Supplementary information for: Analysis of Bonding Motifs in Unusual Molecules I: Planar Hexacoordinated Carbon Atoms

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S1 Geometries

Qualitatively, the RHF/6-31G(d), MP2/ACCD and CCSD(T)/ACCT geometries are similar. The computed CH_3Li geometry is in good agreement with the one previously reported by Kauffman and collaborators,[1] at the MP2/6-31G(d) level of theory. For $CO_3Li_3^+$, the parameters reported by Wu and collaborators[2] at the CCSD(T)/ACCT level of theory are in good agreement with the present results. For $CS_3Li_3^+$, the PBE0-D3/def2-TZVP optimized geometry reported by Leyva-Parra and collaborators[3] predicts C-Li and Li-S bond distances that are too short relative to those predicted by the wave function methods.

A shortening of the C-Li distances is observed in the CCSD(T)/ACCT structures of CH_3Li and $CS_3Li_3^+$, relative to their RHF/6-31G(d) counterparts. Generally, the treatment of electron correlation leads to longer interatomic equilibrium distances, as a result of the introduction of antibonding character into the wave function. However, a shortening may indicate that the CCSD(T) level of theory provides a better description of an attractive interaction that plays a significant role in the bonding of a molecule (e.g., ionic attraction), as it is the case in CH_3Li, in which the C-Li bond is known to have a strong ionic character.[4] The observation of this shortening in $CS_3Li_3^+$ but not in $CO_3Li_3^+$

would indicate the existence of ionic attraction in the former, but not in the latter, in accordance with previous reports.[3]

Table S1 Computed CH_3Li (C_{3v}) $CO_3Li_3^+$ (D_{3h}) and $CS_3Li_3^+$ (D_{3h}) geometrical parameters.

Parameter	RHF/ 6-31G(d)	MP2/ACCD	CCSD(T)/ACCT	Literature
CH_3Li				**MP2/6-31G(d)**[1]
r(C-Li)	2.001	2.016	1.986	2.003
r(C-H)	1.093	1.109	1.100	1.099
∠ H-C-Li	112.60	112.62	112.79	112.0
∠ H-C-H	106.17	106.15	105.96	-
$CO_3Li_3^+$				**CCSD(T)/ACCT**[2]
r(C-O)	1.269	1.304	1.292	1.296
r(C-Li)	2.204	2.237	2.212	2.212
r(Li-O)	1.916	1.946	1.925	1.925
$CS_3Li_3^+$				**PBEO-D3/def2-TZVP**[3]
r(C-S)	1.720	1.728	1.727	1.710
r(C-Li)	2.770	2.770	2.722	2.670
r(Li-S)	2.422	2.424	2.386	2.340

S2 RHF/6-31G(d) QUAO results on the CCSD(T)/aug-cc-pVTZ geometries

RHF/6-31G(d) QUAOs were obtained at the CCSD(T)/aug-cc-pVTZ geometries of all three molecules in the study. For conciseness, the aug-cc-pVTZ basis set is abbreviated as ACCT. Qualitatively, all RHF/6-31G(d)//CCSD(T)/ACCT QUAOs match those presented in Figures 3 to 5 in the main body of this work. Thus, only the quantitative results are presented here. Bond orders (BOs) and kinetic bond orders (KBOs) are presented in Table S2, S5 and S7, for CH_3Li, $CO_3Li_3^+$ and $CS_3Li_3^+$, respectively. Orbital occupations and s and p characters are presented in Tables S3, S6 and S8 for CH_3Li, $CO_3Li_3^+$ and $CS_3Li_3^+$, respectively. Atomic charges computed from QUAO populations for all three molecules are presented in Table S4.

Table S2 RHF/6-31G(d)//CCSD(T)/ACCT bonding interactions and characteristics in CH_3Li. Only interactions with BO > 0.15 and KBO < -1 kcal/mol are listed.

Bond	Orbital I	Orbital J	BO	KBO (kcal/mol)
CHσ	Chσ	Hcσ	0.97	-36.5
CLiσ	Cliσ	Licσ	0.75	-10.6

Table S3 RHF/6-31G(d)//CCSD(T)/ACCT orbital occupations and s- and p- character fractions in CH_3Li.

Orbital	Occupation	Fraction s	Fraction p
Chσ	1.08	0.19	0.81
Hcσ	0.89	1	0
Cliσ	1.64	0.27	0.73
Licσ	0.36	0.81	0.19
Li*nv*	0.02	0.09	0.91

Table S4 RHF/6-31G(d)//CCSD(T)/ACCT atomic partial charges computed from QUAO populations in CH_3Li, $CO_3Li_3^+$ and $CS_3Li_3^+$.

Molecule	CH3Li			CO3Li3+		
Atom	C	H	Li	C	O	Li
Charge	-0.89	+0.11	+0.57	+0.88	-0.68	+0.71
Molecule	CS3Li3+					
Atom	C	S	Li			
Charge	-0.12	-0.12	+0.49			

Table S5 RHF/6-31G(d)//CCSD(T)/ACCT bonding structures and characteristics in $CO_3Li_3^+$. Only interactions with BO larger than 0.15 and KBO lower than -1 kcal/mol are listed. The Li-C interactions are listed despite being below the set threshold.

Bond	Orbital I	Orbital J	BO	KBO
COσ	Coσ	Ocσ	0.93	-66.2
COπ	Coπ	Ocπ	0.54	-13.9
OOπ	Ocπ	Ocπ	0.23	-2.9
O*pl*-Coσ	O*pl*	Coσ	0.19	-2.9
O*pl*-Lioσ	O*pl*	Lioσ	0.43	-12.5
Ocπ-Lioπ	Ocπ	Lioπ	0.16	-1.5
Lioσ-Coσ	Lioσ	Coσ	0.05	-0.6
Lioπ-Coπ	Lioσ	Coπ	0.11	-0.3

Table S6 RHF/6-31G(d)//CCSD(T)/ACCT orbital occupations and s- and p- character fractions in $CO_3Li_3^+$.

Orbital	Occupation	Fraction s	Fraction p
Coσ	0.81	0.29	0.71
Coπ	0.68	0.00	1.00
Ocσ	1.23	0.26	0.74
Ocπ	1.74	0.00	1.00
O*pl*	1.85	0.34	0.66
Lioσ	0.12	0.29	0.71
Lioπ	0.04	0.00	1.00
Li*nv*	0.01	0.36	0.64

Table S7 RHF/6-31G(d)//CCSD(T)/ACCT bonding structures and characteristics in $CS_3Li_3^+$. Only interactions with BO larger than 0.15 and KBO lower than -1 kcal/mol are listed. The Li-C interactions are listed despite being below the set threshold.

Bond	Orbital I	Orbital J	BO	KBO (kcal/mol)
CSσ	Csσ	Scσ	0.96	-40.4
CSπ	Csπ	Scπ	0.54	-9.1
Ssπ	Scπ	Scπ	0.25	-1.8
S*pl*-Lisσ	S*pl*	Lisσ	0.59	-16.7
Scπ-Lisπ	Scπ	Lisπ	0.21	-1.9
Lisσ-Csσ	Lisσ	Csσ	0.04	-0.2
Lisπ-Csπ	Lisπ	Csπ	0.14	-0.2

The RHF/6-31G(d)//CCSD(T)/aug-cc-pVTZ results are essentially the same as the RHF/6-31G(d) ones. Thus, the RHF results are used in the main body of the paper.

S3 Empty orbitals on Li

The orbitals displayed in this section correspond to the RHF/6-31G(d) results reported in the main body of this work. The following orbitals do not participate in any bonding interaction, and thus have been excluded from the figures in the main text.

S3.1 CH_3Li

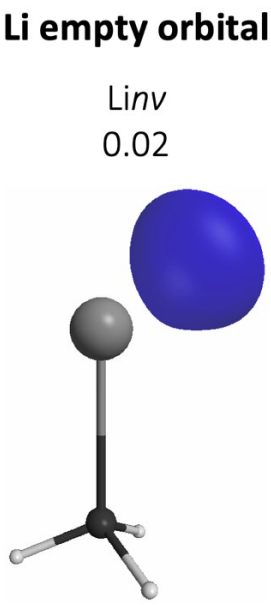

Figure S1 Empty orbital on Li in CH_3Li. The orbital population is shown below the orbital label.

S3.2 $CO_3Li_3^+$

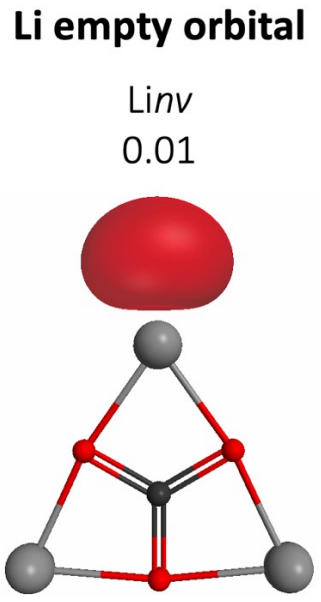

Figure S2 Empty orbital on Li in $CO_3Li_3^+$. The orbital population is shown below the orbital label.

S3.3 $CS_3Li_3^+$

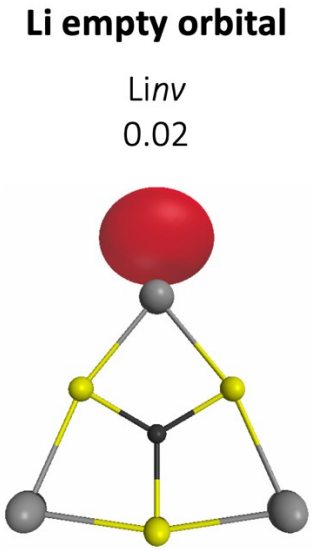

Figure S3 Empty orbital on Li in $CS_3Li_3^+$. The orbital population is shown below the orbital label.

S4 Comparison of the QUAOs of CH3Li obtained from RHF/6-31G(d) and full-valence (8,11)-CASSCF/6-311++G(d,p)//RHF/6-311++G(d,p) wave functions

The CASSCF calculation was ran using the RHF occupied molecular orbitals (MOs) + valence virtual orbitals (VVOs) as starting point. The active space was chosen to be the full valence space; 8 valence electrons in 11 valence orbitals (considering the three 2p orbitals on Li).

The QUAOs are shown in Figures 1, 2, and 3. Bond orders (BOs) are shown in bold above the plotted orbitals. Kinetic bond orders (KBOs) (in kcal/mol) are shown to the right of the respective BO. Bonding interactions, s- and p- characters and partial charges are summarized in Tables 1 to 3. It is evident that the results do not change significantly with respect to the RHF results when a CASSCF wave function is employed.

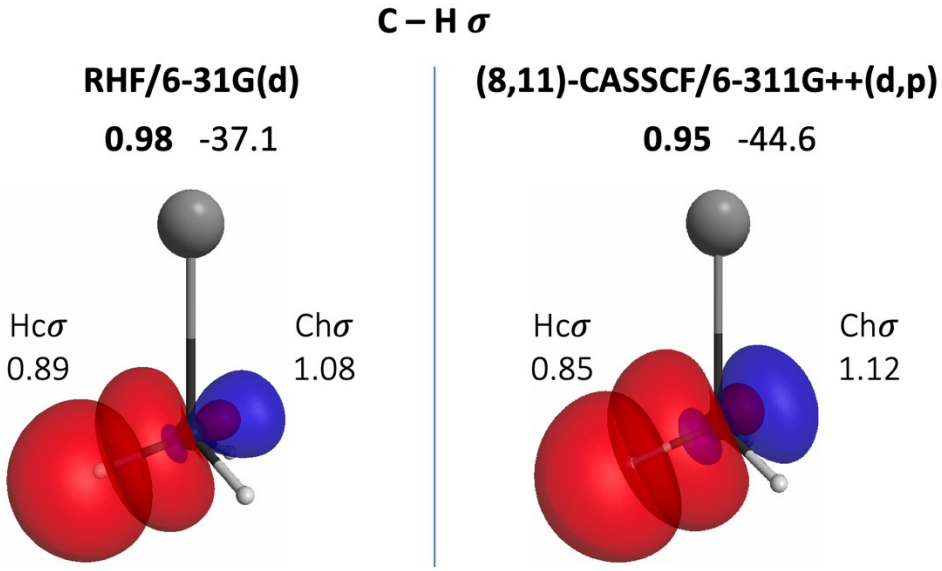

Figure 1 RHF vs CASSCF CHσ interaction in CH3Li. Bond orders are shown in bold above the displayed orbitals. Kinetic bond orders (in kcal/mol) are shown to the right of the corresponding bond order. The labels of the orbitals involved in the interactions are shown to the sides of the displayed orbitals, and orbital populations are shown below the corresponding orbital label.

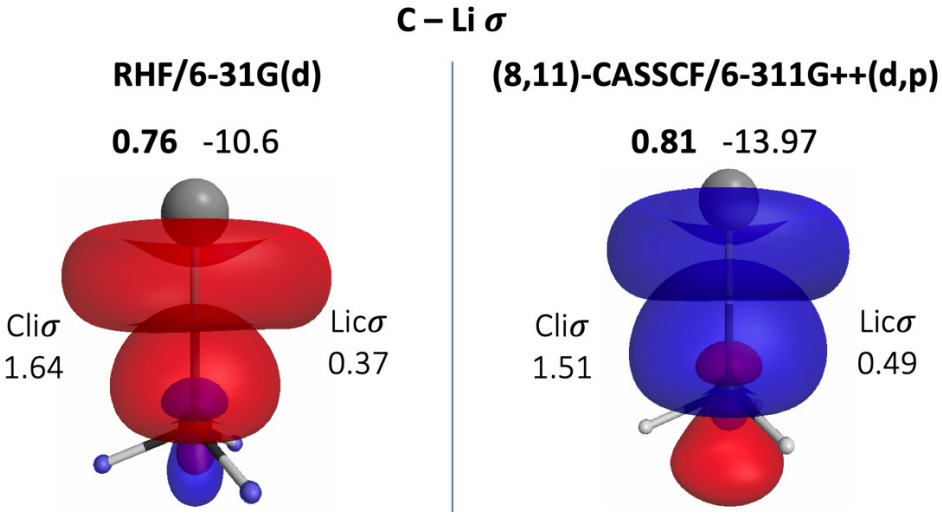

Figure 2 RHF vs CASSCF CLiσ interaction in CH3Li. Bond orders are shown in bold above the displayed orbitals. Kinetic bond orders (in kcal/mol) are shown to the right of the corresponding bond order. The labels of the orbitals involved in the interactions are shown to the sides of the displayed orbitals, and orbital populations are shown below the corresponding orbital label.

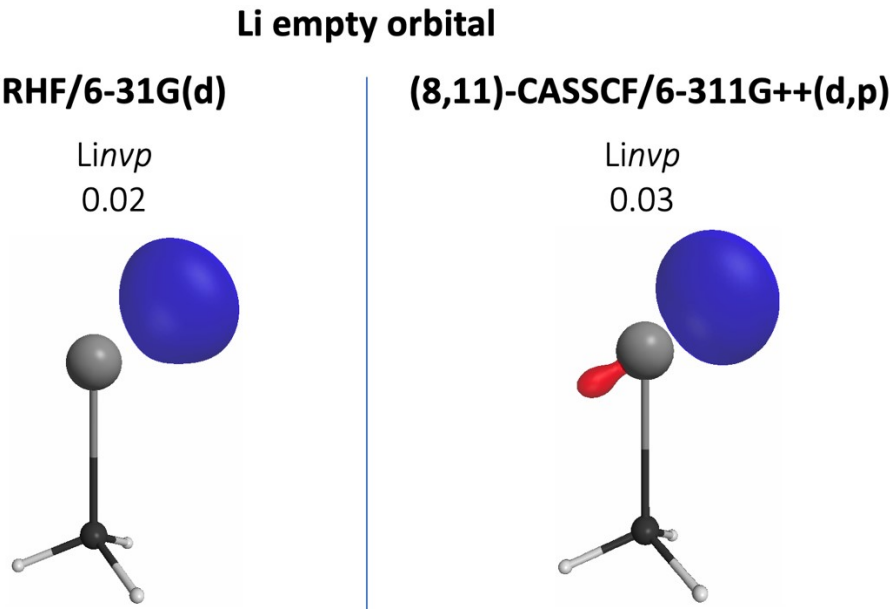

Figure 3 RHF vs CASSCF Li empty orbital in CH3Li. The labels of the orbitals are shown above the displayed orbitals, and orbital populations are shown below the corresponding orbital label.

Table 1 comparison of the bonding interactions and characteristics in CH_3Li. Only interactions with BO > 0.15 and KBO < -1 kcal/mol are listed.

Bond	Orbital I	Orbital J	RHF/6-31G(d)		(8,11)-CASSCF/6-311++G(d,p)	
			BO	KBO	BO	KBO
CHσ	Chσ	Hcσ	0.98	-37.1	0.95	-44.6
CLiσ	Cliσ	Licσ	0.76	-10.6	0.81	-14.0

Table 2 Comparison of the orbital occupations and s- and p- character fractions in CH_3Li.

Orbital	RHF/6-31G(d)			(8,11)-CASSCF/6-311++G(d,p)		
	Occupation	Fraction s	Fraction p	Occupation	Fraction s	Fraction p
Chσ	1.08	0.19	0.81	1.12	0.19	0.81
Hcσ	0.89	1	0	0.85	1.00	0.00
Cliσ	1.64	0.26	0.74	1.51	0.25	0.75
Licσ	0.37	0.81	0.19	0.49	0.86	0.14
Li*nv*	0.02	0.09	0.91	0.03	0.07	0.93

Table 3 Comparison of the atomic partial charges computed from QUAO populations in CH_3Li.

	RHF/6-31G(d)			(8,11)-CASSCF/6-311++G(d,p)		
Atom	C	H	Li	C	H	Li
Charge	-0.89	+0.11	+0.56	-0.88	+0.15	+0.43

References

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