Crystal Structure of the Product Formed by Facile Cleavage of 2,1,1-Cryptand by Dineopentylmagnesium

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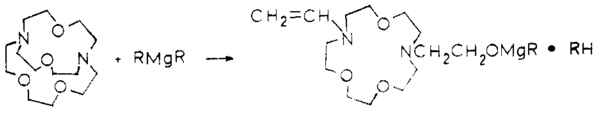
When a diethyl ether–benzene solution of dineopentylmagnesium and 2,1,1-cryptand is heated, one of the short bridges of the cryptand cleaves to vinyl and (metalated) hydroxyethyl groups, producing a species of composition $(CH_3)_3CCH_2MgOCH_2CH_2\overline{[N(CH_2)_2O(CH_2)_2O(CH_2)_2N(CH{=}CH_2)(CH_2)_2OCH_2CH_2]}$. The structure of a crystal obtained from such solutions was determined by single-crystal X-ray diffraction techniques. The crystal is monoclinic, and the space group is $P2_1/n$. The structure is a symmetrical dimer of two of the formula units above, and two of these dimers are in a unit cell with a = 10.203 (2) Å, b = 9.579 (4) Å, c = 23.121 (7) Å, and β = 95.93 (2)°. In the dimer, the oxygens of the two hydroxyethyl groups are each bonded to both magnesiums. Each magnesium is pentacoordinate, the other bonds being to a neopentyl group and to one nitrogen and one oxygen of one of the 15-membered rings.

We have discovered that additions of cryptands to solutions of dialkylmagnesium compounds form new organomagnesium species with interesting reaction behavior and have been trying to establish the structures of these species. For example, a single-crystal X-ray diffraction study has shown that a solid formed from 2,1,1-cryptand and Np_2Mg (Np = neopentyl) consists of $NpMg^+$(cryptand) and Np_3Mg^- ions.[1] Moreover, ^1H NMR spectra of benzene solutions of such solids show that the same ions probably are the dominant species in the solution.[1]

In our first effort at single-crystal X-ray diffraction in this system, however, the crystal that was chosen incorporated monocyclic units (**2**, R = $(CH_3)_3CCH_2$) that formed from 2,1,1-cryptand units (**1**) by a ring cleavage. In recrystallizing the sample to obtain crystals suitable for X-ray analysis, a benzene–diethyl ether solution had been heated in a sealed tube. We have now observed that heating a benzene–diethyl ether solution (1:1 by volume) at 100 °C for 1 h leads to cleavage of the cryptand ring, evident particularly by the appearance of ^1H NMR absorptions of the vinyl group. ^1H NMR absorptions characteristic of solutions[1] containing Np_2Mg and 2,1,1-cryptand are absent and the only absorptions present are identical with those observed for solutions prepared by redissolving crystals of the sort shown by X-ray diffraction to contain only ring-cleaved cryptand units. Therefore, cleavage must be complete. At ambient temperature, however, solutions are relatively stable. ^1H NMR absorptions indicated that cleavage had occurred to the extent of only ~50% in a benzene solution after 60 days.



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1 2

The cleavage of the ether function is remarkably ready. Although organomagnesium compounds have been observed to cleave various saturated dialkyl ethers to alcohols and alkenes, the necessary conditions have been considerably more severe.[2] The greater basicity[3] of solutions of dialkylmagnesium compounds and 2,1,1-cryptand than of typical organomagnesium solutions may be responsible for cleavage being so facile. Encapsulation of an electrophilic magnesium in the cryptand cavity may also contribute by enhancing the leaving-group ability of the ether oxygen or by increasing the ring strain.

The structure in the crystal, shown schematically in **3** (R = $(CH_3)_3CCH_2$), is that of a symmetrical dimer of **2**; for clarity, bonds within the cleaved cryptand units are shown as solid lines and linkages of the heteroatoms to the magnesiums as dashed lines. Bonds from the side-chain alkoxide oxygen of each cryptand unit to both magnesiums join the two units. Each magnesium also is bonded to a neopentyl group and to one nitrogen and one oxygen of one of the rings. A full ORTEP drawing of **3** is shown in

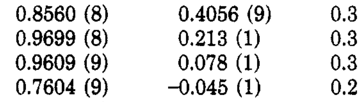

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Table I. Positional Parameters[a]

atom	x	y	z
Mg	0.5108 (2)	0.4549 (3)	0.4377 (1)
O(1)	0.3996 (4)	0.4180 (4)	0.5013 (2)
O(2)	0.6835 (5)	0.3264 (5)	0.4451 (2)
O(3)	0.8578 (6)	0.2902 (7)	0.3490 (3)
O(4)	0.5742 (5)	0.0699 (6)	0.3157 (2)
N(1)	0.4353 (6)	0.2245 (6)	0.4154 (2)
N(2)	0.8585 (7)	−0.0150 (7)	0.3355 (3)
C(1)	0.3149 (7)	0.2234 (8)	0.4458 (3)
C(2)	0.3328 (7)	0.2922 (8)	0.5054 (3)
C(3)	0.5374 (7)	0.1333 (7)	0.4446 (3)
C(4)	0.6726 (7)	0.1772 (7)	0.4365 (3)
C(5)	0.8124 (7)	0.3781 (8)	0.4478 (4)
C(6)	0.8560 (8)	0.4056 (9)	0.3896 (4)
C(7)	0.9699 (8)	0.213 (1)	0.3628 (5)
C(8)	0.9609 (9)	0.078 (1)	0.3253 (4)
C(9)	0.7604 (9)	−0.045 (1)	0.2860 (4)
C(10)	0.6593 (9)	0.065 (1)	0.2720 (4)
C(11)	0.5013 (8)	0.1976 (8)	0.3142 (3)
C(12)	0.3966 (8)	0.1892 (8)	0.3544 (3)
C(13)	0.9650 (9)	−0.107 (1)	0.4216 (5)
C(14)	0.8725 (9)	−0.102 (1)	0.3822 (4)
C(20)	0.4678 (7)	0.5690 (8)	0.3564 (3)
C(21)	0.3430 (7)	0.6588 (8)	0.3477 (3)
C(22)	0.2111 (8)	0.567 (1)	0.3455 (4)
C(23)	0.3323 (8)	0.742 (1)	0.2912 (3)
C(24)	0.3399 (9)	0.7605 (9)	0.3978 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

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[1] Squiller, E. P.; Whittle, R. W.; Richey, H. G., Jr., *J. Am. Chem. Soc.* **1985**, *106*, 432.

[2] Burwell, R. L., Jr. *Chem. Rev.* **1954**, *54*, 615. Meerwein, H. *Methoden Org. Chem.* (*Houben-Weyl*), *4th Ed.* **1965**, *6* (*part 3*), 1. Nützel, K. *Ibid.* **1973**, *13* (*part 2a*), 47. Trofimov, B. A.; Korostova, S. E. *Russ. Chem. Rev.* (*Engl. Transl.*) **1975**, *44*, 75; *Usp. Khim.* **1975**, *44*, 41.

[3] Farkas, J., Jr.; Squiller, E. P.; Richey, H. G., Jr., unpublished observations.

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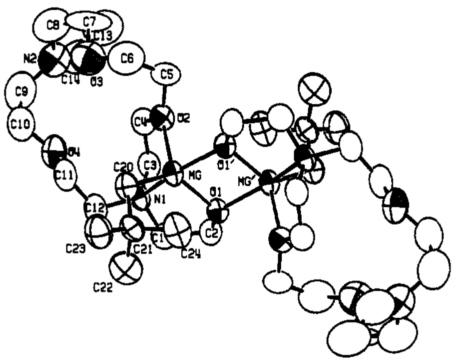


Figure 1. An ORTEP drawing of 3 showing the atom numbering scheme.

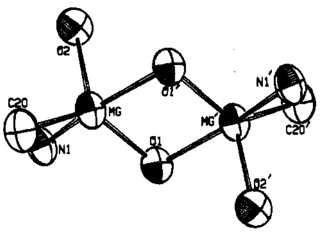


Figure 2. An ORTEP drawing of 3 showing only the magnesiums and the atoms bonded directly to them.

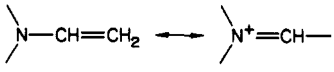
Table II. Selected Bond Lengths (Å) for 3[a]

Mg-Mg'	3.037 (4)	O(2)-C(4)	1.455 (7)
Mg-O(1)	1.979 (4)	O(2)-C(5)	1.401 (7)
Mg-O(1)'	2.010 (4)	N(1)-C(1)	1.478 (7)
Mg-O(2)	2.142 (5)	N(1)-C(3)	1.469 (7)
Mg-N(1)	2.377 (5)	N(1)-C(12)	1.463 (8)
Mg-C(20)	2.181 (6)	N(2)-C(14)	1.359 (11)
O(1)-C(2)	1.392 (7)	C(13)-C(14)	1.243 (11)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Figure 1. The five-coordinate geometry about magnesium is seen more readily in the ORTEP drawing in Figure 2 that includes only the magnesiums and the atoms bonded directly to them.

Coordinates for all atoms are listed in Table I, selected bond lengths in Table II, and selected bond angles in Table III. The distances from magnesium to the methylene carbon of the neopentyl group (2.181 (6) Å), the bridging oxygens (1.979 (4) and 2.010 (4) Å), and the ring oxygen (2.142 (5) Å) are unexceptional. A species having the formula $[t\text{-BuOMgBr(EtOEt)}]_2$ has been shown to have Mg–O–Mg bridge bonding with similar bond lengths (1.91 and 1.91 Å) and bond angles (O–Mg–O = 83.3° and Mg–O–Mg = 96.7°).[4] The bond to a ring nitrogen (2.377 (5) Å) is unusually long, however, though the Mg–N distance (2.385 (3) Å) in the hexacoordinate compound $Mg(C{\equiv}CPh)_2(\text{tetramethylethylenediamine})_2$ is comparable.[5] The carbon–carbon double bond (C(13)–C(14)) is remarkably short (1.243 (11) Å). Due to the possibility of interaction with the adjoining nitrogen (4 ↔ 5), this enamine double



4 5

bond might have been expected to be long. In fact, as expected[6] to result from this sort of interaction, the ^1H NMR absorptions of the $=CH_2$ hydrogens are considerably upfield from those of typical vinyl hydrogens, the nitrogen–carbon bond (N(2)–C(14)) is unusually short (1.359 (11) Å), and the bond angles at the nitrogen (C(8)–N(2)–C(14) = 119.9 (9)°, C(9)–N(2)–C(14) = 120 (1)°, and C(8)–N(2)–C(9) = 116.8 (9)° are approximately 120°. Examination of the distances between atoms indicated no unusual interactions of the double bond atoms with those of neighboring molecules.

It is noteworthy that a dimer structure is found instead of alternative monomer structures in which the magnesium would be bonded to more of the ring heteroatoms. Benzo-15-crown-5, which has a 15-membered ring with the same placement of heteroatoms as does the ring of 2, forms a compound with $Mg(SCN)_2$ in which all five ring oxygens are bonded to the magnesium.[7] The structure is that of a pentagonal bipyramid with the ring oxygens approximately in a plane that includes the magnesium and with the thiocyanate nitrogens occupying the apical positions. In the ion $NpMg^+$(2,1,1-cryptand), all six heteroatoms (including the five heteroatoms of a bridged 15-membered ring) are bonded to the magnesium.[1] On the basis of these examples, a similar structure for 2, the five ring oxygens lying approximately in a plane surrounding the magnesium and the neopentyl group and the oxygen of the $-CH_2CH_2O^-$ side chain occupying apical sites, seemed a possiblity. That the dimer structure is found instead may be a consequence of a predilection for forming a structure which can more fully utilize the bonding potential of the side-chain alkoxide oxygens. Other evidence indicates that formation of alkoxide bridges between magnesiums is particularly favorable.[8]

Is the species found in the crystal also the major species in the solutions from which the crystal was obtained? NMR observations indicate that the solutions have the gross features implied by structure 2—the presence only of neopentyl groups bonded to magnesium and of monocyclic units derived from the cryptand. Many absorptions in the ^1H NMR spectra of diethyl ether or benzene–diethyl ether solutions are obscured by strong diethyl ether absorptions. Not obscured, however, are two doublets for the CH_2 of neopentyl at δ −0.02 and 0.19, positions that indicate that neopentyl is bonded to magnesium, and an absorption at δ 6.04 due to the =CH– of the cleaved cryptand. The absorption areas indicate equal numbers of NpMg– and cleaved cryptand groups. Crystals obtained by cooling benzene–diethyl ether solutions dissolve in benzene to give solutions virtually free of diethyl ether, even when the crystals have not been subjected to reduced pressure. The ^1H NMR spectra of the benzene solutions exhibit absorptions essentially identical with those described for the solutions containing diethyl ether plus, in the proper area ratios, a singlet for the neopentyl CH_3's and a complex group of absorptions for the ring-cleaved cryptand. The same species probably predominates, therefore, in the presence or absence of diethyl ether, suggesting that coordination by the oxygen of diethyl ether is insignificant. We suspect that this species is a dimer, probably with a structure closely resembling that found in the crystal. The absorptions of the $=CH_2$ hydrogens of the vinyl group are far upfield as is characteristic of enamines, presumably because of the 4 ↔ 5 interaction. This suggests that, as in 3, the nitrogen (N(2)) is not bonded to magnesium, since such bonding would reduce this interaction. The nonequivalence of the neopentyl CH_2

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(4) Moseley, P. T.; Shearer, H. M. M. *J. Chem. Soc., Chem. Commun.* **1968**, 279.

(5) Schubert, B.; Behrens, U.; Weiss, E. *Chem. Ber.* **1981**, *114*, 2640.

(6) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164.

(7) Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1418.

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Table III. Selected Bond Angles (deg) for 3[a]

O(1)–Mg–O(1)′	80.8 (2)	O(2)–Mg–C(20)	116.6 (2)	Mg–N(1)–C(3)	104.7 (4)
O(1)–Mg–O(2)	111.6 (2)	N(1)–Mg–C(20)	104.3 (2)	Mg–N(1)–C(12)	118.2 (4)
O(1)′–Mg–O(2)	89.0 (2)	Mg–O(1)–Mg′	99.2 (2)	Mg–C(20)–C(21)	119.0 (4)
O(1)–Mg–N(1)	78.3 (2)	Mg–O(1)–C(2)	121.8 (4)	C(8)–N(2)–C(9)	116.8 (9)
O(1)′–Mg–N(1)	146.0 (2)	Mg–O(1)′–C(2)	131.9 (4)	C(8)–N(2)–C(14)	119.9 (9)
O(1)–Mg–C(20)	130.6 (2)	Mg–O(2)–C(4)	120.4 (4)	C(9)–N(2)–C(14)	120 (1)
O(1)′–Mg–C(20)	109.7 (2)	Mg–O(2)–C(5)	124.1 (4)	N(2)–C(14)–C13)	128 (1)
O(2)–Mg–N(1)	74.3 (2)	Mg–N(1)–C(1)	99.8 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

hydrogens requires a structure in which these hydrogens occupy different environments and do not exchange on the NMR time scale. Structure 3 certainly qualifies, though probably not uniquely.

Experimental Section

^{1}H NMR spectra were taken at 200 or 360 MHz with C_6H_6 (δ 7.15) as an internal standard and C_6D_6 as an internal lock. Absorptions are reported with the following notations: s, singlet; d, doublet; t, triplet; q, quartet; c, complex overlapping absorptions.

Preparation of Dineopentylmagnesium. The preparation was based on one already reported.[9] A Grignard solution was prepared by addition first of 1,2-dibromoethane (0.5 mL) as an initiator followed by dropwise addition over 1 h of a solution of neopentyl chloride (10.65 g, 0.10 mol) in diethyl ether (50 mL) to a stirred mixture of magnesium (Johnson Matthey Puratronic, 2.67 g, 0.11 mol) in diethyl ether (50 mL). The flask then was heated at reflux temperature for 15 h. The concentration of the Grignard reagent was determined by hydrolysis of an aliquot followed by titration with a standard hydrochloric acid solution. Yields of Grignard reagent (typically about 75%) were generally highest if relatively concentrated (0.8–2.0 M) rather than less concentrated solutions were prepared. Then a solution of dioxane (exactly 1 mol/mol of RMgCl) in diethyl ether (100 mL) was added dropwise over 2 h to the stirred Grignard solution. The resulting white slurry was stirred for an additional 24 h and then transferred to centrifuge tubes and centrifuged. The clear, colorless solution was decanted and placed in a storage bottle. Evaporation of the diethyl ether at reduced pressure left a white amorphous solid which was sublimed (80 °C ($<10^{-3}$ torr)) before use. If more dioxane was used, the sublimed material contained dioxane and was less soluble in benzene than was the dioxane-free material; the portion that dissolved in benzene exhibited a complicated ^{1}H NMR spectrum.

Preparation of the Ring-Cleaved Product 2 (3). The preparative procedures were performed in a glovebox under a nitrogen atmosphere. A solution of 2,1,1-cryptand (Parish Chemical, 100 mg, 0.356 mmol) in diethyl ether (5 mL) was added dropwise to a solution prepared by dissolving solid dineopentylmagnesium (57.6 mg, 0.356 mmol) in diethyl ether (3 mL). The diethyl ether was distilled from sodium benzophenone ketyl prior to use. Benzene (8 mL) was added, and the tube was sealed and heated at 100 °C for 1 h. The resulting solution exhibited the following ^{1}H NMR absorptions (200 MHz, EtOEt–C_6D_6): δ −0.02 (d, 1 H, J = 12.3 Hz, C*H*HMg), 0.19 (d, 1 H, J = 12.3 Hz, CH*H*Mg), 1.11 (t, EtOEt), 3.25 (q, EtOEt), 6.04 (d of d, 1 H, J = 8.8 and 15.1 Hz, =CHN). Cooling this solution resulted in the formation of crystals which were removed by filtration: ^{1}H NMR (360 MHz, C_6D_6) δ −0.02 (d, 1 H, J = 12.3 Hz, C*H*HMg), 0.19 (d, 1 H, J = 12.3 Hz, CH*H*Mg), 1.53 (s, 9 H, CH_3), 2.4–3.8 (c, ~26 H), 6.04 (d of d, 1 H, J = 8.8 and 15.1 Hz).

Single-Crystal X-ray Structure Determination. Cooling a benzene–diethyl ether solution (prepared as described above) at −10 °C for 1 week furnished clear, colorless crystals suitable for X-ray analysis. A crystal of approximate dimensions 0.14 × 0.27 × 0.66 mm was sealed in a glass capillary under a nitrogen atmosphere. The capillary containing the crystal was then mounted onto an eucentric goniometer. Diffraction data were collected with an Enraf-Nonius CAD-4 automatic diffractometer controlled by a Digital Equipment PDP8a computer coupled to a PDP11/34a computer. The program SEARCH[10] was used to obtain 25 accurately centered reflections which were then used in the program INDEX[10] to obtain an orientation matrix for data collection and to provide cell dimensions. Unit cell parameters indicated a monoclinic crystal system. A small test data set (zero and axial reflections) showed systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) which uniquely determined the nonstandard setting of the monoclinic space group $P2_1/n$ (No. 14, C_{2h}^5).[11] Crystal data and data collection parameters are listed in Table IV.

Table IV. Crystal Data and Data Collection Parameters for 3

mol formula	$C_{38}H_{76}Mg_2N_4O_8$
mol wt	765.04
cryst system	monoclinic
space group	$P2_1/n$
unit cel dimens	
a, Å	10.203 (2)
b, Å	9.579 (4)
c, Å	23.121 (7)
β, deg	95.93 (2)
V, Å^3	2248 (2)
formula units per unit cell (Z)	2
D(calcd), g cm^{-3}	1.134
abs coeff (μ), cm^{-1}	0.97
temp, °C	22 (1)
radiatn, Å	Mo Kα, 0.71073
monochromator	graphite
scan type	θ–2θ
scan speed, deg min^{-1}	1.0–5.0
scan width, deg	1.3 + 0.347 tan θ
takeoff angle, deg	2.8
std reflctns, h^{-1}	3
data limits, deg	$1.6 \leq \theta \leq 21.56$
reflctns measd	3143
unique reflctns	2754
means discrepancy of multiply measd reflctns	0.029
reflctns obsd, $I > 2\sigma(I)$	1217
drift correctns (from stds)	
empirical	1.000–1.000
anisotropic	0.969–1.023

No absorption corrections were applied since the value of μ (0.97 cm^{-1}) indicated that absorption was not severe. The Mg atomic coordinates were determined by Patterson heavy-atom techniques. The remaining non-hydrogen atomic positions were then found from subsequent least-squares refinements and difference Fourier electron density maps and were refined. In the final cycles of least-squares refinement, 235 parameters were varied including the positional parameters and anisotropic thermal parameters of all non-hydrogen atoms. The methylene and vinyl hydrogens were fixed at their calculated positions with C–H = 0.97 Å and given fixed isotropic temperature factors (B = 5.0 Å^2). The methyl hydrogens were calculated and fixed (C–H = 0.97 Å, B = 5.0 Å^2) to give the best possible agreement with those located from a difference Fourier map. Convergence was achieved with the use of a weighting scheme[12] where ρ, the ignorance factor, was set equal

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(9) Anderson, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 809.

(10) All programs used in this study are part of the Enraf-Nonius Structure Determination Package (SDP-PLUS, version 1.0), Delft, 1982.

(11) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, United Kingdom, 1969; Vol. I.

(12) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

to 0.04. The discrepancy indices were $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.071$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.067$. In the last cycle of refinement, the maximum shift per error was 0.03. A final difference Fourier map showed the largest peak to be less than 0.24 e Å^{-3}. The final error of an observation of unit weight was 1.71.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers.

Registry No. 1, 31250-06-3; 3, 96165-39-8; dineopentylmagnesium, 19978-31-5; neopentyl chloride, 753-89-9.

Supplementary Material Available: Tables for 3 of all bond angles and bond lengths, anisotropic thermal parameters, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

Thermal Rearrangement, Oxypalladation, and Molecular Structure of "Boat–Chair" Dichloro(3-methylcycloocta-1,4-diene)palladium(II)

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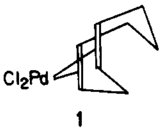
In contrast to cycloocta-1,4-diene, which is found chelated to $PdCl_2$ in a high-energy boat–boat conformation, the methylated analogue dichloro(3-methylcycloocta-1,4-diene)palladium(II) (i.e., [$PdCl_2$·MeCOD-1,4]) has the hydrocarbon moiety chelated in the more stable boat–chair conformation, with the methyl group in the equatorial position. These structural results are discussed in terms of the free 1,4-diene conformational profile derived experimentally and theoretically by Anet and Yavari (*J. Am. Chem. Soc.* 1977, *99*, 6986–6991). The molecular structure of [$PdCl_2$·MeCOD-1,4] was determined by X-ray crystallography. Crystal data: space group $P2_1/n$ with $a = 8.113$ (1) Å, $b = 10.875$ (3) Å, $c = 11.758$ (2) Å, $\beta = 91.21$ (1)°, $V = 1037.1$ (6) Å^3, $Z = 4$. The refinement was based on 2088 reflections with $I > 3\sigma(I)$ with final $R = 2.3\%$ and $R_w = 3.8\%$. Structural parameters are compared with a related series of [$PdCl_2$·diene] complexes. The complex [$PdCl_2$·MeCOD-1,4] rearranges thermally via allylic hydrogen migration to dichloro(*eq*-3-methylcycloocta-1,5-diene)palladium(II), followed by equilibration of the latter with dichloro(*ax*-3-methylcycloocta-1,5-diene)palladium(II) (the eq/ax equilibrium mixture is ca. 1.8:1 at 45 °C). Reaction of [$PdCl_2$·MeCOD-1,4] with methoxide leads to methoxypalladation to form a 1,4,5-η^3-σ,π-cyclooctenyl chelate.

Introduction

In a previous report from this laboratory[1] we explored medium-ring diene conformational effects on the kinetics and thermodynamics of the metal chelation process. We have shown that a much better understanding of the rates and structural results of diene chelation can be accomplished through consideration of the conformational profiles of the free dienes. One very intriguing result of the previous study[1] was the finding that cycloocta-1,4-diene (COD-1,4) binds $PdCl_2$ in the unexpected boat–boat (BB) conformation 1. The BB conformation is an energy maximum for free COD-1,4, and our analysis led to the conclusion that 1 arises from initial monodentate chelation of twist boat (TB) COD-1,4, followed by kinetic trapping of BB at the second substitution (chelation) step.



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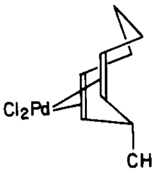
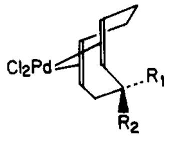
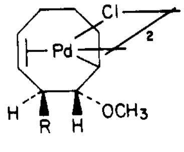
We now report the synthesis and structural characterization of dichloro(3-methylcycloocta-1,4-diene)palladium(II), [$PdCl_2$·MeCOD-1,4], 2. We find that the methyl group has perturbed the 1,4-diene conformational energy profile such that we now obtain exclusively the complexed boat–chair (BC) conformation 2. We also report observations on the thermal rearrangement of 2 to **3eq** and **3ax**, and we establish **4a** as the product of methoxide attack on 2 and **4b** as the product of methoxide attack on 1.



2



3eq, $R_1 = H$, $R_2 = CH_3$
3ax, $R_1 = CH_3$, $R_2 = H$



4a, R = CH_3
4b, R = H

Experimental Section

General Data. NMR spectra were determined by using a Varian EM 390 instrument (90-MHz ^1H) or a JEOL 200 FX instrument (200-MHz ^1H). [$PdCl_2$·COD-1,4][2] and bis(benzo-

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(1) Rettig, M. F.; Wing, R. M.; Wiger, G. R. *J. Am. Chem. Soc.* 1981, *103*, 2980–2986.

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