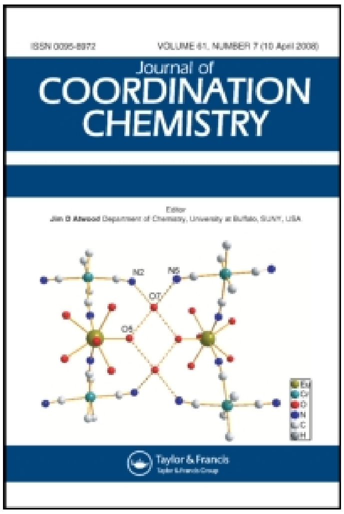

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The metal influence on the structural chemistry of alkynes: synthetic, spectroscopic and structural studies on magnesium acetylides

Marites A. Guino-o[a]; Eva Baker[a]; Karin Ruhlandt-Senge
[a] Department of Chemistry, 1-014 Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100

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The metal influence on the structural chemistry of alkynes: synthetic, spectroscopic and structural studies on magnesium acetylides†

MARITES A. GUINO-O, EVA BAKER
and KARIN RUHLANDT-SENGE*

Department of Chemistry, 1-014 Center for Science and Technology,
Syracuse University, Syracuse, New York 13244-4100

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A family of magnesium acetylides was prepared by treating Bu_2Mg with two equivalents of various alkyne ligands in the presence of different donors. The resulting complexes were examined for the influence of ligand and donors on the spectroscopic and structural properties of the target compounds. The magnesium complexes are compared to the heavier alkaline earth metal analogs.

Keywords: Magnesium; Alkynes; Donor effects; Alkane elimination; Structure elucidation

1. Introduction

The organometallic chemistry of the heavy alkaline earth metals has emerged from obscurity with a small group of partially characterized compounds to a vibrant area of chemistry [1, 2]. Contributing to this transformation is the development of viable synthetic routes that allow the preparation and in depth characterization of the target compounds [3]. As such, much has been learned about the properties of these highly reactive compounds, leading to an array of exciting opportunities in synthetic and polymer chemistry [1, 2].

Among the compounds prepared and analyzed are several families of alkaline earth metal acetylides that have attracted attention due to unexpected structural properties [4]. The heavy metal complexes of the general formula $M(18\text{-crown-6})(C{\equiv}CR)_2$ ($M = Ca$, Sr, Ba; $R = SiPh_3$ [4], 4-${}^tBuC_6H_4$ and ${}^tBu$ [5], contain the multidentate crown ether, 18-crown-6, to kinetically stabilize the large alkaline earth metal centers. This arrangement places the crown ether in the equatorial plane of the complexes, with expected trans angles (C–M–C) of 180°. Other predicted structural features include the linear geometry at the ipso carbon atom, and thus a 180° angle for the $M{-}C{\equiv}C$ moiety. Unexpectedly, significant deviation from these geometries were observed, noticeably,

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*Corresponding author. Tel.: 315-443-1306. Fax: 315-443-4070. Email: kruhland@syr.edu
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Table 1. Numbering scheme for magnesium acetylides.

Alkyne	Magnesium acetylide
$HC{\equiv}CSi(C_6H_5)_3$	$Mg(THF)_4(C{\equiv}CSi(C_6H_5)_3)_2$ (**1a**) $Mg(TMEDA)_2(C{\equiv}CSi(C_6H_5)_3)_2$ (**1b**)
$HC{\equiv}C\text{-}4\text{-}^tBuC_6H_4$	$Mg(15\text{-crown-}5)(C{\equiv}C\text{-}4\text{-}\ ^tBuC_6H_4)_2$ (**2**)
$HC{\equiv}C^tBu$	$Mg(TMEDA)_2(C{\equiv}C^tBu)_2$ (3)
$HC{\equiv}CSiMe_3$	$Mg(TMEDA)_2(C{\equiv}CSiMe_3)_2$ (**4**)

the deviations increased with increasing molecular weight of the central metal centers. Distinguishable structural features include a bent angle at the ipso carbon of 126.6° for $Ba(18\text{-crown-}6)(C{\equiv}CSiPh_3)_2$ in addition to a less dramatic, but still noticeable decrease in the linear trans angle (C–M–C), with values as low as 162.7° for $Ba(18\text{-crown-}6)(C{\equiv}CSiPh_3)_2$.

In an effort to analyze the metal dependency of these geometrical features, we extended our studies on acetylide derivatives of the alkaline earth metals to the lighter congener, magnesium.

Previous examples on terminal and/or bridging magnesium acetylides include monomeric $Mg(TMEDA)_2(C{\equiv}C^tBu)_2$ (where TMEDA = N,N,N',N'-tetramethylethylenediamine) [6], and $Mg(TMEDA)_2(C{\equiv}CC_6H_5)_2$ [7]; dimeric $[Mg(C{\equiv}CSiMe_3)_2(\mu\text{-}N^iPr_2)(THF)]_2$ [8], $[Mg(C{\equiv}CC_6H_5)_2(\mu\text{-}N^iPr_2)(THF)]_2$ [8], and $[CpMg(\mu_2\text{–}C{\equiv}CC_6H_5)(THF)]_2$ (where $Cp = C_5H_5$) [9]; tetrametric $[CpMg(\mu_3\text{–}C{\equiv}C\text{–}C_6H_5)]_4$ [9], and $[CpMg(\mu_3\text{-}C{\equiv}CC_5H_4FeCp)]_4$ [9]; and the polymeric $[(^tBuC{\equiv}C)(THF)Mg(\mu\text{-}C{\equiv}C^tBu)(\mu\text{-}N^iPr_2)\ Mg(\mu\text{-}C{\equiv}C^tBu)(\mu\text{-}N^iPr_2)Mg(THF)(C{\equiv}C^tBu)]$ [8].

In here, we report on the synthesis, spectroscopic and structural characterization of five magnesium acetylides, including two compounds bearing the $HC{\equiv}CSiPh_3$ ligand, $Mg(THF)_4(C{\equiv}CSiPh_3)_2$ (**1a**), $Mg(TMEDA)_2(C{\equiv}CSiPh_3)_2$ (**1b**), in addition to $Mg(15\text{-crown-}5)(C{\equiv}C\text{-}4\text{-}^tBuC_6H_4)_2$ (**2**), $Mg(TMEDA)_2(C{\equiv}C^tBu)_2$ (**3**), and $Mg(TMEDA)_2(C{\equiv}CSiMe_3)_2$ (**4**).

Compound **3** was previously reported by Geissler *et al.* including a room temperature X-ray data collection [6]. Since geometrical data are affected by crystal temperature, we prepared the compound using a slightly modified procedure and obtained crystallographic data at low temperature to allow for a direct comparison of geometrical values.

2. Experimentals

2.1. *Materials and measurements*

All manipulations were carried out under inert gas conditions with the use of a Schlenk line and standard dry box techniques. All solvents including tetrahydrofuran, toluene, benzene, and hexane were distilled over Na/K alloy and degassed prior to use. The acetylenes and donors including TMEDA and 15-crown-5 were obtained commercially and dried over calcium hydride before using. Dibutylmagnesium (a statistical mixture of secondary butyl and n-butyl) was obtained commercially as a 1.0 M heptane solution packaged under argon. It was used as received.

Table 2. Crystallographic data.

	1a	**1b**	**2**	**3**	**4**
Formula	$MgSi_2O_4C_{58}H_{62}$	$MgSi_2N_4C_{42}H_{62}$	$MgO_5C_{42}H_{54}$	$MgN_4C_{24}H_{52}$	$MgSi_2N_4C_{22}H_{50}$
Formula weight ($g\,mol^{-1}$)	439.77	411.77	559.031	418.99	451.15
Unit cell dimensions (Å,°)					
a	9.1068(7)	8.5713(1)	6.8605(7)	8.7611(2)	9.6060(1)
b	9.7040(7)	9.4404(1)	14.5838(2)	9.3003(2)	15.670(2)
c	17.0416(1)	16.441(3)	19.594(2)	9.811(2)	16.230(2)
α	75.6600(1)	77.508(4)	77.144(2)	74.96(3)	111.512(2)
β	75.3690(1)	88.217(4)	81.524(2)	70.40(3)	94.834(3)
γ	81.1240(1)	64.752(4)	80.423(2)	69.43(3)	101.961(3)
Volume ($Å^3$)	1405.0(2)	1172.0(3)	1872.2(3)	695.9(2)	2188.8(6)
Z	2	2	2	1	3
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$\rho_{(Calcd)}$ ($Mg\,m^{-3)}$	1.040	1.167	1.155	0.990	1.027
Temperature (K)	103(2)	95(2)	98(2)	100(2)	89(2)
2θ range (°)	2.18–28.30	2.45–25.00	1.62–28.35	2.23–25.00	1.45–25.00
No. of independent reflections	6902	4128	9259	2443	7713
Data/restraints/parameters	6902/0/286	4128/31/341	9259/0/424	2443/0/161	7713/0/464
R_1, wR_2 (all data)	$R_1 = 0.0480$, $wR_2 = 0.1278$	$R_1 = 0.0760$, $wR_2 = 0.1553$	$R_1 = 0.0592$, $wR_2 = 0.1310$	$R_1 = 0.0634$, $wR_2 = 0.1621$	$R_1 = 0.0551$, $wR_2 = 0.1812$
R_1, wR_2 ($>2\sigma$)	$R_1 = 0.0557$, $wR_2 = 0.1330$	$R_1 = 0.1237$, $wR_2 = 0.1767$	$R_1 = 0.0812$, $wR_2 = 0.1422$	$R_1 = 0.0713$, $wR_2 = 0.1688$	$R_1 = 0.1081$, $wR_2 = 0.2226$

^{1}H NMR and ^{13}C NMR were collected on a Bruker DPX-300 spectrometer with the use of benzene [D_6] as the NMR solvent. The chemical shifts were referenced to the residual solvent signals ([D_6] benzene: $\delta_H = 7.16$, $\delta_C = 128.38$). Infrared spectra were obtained on a Perking-Elmer Paragon 1000 FT-IR using KBr plates. Melting points were acquired on a MelTemp apparatus in capillaries sealed under nitrogen and are uncalibrated. Elemental analyses were conducted of all compounds, after ^{1}H and ^{13}C NMR data indicated clean samples. In all but one case (compound **4**), the carbon content was significantly lower than predicted, confirming earlier observations that elemental analysis on alkaline earth metal compounds frequently results in the formation of non-volatile carbonates, that cannot be detected by the analyzer. This result remains identical if a combustion aid is applied, suggesting that elemental analysis is an unreliable method to confirm the purity of alkaline earth metal containing bulk samples, as noted previously [3]. Yields reported are not optimized and pertain to the crystals grown and isolated for crystallographic studies. Typically crystal yields are low because of the prevailing powder formation of most of the target compounds in any organic solvent used. However, no unreacted alkynes was identified in the mother liquor, so quantitative transformations are assumed. All crystal data were collected using Bruker SMART system with 3-circle goniometer and a SMART 1K or APEX-CCD detector. Data were collected using MoKα radiation at low temperatures using a low temperature device build by H. Hope (UC Davis).

The crystals were submerged under inert gas in highly viscous hydrocarbon oil (Infineum), mounted on a glass fiber and placed in the low temperature stream on the diffractometer, as described in detail previously [10]. Data collection parameters and refinement details have been described in detail [10] with all crystal structures solved using Direct methods and subsequent refinement by full-matrix least-squares method on F^2 [11]. All non-hydrogen atoms were refined anisotropically. In compound **1a**, one solvent of crystallization, THF, displayed unresolvable disorder. It was removed from the refinement using "squeeze" as available in the Platon program suite [12, 13]. The TMEDA donors in compounds **1b**, **3**, and **4** were disordered. Refinement included the introduction of split position and refinement of the respective occupancies (90/10, 60/40, 50/50, respectively). The asymmetric unit in **4** contains one and one half molecule wherein the second magnesium atom resides on the center of symmetry. Further details about the refinements and how disorder was handled are outlined in the Supplementary material. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementarypublication nos. listed as follows: **1a** – 6,49,172, **1b** – 6,49,173, **2** – 6,49,174, **3** – 6,49,175, and **4** – 6,49,176. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

2.2. *Synthesis and characterization*

2.2.1. General procedure. Dibutylmagnesium (1 mmol, 1.00 mL) is slowly added by syringe to a solvent while stirring at room temperature. To the resulting solution, stoichiometric amounts of the corresponding ligand and donor were added (see below for specific amounts). The reaction mixtures were stirred overnight at room temperature and filtered using a Celite padded filter frit. The resultant clear solutions were stored in a 7°C refrigerator. Clear, colorless crystals formed within a few days.

2.2.2. $\mathbf{Mg(THF)_4(C{\equiv}CSiPh_3)_2}$ (1a). Solvent: THF, $HC{\equiv}CSiPh_3$ (2 mmol, 0.57 g). Yield: 0.10 g (12%). Block-like crystals. M.p.: 155°C. ^1H NMR (300 MHz, 25°C, C_6D_6): $\delta = 1.40$ (m, THF, 16H), 3.75 (t, THF, 16H), 7.26 (m, Ph, 18H), 8.09 (d, Ph, 12H). ^{13}C NMR (75 MHz, 25°C, C_6D_6): $\delta = 25.81$ (THF), 69.09 (THF), 128.35, 129.70, 136.55, 137.88 (Ph).

2.2.3. $\mathbf{Mg(TMEDA)_2(C{\equiv}CSiPh_3)_2}$ (1b). Solvent: Toluene, $HC{\equiv}CSiPh_3$ (2 mmol, 0.57 g), TMEDA (2 mmol, 0.30 mL). Yield: 1.10 g (63%). Block-like crystals. M.p.: 170°C. IR (Nujol): 2886.7 (s), 2149.4 (s), 2013.1 (w), 1891.0 (w), 1823.9 (w), 1661.3 (w), 1456.5 (m), 1376.8 (m), 1298.8 (s), 1260.0 (s) cm^{-1}. ^1H NMR (300 MHz, 25°C, C_6D_6): $\delta = 2.17$ (s, TMEDA, 8H), 2.25 (S, TMEDA, 24H), 7.16 (m, Ph, 18H), 7.99 (d, Ph, 12H). ^{13}C NMR (75 MHz, 25°C, C_6D_6): $\delta = 25.81$ (THF), 69.09 (THF), 128.35, 129.70, 136.55, 137.88 (Ph).

2.2.4. $\mathbf{Mg(15\text{-}crown\text{-}5)(C{\equiv}C\text{-}4\text{-}{}^tBuC_6H_4)_2}$ (2). Solvent: Toluene, $HC{\equiv}C4\text{-}{}^tBuC_6H_4$ (2 mmol, 0.36 mL), 15-crown-5 (1 mmol, 0.29 mL). Yield: 0.20 g (18%). Plate-like crystals. M.p.: 185–190°C. IR (Nujol): 3313.5 (s), 2921.5 (s), 2051.2 (s), 1459.1 (m), 1373.7 (m), 1265.3 (s) cm^{-1}. ^1H NMR (300 MHz, 25°C, C_6D_6): $\delta = 1.14$ (s, CH_3, 18H), 3.43 (t, 15-crown-5, 20H), 7.14–7.65 (m, C_6H_4, 8H). ^{13}C NMR (75 MHz, 25°C, C_6D_6): $\delta = 31.89$ (CH_3), 34.70 ($C(CH_3)_3$), 68.12 (15-crown-5), 107.98, 126.02, 131.75, 146.68 (C_6H_4).

2.2.5. $\mathbf{Mg(TMEDA)_2(C{\equiv}C^tBu)_2}$ (3). Solvent: Hexane, $HC{\equiv}C^tBu$ (2 mmol, 0.25 mL), TMEDA (2 mmol, 0.30 mL). Yield: 0.06 g (15%). Block-like crystals. M.p.: 108–113°C. IR (Nujol): 3313.9 (s), 2922.8 (s), 2245.1 (w), 2064.1 (s), 1459.0 (m), 1375.8 (m), 1291.7 (s) cm^{-1}. ^1H NMR (300 MHz, 25°C, C_6D_6): $\delta = 1.11$ (s, 18H, CH_3), 1.48 (s, 24H, THF), 2.14 (t, 8H, THF). ^{13}C NMR(75 MHz, 25°C, C_6D_6): $\delta = 31.27$ ($C(CH_3)_3$), 33.41 (CH_3), 46.65 (CH_3-TMEDA), 58.07 (CH_2-TMEDA).

2.2.6. $\mathbf{Mg(TMEDA)_2(C{\equiv}CSiMe_3)_2}$ (4). Solvent: Hexane, $HC{\equiv}CSiMe_3$ (2 mmol, 0.28 mL), TMEDA (2 mmol, 0.30 mL). Yield: 0.25 g (28%). Anal. Calcd for [$MgSi_2N_4C_{22}H_{50}$] %: C, 58.57; H, 11.19; Mg, 5.39; Si, 12.45; N, 12.42. Found: C, 58.63; H, 11.38; Mg, 5.28; Si, 12.52; N, 12.17. Block-like crystals. M.p.: 115–120°C. IR (Nujol): 2923.5 (s), 2013.2 (s), 1458.5 (m), 1375.6 (m), 1292.6 (s) cm^{-1}. ^1H NMR (300 MHz, 25°C, C_6D_6): $\delta = 0.35$ (s, CH_3, 18H), 2.16 (s, TMEDA, 24H), 2.32 (t, TMEDA, 8H). ^{13}C NMR (75 MHz, 25°C, C_6D_6): $\delta = 2.04$ (CH_3), 48.06 (CH_3-TMEDA), 57.62 (CH_2-TMEDA), 115.33 ($C{\equiv}C$).

3. Results and discussion

3.1. *Synthetic aspects*

The acetylide magnesium target compounds have been obtained by simple alkane elimination, utilizing the commercially available Bu_2Mg as a statistical mix of *n*- and *sec*-butyl. The significant difference in acidity between $^{n}Bu/^{sec}BuH$ ($pKa = \sim 53$) and $HC{\equiv}CR$ ($R = SiPh_3$, $SiMe_3$, ^{t}Bu, $4\text{-}^{t}BuC_6H_4$; $pKa = \sim 23$) ensures a smooth reaction (Eq. 1), further facilitated by the small steric requirement of the alkyne ligand.

$$Bu_2Mg + 2HCCR \underset{\substack{R=SiPh_3,SiMe_3,{}^{t}BuC_6H_4\\ donor=THF,TMEDA,15-crown-5}}{\overset{donor}{\longrightarrow}} Mg(CCR)_2(donor)_n + 2BuH$$

Equation 1. General equation for alkane elimination

Work-up of the reaction is facile due to the low boiling point of $^{n/sec}$butane. This route has been utilized to prepare a large variety of magnesium derivatives, including amides [14], alkoxides [15], aryloxides [16–21], thiolates [22–24], selenolates [24, 25] and others [25].

Four of the five target compounds contain a coligand, introduced by addition of a stoichiometric quantity to the reaction mixture. Stoichiometric considerations were based on the assumption that magnesium, in the presence of the small alkynes might prefer a coordination number of six, as also confirmed by prior work on related magnesium acetylides [26]. As such, two equivalents of TMEDA, or one equivalent of 15-crown-5 were introduced to the reaction mixture.

3.2. *Spectroscopic analysis*

All compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, confirming the purity of the bulk sample. However, due to difficulties in the observation of the acetylenic carbon atoms (even after applying increased relaxation delays and extensive run times), the ^{13}C NMR spectrum only show signals for donors and acetylide substituents. Further spectroscopic analysis was conducted by IR spectroscopy with the clear identification of the C≡C stretching frequency, identified in the range of 2013 to 2075 cm^{-1}, with the silyl substituted compounds **1a**, **1b** and **4** being recorded on the lower end of the scale. Table 3 summarizes the values for compounds **1–4** and lists some related species.

In all cases, a decrease in stretching frequency as compared to the free alkyne is observed, this decrease may be as small as nine wavenumbers, but may be as large as 66. Aside from the low stretching frequencies for the silyl substituted compounds, no other trends are apparent.

3.3. *Structural studies*

All compounds reported here display trans geometry, with either six coordinate metal centers for compounds bearing THF or TMEDA donors, namely **1a** (figure 1), **1b** (figure 2), **3** (figure 3) and **4** (figure 4), while introduction of 15-crown-5 macrocycle

Table 3. Comparative IR data.

ν (C≡C) (cm $^{-1}$)					
HC≡CR		Mg(donor)$_x$ (C≡CR)$_2$		$\Delta\nu$ (cm $^{-1}$)	Ref
R = Si(C$_6$H$_5$)$_3$	2034	**1b**	2013	21	*
R = 4- ^{t}BuCC$_6$H$_4$	2109	**2**	2051	58	*
R = ^{t}Bu	2108	**3**	2064	44	*
R = SiMe$_3$	2037	**4**	2013	24	*
		[Mg(C≡CSiMe$_3$)$_2$ (μ-N^{i}Pr$_2$)(THF)]$_2$	2028	9	[8]
R = C$_6$H$_5$	2110	[Mg(C≡CC$_6$H$_5$)$_2$ (μ-N^{i}Pr$_2$)(THF)]$_2$	2075	35	[8] [9]
		[CpMg (μ_3-C≡CC$_6$H$_5$)]$_4$	2052	58	
R = C$_5$H$_4$FeC$_5$H$_5$	2105	[CpMg (μ_3-C≡CC$_5$H$_4$-FeCp)]$_4$	2039	66	[9]

*=this work.

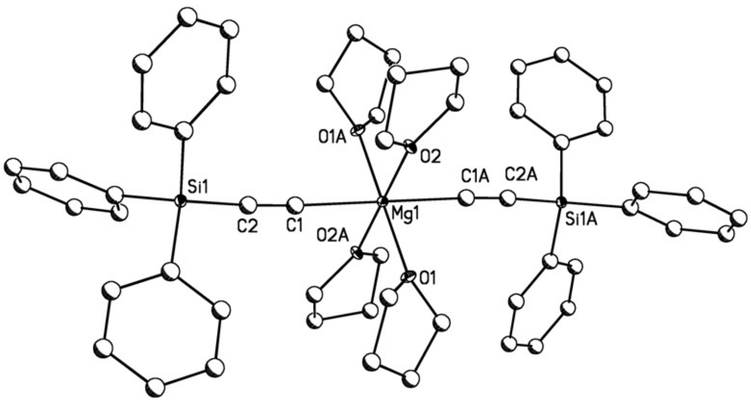

Figure 1. Solid-state structure of *bis*(triphenylsilylethynide)tetra(oxacyclopentane) magnesium (**1a**) Hydrogen atoms are omitted for clarity.

results in the seven coordinate **2** (figure 5). Cisoid geometry as suggested earlier for Mg(THF)$_4$(C≡CPh)$_2$ was not confirmed [27].

Compounds **1a**, **1b**, **3** and **4** exhibit a close to ideal octahedral geometry, with linear trans angles, as mandated in **1** and **3** through an inversion center at the metal center. The trans angles in **2** and **4** are 174.1(7) and 179.3(3)°. Ideal geometry in the equatorial plane is only possible for **1a**, where no constraints due to narrow bite angles imposed by the donors is apparent (O(THF)–Mg–O(THF) 89.76(4), 90.24(4)°). N(TMEDA)–Mg–N(TMEDA) bite angles center close to 80° (79.9(3)°, **1b**; 80.39(7)°, **3**; and 80.58(19), 80.62(19), 80.68(18)°, **4**). Consequently, angles between the two TMEDA donors exceed this value with angles close to 100° (100.1(3)°, **1b**; 99.61(7)°, **3**; and 99.39(19), 99.40(19), 99.33(18) °, **4**); thus ensuring an angle sum of close to 360°.

Structural data for **3** and the earlier room temperature structure Mg(TMEDA)$_2$(C≡C^{t}Bu)$_2$ [6] reveal minor differences, with both compounds displaying trans geometry and the magnesium atoms located on an inversion center. The Mg–C and C≡C bond length values between **3** *versus* literature example are as follows:

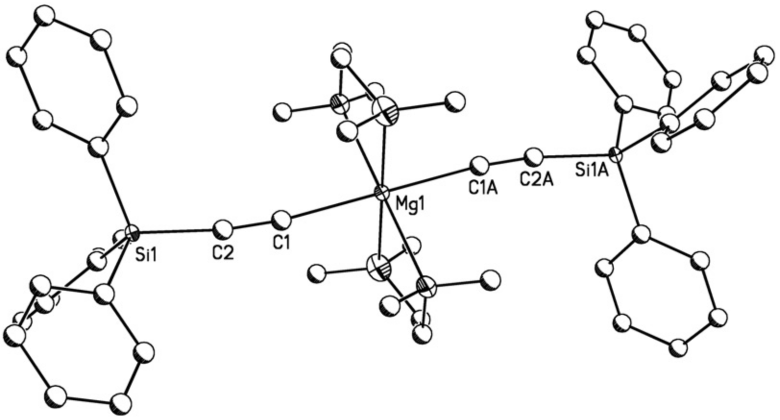

Figure 2. Solid-state structure of *bis*(triphenylsilylethynide)*bis*(*N*′,*N*′,*N*″,*N*″-tetramethylethylenediamine) magnesium (**1b**). Hydrogen atoms are omitted for clarity.

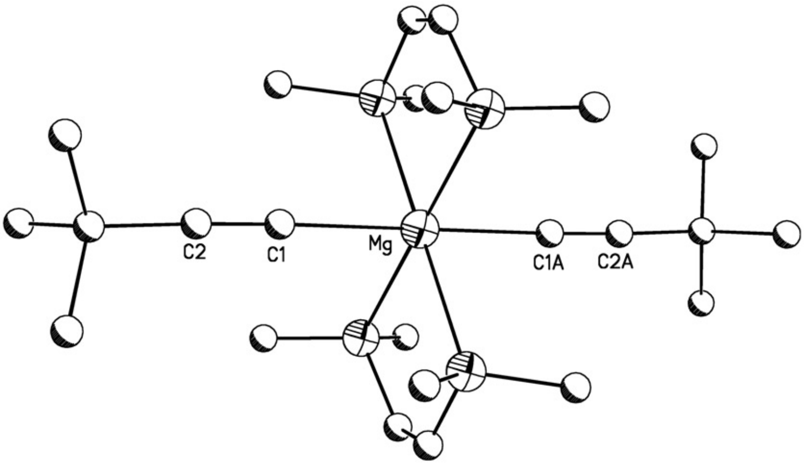

Figure 3. Solid-state structure of *bis*(tert-butylethynide)*bis*(*N*′,*N*′,*N*″,*N*″-tetramethylethylenediamine)magnesium (**3**). Hydrogen atoms are omitted for clarity.

2.175(4) *versus* 2.180(2) Å and 1.216(3) *versus* 1.207(5) Å, with Mg–C≡C angles being 176.0(2) and 175.6(4)°, respectively (see to table 4) [6]. All values fall within the standard deviation values.

Compound **2** is seven-coordinate, with 15-crown-5 in the equatorial plane and the two acetylide ligands in trans positions (174.1(7)°). The five crown oxygen atoms fit nicely in the equatorial plane with O(crown)–Mg–O(crown) angles close to 70°, a typical value for crown complexes [4].

With overall octahedral geometry close to the values, deviations from linear (sp) geometry for the Mg–C≡C moiety for compounds **1a**, **1b**, **3** and **4** are also close to expected values (see table 4). Noticeably, the two Mg–C≡C angles in a given compound may deviate quite significantly, as observed in **2** with 164.41(14) and 172.69(14)°. Noticeably, compound **2** also exhibits the most significant deviations from ideal trans geometry. Detailed analysis of close contact interactions in **2** reveals several intra- and

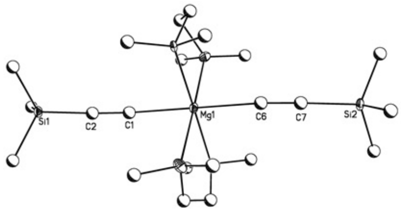

Figure 4. Solid-state structure of *bis*(trimethylsilylethynide)*bis*(N',N',N'',N''-tetramethylethylenediamine)-magnesium (**4**). Hydrogen atoms are omitted for clarity.

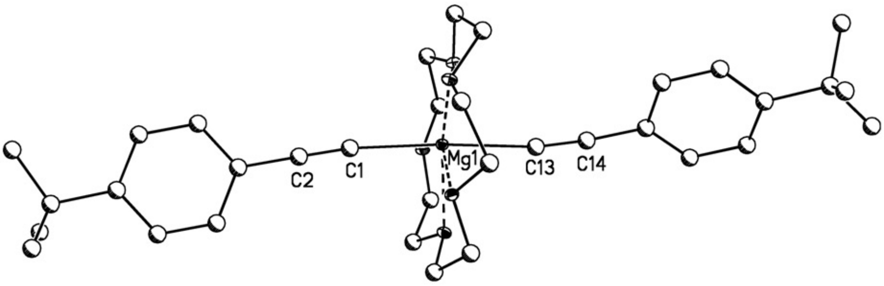

Figure 5. Solid-state structure of *bis*(4-tertbutylphenyl-1-ethynide)(1,4,7,10,13-pentaoxacyclopentadecane)-magnesium (**2**). Hydrogen atoms are omitted for clarity.

Table 4. Selected bond lengths and angles in magnesium acetylides.

Mg acetylide	CN	Ae-C$^{\mathrm{t,br}}$ (Å)	C–Ae–C (°)	Ae–C≡C (°)	C≡C (Å)	Ref
1a	6	2.238(1)$^{\mathrm{t}}$	180.0	173.3(1)	1.226(2)	*
1b	6	2.214(4)$^{\mathrm{t}}$	180.0	173.9(4)	1.221(5)	*
2	7	2.222(2)$^{\mathrm{t}}$	174.1(7)	164.4(1)	1.220(1)	*
				172.7(1)		
3	6	2.180(2)$^{\mathrm{t}}$	180.0	175.6(4)	1.207(5)	[6]
		2.175(4)$^{\mathrm{t}}$	180.0	176.0(2)	1.216(3)	*
$[(^t\mathrm{BuC{\equiv}C})(\mathrm{THF})\mathrm{Mg}$	4	2.100(2)$^{\mathrm{t}}$	108.4(0)	φ 92.4(2)	1.222(3)	[8]
$(\mu\text{-}\mathrm{C{\equiv}C}^t\mathrm{Bu})(\mu\text{-}\mathrm{N}^i\mathrm{Pr}_2)$		2.092(2)$^{\mathrm{t}}$	128.0(1)	96.4(2)	1.220(3)	
$\mathrm{Mg}(\mu\text{-}\mathrm{C{\equiv}C}^t\mathrm{Bu})$		2.203(2)$^{\mathrm{br}}$	128.0(1)	θ 173.2(2)		
$(\mu\text{-}\mathrm{N}^i\mathrm{Pr}_2)\mathrm{Mg}(\mathrm{THF})$		2.225(2)$^{\mathrm{br}}$		163.6(2)		
$(\mathrm{C{\equiv}C}^t\mathrm{Bu})]$						
4	6	2.202(6)$^{\mathrm{t}}$	179.3(3)	172.8(5)	1.220(8)	*
		2.198(6)$^{\mathrm{t}}$	180.0	173.5(5)	1.224(8)	
		2.20(2)$^{\mathrm{t}}$		173.1(1)	1.224(8)	
$[\mathrm{Mg}(\mathrm{C{\equiv}CSiMe}_3)_2$	4	2.202(6)$^{\mathrm{t}}$	179.3(3)	172.8(5)	1.220(8)	[8]
$(\mu\text{-}\mathrm{N}^i\mathrm{Pr}_2)(\mathrm{THF})]_2$		2.198(6)$^{\mathrm{t}}$		173.5(5)	1.224(8)	
$\mathrm{Mg}(\mathrm{TMEDA})_2$	6	2.176(6)$^{\mathrm{t}}$	180.0	–	1.219(8)	[7]
$(\mathrm{C{\equiv}CC}_6\mathrm{H}_5)_2$		2.200(6)$^{\mathrm{t}}$			1.213(8)	
$[\mathrm{CpMg}(\mu_3\text{-}\mathrm{C{\equiv}CC}_6\mathrm{H}_5)]_4$	8	2.248(2)		100.5(1)	1.214(3)	[9]
		2.348(2)$^{\mathrm{tet,br}}$		111.0(2)		
				152.4(2)		
$[\mathrm{CpMg}(\mu_2\text{-}\mathrm{C{\equiv}CC}_6\mathrm{H}_5)$	8	2.185(2)$^{\mathrm{t}}$		108.0(2)	1.202(3)	[9]
$(\mathrm{THF})]_2$		2.277(3)		110.0(2)	1.200(3)	
				161.2(2)		
				166.0(2)		
$[\mathrm{Mg}(\mathrm{C{\equiv}CC}_6\mathrm{H}_5)_2$	4	2.134(5)$^{\mathrm{t}}$	–	172.8(5)	1.195(6)	[8]
$(\mu\text{-}\mathrm{N}^i\mathrm{Pr}_2)(\mathrm{THF})]_2$						

t = terminal acetylide; br = bridging acetylide; tet = tetrameric; * = this work.

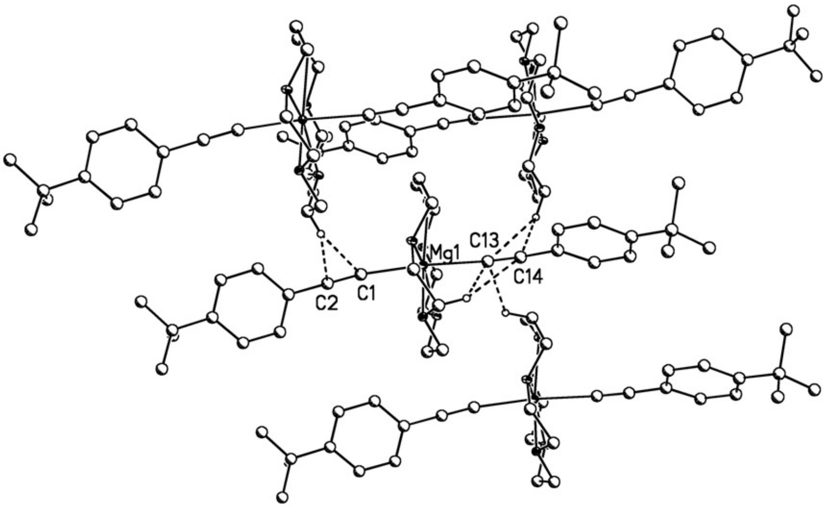

Figure 6. Intra- and intermolecular $C_{C\equiv C}-CH_{crown}$ contacts in **2**. Hydrogen atoms not involved in the short contacts are omitted for clarity.

Table 5. Intra- and intermolecular $C_{c\equiv c}$- CH_{crown}contacts in compound **2**.

	Length (Å)
Intramolecular	2.660
C13–H32b	
C14–H32b	2.877
Intermolecular	2.839
C1–H34a	
C2–H34a	2.892
C13–H28d	2.909
C14–H28d	2.741
C13–H29e	2.879

intermolecular interactions (see figure 5), possibly responsible for the deviation: intramolecular interactions between a CH moiety on the crown ether with the acetylide π-systems are observed as short as 2.660 Å (C13–H32b). Several intermolecular contacts are also apparent with values as short as 2.741 Å (C14–H28d), again between crown ether CH moieties and the acetylide π-system (see figure 6 and table 5).

Corresponding analysis of the other magnesium acetylide derivatives did not indicate close inter- and intramolecular interactions, but in the heavier alkaline earth metal acetylides M(18-crown-6)(C≡CSiPh$_3$)$_2$ (M = Ca, Sr, Ba), noted for their significant degree of distortion, a multitude of weak intra- and intermolecular interactions is apparent, possibly providing a rationale for their unexpected geometry.

Magnesium–carbon bond lengths in **1**–**4** lie in a narrow range, with the shortest at 2.175(4)Å for **3**, and 2.37(5)Å for **1a**. Noticeably, the Mg–C bond length for the seven coordinate **2** falls in this range, confirming earlier studies that an increase in coordination number as achieved by replacing four THF's by either 15-crown-5 or 18-crown-6 has a minimal effect on bond length. A similar observation was made earlier when comparing Ba-Se bond lengths in the eight coordinate Ba(18-crown-6)(Se-2,4,6^{i}Pr$_3$C$_6$H$_2$)$_2$ (3.23 Å) with the six coordinate Ba(thf)$_4$(Se-2,4,6^{t}Bu$_3$C$_6$H$_2$)$_2$

(3.28 Å) [28]. This puzzling observation may be rationalized by the location of the crown in the equatorial plane, as made possible by narrow O–M–O bite angles, leading to a steric demand that is comparable to either four THF or two TMEDA donors. Consequently, it appears that the bulkiness of the ligand, rather than the increase in coordination number affects the bond length, thus explaining the slightly longer M–C distance in **1a**, despite the lower coordination number.

In analogy with Mg–C distances, C≡C bond lengths in **1**–**4** lie in a very narrow range and compare well with related species (see table 4).

We now confirm that distortion from ideal geometry upon descending group 2 is apparent. Interestingly, a comparison of structural features in alkaline earth metal halides and cyclopentadienide derivatives indicates similar trends; an increase in bent geometry as descending group 2. As an example, $Mg(C_5H_5)_2$ is linear, while the barium analog has a Ba–C_5Me_5 (centroid) angle of 130.1° [29]. Future studies will link these observations with the presence of intra- and intermolecular interactions.

4. Conclusion and remarks

Five magnesium acetylides bearing four different ligand systems and three different donors were prepared by alkane elimination to analyze the effect of the donor and ligand on the structural chemistry of the compounds. The compounds display a very close range of geometrical features, indicating a minimal impact of ligands and donors on structural features. In all cases, trans geometry with close to ideal values were observed supporting the earlier assumption that deviation from ideal geometry becomes more apparent for the heavier alkaline earth metal compounds.

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