

Structure, bonding and energetics of N-heterocyclic carbene (NHC) stabilized low oxidation state group 2 (Be, Mg, Ca, Sr and Ba) metal complexes: A theoretical study

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Abstract. A series of N-heterocyclic carbene stabilized low oxidation state group 2 metal halide and hydrides with metal-metal bonds ($[L(X)M-M(X)L]$; $L = \text{NHC} ((\text{CHNH})_2\text{C}:)$, $M = \text{Be, Mg, Ca, Sr and Ba}$, and $X = \text{Cl or H}$) has been studied by computational methods. The main objective of this study is to predict whether it is possible to stabilize neutral ligated low oxidation state alkaline-earth metal complexes with metal-metal bonds. The homolytic metal-metal Bond Dissociation Energy (BDE) calculation, Natural Bond Orbital (NBO) and Energy Decomposition Analyses (EDA) on density functional theory (DFT) optimized $[L(X)M-M(X)L]$ complexes revealed that they are as stable as their β -diketiminato, guanidinate and α -diimine counterparts. The optimized structures of the complexes are in trans-linear geometries. The bond order analyses such as Wiberg Bond Indices (WBI) and Fuzzi Bond Order (FBO) confirm the existence of single bond between two metal atoms, and it is covalent in nature.

Keywords. Alkaline earth metals, low oxidation state, NHC.

1. Introduction

The seminal breakthrough came in 1991, when Arduengo and co-workers synthesized and isolated the first stable N-heterocyclic carbene (NHC), i.e. 1,3-bis(adamantyl)imidazol-2-ylidene.¹ In recent years, in the s- and p- block chemistry, synthetic main group chemists employed various monoanionic (like β -diketiminato, amidinate, guanidinate, terphenyl), dianionic (like α -diimine) and neutral ligands (like NHCs) to isolate very reactive species of main group elements. By utilizing such ligands, chemists synthesized and isolated very reactive and unusual low oxidation state metal complexes with metal-metal (element-element) single or multiple bonds and metal (element) with non-bonded electrons and/or both.^{2–17}

From the past one decade, NHCs turned out to be key to the isolation of reactive and unusual compounds of p- block elements. Heavier group 14 dichlorides of germanium, tin and lead are stable at room temperature and commercially available, whereas lighter dichlorides of carbon and silicon are not stable at room temperature. However, in 2009 Roesky and co-workers isolated the

NHC stabilized silicon dichloride (dichlorosilylene),¹⁸ where silicon oxidation state is +2. Many silylenes are known in the literature and most of them are prepared by reductions of their parent compounds using strong reducing agents like potassium metal or KC_8 (potassium graphite is a strong one electron reductant). Dichlorosilylene was formed by reductive elimination of HCl from trichlorosilane in the presence of bulky N-heterocyclic carbene. In addition to this they also have shown that the reduction of NHC adduct of silicon tetrachloride in toluene led to the formation of NHC stabilized dichlorosilylene. In the same year Filippou *et al.*¹⁹ reported the bulky NHC adduct of dibromosilylene.

In 2008, Robinson and co-workers succeeded in isolating the NHC stabilized Si (0) compound with a Si-Si double bond, representing a truly landmark breakthrough in silicon chemistry.²⁰ It was formed by the KC_8 reduction of NHC adduct of silicon tetrachloride in tetrahydrofuran. Closely related to silicon (0), Robinson and co-workers were successful in isolating other main group low oxidation state compounds (B, P, and As).^{21–23}

Very recently, Braunschweig *et al.*,²⁴ reported the bulky NHC stabilized boron compound containing boron-boron triple bond core.²⁵ It indicates the donor

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strength of the NHC ligand and it also gives a clue to the isolation of other reactive NHC stabilized main group compounds.²⁶

Jones and co-workers isolated NHC stabilized digermanium (0) compound. It was obtained by the reduction of NHC adduct of germanium dichloride in the presence of 2c/2e reductant, i.e. (^{mes}nacnacMg(I))₂.²⁷ They also reported the stable adduct of dialane (4), i.e., (Al₂H₄).²⁸ It was achieved by the reaction of NHC: AlH₃ adduct with (^{mes}nacnacMg (I))₂. The same research group further explored the usage of soluble 2c/2e Mg(I) as reducing agent in the isolation of soluble allotrope of tin.²⁹

The research activities mentioned above suggest that NHC ligated chemistry is growing rapidly for the stabilization of low oxidation state of p- block elements, their use in s- block elements is essentially unknown, although there are some reports on the NHC stabilized group 1 and group 2 metal complexes.^{30–37}

Soon after the unprecedented synthesis of decamethyl dizincocene compound, Cp*Zn-ZnCp* (Cp* = C₅Me₅), containing a Zn-Zn bond by Carmona and co-workers in 2004,³⁸ theoreticians predicted thermally stable low oxidation state group 2 compounds with metal-metal bonds should be isolable.

Indeed, a few reports are there on computational studies of low oxidation state group 2 metal complexes with metal-metal bonds.^{39–41} Notably, in 2005 Xie *et al.*⁴² reported a series of stable species containing group 2 elements, CpMMcP [(Cp) = C₅H₅; M = Be, Mg, Ca], by theoretical methods. Zhang and co-workers have studied the binuclear metallocenes using DFT methods,⁴³ and concluded the existence of single bond between the metal-metal atoms and a predominant ionic bond between metal and the ligand.

New era in the group 2 low oxidation state compounds with metal-metal bonds was shown by Jones and co-workers in 2007, by synthesizing well-defined stable dimeric magnesium (I) compounds.⁴⁴ Also, in their later reports, they showed a handful of magnesium (I) dimers, that are stabilized by monoanionic and bidentate β-diketiminato ligands.^{12,45} Liu *et al.* reported magnesium (I) complex which is stabilized by the α-diimine ligand.⁴⁶ Recently, Westerhausen reported inverse sandwich complex [(THF)₃Ca₂C₆H₃Ph₃] as black pyrophoric crystals, which was formed by the reaction of 1,3,5-triphenylbenzene with activated calcium in THF, in the presence of catalytic amounts of 1-bromo-2,4,6-triphenylbenzene.⁴⁷

To our knowledge, there is only one report on NHC stabilized complexes with Be-Be bonds.⁴⁸ It has been recently shown theoretically that in the case of group 14 low oxidation state compounds, NHCs are better

ligands than other neutral ligands such as phosphines.⁴⁹ In the present work, NHC stabilized low oxidation state alkaline earth metal complexes with M-M bonds (M = Be, Mg, Ca, Sr, and Ba) are studied comprehensively to explore their structures, stabilities, bonding *via* density functional theory (DFT) methods.

2. Theoretical Methods

The DFT calculations were performed using Gaussian-03⁵⁰/09⁵¹ and GAMESS^{52,53} ab initio quantum chemistry packages. The geometry optimization was carried out with Gaussian software with the default convergence criteria. Subsequent frequency analyses on the optimized structure were performed to establish that the optimized structures are true minima. The dispersion corrected hybrid DFT functional, ω-B97X-D⁵⁴ as well as B3LYP^{55,56} and BP86^{57,58} functionals were used for geometry optimization and frequency calculation. The def2-TZVP⁵⁹ basis set was used for Be, Mg, and Ca. For Sr and Ba, the def2-TZVP basis set with the effective core potential was employed. The Natural Bond Orbital (NBO)^{60,61} analysis was also performed to get a clear insight to bonding properties like Natural Population Analysis (NPA), Wiberg Bond Index (WBI)⁶² and donor-acceptor interaction energy.⁶¹ The NBO calculations were done using Gaussian NBO Version 3.1 as implemented in Gaussian-09. To understand the nature of metal-metal bonding interaction in complexes and the contribution of different energy terms to the total metal-metal bond dissociation energy, the localized molecular orbital energy decomposition analysis (LMO-EDA)⁶³ analyses were carried out using the Gamess software.

3. Results and Discussion

3.1 Structure

The schematic representation of the complexes is shown in figure 1 (M = Be, Mg, Ca, Sr, and Ba; X = Cl and H; L = NHC). The double headed arrow indicates the bond angles. Figure 2 shows the ω-B97X-D/def2-TZVP optimized structure of [(Cl) (NHC) Mg-Mg (NHC) (Cl)] and [(H) (NHC) Mg-Mg (NHC) (H)] complexes. The important structural parameters of [(Cl) (NHC) M-M (NHC) (Cl)] and [(H) (NHC) M-M (NHC) (H)] are presented in tables 1 and 2, respectively. We have tried several DFT functionals like B3LYP, BP86 and PBE0 with def2-TZVP basis set (not presented here) for the geometry optimization and binding energy calculation. However, we have chosen ω-B97X-D as it

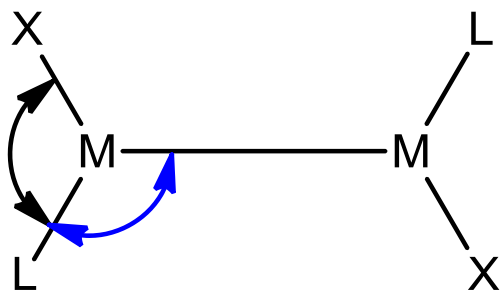


Figure 1. Schematic representation of [(X) (L) M-M (L) (X)] complex, where X = H or Cl, L = NHC, M = Be, Mg, Ca, Sr, and Ba. The bond angles are indicated by double-headed arrow.

is shown to predict bond dissociation energy (BDEs) of metal complexes within 1 kcal/mol of CCSD(T) level BDEs.⁶⁴ The choice is further justified by comparing the computed structural parameters of a model compound $K_2[(NHCH)_2-Mg-Mg-(NHCH)_2]$ with those of crystallographic data of $[K(THF)_3]_2[LMg-MgL]$; L = $[(2,6-iPr_2C_6H_3)NC(Me)]_2^{2-}$.⁴⁶ The important structural parameters around the metal atoms are provided in table 3. It can be seen from the table that ω -B97X-D/def2-TZVP is good enough to predict the structure of alkaline earth metal complexes. Except

the Ba complexes (see the dihedral angle L-M-M-L in tables 2 and 3), all other complexes are trans-linear structure. Longer bond distances of M-L, M-X and M-M bonds were observed, when going down the group (Be to Ba). The M-M and M-L bond lengths of [(Cl) (NHC) M-M (NHC) (Cl)] are slightly shorter than the corresponding M-M bond length in [(H) (NHC) Mg-Mg (NHC) (H)], suggesting that Cl atoms strengthen both M-M and M-L bonds. This is further confirmed by NBO analysis and BDEs, *vide infra*. The M-M bond distances can be compared with those of α -diimine complexes of alkaline earth metals. The NHC stabilized M-M bonds are slightly shorter than α -diimine complexes.^{46,65} The computed Mg-Mg bond distances are within the range 2.845 – 3.196 Å observed experimentally for binuclear Mg complexes.^{12,44,66} The structural analysis of the optimized metal complexes provides a direct clue that NHC stabilized Group 2 binuclear metal complexes can be synthesized in the laboratory.

3.2 Bonding

The natural bond orbital analysis has been performed to understand the bonding nature of these complexes.

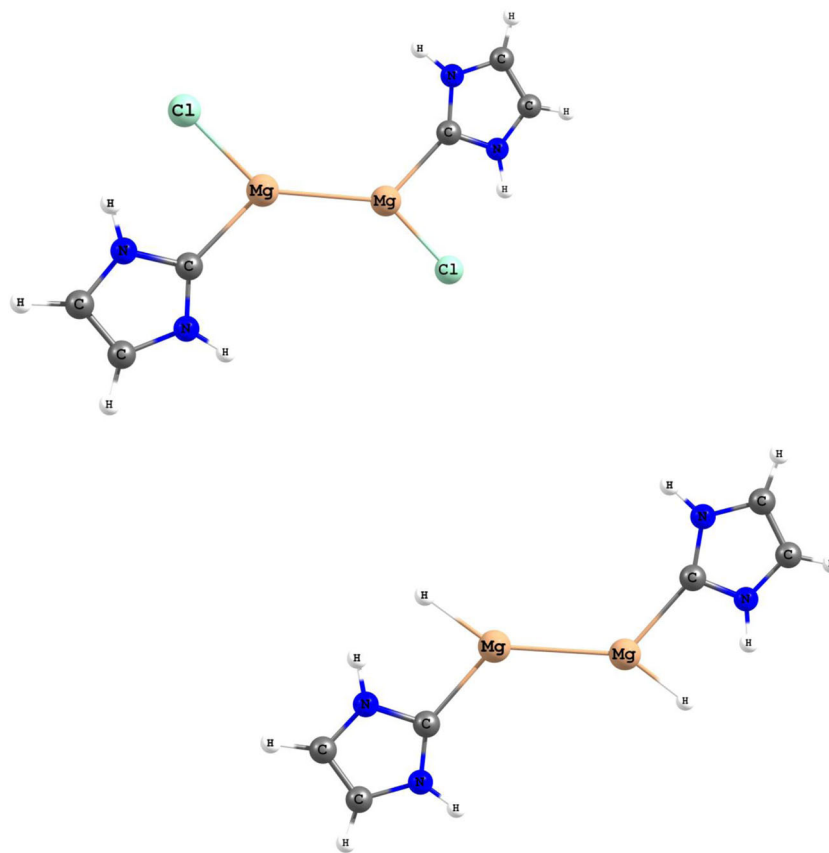


Figure 2. ω -B97X-D/def2-TZVP-optimized geometries of [(Cl) (NHC)-Mg-Mg-(Cl) (NHC)] and [(H) (NHC)-Mg-Mg-(H) (NHC)].

Table 1. Selected bond lengths (Å), angles (deg.) and dihedral angles (deg.) in [(H) (NHC)-M-M-(H) (NHC)] as obtained from the ω -B97X-D/def2-TZVP-optimized structures.

Species	X = H, L = NHC					
	M-L	M-X	M-M	L-M-X	L-M-M	L-M-M-L
[(X)(L)-Be-Be-(L)(X)]	1.812	1.411	2.196	111.9	103.8	180.0
[(X)(L)-Mg-Mg-(L)(X)]	2.277	2.277	2.937	87.1	125.9	180.0
[(X)(L)-Ca-Ca-(L)(X)]	2.574	2.133	3.836	78.0	132.0	180.0
[(X)(L)-Sr-Sr-(L)(X)]	2.754	2.308	4.196	74.3	134.7	180.0
[(X)(L)-Ba-Ba-(L)(X)]	2.927	2.452	4.542	69.9	124.7	82.3

Table 2. Selected bond lengths (Å), angles (deg.) and dihedral angles (deg.) in [(Cl) (NHC)-M-M-(Cl) (NHC)] as obtained from the ω -B97X-D/def2-TZVP-optimized structures.

Species	X = Cl, L = NHC					
	M-L	M-X	M-M	L-M-X	L-M-M	L-M-M-L
[(X)(L)-Be-Be-(L)(X)]	1.792	1.977	2.128	113.3	116.06	180.0
[(X)(L)-Mg-Mg-(L)(X)]	2.245	2.341	2.881	92.1	133.302	180.0
[(X)(L)-Ca-Ca-(L)(X)]	2.563	2.580	3.788	84.7	127.054	180.0
[(X)(L)-Sr-Sr-(L)(X)]	2.754	2.740	4.148	81.1	134.257	168.8
[(X)(L)-Ba-Ba-(L)(X)]	2.913	2.878	4.507	77.1	113.942	106.6

The Wiberg bond indices (WBI) and the charge on the metal atom are presented in table 4. The WBI of M-M bond are very close to one (0.932 – 0.975). This indicates the presence of single bond between two metal atoms and it is covalent in nature. The WBI of M-X bond except Be complexes are below 0.5, suggesting that these bonds are weaker than M-M bond and can be coordinate bonds rather than co-valent bonds. In addition, Fuzzy bond order (FBO) analysis was done with Multiwfn software.⁶⁷ The FBO bond order has been found to be more accurate and appropriate over Mayer bond order and AIM indices. It is also relatively less sensitive to basis functions.⁶⁸ The FBO is also consistent with WBI. The donor-acceptor NBO second order interaction (ΔE_{ij})⁶¹ energies have also been estimated. It is noticed that there is non-covalent interaction between N-H group of NHC and X, forming some sort of weak hydrogen/dihydrogen bonds. For instance, in [(X)(L)-Mg-Mg-(L)(X)] complexes, lone pair (LP) of the Cl atom (LP_{Cl}) interacts with the sigma

antibonding orbital of N-H bond (σ^*_{N-H}), similarly the sigma bonding orbital of Mg-H (σ_{Mg-H}) interacts with the σ^*_{N-H} . The ΔE_{ij} values for the above mentioned two interactions are 3.9 and 4.2 kJ/mol, respectively. The striking results obtained from the NBO analysis is the strengthening of the M-M bond by the presence of Cl atoms. This is confirmed by the donor-acceptor interaction energy between Cl and metal atoms. The LP_{Cl} interacts with the sigma anti bonding orbital of M-C (NHC) (σ^*_{M-C}) bond and with the empty non-lewis NBOs of the metals atoms (LP^*_M). The interaction energy for LP_{Cl} and σ^*_{M-C} is 17.62 kJ/mol, while that is 88.63 kJ/mol for LP_{Cl} and LP^*_{Mg} interaction.

The low oxidation state of the metal in the complexes is verified by the natural population analysis within the NBO framework. The computed natural charges of metals are given in table 4. The natural charge of metals (q_M) except Be is within the range of +0.45 to +0.75 au and q_H and q_{Cl} values range from -0.43 to -0.75 and -0.58 to -0.82, respectively. The low positive charge

Table 3. Selected bond lengths and angles in $K_2[(CHNH)_2-Mg-Mg-(CHNH)_2]$ are compared with the corresponding crystallographic data⁴⁶ $[K(THF)_3]_2[LMg-MgL]$; L = [(2,6— $Pr^2C_6H_3$)NC(Me)]₂²⁻.

Methods	$K_2[(CHNH)_2-Mg-Mg-(CHNH)_2]$			
	Mg-Mg (Å)	Mg-N (Å)	N-Mg-Mg (deg)	N-Mg-N (deg)
Theoretical (ω -B97X-D/def2-TZVP)	2.939	2.045	135.8	81.2
Experimental	2.937	2.047 ^a	138.9 ^a	81.5 ^a

^aArithmetic mean of the two bond lengths/angles

Table 4. The Fuzzy Bond Order (FBO), Wiberg Bond Index (WBI) of metal-metal bond (M-M) and natural charge of metal q_M in atomic unit in [(X) (L)-M-M-(L) (X)] complexes.

Species	X = H, L = NHC			X = Cl, L = NHC		
	FBO (M-M)	WBI (M-M)	q_M	FBO (M-M)	WBI (M-M)	q_M
[(X)(L)-Be-Be-(L)(X)]	0.784	0.846	0.146	0.735	0.842	0.295
[(X)(L)-Mg-Mg-(L)(X)]	0.908	0.998	0.477	0.882	0.971	0.581
[(X)(L)-Ca-Ca-(L)(X)]	0.958	1.014	0.606	0.930	1.002	0.627
[(X)(L)-Sr-Sr-(L)(X)]	0.988	1.060	0.676	0.970	1.046	0.692
[(X)(L)-Ba-Ba-(L)(X)]	1.019	1.099	0.713	0.984	1.085	0.739

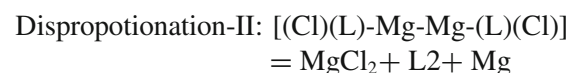
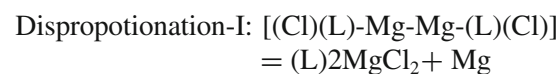
on metal atom suggests that they are in low oxidation state (+1).

3.3 Energetics

The dimerisation energies or metal-metal bond dissociation energies (BDEs) of the complexes were calculated using the dimerisation scheme as [(X)(L)-M-M-(L)(X)] = 2[(X)(L)-M]. The zero point vibrational energy (ZPVE) contribution is also incorporated in all BDE calculations. The BDE, enthalpy (ΔH) and free energy (ΔG) of bond dissociation are given in table 5. To ensure about the reliability of current level of theory in predicting BDE correctly, the BDE for Mg_2Cl_2 has been calculated compared with the experimental value obtained from Mg-Mg stretching vibration and its overtones.⁶⁹ The computed value of Mg-Mg bond energy in Mg_2Cl_2 is -198.8 kJ/mol, which is about 2 kJ/mol higher than the experimental value (-197 kJ/mol). This establishes the current level of theory can be used for the precise prediction BDEs. The BDE, ΔH , and ΔG decreases down the group i.e. from Be-Be to Ba-Ba. This trend was previously reported in other complexes of binuclear alkaline earth metals. The M-M BDE for [(Cl)(NHC)M-M(NHC)(Cl)] are higher compared to that of [(H)(NHC)M-M(NHC)(H)] complexes. This has already been noticed in shorter M-M bond length in [(Cl) (NHC) M-M (NHC) (Cl)] than in [(H) (NHC) M-M (NHC) (H)] complexes. The reason for larger BDE in [(Cl) (NHC) M-M (NHC) (Cl)] is

the LP_{Cl} and LP^*_M interactions which is lacking in [(H) (NHC) M-M (NHC) (H)] complexes (vide supra).

The disproportionation of [(Cl)(L)-Mg-Mg-(L)(Cl)] has also been considered for the comparison with the dimerisation. The disproportionation energy (DPE) has been determined by the two schemes shown below.



The disproportionation energy, enthalpy and free energy are given in table 7. For the scheme I the DPE is endothermic and for scheme II it is exothermic. However, the exothermic disproportionation energy (~ -75 kJ/mol) is almost one-third of the BDE and half of atomization energy (~ -148 kJ/mol) of $(Mg)_n$ cluster. Comparing these values (scheme I and II) with the dimerisation energy, it can be concluded that dimerisation is thermodynamically more favourable than the disproportionation.

To understand the nature of the M-M bond and contribution of different energy components such as the electrostatic energy (ΔE_{ES}), the exchange energy (ΔE_{EX}), the repulsion energy (ΔE_{Rep}), the polarization energy (ΔE_{POL}) and the dispersion energy (ΔE_{Disp}) to the total interaction energy (ΔE_{Int}), LMO-EDA calculation was performed at the B97-D/def2-TZVP level. The different energy contributions for [(Cl) (NHC) Mg-Mg

Table 5. ω -B97X-D/def2-TZVP-calculated bond dissociation energies (BDE in kJ/mol), enthalpy (ΔH in kJ/mol) and free energies (ΔG in kJ/mol) of the fragmentation of the complex [(X) (L)-M-M-(L) (X)] \rightarrow 2[(X) (L)-M].

Species	X = H, L = NHC			X = Cl, L = NHC		
	BDE	ΔH	ΔG	BDE	ΔH	ΔG
[(X)(L)-Be-Be-(L)(X)]	-189.1	-193.8	-138.6	-296.7	-295.6	-247.8
[(X)(L)-Mg-Mg-(L)(X)]	-193.3	-191.7	-149.2	-211.8	-209.5	-166.1
[(X)(L)-Ca-Ca-(L)(X)]	-144.2	-141.0	-108.6	-152.5	-149.0	-113.4
[(X)(L)-Sr-Sr-(L)(X)]	-126.7	-123.8	-84.6	-136.1	-132.1	-98.0
[(X)(L)-Ba-Ba-(L)(X)]	-120.4	-117.7	-75.6	-127.3	-124.0	-83.2

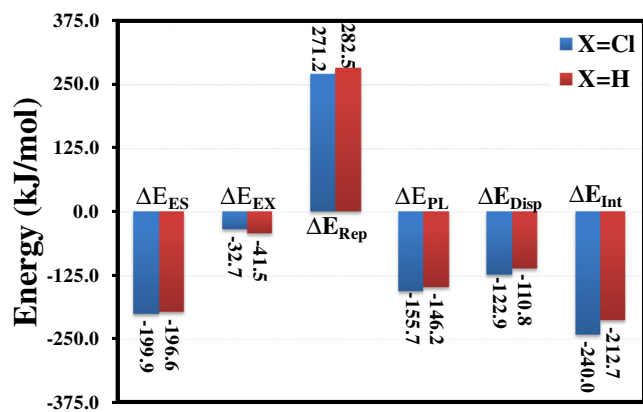


Figure 3. Different energy components as obtained from LMO-EDA calculation at the ω -B97X-D/def2-TZVP level of theory for [(Cl)(NHC)-Mg-Mg-(Cl)(NHC)] and [(H)(NHC)-Mg-Mg-(H)(NHC)].

(NHC) (Cl)] and [(H) (NHC) Mg-Mg (NHC) (H)] are represented graphically in figure 3. It can be seen from the LMO-EDA that the Mg-Mg interaction is not completely electrostatic in nature, although it is the major contributor to the total interaction energy. The contributions from polarization as well as from dispersion are also significant. The polarization and dispersion energy contribution for [(Cl) (NHC) Mg-Mg (NHC) (Cl)] is ~ 21 kJ/mol more than that for [(H) (NHC) Mg-Mg (NHC) (H)] which also accounts for the ~ 27 kJ/mol total interaction energy difference between these two complexes.

Finally a comparative study of NHC stabilized Mg (I)-Mg (I) complexes and Cp-Mg-Mg-Cp and $\text{Na}_2[(\text{NHCH})_2\text{-Mg-Mg-(NHCH)}_2]$ is presented. The

ω -B97X-D/def2-TZVP level of theory was used for the geometry optimization, WBI and BDE calculation of the complexes. These values along with previously reported values are presented in tables 6 and 7. The BDEs of [(Cl)(NHC)Mg-Mg(NHC)(Cl)] and Cp-Mg-Mg-Cp are ~ -210 kJ/mol while those for [(H)(NHC)Mg-Mg(NHC)(H)] and $\text{Na}_2[(\text{NHCH})_2\text{-Mg-Mg-(NHCH)}_2]$ are ~ -190 kJ/mol. The BDEs of Cp-Mg-Mg-Cp and $\text{Na}_2[(\text{NHCH})_2\text{-Mg-Mg-(NHCH)}_2]$ at the ω -B97X-D/def2-TZVP level are ~ -20 kJ/mol more than those obtained at the BP86/TZ2P⁷⁰ and B3LYP/def2TZVPP⁶⁵ level of theory, respectively. However, the trend of stabilization of the complexes follows the same order irrespective of the level of theory. The BDEs of [(Cl)(NHC)Mg-Mg(NHC)(Cl)] and [(H)(NHC)Mg-Mg(NHC)(H)] at B3LYP/def2-TZVP level are -193.5 and -175.7 kJ/mol respectively and those at the BP86/def2-TZVP level are -188.1 and -173.0 kJ/mol, respectively. The WBI of all the complexes are very close to one which infers that NHC stabilized low oxidation state binuclear Mg-Mg complexes are stable and can be synthesized in the laboratory.

4. Conclusions

Low oxidation state group 2 metals with metal-metal bonds (Be, Mg, Ca, Sr, and Ba) are strongly stabilized by the neutral N-heterocyclic carbene ligand. All metal-metal bonded low oxidation state compounds are trans-linear in geometry. The WBIs of M-M bonds are close to one, indicating the existence of single bond between two metal atoms. The stability (in terms of BDE) of

Table 6. Comparison of the ω -B97X-D/def2-TZVP-estimation of bond dissociation energy (BDE in kJ/mol), Wiberg Bond Index and bond length (Å) of Mg-Mg bond with those in the related Mg (I)-Mg (I) systems reported in the literature.

Species	This Work			Previous Work		
	Mg-Mg	BDE	WBI (Mg-Mg)	Mg-Mg	BDE	WBI (Mg-Mg)
(H)(NHC)-Mg-Mg-(H)(NHC)	2.937	-193.3	0.998			
(Cl)(NHC)-Mg-Mg-(Cl)(NHC)	2.881	-211.8	0.971			
Cp-Mg-Mg-Cp	2.811	-210.3	0.986	2.790	-186.35	
$\text{Na}_2[(\text{CHNH})_2\text{-Mg-Mg-(CHNH)}_2]$	2.921	-193.0	0.921	2.887	-167.36	0.886

Table 7. Comparison of the ω -B97X-D/def2-TZVP-estimation of bond dissociation energy, enthalpy, free energy with disproportionation energy, enthalpy, free energy (all the energies and enthalpy are in kJ/mol). The atomic energy of Mg atom was taken from reference.⁶⁹

[(Cl)(L)-Mg-Mg-(L)(Cl)], L=NHC	ΔE (ZPE)	ΔH	ΔG
Dimerisation, [(Cl)(L)-Mg-Mg-(L)(Cl)] = 2(Cl)(L)-Mg	-211.8	-209.5	-166.1
Disproportionation-I, [(Cl)(L)-Mg-Mg-(L)(Cl)] = (L) ₂ MgCl ₂ + Mg	193.1	198.6	181.3
Disproportionation-II, [(Cl)(L)-Mg-Mg-(L)(Cl)] = MgCl ₂ + 2L + Mg	-74.6	-68.4	-47.9

$[(Cl)(NHC)Mg-Mg(NHC)(Cl)]$ is higher than that of $Na_2[(NHCH)_2-Mg-Mg-(NHCH)_2]$ (a model compound used for the computational study of $[K(THF)_3]_2[LMg-MgL]$; $L = [(2,6-iPr_2C_6H_3)NC(Me)]_2^{2-}$, whose synthesis and structure have already been reported)⁴⁷ emphasizing the possibility of synthesizing such complexes in the laboratory. The disproportionation energies are smaller than BDE. The LMO-EDA shows that polarization and dispersion have significant contribution to the stabilization of the Mg-Mg bond. The results presented in this paper shed light on the room temperature stable isolation of NHC stabilized low oxidation state group 2 metal complexes, which are not yet reported experimentally.

Supplementary information

The optimized structure and the Cartesian coordinates of the complexes computed at the ω -B97X-D /def2-TZVP level of theory. The electronic supporting information can be seen at www.ias.ac.in/chemsci.

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