Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

System	Method	Basis set	Binding energy (kcal/mol)	Binding energy corrected (kcal/mol)
$1_{li\text{-}ben}$	B3LYP	6-31G(d)	-2.32	-1.93
		6-311+G(d,p)	-2.73	-2.58
		TZVP	-2.67	-2.44
	MP2	6-31G(d)	-2.42	-1.49
		6-311+G(d,p)	-3.35	-2.52
		TZVP	-2.67	-2.16
	B2PLYPD	6-31G(d)	-3.66	-3.09
		6-311+G(d,p)	-4.46	-4.05
		TZVP	-4.15	-3.79
$1_{li\text{-}aniline}$	B3LYP	6-31G(d)	-2.06	-1.68
		6-311+G(d,p)	-2.43	-2.28
		TZVP	-2.40	-2.17
	MP2	6-31G(d)	-2.22	-1.26
		6-311+G(d,p)	-3.09	-2.27
		TZVP	-2.38	-1.69
	B2PLYPD	6-31G(d)	-3.38	-2.79
		6-311+G(d,p)	-4.12	-3.71
		TZVP	-3.85	-3.44
$1_{li\text{-}methyl}$	B3LYP	6-31G(d)	-2.19	-1.80
		6-311+G(d,p)	-2.58	-2.45
		TZVP	-2.53	-2.30
	MP2	6-31G(d)	-2.34	-1.39
		6-311+G(d,p)	-3.24	-2.44
		TZVP	-2.58	-2.08
	B2PLYPD	6-31G(d)	-3.57	-2.99
		6-311+G(d,p)	-4.34	-3.96
		TZVP	-4.05	-3.69
$1_{li\text{-}cyano}$	B3LYP	6-31G(d)	-2.58	-2.21
		6-311+G(d,p)	-3.07	-2.94
		TZVP	-2.93	-2.70
	MP2	6-31G(d)	-2.55	-1.66
		6-311+G(d,p)	-3.56	-2.79
		TZVP	-2.85	-2.34
	B2PLYPD	6-31G(d)	-3.82	-3.24
		6-311+G(d,p)	-4.62	-4.24
		TZVP	-4.31	-3.93
	B3LYP	6-31G(d)	-2.34	-1.94
		6-311+G(d,p)	-2.81	-2.69
		TZVP	-2.72	-2.49

$1_{li\text{-}benzoic}$	MP2	6-31G(d)	-2.41	-1.48
		6-311+G(d,p)	-3.36	-2.58
		TZVP	-2.76	-2.19
	B2PLYPD	6-31G(d)	-3.64	-3.04
		6-311+G(d,p)	-4.52	-4.15
		TZVP	-4.10	-3.71

Table S1. Binding energy values (kcal/mol) for $C_6H_6{-}Li^+$ and $C_6H_5X{-}Li^+$ complexes at *ab initio* and different density functional methods in conjunction with 6-31G(d), 6-311+G(d,p) and TZVP basis sets.

System	Method	Basis set	Binding energy (kcal/mol)	Binding energy corrected (kcal/mol)
$1_{mg\text{-}ben}$	B3LYP	6-31G(d)	-11.74	-11.36
		6-311+G(d,p)	-13.45	-13.24
		TZVP	-11.94	-11.87
	MP2	6-31G(d)	-11.16	-9.98
		6-311+G(d,p)	-12.99	-12.18
		TZVP	-10.78	-10.30
	B2PLYPD	6-31G(d)	-12.21	-11.63
		6-311+G(d,p)	-14.00	-13.60
		TZVP	-12.17	-11.97
$1_{mg\text{-}aniline}$	B3LYP	6-31G(d)	-10.22	-9.85
		6-311+G(d,p)	-11.86	-11.67
		TZVP	-10.38	-10.30
	MP2	6-31G(d)	-9.95	-8.81
		6-311+G(d,p)	-11.88	-11.10
		TZVP	-9.53	-9.06
	B2PLYPD	6-31G(d)	-10.82	-10.26
		6-311+G(d,p)	-12.65	-12.27
		TZVP	-10.74	-10.53
$1_{mg\text{-}methyl}$	B3LYP	6-31G(d)	-11.16	-10.78
		6-311+G(d,p)	-12.82	-12.41
		TZVP	-11.35	-11.28
	MP2	6-31G(d)	-10.69	-9.51
		6-311+G(d,p)	-12.54	-11.73
		TZVP	-10.37	-9.89
	B2PLYPD	6-31G(d)	-11.71	-11.12
		6-311+G(d,p)	-13.31	-12.91
		TZVP	-11.66	-11.46
$1_{mg\text{-}cyano}$	B3LYP	6-31G(d)	-12.07	-11.69
		6-311+G(d,p)	-13.91	-13.70
		TZVP	-12.38	-12.32
	MP2	6-31G(d)	-11.44	-10.28
		6-311+G(d,p)	-13.35	-12.54
		TZVP	-11.21	-10.73
	B2PLYPD	6-31G(d)	-12.53	-11.94
		6-311+G(d,p)	-14.41	-14.00
		TZVP	-12.66	-12.46

Table S2. Binding energy values (kcal/mol) for C_6H_6–Mg^{2+} and C_6H_5X–Mg^{2+} complexes at *ab initio* and different density functional methods in conjunction with 6-31G(d), 6-311+G(d,p) and TZVP basis sets

System	ρ	$\nabla^2\rho$
$1_{li\text{-}ben}$	0.0154	0.0824
$2_{li\text{-}ben}$	0.0138	0.0753
	0.0138	0.0753
$3_{li\text{-}ben}$	0.0123	0.0682
	0.0123	0.0682
	0.0123	0.0682
$4_{li\text{-}ben}$	0.0123	0.0687
	0.0124	0.0686
	0.0122	0.0679

System	ρ	$\nabla^2\rho$
$1_{li\text{-}methyl}$	0.0153	0.0823
$2_{li\text{-}methyl}$	0.0139	0.0760
	0.0135	0.0744
$3_{li\text{-}methyl}$	0.0123	0.0687
	0.0123	0.0686
	0.0120	0.0668
$4_{li\text{-}methyl}$	0.0124	0.0692
	0.0120	0.0665
	0.0124	0.0692

System	ρ	$\nabla^2\rho$
$1_{li\text{-}benzoic}$	0.0155	0.0827
$2_{li\text{-}benzoic}$	0.0139	0.0755
	0.0142	0.0773
$3_{li\text{-}benzoic}$	0.0128	0.0709
	0.0126	0.0697
	0.0125	0.0682
$4_{li\text{-}benzoic}$	0.0127	0.0704
	0.0127	0.0704
	0.0126	0.0691

System	ρ	$\nabla^2\rho$
$1_{li\text{-}aniline}$	0.0152	0.0822
$2_{li\text{-}aniline}$	0.0143	0.0782
	0.0136	0.0733
$3_{li\text{-}aniline}$	0.0125	0.0702
	0.0122	0.0664
	0.0125	0.0699
$4_{li\text{-}aniline}$	0.0125	0.0700
	0.0123	0.0672
	0.0125	0.0702

System	ρ	$\nabla^2\rho$
$1_{li\text{-}cyano}$	0.0156	0.0828
$2_{li\text{-}cyano}$	0.0141	0.0762
	0.0142	0.0771
$3_{li\text{-}cyano}$	0.0127	0.0704
	0.0128	0.0706
	0.0127	0.0698
$4_{li\text{-}cyano}$	0.0129	0.0710
	0.0128	0.0713
	0.0125	0.0688

Table S3. Electron density and Laplacian of electron density at the BCP of $(H)_2$-Li^+ for all the C_6H_6-Li^+ and C_6H_5X-Li^+ complexes.

System	ρ	$\nabla^2\rho$
$1_{mg\text{-}ben}$	0.0220	0.1040
$2_{mg\text{-}ben}$	0.0192	0.0911
	0.0187	0.0876
$3_{mg\text{-}ben}$	0.0167	0.0793
	0.0167	0.0793
	0.0167	0.0793
$4_{mg\text{-}ben}$	0.0140	0.0655
	0.0140	0.0655
	0.0140	0.0655
	0.0140	0.0655
$5_{mg\text{-}ben}$	0.0143	0.0671
	0.0135	0.0628
	0.0132	0.0609
	0.0157	0.0745

System	ρ	$\nabla^2\rho$
$1_{mg\text{-}aniline}$	0.0214	0.1012
$2_{mg\text{-}aniline}$	0.0186	0.0880
	0.0181	0.0857
$3_{mg\text{-}aniline}$	0.0166	0.0789
	0.0166	0.0790
	0.0160	0.0750
$4_{mg\text{-}aniline}$	0.0130	0.0597
	0.0148	0.0699
	0.0143	0.0671
	0.0126	0.0543
$5_{mg\text{-}aniline}$	0.0125	0.0570
	0.0161	0.0770
	0.0143	0.0671
	0.0125	0.0538

System	ρ	$\nabla^2\rho$
$1_{mg\text{-}methyl}$	0.0217	0.1024
$2_{mg\text{-}methyl}$	0.0191	0.0906
	0.0183	0.0856
$3_{mg\text{-}methyl}$	0.0165	0.0786
	0.0165	0.0785
	0.0163	0.0775
$4_{mg\text{-}methyl}$	0.0136	0.0628
	0.0144	0.0677
	0.0142	0.0667
	0.0132	0.0602
$5_{mg\text{-}methyl}$	0.0127	0.0583
	0.0161	0.0770
	0.0143	0.0676
	0.0127	0.0575

System	ρ	$\nabla^2\rho$
$1_{mg\text{-}cyano}$	0.0225	0.1048
$2_{mg\text{-}cyano}$	0.0194	0.0907
	0.0195	0.0925
$3_{mg\text{-}cyano}$	0.0173	0.0816
	0.0173	0.0822
	0.0172	0.0814
$4_{mg\text{-}cyano}$	0.0143	0.0656
	0.0147	0.0687
	0.0147	0.0690
	0.0146	0.0681
$5_{mg\text{-}cyano}$	0.0143	0.0666
	0.0147	0.0687
	0.0142	0.0658
	0.0159	0.0743

Table S4. Electron density and Laplacian of electron density at the BCP of $(H)_2$-Mg^{2+} for C_6H_6−Mg^{2+} and C_6H_5X−Mg^{2+} complexes.