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Steric Blocking of Methyl Bridging: The Syntheses and X-ray Crystal Structures of a Three-Coordinate Methyl Magnesium Complex and Its THF Adduct

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Summary: Treatment of dimethylmagnesium with $Ar'N{=}C(^tBu)CHC(^tBu)NHAr'$ ($Ar' = 2,6$-diisopropylphenyl) in THF provides the β-diketiminate complex $[CH_3Mg(THF)\{\eta^2\text{-}(Ar'NC^tBu)_2CH\}]$. The THF ligand may be removed from this complex at 150 °C under vacuum to provide the three-coordinate complex $[CH_3Mg\{\eta^2\text{-}(Ar'NC^tBu)_2CH\}]$. Both species have been structurally characterized by X-ray crystallography, which shows that the Mg−C bond decreases from 2.189(4) to 2.077(2) Å on removal of the THF ligand, and this is accompanied by a change in magnesium coordination geometry from distorted tetrahedral to trigonal planar.

Introduction

Given the ubiquity of Grignard reagents, it is unsurprising that the organometallic chemistry of magnesium with oxygen donor ancillary ligands is a well-developed field.[1] The amide coordination chemistry of magnesium and organomagnesium species is also now attracting interest, driven by the differing selectvities and reactivities these systems exhibit as basic reagents compared with their well-established lithium counterparts[2] and the commercial availability of the hydrocarbon soluble Mg^nBu^sBu as a convenient precursor. A better understanding of structural and bonding parameters in these systems is fundamental to delineating the factors responsible for these differences and for the development of new applications of such species. The coordination chemistry of magnesium with other anionic nitrogen donor ligand systems, however, remains relatively poorly explored. The β-diketiminate ligand system has attracted increasing attention in both transition metal[3] and main group[4] coordination chemistry. The formation of a stable six-membered chelate, coupled with the potential for variation of the steric and electronic properties of the nitrogen substituents, and the more subtle effects that may be achieved by substitution of the ligand carbon backbone provide for a useful range of steric and electronic properties essential for the fine-tuning of structure and reactivity. Sometime ago we realized that the known ability of Grignard reagents to effect carbomagnesation of certain alkenes[5] and the limited work demonstrating the ability of some magnesium dialkyls to oligomerize ethene[6] suggested the possibility that organomagnesium species, supported by a suitable ligand system, could be induced to exhibit alkene polymerization activity. At the time such activity was restricted to complexes of the early transition and lanthanide metals. However, soon afterward Jordan reported the ability of certain cationic methyl aluminum amidinate complexes to catalyze ethene polymerization,[7] the first such main group metal system to do so, and Brookhart and Gibson extended activity to the later transition metals.[8] Consequently, the only groups of metals in the periodic table yet to be shown to exhibit alkene polymerization activity are those of the *s*-block, and an investigation of their potential is overdue. This paper reports the results of our initial investigation of complexes synthesized with this objective in mind. We have previously reported a number of complexes

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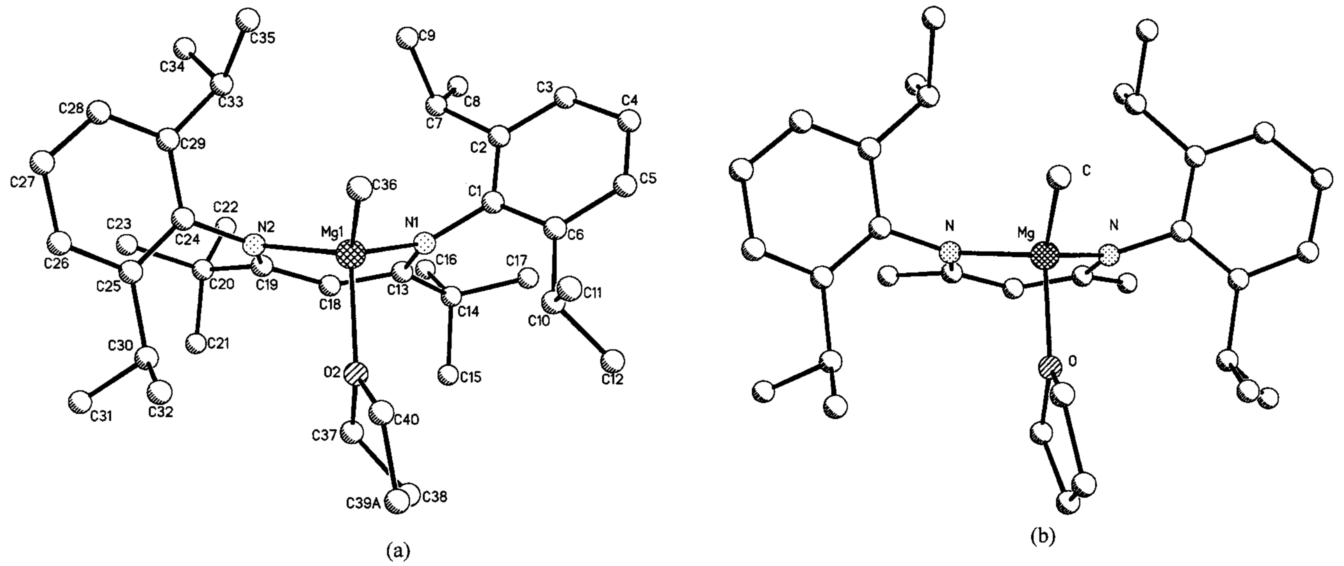
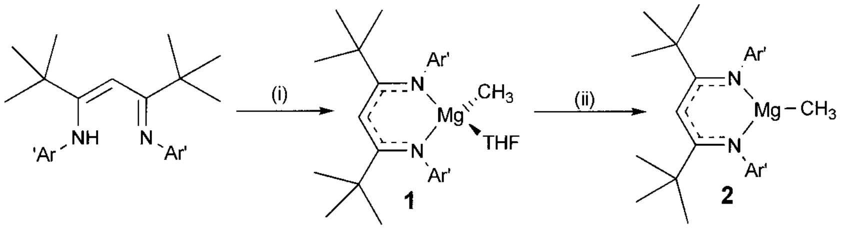


Figure 1. (a) Molecular structure of [$CH_3Mg(THF)\{\eta^2\text{-}(Ar'NC^tBu)_2CH\}$] (**1**) with hydrogen atoms omitted for clarity. (b) Molecular structure of [$CH_3Mg(THF)\{\eta^2\text{-}(Ar'NCMe)_2CH\}$] for comparison.[9]

Scheme 1[a]



(Ar' = 2,6-diisopropylphenyl)

[a] (i) $MgMe_2$, THF, 20 °C; (ii) 150 °C, 10^{-2} Torr, 1 h.

[(L−X)$MgCH_3$] (L−X = β-diketiminate, α-aminotroponiminate) in the form of their THF adducts and as methyl-bridged dimers,[9] both containing four-coordinate magnesium, and here we report the synthesis and characterization of further members of this group and a rare example of a three-coordinate, nitrogen-ligated organomagnesium species.

Results and Discussion

Treatment of dimethylmagnesium with Ar′N=C(^{t}Bu)-CHC(^{t}Bu)NHAr′ (Ar′ = 2,6-diisopropylphenyl)[3c] in THF provides the β-diketiminate complex [$CH_3Mg(THF)\{\eta^2\text{-}(Ar'NC^tBu)_2CH\}$] (**1**) (Scheme 1). We have previously reported the analogous complex with methyl groups in place of *tert*-butyl in the 1,3-positions on the ligand backbone,[9] and our intention in preparing **1** was to increase the steric bulk around the magnesium to prevent THF coordination. However, the NMR spectra of **1** clearly show the presence of coordinated THF. The X-ray crystal structure of **1** is given in Figure 1 alongside that of the previously reported analogous complex with backbone methyl substituents in place of *tert*-butyl for comparison.[9] Selected bond lengths and angles are given in Table 1. The coordination geometry of the magnesium is considerably distorted from tetrahedral. The N(1)−Mg−N(2) ligand chelate angle of 94.51(12)° is significantly less than the ideal tetrahedral angle; however this does not result in a corresponding widening of all of the remaining angles around Mg. Indeed the angles N(1)−Mg−O(2) [103.93(11)°], N(2)−Mg−O(2) [103.98(12)°], and C(36)−Mg−O(2)-[105.63(13)°] are all compressed from the ideal, while both N(1)−Mg−C(36) and N(2)−Mg−C(36) are expanded to 125.11(14)° and 121.05(13)°, respectively. Comparison of the structure of this complex with that containing the backbone methyl-substituted ligand indicates the effect which increasing the steric bulk in this position has upon the coordination environment of the magnesium. Similar, although less pronounced, distor-

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 2

1	2
Mg(1)−C(36) 2.189(4)	Mg(1)−C(1M) 2.077(2),
Mg(1)−O(2) 2.097(3)	Mg(1)−N(1) 2.0163(18),
Mg(1)−N(1) 2.063(3),	Mg(1)−N(5) 2.0137(17),
Mg(1)−N(2) 2.083(3),	N(1)−C(2) 1.335(2),
C(13)−N(1) 1.344(4),	N(5)−C(4) 1.335(2),
C(19)−N(2) 1.331(4)	C(2)−C(3) 1.417(3),
N(2)−Mg(1)−C(36) 121.05(13)	C(3)−C(4) 1.406(3),
N(1)−Mg(1)−N(2) 94.51(12)	N(1)−Mg(1)−N(5) 95.68(7),
N(1)−Mg(1)−O(2) 103.93(11)	N(1)−Mg(1)−C(1M) 134.62(8),
C(18)−C(19) 1.418(5)	N(5)−Mg(1)−C(1M) 129.68(8),
C(13)−C(18) 1.409(4)	C(1A)−N(1)−Mg(1) 110.02(11),
N(1)−Mg(1)−C(36) 125.11(4)	C(2)−N(1)−C(1A) 125.92(16),
N(2)−Mg(1)−O(2) 103.98(12)	C(1B)−N(5)−Mg(1) 110.91(11),
C(36)−Mg(1)−O(2) 105.63(13)	C(4)−N(5)−C(1B) 125.44(15)
C(1)−N(1)−Mg(1) 120.5(3)	
C(24)−N(2)−Mg(1) 115.1(2)	
C(13)−N(1)−C(1) 122.8(3)	
C(19)−N(2)−C(24) 125.9(3)	

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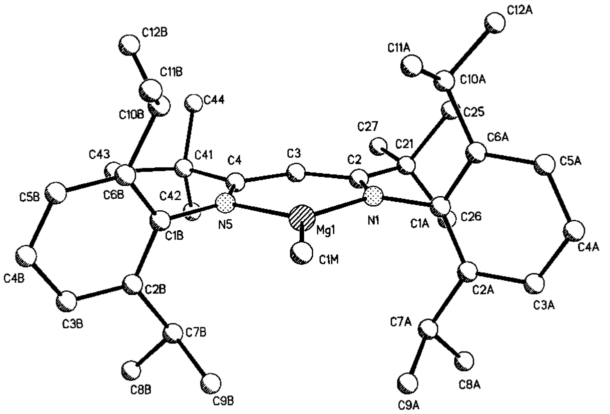

Figure 2. Molecular structure of [$CH_3Mg\{\eta^2\text{-}(Ar'NC^t\text{-}Bu)_2CH\}$] (**2**) with hydrogen atoms omitted for clarity.

tions of the magnesium coordination geometry are observed in this species. In **1** the C(1)−N(1)−C(13) and C(24)−N(2)−C(19) angles are 122.8(3)° and 125.9(3)°, respectively, and this compares with values of 117.7(4)° and 119.6(4)° for the corresponding angles in the complex with the less bulky methyl substituents, clearly indicating a forcing of the aromatic groups toward the magnesium by the backbone *tert*-butyl groups in **1**. This increased congestion of the magnesium site is reflected not only in the severe angle distortions around Mg, but also by increases in the Mg−O and Mg−C distances: from 2.066(4) to 2.097(3) Å and 2.107(6) to 2.189(4) Å, respectively. The THF and, in particular, the methyl ligand are therefore forced away from the magnesium by the nitrogen substituents. The overall picture is therefore one in which the Mg, the two N atoms, and the methyl ligand C atom are distorted toward planarity and their deviation from planarity is induced by the weak coordination of THF. This situation is best characterized by the angle between the N−Mg−N plane and the Mg−C vector, which is 36.4° in **1** and compares with 39.3° in the less bulky methyl-substituted ligand complex (cf. the ideal of 54.8° for a tetrahedron).

Given the steric crowding present in **1**, it is unsurprising that the coordinated THF in this complex may be removed by heating to 150 °C under vacuum to provide a complex (**2**) whose NMR spectrum in benzene-d_6 solution contains no signals for THF (Scheme 1). However, on the basis of these spectra, it is not possible to deduce whether this species is a three-coordinate monomer or a methyl-bridged dimer with four-coordinate Mg centers analogous to that formed by removal of THF from [$CH_3Mg(THF)\{\eta^2\text{-}(Ar'NCMe)_2CH\}$].[9] The X-ray crystal structure of **2** does indeed show it to contain a planar, tricoordinate magnesium center with the angles around magnesium totaling 360° (Figure 2). Selected bond lengths and angles are given in Table 1. The increase in electronic unsaturation at Mg effected by the removal of the THF ligand from **1** is reflected in the shortening of the Mg−C bond distance from 2.189(4) to 2.077(2) Å. It is also apparent that the electron deficiency is compensated by increased donation by the β-diketiminate ligand as the Mg−N bond distances are decreased from 2.063(3) and 2.083(3) Å in **1** to 2.0163(18) and 2.0137(17) Å in **2**. The removal of the THF also leads to a further increase in the steric shielding of the Mg−CH_3 unit by the nitrogen substituent groups, as reflected by the decrease in the 2,6-diisopropylphenyl *ipso*-carbon−N−Mg angles from 120.5(2)° and 115.1(2)° in **1** to 110.02(11)° and 110.91(11)° in **2**. It is this shielding that prevents the dimerization of **2** by formation of methyl bridges, a process that occurs spontaneously on removal of THF from [$CH_3Mg(THF)\{\eta^2\text{-}(Ar'NCMe)_2CH\}$].[9] The corresponding angles in the resulting dimeric species are 123.3(2)° and 120.5(2)°.

To our knowledge, only three other nitrogen-ligated, three-coordinate organomagnesium species have been characterized to date, and in two of these the necessary steric shielding is provided by bis(trimethylsilyl)amido ligands. The treatment of hexamethyldisilazane with Mg^nBu^sBu provides the dimeric species [$Mg^sBu\{\mu\text{-}N(SiMe_3)_2\}]_2$, which exhibits a similarly short Mg−C bond distance of 2.08(1) Å.[10] A Mg−C distance of 2.16(1) Å is observed in [$\{(\mu\text{-}R_2N)Mg(\mu\text{-}Me)\}_2\{Mg(NR_2)(NR_2AlMe_3)\}_2$] ($R = SiMe_3$), formed by treatment of [$\{Mg(NR_2)_2\}_2(1,4\text{-dioxane})$] with $AlMe_3$; however the methyl ligands bridge between magnesium ions in this structure and a comparison with **2** is therefore not valid.[11] During the preparation of the manuscript for this publication a paper reporting the structural characterization of [$^tBuMg\{\eta^2\text{-}(Ar'NCMe)_2CH\}$], another three-coordinate magnesium alkyl β-diketiminate complex, was published. In this species the unsaturated trigonal magnesium center is stabilized, not by increasing the steric requirements of the chelating ligand as in our case, but rather by increasing the size of the alkyl ligand from methyl to *tert*-butyl.[12] The Mg−C bond distance in this species was found to be 2.140(4) Å and is thus significantly longer than that found in **1**. Interestingly, these authors also report the X-ray crystal structure of the dimer of the corresponding methyl complex [$(\mu\text{-}CH_3)Mg\{\eta^2\text{-}(Ar'NCMe)_2CH\}]_2$, which we had previously published,[9] although as a different polymorph. The monomeric units in the tetramer [$Me_2Al\{(\mu\text{-}{}^iPr_2N)_2\}_2MgMe]_4$ contain three-coordinate Mg−Me units (Mg−C = 2.151(6) Å); however, the tetramer is linked together via weak Mg(μ-Me)Mg bridges (Mg−C = 2.493(6) Å), and the [$\eta^2\text{-}Me_2Al({}^iPr_2N)_2]^-$ “ligands” are therefore insufficiently bulky to prevent methyl bridging from occurring.[13]

Neither **1** or **2** shows any reactivity toward ethene up to 80 °C and 30 bar pressure in toluene solution. Given the reported ability of dialkylmagnesium species (e.g., $MgEt_2$) in hydrocarbon solution to insert ethene into the Mg−C σ-bond to provide liquid hydrocarbons ranging from C_{10} up,[6] we ascribe this failure to the steric congestion around the Mg−CH_3 unit in these complexes. Although this difference in reactivity could also be ascribed to electronic changes brought about by the nitrogen ligation of the Mg ion. These results therefore seem to suggest that, for neutral methylmagnesium complexes, the steric congestion required to stabilize a three-coordinate Mg center is greater than that which will allow ethene to approach sufficiently closely to insert into the Mg−C bond. We are currently investigat-

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ing the reactivity of **2** with other small molecules and exploring strategies for overcoming the problems identified by these results.

Experimental Section

General Comments. All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk and glovebox techniques and solvents that were distilled from appropriate drying agents under nitrogen immediately prior to use. NMR spectra were recorded on Varian Gemini 200 or Bruker AC 250 spectrometers and were referenced relative to the signals due to the residual protonated solvent. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. The ligand Ar′N═C(^{t}Bu)CHC(^{t}Bu)NHAr′ (Ar′ = 2,6-diisopropylphenyl) was prepared by the literature proceedure,[3c] while dimethylmagnesium was prepared as outlined previously.[9]

[CH$_3$Mg(THF){η^2-(Ar′NC^{t}Bu)$_2$CH}], 1. To a solution of Ar′N═C(^{t}Bu)CHC(^{t}Bu)NHAr′ (Ar′ = 2,6-diisopropylphenyl) (1 g, 1.98 mmol) in THF at room temperature was added Me$_2$Mg (0.10 g, 1.98 mmol). The mixture was stirred for 1 h, and the volatiles were removed under vacuum. The resulting yellow solid was redissolved in hexane and stored at −10 °C. Compound **1** was obtained as a yellow crystalline solid in a 85% yield (1.03 g) by filtration. ^{1}H NMR (THF$_d$): δ −2.10 (s, 3H, CH$_3$), 1.04 (s, 18H, CH$_3$), 1.08−1.23 (2 d, 24H, CH$_3$, $^3J_{H-H}$ = 6.6 Hz), 1.69 (m, 4H, CH$_2$), 3.19 (spt, 4H, CH, $^3J_{H-H}$ = 6.6 Hz), 3.54 (m, 4H, CH$_2$), 5.33 (s, 1H, CH), 6.80−7.10 (m, 6H, CH arom.). ^{13}C{^{1}H} NMR (THF$_d$): δ −18.1 (CH$_3$), 32.9 (CH$_3$), 25.8 (CH$_2$), 26.4 and 27.9 (CH$_3$), 28.7 (CH), 44.0 (C), 67.6 (CH$_2$), 96.3 (CH), 122.7, 123.3−124.1 (C$_m$, C$_p$), 142.2 (C$_o$), 146.6 (C$_{ipso}$), 175.5 (C$_\alpha$). Despite the absence of signals due to impurities in the NMR spectra, a consistent set of elemental analytical data could not be obtained. We attribute this problem to the extreme air sensitivity of **1**.

[CH$_3$Mg{η^2-(Ar′NC^{t}Bu)$_2$CH}], 2. Yellow crystals of **1** (2 g, 3.2 mmol) were heated at 150 °C under dynamic vacuum (10^{-2} Torr) for 1 h to afford compound **2** as a yellow microcrystalline solid in quantitative yield (1.76 g). ^{1}H NMR (C$_6$D$_6$): δ −1.37 (s, 3H, CH$_3$), 1.31 (s, 18H, CH$_3$), 1.38 (d, 24H, CH$_3$, $^3J_{H-H}$ = 6.8 Hz), 3.41 (spt, 4H, CH, $^3J_{H-H}$ = 6.8 Hz), 5.53 (s, 1H, CH), 7.11−7.28 (m, 6H, CH arom.). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ −16.8 (CH$_3$), 23.5−25.4 (CH$_3$), 28.5 (CH), 33.1 (CH$_3$), 44.1 (C), 94.9 (CH), 123.2, 123.8−125.5 (C$_m$, C$_p$), 141.4 (C$_o$), 145.0 (C$_{ipso}$), 176.3 (C$_\alpha$). Despite the absence of signals due to impurities in the NMR spectra a consistent set of elemental analytical data could not be obtained. We attribute this problem to the extreme air sensitivity of **2**.

Crystallography. Crystals of **1** suitable for X-ray-diffraction analysis were obtained from a saturated toluene solution at −20 °C. Crystal data for **1**: $C_{40}H_{64}MgN_2O$, M_r = 613.24, monoclinic, space group $P2(1)/n$, a = 12.522(3) Å, b = 15.590(4) Å, c = 19.983(6) Å, β = 102.84(2)°, V = 3803.4(17) Å^3, Z = 4, ρ_{calc} = 1.071 g cm^{-3}, T = 150 K. Structure solution and refinement for **1**: Data were collected on a Stoe Stadi-4 diffractometer using graphite-monochromated Mo Kα radiation and $\omega-\theta$ scans. The structure was solved by direct methods and refined against F^2 (SHELXTL),[14] yielding R = 0.0677, for 3546 independent reflections with $F > 4\delta(F)$, R_w = 0.1710 for 6730 observed reflections. The molecule contained a disordered ligand of thf which was modeled over two positions. All non-H atoms were refined with anisotropic thermal parameters, with the H atoms placed in calculated positions.

Crystals of **2** suitable for X-ray crystallography were obtained from a saturated solution of **2** in toluene at −20 °C. Crystal data for **2**: $C_{36}H_{56}MgN_2$, M_r = 541.14, triclinic (twinned via a 2-fold about the [1−10] reciprocal axis direction), space group $P\bar{1}$, a = 10.498(3) Å, b = 12.545(5) Å, c = 14.243(5) Å, α = 98.990(18)°, β = 107.35(2)°, γ = 101.102(16)° V = 1710.6(10) Å^3, Z = 2, ρ_{calc} = 1.051 g cm^{-3}, T = 150 K. Structure solution and refinement for **2**: Following correction for absorption using ψ-scan data (T = 0.353−0.605), the structure was solved by direct methods and refined by full-matrix least-squares against F^2.[14] The twin law was derived using the programs DIRAX and 2VIEW[15] using the initial reflection search results. It was possible to index the list of reflections using two orientation matrixes related by a 2-fold rotation about the [1−10] reciprocal lattice direction; diffraction data were collected on one of these. Several other crystals from the sample were also investigated, and all showed the same twinning effect. The matrix corresponding to the twin operation is (0.278 −0.722 0.179/−1.278 −0.278 −0.179/0 0 −1). Transformed h and k indices lay within 0.15 of integral values for 2088 data originally collected, and it was found that by far the most effective means for treating these was simply to omit them. The crystal diffracted strongly, and the ratio of the number of data with $F > 4\sigma(F)$ to the number of parameters is over 10:1 even after omitting this large number of data. The final conventional R factor (based on F) was 4.75%, wR2 = 13.15% (based on F^2 and all 4547 data); the final difference map extremes were +0.22 and −0.18 e Å^{-3}. Crystallographic data (excluding structure factors) for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC-147088 and -147089. Copies of the data may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables showing details of crystal structure determinations, atom coordinates, equivalent isotropic displacement factors, bond lengths, angles, and hydrogen atom positions for **1** and **2**. This information is available free of charge via the Internet at http://pubs.acs.org.

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