up to 2θ=45°

by the θ-2θ scan method, of which 1362 were observed ($|Fo| \geqq 3\sigma(Fo)$) and were used for the structure refinement. The structure was solved by the direct method (*MULTAN*-78)[10] and refined by the block-diagonal least-squares (*HBLS*-V)[11] (only non-hydrogen atoms anisotropically) to the *R* index of 0.139. The final atomic coordinates are listed in Table 1.

Table 1. Fractional atomic coordinates with *e.s.d.*'s in parentheses. $B_{eq}=\frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}a_i\cdot a_j$

Atom	x	y	z	$B_{eq}/\mathrm{\AA}^2$
Mg	0.2625(5)	0.4003(4)	0.2063(6)	5.0
C(1)	0.1591(12)	0.2911(10)	0.2155(17)	6.0
C(2)	0.2123(14)	0.2508(11)	0.1404(19)	7.2
C(3)	0.3123(14)	0.2521(11)	0.1734(17)	6.6
C(4)	0.3610(12)	0.2955(10)	0.2829(16)	5.7
C(41)	0.0562(14)	0.2971(11)	0.1705(17)	7.0
C(42)	-0.0053(14)	0.3159(13)	0.2503(20)	7.6
C(43)	-0.1096(16)	0.3187(15)	0.2023(23)	10.1
C(44)	-0.1454(17)	0.3098(15)	0.0838(20)	9.5
C(45)	-0.0868(14)	0.2935(12)	0.0051(18)	7.6
C(46)	0.0109(13)	0.2868(10)	0.0462(17)	6.5
C(51)	0.4635(12)	0.3026(10)	0.2919(15)	5.1
C(52)	0.5062(13)	0.3072(13)	0.1951(17)	7.0
C(53)	0.6071(14)	0.3151(13)	0.2161(19)	7.8
C(54)	0.6611(14)	0.3195(15)	0.3276(21)	9.6
C(55)	0.6190(16)	0.3167(15)	0.4291(20)	9.4
C(56)	0.5203(12)	0.3088(12)	0.4104(17)	6.6
O(1)	0.3659(9)	0.5005(8)	0.2157(11)	7.4
C(11)	0.3846(20)	0.5629(19)	0.1304(24)	13.7
C(12)	0.4882(19)	0.5765(16)	0.1627(24)	12.6
C(13)	0.5163(18)	0.5502(18)	0.2854(25)	12.5
C(14)	0.4325(16)	0.5138(16)	0.3268(19)	9.4
O(2)	0.2201(9)	0.4345(8)	0.0298(10)	6.2
C(21)	0.1294(13)	0.4668(14)	-0.0246(19)	8.1
C(22)	0.1192(19)	0.4504(16)	-0.1573(20)	11.2
C(23)	0.2172(21)	0.4427(16)	-0.1719(19)	11.4
C(24)	0.2668(18)	0.3998(15)	-0.0603(18)	9.6
O(3)	0.2089(9)	0.4817(8)	0.3224(11)	7.3
C(31)	0.2106(20)	0.4595(18)	0.4427(19)	11.8
C(32)	0.1417(22)	0.5092(18)	0.4804(24)	13.2
C(33)	0.1110(18)	0.5701(16)	0.3970(20)	11.1
C(34)	0.1541(19)	0.5575(14)	0.2892(23)	12.1

The molecular structure obtained is shown in Figure 1. One of the important features of the present molecule is that the magnesium atom is penta-coordinated by three oxygen atoms of THF ligands and C(1) and C(4) atoms of the butadiene ligand. The coordination geometry of magnesium is distorted trigonal bipyramid. The C(1) and C(4) atoms of butadiene ligand occupy the axial and equatorial positions, respectively. The only previous X-ray example of penta-coordinated organomagnesium complex is $MgBr(CH_3)(THF)_3$,[12] in which magnesium takes trigonal bipyramidal coordination with Br and methyl ligands on the equatorial positions.



C(1)-Mg-O(1)=174.4°
C(1)-Mg-C(4)= 77.9
C(1)-Mg-O(2)=100.3
C(1)-Mg-O(3)= 96.0
O(1)-Mg-C(4)= 98.5
O(1)-Mg-O(2)= 85.3
O(1)-Mg-O(3)= 82.0
C(4)-Mg-O(2)=127.8
C(4)-Mg-O(3)=119.7
O(2)-Mg-O(3)=112.3

Mg-O(1)=2.18 Å
Mg-O(2)=2.06
Mg-O(3)=2.12

Figure 1. Molecular structure of $Mg(THF)_3$(*s-cis*-PhCH=CH-CH=CHPh). Thermal ellipsoids are drawn at the 20% probability level.

The butadiene ligand takes *s-cis* conformation with four carbon atoms of C(1) to C(4) on a plane, from which magnesium atom deviates 1.71 Å away. The Mg-C(1) bond (2.32 Å) is slightly longer than Mg-C(4) bond (2.26 Å), the former locating on the axial and the latter on the equatorial position, respectively. The Mg-C(2) (2.56 Å) and Mg-C(3) (2.52 Å) bonds are longer than the Mg-C(1) and Mg-C(4) bonds. The observed Mg-C distances are significantly longer than those found in $MgPh_2$·TMEDA (Mg-C=2.167(3) Å)13) and $MgMe_2$·TMEDA (Mg-C=2.166(6) Å).14) The C(2)-C(1)-Mg and C(3)-C(4)-Mg bond angles are 82.7 and 82.1°, respectively. These angles are very close to the corresponding angle of η^4-coordinated diene complex of $ZrCp_2$(2,3-dimethyl-1,3-butadiene) (84.4°)9) and are larger than those of $Fe(CO)_3$(1,4-diphenyl-1,3-butadiene) (66.3, 67.1°).15)

The geometry of butadiene ligand is also interesting. The C(1)-C(2) (1.42 Å) and C(2)-C(3) (1.42 Å) bond distances are identical with each other but slightly shorter than that of C(3)-C(4)(1.48 Å). The C(2)-C(1)-C(41) bond angle (117.1°) is close to that of the *sp*^{2} carbon in contrast to the C(3)-C(4)-C(51) bond angle (113.2°) being close to that of the *sp*^{3} carbon. The relatively large deformation of butadiene ligand from the geometry of conventional η^4-diene or 2-buten-1,4-diyl coordination may result from the trigonal bipyramidal coordination of magnesium atom. The *e.s.d.*'s of the Mg-O, Mg-C, and C-C distances are 0.01, 0.02 and 0.03-0.04 Å, respectively. Though rather low accuracy of the molecular parameters was observed in the present study as has commonly found in the organomagnesium complexes, the structure determination of this complex is valuable to understand the correlation between the structure and the unique chemical behavior observed generally for magnesium-diene complexes.

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