

Ab Initio Predictions of New Carbon Hypermagnesium Species: Mg₂C and Mg₃C

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The ground and very low-lying excited states of new Mg₂C and Mg₃C molecules have been studied using high-level ab initio techniques. Four structures of Mg₂C, (*C*_{2*v*}, ¹A₁), (*C*_{2*v*}, ³B₁), (*D*_{∞*h*}, ³Σ_g[−]), and (*D*_{∞*h*}, ⁵Σ_u[−]), were found to lie within 4 kcal/mol (at QCISD(T)/6-311+G(2df)) of one another. A *C*_{3*v*} (¹A₁) structure was found to be the only low-energy structure for Mg₃C. Both Mg₂C and Mg₃C were found to be thermodynamically stable with respect to all dissociation channels. Dissociation energies are found to be, for Mg₂C (*C*_{2*v*}, ¹A₁) → MgC (³Σ[−]) + Mg (¹S), 24.6 kcal/mol and, for Mg₃C (*C*_{3*v*}, ¹A₁) → Mg₂C (*C*_{2*v*}, ¹A₁) + Mg (¹S), 41 kcal/mol at the QCISD(T)/6-311+G(2df)+ZPE level.

I. Introduction

Recently, the stable hypermagnesium oxides Mg₂O, Mg₂O⁺, Mg₃O, and Mg₃O⁺ have been studied theoretically^{1,2} and experimentally.^{3–7} While the usual valences of oxygen and magnesium are formally satisfied in MgO, it was somewhat surprising that the hyperstoichiometric molecules Mg₂O and Mg₃O were both found in theoretical and experimental studies to be quite stable. More recently, a hyperberyllium molecule Be₂O has also been studied theoretically^{8,9} and experimentally⁸ and was found to be thermodynamically very stable.

Two main factors have been found to be responsible for the stability of these hyperstoichiometric molecules. The first is the atomic charge on the oxygen (−1 instead of −2) in MgO and BeO, which makes it possible for oxygen to form one more bond such as those in Mg₂O and Be₂O, respectively. The second factor is the bonding interactions among the Mg centers in Mg₃O. With these thoughts in mind, we decided to see whether other hypermagnesium molecules with a different central atom could be stable. In particular, we decided to explore Mg₂C and Mg₃C because carbon, like oxygen, is multivalent and thus may be able to form various kinds of bonds with Mg in various charge states.

II. Computational Methods

The geometries and harmonic vibrational frequencies of Mg₂C and Mg₃C were first optimized by employing analytical gradients¹⁰ with a polarized split-valence basis set (6-311+G*¹¹) at the MP2 (full, including core orbitals and all double excitations) level. The geometries of Mg₂C were then reoptimized at the QCISD level with frozen C 1s and Mg 1s, 2s, and 2p orbitals, where numerical second derivatives were employed. The fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods. The resultant QCISD/6-311+G* geometries for Mg₂C and the MP2(full)/6-311+G* geometries for Mg₃C were then used to evaluate higher level *valence* electron correlation both by Møller–Plesset perturbation theory to full fourth order¹² and by the (U)QCISD(T) method¹³ using 6-311+G-(2df) basis sets but with the C 1s and Mg 1s, 2s, and 2p orbitals now frozen. The unrestricted Hartree–Fock (UHF) wave functions for open-shell systems were projected to pure spectroscopic states (PUHF, PMP2, PMP3, and PMP4¹⁴). All

calculations were carried out with the GAUSSIAN 94¹⁵ suite of programs unless otherwise specified.

III. Results

A. MgC. This molecule was recently predicted computationally to have a ³Σ[−] ground electronic state with a valence electron configuration¹⁶ denoted as 1σ²2σ²1π² and a bond length and dissociation energy of 2.10 Å and 34.5 kcal/mol. Throughout this work, the C 1s and Mg 1s, 2s, and 2p core orbital occupancies could be represented as [] = 1σ²2σ²3σ²1π⁴4σ² in which case the valence configuration given earlier would read [] = 5σ²6σ²2π². However, we prefer to shorten the notation and to focus attention on the valence orbitals by (i) ignoring [] in writing the configuration and (ii) beginning the numbering of orbitals with the valence orbitals. Within this notational scheme, the lowest excited state was found to be the high-spin ⁵Σ[−] (1σ²2σ¹1π²3σ¹) state, which lies just 10.5 kcal/mol above the ³Σ[−] state (all data at the QCISD(T)/6-311+G(2df) level detailed in section II).

B. Mg₂C. For this molecule and for Mg₃C, we examined a wide variety of geometrical structures. In each case, we considered singlet, triplet, and quintet spin states and then focused only on candidates for the lowest energy states. This process generated twelve electronic state and geometrical structure combinations for Mg₂C at the MP2(full)/6-311+G* level: MgCMg (*D*_{∞*h*}, ¹Σ_g⁺), MgCMg (*D*_{∞*h*}, ³Σ_g[−]), MgCMg (*D*_{∞*h*}, ⁵Σ_u[−]), Mg₂C (*C*_{2*v*}, ¹A₁), Mg₂C (*C*_{2*v*}, ³B₁), Mg₂C (*C*_{2*v*}, ³B₂), Mg₂C (*C*_{2*v*}, ³A₂), Mg₂C (*C*_{2*v*}, ⁵A₁), Mg₂C (*C*_{2*v*}, ⁵B₂), CMgMg (*C*_{∞*v*}, ¹Σ⁺), CMgMg (*C*_{∞*v*}, ³Σ[−]), and CMgMg (*C*_{∞*v*}, ⁵Σ[−]). The optimal geometries, vibrational frequencies, and relative energies for the lowest eight are presented in Table 1.

The MgCMg (*D*_{∞*h*}, ¹Σ_g⁺) structure is found to be a saddle point (it has two imaginary frequencies) and is higher in energy (by 52.2 kcal/mol at QCISD/6-311+G*) than the (*C*_{2*v*}, ¹A₁) minimum, which connects to this saddle point. In contrast, the MgCMg (*D*_{∞*h*}, ³Σ_g[−]), MgCMg (*D*_{∞*h*}, ⁵Σ_u[−]), CMgMg (*C*_{∞*v*}, ⁵Σ[−]), Mg₂C (*C*_{2*v*}, ¹A₁), Mg₂C (*C*_{2*v*}, ³A₂), Mg₂C (*C*_{2*v*}, ³B₁), Mg₂C (*C*_{2*v*}, ³B₂), and Mg₂C (*C*_{2*v*}, ⁵A₁) structures were found to be minima, and the Mg₂C (*C*_{2*v*}, ¹A₁), MgCMg (*D*_{∞*h*}, ³Σ_g⁺), MgCMg (*D*_{∞*h*}, ⁵Σ_u[−]), CMgMg (*C*_{∞*v*}, ⁵Σ[−]), and Mg₂C (*C*_{2*v*}, ³B₁) structures were found to be substantially more stable than the others, as seen in Table 1.

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TABLE 1: Calculated Molecular Properties of Mg₂C

property	Mg ₂ C (C _{2h} , ¹ A ₁) 1a ₁ ² 1b ₂ ² 1b ₁ ² 2a ₁ ²	Mg ₂ C (C _{2h} , ³ B ₁) 1a ₁ ² 2a ₁ ² 1b ₂ ² 1b ₁ ² 3a ₁ ¹	MgCMg (D _{3h} , ³ Σ _g ⁻) 1σ _g ² 1σ _u ² 2σ _g ² 1π _u ²	MgCMg (D _{3h} , ⁵ Σ _g ⁻) 1σ _g ² 1σ _u ² 2σ _g ² 1π _u ²	MgCMg (D _{3h} , ⁵ Σ _u ⁻) 1σ _g ² 1σ _u ² 2σ _g ² 1π _u ² 2σ _u ¹	Mg ₂ C (C _{2h} , ³ A ₂) 1a ₁ ² 1b ₂ ² 2a ₁ ² 1b ₁ ² 2b ₂ ¹	CMgMg (C _{2v} , ⁵ Σ ⁻) 1σ ² 2σ ² 3σ ¹ 1π ² 4σ ¹	Mg ₂ C (C _{2v} , ³ B ₂) 1a ₁ ² 1b ₂ ² 2a ₁ ² 3a ₁ ¹ 2b ₂ ¹	Mg ₂ C (C _{2v} , ⁵ A ₁) 1a ₁ ² 1b ₁ ² 1b ₂ ² 2a ₁ ² 3a ₁ ¹ 2b ₂ ¹	
R(Mg-Mg), Å	2.990	3.144	4.328	4.198	3.368	3.368	2.951	4.018	3.630	
R(Mg-C), Å	2.047	2.127	2.164	2.099	2.156	2.156	2.072	2.113	2.043	
E _{mp2} (⁰), kcal/mol	-437.351 97	-437.326 14	-437.341 65	-437.368 20	-437.318 91	-437.318 91	-437.336 67	-437.311 89	-437.292 53	
$\langle S^2 \rangle$		2.997	2.585	6.039	2.856	2.856	6.031	2.034	6.055	
ν_1 , cm ⁻¹	567 [ν ₁ (a ₁)]	415 [ν ₁ (a ₁)]	242 [ν ₁ (σ _g)]	342 [ν ₁ (σ _g)]	361 [ν ₁ (a ₁)]	361 [ν ₁ (a ₁)]	593 [ν ₁ (σ)]	462 [ν ₁ (a ₁)]	489 [ν ₁ (a ₁)]	
ν_2 , cm ⁻¹	221 [ν ₂ (a ₁)]	127 [ν ₂ (a ₁)]	516 [ν ₂ (σ _u)]	736 [ν ₂ (σ _u)]	115 [ν ₂ (a ₁)]	115 [ν ₂ (a ₁)]	221 [ν ₂ (σ)]	100 [ν ₂ (a ₁)]	101 [ν ₂ (a ₁)]	
ν_3 , cm ⁻¹	646 [ν ₃ (b ₂)]	512 [ν ₃ (b ₂)]	105 [ν ₃ (π _u)]	148 [ν ₃ (π _u)]	547 [ν ₃ (a ₁)]	547 [ν ₃ (a ₁)]	95 [ν ₃ (π)]	721 [ν ₃ (b ₂)]	682 [ν ₃ (b ₂)]	
ZPE, kcal/mol	2.05	1.50	1.38	1.96	1.46	1.46	1.43	1.83	1.82	
ΔE _{mp2} (⁰), kcal/mol	10.2	26.4	16.7	0.0	30.9	30.9	19.8	35.3	47.5	
				MP2(full)/6-311+G*/MP2(full)/6-311+G*						
				QCISD/6-311+G*/QCISD/6-311+G*						
R(Mg-Mg), Å	2.999	3.168	4.308	4.220	3.456	3.456	2.967	3.605	3.555	
R(Mg-C), Å	2.057	2.115	2.154	2.110	2.156	2.156	2.074	2.221	2.058	
E _{qsid} (⁰), kcal/mol	-437.107 82	-437.111 82	-437.112 44	-437.116 29	-437.092 19	-437.092 19	-437.092 76	-437.069 70	-437.042 13	
$\langle S^2 \rangle$		2.989	2.581	6.014	2.871	2.871	6.032	2.260	6.065	
ν_1 , cm ⁻¹	548 [ν ₁ (a ₁)]	478 [ν ₁ (a ₁)]	274 [ν ₁ (σ _g)]	326 [ν ₁ (σ _g)]	401 [ν ₁ (a ₁)]	401 [ν ₁ (a ₁)]	589 [ν ₁ (σ)]	468 [ν ₁ (a ₁)]	468 [ν ₁ (a ₁)]	
ν_2 , cm ⁻¹	181 [ν ₂ (a ₁)]	126 [ν ₂ (a ₁)]	575 [ν ₂ (σ _u)]	683 [ν ₂ (σ _u)]	110 [ν ₂ (a ₁)]	110 [ν ₂ (a ₁)]	209 [ν ₂ (σ)]	102 [ν ₂ (a ₁)]	102 [ν ₂ (a ₁)]	
ν_3 , cm ⁻¹	598 [ν ₃ (b ₂)]	506 [ν ₃ (b ₂)]	74 [ν ₃ (π _u)]	134 [ν ₃ (π _u)]	596 [ν ₃ (b ₂)]	596 [ν ₃ (b ₂)]	69 [ν ₃ (π)]	650 [ν ₃ (b ₂)]	650 [ν ₃ (b ₂)]	
ZPE, kcal/mol	1.90	1.59	1.42	1.82	1.58	1.58	1.34	1.74	1.74	
ΔE _{qsid} (⁰), kcal/mol	5.3	2.8	2.4	0.0	15.1	15.1	14.8	29.2	46.5	
				QCISD(T)/6-311+G(2df)/QCISD/6-311+G*						
E _{mp2} , kcal/mol	-437.103 80	-437.081 02	-437.095 97	-437.119 78	-437.067 25	-437.067 25	-437.083 16	-437.061 15	-437.047 49	
E _{mp3} , kcal/mol	-437.105 15	-437.102 38	-437.118 15	-437.136 11	-437.091 76	-437.091 76	-437.104 95	-437.082 27	-437.063 68	
E _{mp4} , kcal/mol	-437.145 09	-437.118 85	-437.132 00	-437.144 50	-437.106 49	-437.106 49	-437.112 58	-437.094 66	-437.072 66	
E _{qsid} , kcal/mol	-437.131 39	-437.133 46	-437.132 70	-437.138 92	-437.113 01	-437.113 01	-437.110 94	-437.091 89	-437.067 13	
E _{qsid} (⁰), kcal/mol	-437.152 92	-437.152 05	-437.149 86	-437.146 92	-437.130 41	-437.130 41	-437.116 27	-437.102 15	-437.076 35	
ΔE _{mp4} , kcal/mol	0.0	16.5	8.2	0.4	24.2	24.2	20.4	31.6	45.5	
ΔE _{qsid} (⁰), kcal/mol	0.0	0.6	1.9	3.8	14.1	14.1	23.0	31.9	48.0	

TABLE 3: Calculated Effective Atomic Charges in MgC, CH₃MgH, Mg₂C, and Mg₃C

method	Q_C		$Q(\text{Mg}-\text{Mg})$ Mulliken	Q_C				Q_{Mg}				
	Mulliken ^d	Mulliken		dipole ^e	CHelpG ^f	MK ^g	NBO ^h	Mulliken ^d	dipole ^e	CHelpG ^f	MK ^g	NBO ^h
MgC ($^3\Sigma^-$) ^a												
MP2/6-311+G*	-0.311	0.155		-0.508	-0.496	-0.565	-0.856	+0.311	+0.508	+0.496	+0.565	+0.856
QCISD/6-311+G*	-0.290	0.177		-0.352	-0.373	-0.437	-0.734	+0.290	+0.352	+0.373	+0.437	+0.734
CH ₃ MgH ($C_{3v}, ^1A_1$) ^b												
MP2/6-311+G*	-0.822	0.321		-0.922	-0.730	-0.881	-1.356	+0.673	+1.004	+0.911	+0.993	+1.463
QCISD/6-311+G*	-0.763	0.304		-0.896	-0.704	-0.852	-1.319	+0.644	+0.989	+0.896	+0.977	+1.445
HMgMgH ($D_{\infty h}, ^1\Sigma_g^+$) ^b												
MP2/6-311+G*			0.466					+0.284	+0.381	+0.348	+0.381	+0.758
QCISD/6-311+G*			0.457					+0.268	+0.371	+0.338	+0.371	+0.737
CMg ₂ ($C_{2v}, ^1A_1$) ^c												
MP2/6-311+G*	-0.365	0.217	0.100	-0.733	-0.711	-0.850	-2.122	+0.183	+0.367	+0.356	+0.425	+1.061
QCISD/6-311+G*	-0.300	-0.006	0.271	-0.417	-0.526	-0.640	-1.885	+0.150	+0.209	+0.263	+0.320	+0.943
CMg ₂ ($C_{2v}, ^3B_1$) ^c												
MP2/6-311+G*	-0.161	-0.063	0.257	-0.419	-0.491	-0.601	-1.578	+0.081	+0.210	+0.246	+0.300	+0.789
QCISD/6-311+G*	-0.181	-0.054	0.228	-0.382	-0.453	-0.564	-1.538	+0.091	+0.191	+0.227	+0.282	+0.769
MgCMg ($^3\Sigma_g^-$) ^c												
MP2/6-311+G*	+0.147	-0.162		-0.365	-0.274	-0.365	-1.300	-0.074	+0.183	+0.137	+0.183	+0.650
QCISD/6-311+G*	-0.079	-0.001		-0.284	-0.220	-0.284	-1.346	+0.040	+0.142	+0.110	+0.142	+0.673
MgCMg ($^5\Sigma_u^-$) ^c												
MP2/6-311+G*	-0.455	0.293		-0.229	-0.209	-0.229	-1.621	+0.228	+0.115	+0.105	+0.115	+0.811
QCISD/6-311+G*	-0.409	0.249		-0.210	-0.187	-0.210	-1.546	+0.204	+0.105	+0.094	+0.105	+0.773
CMg ₃ ($C_{3v}, ^1A_1$) ^b												
MP2/6-311+G*	-0.195	-0.073	0.152	-0.885	-0.764	-0.927	-3.000	+0.065	+0.295	+0.255	+0.309	+1.000
QCISD/6-311+G*	-0.112	-0.184	0.184	-0.748	-0.745	-0.870	-2.877	+0.037	+0.249	+0.248	+0.290	+0.959

^a At QCISD(T)/6-311+G(2df) geometry. ^b At MP2(full)/6-311+G* geometry. ^c At QCISD/6-311+G* geometry. ^d Mulliken population analysis. ^e Fitting charges to the potential, constrain them to reproduce the dipole moment. ^f Fitting charges to the potential at points selected according to the ChelpG scheme. ^g Fitting charges to the electrostatic potential at points selected according to the Merz-Singh-Kollman scheme. ^h Natural population analysis.

C. Mg₃C. For this stoichiometry, we also studied several structures and states as discussed earlier. This process caused us to focus on four singlets D_{3h} ($^1A_1'$: $1a_1'^2 1e'^4 1a_2''^2 2a_1'^2$), C_{3v} (1A_1 : $1a_1^2 1e^4 2a_1^2 3a_1^2$), C_{2v} , T (1A_1 : $1a_1^2 1b_2^2 2a_1^2 1b_1^2 3a_1^2$), and C_{2v} , Y (1A_1 : $1a_1^2 2a_1^2 1b_2^2 1b_1^2 3a_1^2$), three triplets C_{2v} , T (3B_2 : $1a_1^2 1b_2^2 2a_1^2 1b_1^2 3a_1^2 1b_1^2$), C_{2v} , Y (3A_1 : $1a_1^2 2a_1^2 1b_2^2 1b_1^2 3a_1^2 1a_1^2$), and D_{3h} ($^3A_1'$: $1a_1'^2 1e'^4 1a_2''^2 2e'^2$), and one quintet D_{3h} ($^5A_2''$: $1a_1'^2 1e'^4 1a_2''^2 2a_1'^2 2e'^2$).

We were not able to find any stable structure of C_{2v} symmetry with the carbon atom coordinated outside of a Mg₃ cluster. Upon geometry optimization such structures dissociated into Mg₂C + Mg. The final geometries (at the MP2(full)/6-311+G* level) of all of the stable Mg₃C structures that we were able to locate are shown in Figure 1 and their total and relative energies and harmonic frequencies are presented in Table 2.

According to our calculations, the singlet states lie lowest, with the pyramidal C_{3v} (1A_1) structure the most stable. The D_{3h} ($^1A_1'$) planar structure was found to be a third-order saddle point and therefore cannot even be a transition state for the inversion of the C_{3v} (1A_1) structure. Distortions of the D_{3h} ($^1A_1'$) species toward C_{2v} symmetry lead to two types of structures: C_{2v} , T (1A_1) and C_{2v} , Y (1A_1). The former is a true saddle point (with one imaginary frequency), and the second is a second-order saddle point.

However, at levels of theory above MP2 (see Table 2a), a D_{3h} ($^1A_1'$) structure was found to be the most stable singlet planar structure, and inversion of the C_{3v} (1A_1) Mg₃C pyramid was found to occur through this D_{3h} ($^1A_1'$) structure. At our highest level of theory (QCISD(T)/6-311+G(2df)), the inversion barrier is only 1.11 kcal/mol (389 cm⁻¹). Considering the value of the inversion vibrational quantum 110 cm⁻¹, we expect that only three or four inversion vibrational levels are located below the barrier.

Among the low-energy triplet species identified, C_{2v} , T (3B_2), C_{2v} , Y (3A_1), and D_{3h} ($^3A_1'$), the first is a true local minimum

with the others being saddle points. However, even the most stable triplet C_{2v} , T (3B_2) structure is less stable than the C_{3v} (1A_1) global minimum structure by 15 kcal/mol. The lowest quintet, which is of D_{3h} ($^5A_2''$) structure, is a minimum but is higher in energy than the global minimum by 18.9 kcal/mol (all data at the QCISD(T)/6-311+G(2df) level).

We also calculated the dissociation energy D_e for the ground-state singlet Mg₃C ($C_{3v}, ^1A_1$) state into ground-state singlet Mg₂C ($C_{2v}, ^1A_1$) + Mg (1S) to be 41 kcal/mol at the QCISD(T)/6-311+G(2df)+ZPE level. Surprisingly, this dissociation energy of Mg₃C is larger than the Mg atom loss energies of Mg₂C (24.6 kcal/mol) and MgC (34.5 kcal/mol).

IV. Nature of the Bonding in MgC, Mg₂C, and Mg₃C

An ionic model for bonding in MgC transfers two electrons from Mg to C, giving Mg²⁺ (1S), and C²⁻ (3P) and predicts a $^3\Sigma^-$ ground state with atomic charges near ± 2 . Alternatively, a dative bonding picture describes MgC as involving a single two-electron dative bond with Mg serving as the electron pair donor and the empty 2p orbital of C the electron pair acceptor. This model also predicts a $^3\Sigma^-$ ground state. Both models view Mg as providing two valence electrons and one active valence orbital, and both leave the two unpaired electrons on the C center.

Allowing the Mg atom's electronic configuration to be "promoted" to $3s^1 3p^1$ and thus utilizing sp hybridization, MgC might be expected to have one σ bond, an sp σ unpaired electron on Mg, a nonbonding σ pair on C, and a $p\pi$ electron on C and hence a $^3\Pi$ state. However, this same promoted Mg $3s^1 3p^1$ configuration could combine with 3P C to form one σ bond, a σ lone pair on C, and two $p\pi$ electrons (one from Mg and one from C) and thus a $^3\Sigma^-$ state. In this model, both the $^3\Pi$ and $^3\Sigma^-$ states have unpaired electron density on both Mg and C.

According to our calculations and those of others, the ground electronic state of MgC has two doubly occupied sigma ($1\sigma^2$

and $2\sigma^2$) orbitals and one partially occupied π orbital ($1\pi^2$)¹⁶ composed almost completely of $2p_\pi$ AOs of the carbon atom. Only the 2σ MO has significant bonding character, so we view MgC as a singly bound species with its two unpaired nonbonding π electrons on C.

Additional information about the bonding can be obtained from atomic population analysis. Many different methods have been developed for the quantum chemical calculation of atomic charges. We explored five popular methods: Mulliken population analysis,¹⁷ the Merz–Kollman method,^{18,19} which produces partial charges fit to the electrostatic potential at points selected according to the Merz–Singh–Kollman scheme, the CHelpG method that produces charges fit to the electrostatic potential at points selected according to the CHelpG scheme,¹⁹ the dipole method that produces charges to fit the potential constrained to reproduce the dipole moment,²⁰ and the natural bond analysis²¹ method of Weinhold. We examined all of these methods to make certain that any conclusions we draw do not depend on using any particular definition of atomic charges.

A. MgC. Our results on MgC are presented in Table 3. As expected, the calculated effective atomic charges vary substantially from method to method, ranging from ± 0.29 (Mulliken) to ± 0.73 (NBO), all of which mean a substantial covalent character of the bonding in MgC. These charges can be compared with the atomic charges of C (varies from -0.76 (Mulliken) to -1.32 (NBO)) and Mg (varies from $+0.64$ (Mulliken) to $+1.44$ (NBO)) in CH_3MgH , where a single bond is clearly responsible for the Mg–C bonding. Also the overlap population $Q(\text{Mg}-\text{C}) = 0.177$ in MgC is even lower than that, $Q(\text{Mg}-\text{C}) = 0.304$, in CH_3MgH (at QCISD(T)/6-311+G*). The bond length of MgC (${}^3\Sigma^-$) ($R_e = 2.087$ Å, at MP2(full)/6-311+G*) is very close to the Mg–C bond length in the $\text{CH}_3\text{-MgH}$ molecule ($R_e = 2.100$ Å at the same level of theory), and the dissociation energy of MgC (${}^3\Sigma^-$) into Mg (3P) + C(3P) ($D_e = 94.6$ kcal/mol) can be compared with the dissociation energy of the single Mg–C bond in CH_3MgH (into $\text{CH}_3 + \text{MgH}$; $D_e = 64.9$ kcal/mol, at QCISD(T)/6-311++G(2df,2pd)). From all of these data, one concludes that MgC has a *single* bond and atomic charges of less than ± 1 (and certainly not close to ± 2).

B. Mg₂C. As detailed in Table 3, in the most stable cyclic Mg₂C (C_{2v} , 1A_1) structure, the carbon has two Mg–C bonds and a lone pair, and the two magnesium atoms are bonded by a single Mg–Mg bond. The carbon center is thus much like an organic carbene.

As in conventional carbenes, one of the lone pair electrons on carbon can be promoted into the empty b_1 $p\pi$ orbital, producing a Mg₂C (C_{2v} , 3B_1) triplet state which is almost the same in energy. Both of the unpaired electrons in the Mg₂C (C_{2v} , 3B_1) state are located on the carbon atom according to our calculated spin densities.

C. Mg₃C. In the case of Mg₃C, the singlet (C_{3v} , 1A_1) structure has the lowest energy. In this molecule, the atomic

charge on carbon is the most negative among the molecules studied and is -3.00 in the NBO scheme. Magnesium–magnesium bonding interactions are important contributors to the stability of this structure. Moreover, these interactions are responsible for an unusual flatness of the inversion potential energy surface in the area of the Mg₃C (D_{3h} , 1A_1) transition-state structure of this molecule. Overall, the ionic bonding between the valence unsaturated carbon atom and magnesium–magnesium bonding interactions are responsible for the stability of the hyperstoichiometric Mg₃C molecule in its C_{3v} (1A_1) state.

Although we used sophisticated ab initio techniques in our computational predictions of new Mg₂C and Mg₃C molecules, experimental verification of our results are certainly desired.

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