Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

On single-electron magnesium bonding formation and the effect of methyl substitution

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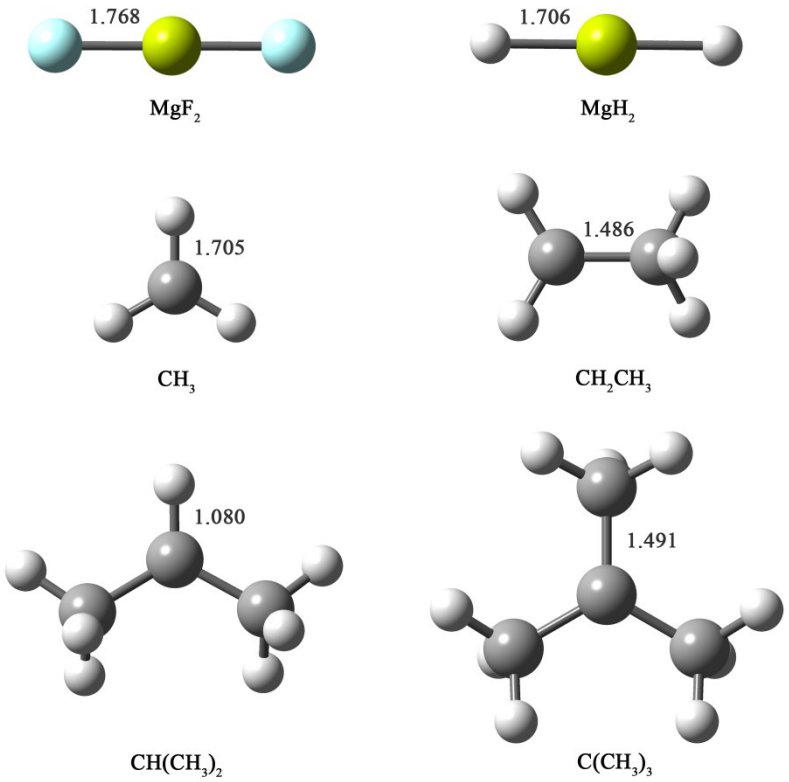

Figure S1. The optimized geometries of the MgX_2 (X = F, H) molecules and CH_3, CH_2CH_3, $CH(CH_3)_2$ and $C(CH_3)_3$ radicals at the MP2/aug-cc-pVTZ level.

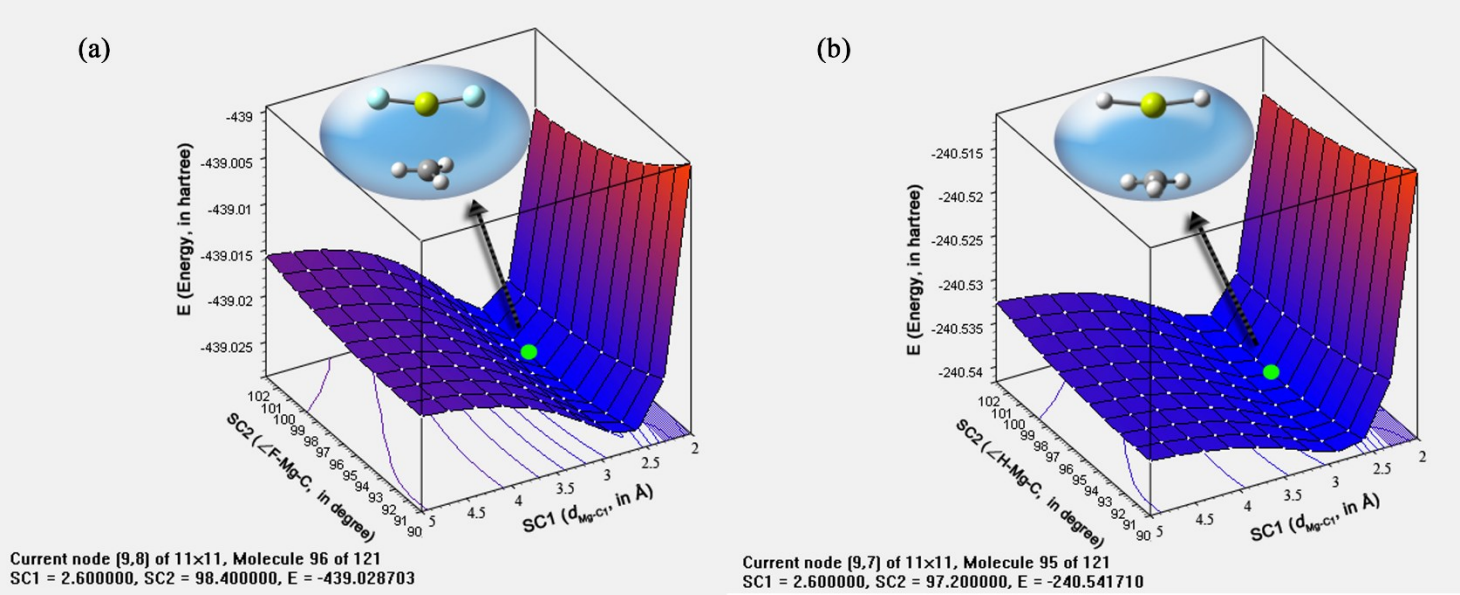

Fig S2. (a) Potential energy scan for **I**, (b) Potential energy scan for **I′**. SC1 and SC2 represent the distance between Mg and C atoms and the X-Mg-C (X = F, H) angle, respectively. Distances in Å and angles in degrees.

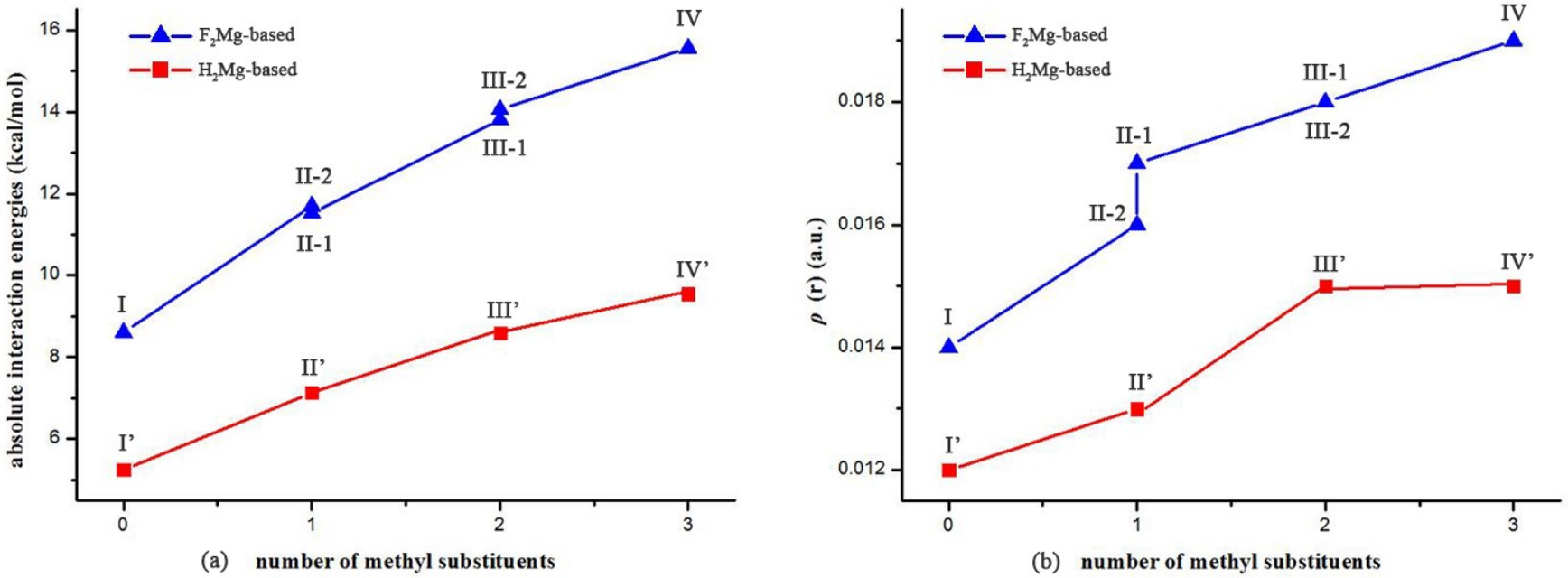

Fig. S3 (a) The relationship between interaction energy and the number of methyl substituents, (b) the relationship between electron density (ρ) at the Mg···C1 BCP and the number of methyl substituents of the $X_2Mg\cdots Y$ [X = F, H; Y = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$] complexes.

Table S1 The symmetry, distance between Mg and C1 atoms ($d_{Mg\text{-}C1}$, in Å), X-Mg-X angle (α, in degree), Mg-X1/X2 bond length ($R_{Mg\text{-}X1}$, in Å), and the $D_{X1\text{-}Mg\text{-}C1\text{-}H1}$ dihedral angle (in degree) of the $X_2Mg\cdots Y$ [X = F, H; Y = CH_3, CH_2CH_3] complexes obtained by using different methods with the same aug-cc-pVTZ basis set.

Complex	Method	*Symmetry*	$d_{Mg\text{-}C1}$	α	$R_{Mg\text{-}X1}$	$R_{Mg\text{-}X2}$	$D_{X1\text{-}Mg\text{-}C1\text{-}H1}$
I	MP2	C_s	2.573	163.0	1.778	1.779	0.0
	wB97XD	C_s	2.527	164.9	1.767	1.768	0.0
	M06-2X	C_s	2.506	165.1	1.752	1.754	0.0
	B3LPY-D3(BJ)	C_s	2.514	162.2	1.767	1.768	0.0
	B2PLYPD3	C_s	2.525	162.5	1.768	1.769	0.0
II-1	MP2	C_s	2.509	160.1	1.781	1.781	32.2
	wB97XD	C_s	2.475	161.5	1.770	1.770	32.0
	M06-2X	C_s	2.443	161.5	1.756	1.756	30.2
	B3LPY-D3(BJ)	C_s	2.458	158.6	1.770	1.770	32.2
	B2PLYPD3	C_s	2.466	159.3	1.771	1.771	32.1
II-2	MP2	C_1	2.521	160.1	1.780	1.783	12.3
	B3LPY-D3(BJ)	C_1	2.465	158.3	1.769	1.772	6.0
	B2PLYPD3	C_1	2.473	159.0	1.771	1.773	8.8
I′	MP2	C_s	2.707	166.6	1.717	1.717	89.9
	wB97XD	C_s	2.590	165.4	1.719	1.719	89.9
	M06-2X	C_s	2.608	165.2	1.704	1.704	89.8
	B3LPY-D3(BJ)	C_s	2.551	162.8	1.716	1.716	89.9
	B2PLYPD3	C_s	2.629	165.1	1.712	1.712	89.9
II′	MP2	C_s	2.644	164.3	1.719	1.719	31.8
	wB97XD	C_s	2.583	163.3	1.719	1.719	31.9
	M06-2X	C_s	2.579	163.4	1.706	1.706	31.8
	B3LPY-D3(BJ)	C_s	2.581	161.7	1.715	1.715	32.1
	B2PLYPD3	C_s	2.607	162.9	1.713	1.713	32.0