Supporting Information for

Comment on "The oxidation state in low-valent beryllium and magnesium compounds" by M. Gimferrer, S. Danés, E. Vos, C. B. Yildiz, I. Corral, A. Jana, P. Salvador and D. M. Andrada, Chem. Sci., 2022, 13, 6583

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Computational details

The geometry optimizations followed by the frequency calculations for $Be(CAAC^{Dip})_2$ were done at the BP86-D3(BJ)/def2-SVP level[1] using Gaussian 16 program[2] (see Figure S1 for the minimum energy geometry). The energy decomposition analysis (EDA)[3] in combination with natural orbital for chemical valence (NOCV) theory[4] was performed at the BP86-D3(BJ)/TZ2P//BP86-D3(BJ)/def2-SVP level using ADF2018.105 program package[5] (see Table S1).

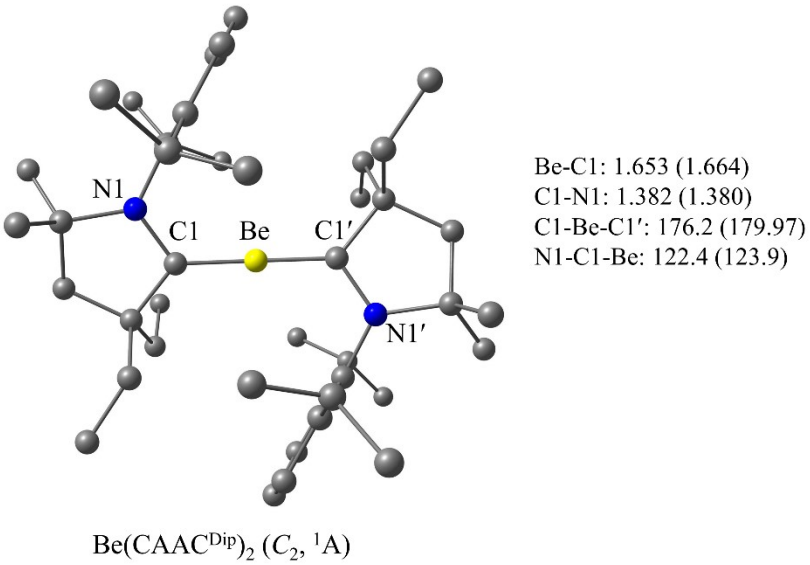

Figure S1. The minimum energy geometries of closed-shell singlet of $Be(CAAC^{Dip})_2$ complex at the BP86-D3(BJ)/def2-SVP level. The distances are in Å and angles are in degree. The experimental values are given in parentheses.

Table S1. EDA-NOCV results for $Be(CAAC^{Dip})_2$ complex at the BP86-D3(BJ)/TZ2P//BP86-D3(BJ)/def2-SVP level. Energies in kcal/mol.

Energy terms	Be^+ [D, $(2s)^0(2p_\perp)^1$] + $(CAAC^{Dip})_2^-$ [D]	Be [S, $(2s)^0(2p_\perp)^2$] + $(CAAC^{Dip})_2$ [S]	Be [T, $(2s)^1(2p_\perp)^1$] + $(CAAC^{Dip})_2$ [T]	Be [T, $(2p_\sigma)^1(2p_\perp)^1$] + $(CAAC^{Dip})_2$ [T]	Be^+ [D, $(2s)^1(2p)^0$] + $(CAAC^{Dip})_2^-$ [D]	Be^+ [D, $(2s)^0(2p_\sigma)^1$] + $(CAAC^{Dip})_2^-$ [D]	Be^{2+} [S, $(3s)^0(3p)^0$] + $(CAAC^{Dip})_2^{2-}$ [S]
ΔE_{int}	-423.3	-293.8	-252.2	-310.2	-407.9	-460.6	-834.6
ΔE_{Pauli}	93.3	155.9	177.8	317.9	121.4	229.9	105.3
ΔE_{disp}[a]	-11.8 (2.3%)	-11.8 (2.6%)	-11.8 (2.7%)	-11.8 (1.9%)	-11.8 (2.2%)	-11.8 (1.7%)	-11.8 (1.3%)
ΔE_{elstat}[a]	-268.6 (52.0%)	-199.2 (44.3%)	-177.9 (41.4%)	-347.4 (55.3%)	-239.0 (45.2%)	-395.0 (57.2%)	-515.4 (54.8%)
ΔE_{orb}[a]	-236.1 (45.7%)	-238.7 (53.1%)	-240.3 (55.9%)	-268.8 (42.8%)	-278.5 (52.6%)	-283.6 (41.1%)	-412.7 (43.9%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

Table S2. Cartesian coordinate and energy of $Be(CAAC^{Dip})_2$ complex at the BP86-D3(BJ)/def2-SVP level.

E = -1841.9563693 au

Be	0.000000000	0.000000000	0.187587000
C	0.717243000	1.488553000	0.133672000
C	2.195683000	1.885903000	0.289420000
C	2.162477000	3.442674000	0.331542000
H	2.214010000	3.796688000	1.380175000
H	3.021974000	3.896492000	-0.200876000
C	0.815775000	3.892008000	-0.282353000
C	0.985477000	4.260061000	-1.772277000
H	1.680391000	5.120216000	-1.863046000
H	0.022674000	4.556866000	-2.229055000
H	1.408129000	3.419373000	-2.355406000
C	0.199925000	5.096010000	0.443792000
H	0.173881000	4.944285000	1.538998000
H	-0.834881000	5.286487000	0.091055000
H	0.800354000	6.005910000	0.240379000
C	2.993843000	1.349124000	-0.932266000
H	2.820372000	0.255892000	-0.983784000
H	2.537966000	1.765775000	-1.854554000
C	4.503301000	1.610720000	-0.946206000
H	5.026912000	1.065168000	-0.135043000
H	4.747898000	2.689506000	-0.839169000
H	4.944648000	1.267967000	-1.905287000
C	2.811486000	1.295295000	1.588263000
H	2.815981000	0.188165000	1.481055000
H	3.879898000	1.599230000	1.643303000
C	2.115535000	1.681057000	2.893743000
H	1.047827000	1.387753000	2.868658000

H	2.161037000	2.772902000	3.089921000
H	2.588329000	1.176873000	3.760725000
C	-1.430654000	2.563867000	-0.150191000
C	-2.167521000	2.657374000	1.068322000
C	-3.568950000	2.511640000	1.025670000
H	-4.146682000	2.590417000	1.960196000
C	-4.236561000	2.272654000	-0.182353000
H	-5.332582000	2.165702000	-0.198143000
C	-3.502512000	2.161153000	-1.368472000
H	-4.029253000	1.957679000	-2.314113000
C	-2.095782000	2.282085000	-1.379381000
C	-1.362583000	2.118913000	-2.706691000
H	-0.280752000	2.206183000	-2.494455000
C	-1.583063000	0.730511000	-3.334477000
H	-1.198847000	-0.061983000	-2.663937000
H	-1.047334000	0.660249000	-4.303498000
H	-2.657970000	0.532555000	-3.530691000
C	-1.769515000	3.223918000	-3.703378000
H	-2.822138000	3.094452000	-4.032923000
H	-1.129711000	3.191549000	-4.610159000
H	-1.688945000	4.237048000	-3.259752000
C	-1.493150000	2.919604000	2.410877000
H	-0.415985000	3.073124000	2.207700000
C	-1.597285000	1.702064000	3.344185000
H	-2.654122000	1.455820000	3.581131000
H	-1.071441000	1.896857000	4.302139000
H	-1.134917000	0.815173000	2.869810000
C	-2.046424000	4.185528000	3.092880000
H	-2.001502000	5.067841000	2.423509000

H	-1.466171000	4.417700000	4.010574000
H	-3.105861000	4.052079000	3.397725000
C	-0.717243000	-1.488553000	0.133672000
C	-2.195683000	-1.885903000	0.289420000
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H	-1.408129000	-3.419373000	-2.355406000
C	-2.993843000	-1.349124000	-0.932266000
H	-2.820372000	-0.255892000	-0.983784000
H	-2.537966000	-1.765775000	-1.854554000
C	-4.503301000	-1.610720000	-0.946206000
H	-4.747898000	-2.689506000	-0.839169000
H	-4.944648000	-1.267967000	-1.905287000
H	-5.026912000	-1.065168000	-0.135043000
C	-2.811486000	-1.295295000	1.588263000
H	-2.815981000	-0.188165000	1.481055000
H	-3.879898000	-1.599230000	1.643303000
C	-2.115535000	-1.681057000	2.893743000
H	-2.161037000	-2.772902000	3.089921000
H	-2.588329000	-1.176873000	3.760725000

H	-1.047827000	-1.387753000	2.868658000
C	1.430654000	-2.563867000	-0.150191000
C	2.167521000	-2.657374000	1.068322000
C	3.568950000	-2.511640000	1.025670000
H	4.146682000	-2.590417000	1.960196000
C	4.236561000	-2.272654000	-0.182353000
H	5.332582000	-2.165702000	-0.198143000
C	3.502512000	-2.161153000	-1.368472000
H	4.029253000	-1.957679000	-2.314113000
C	2.095782000	-2.282085000	-1.379381000
C	1.362583000	-2.118913000	-2.706691000
H	0.280752000	-2.206183000	-2.494455000
C	1.583063000	-0.730511000	-3.334477000
H	1.198847000	0.061983000	-2.663937000
H	1.047334000	-0.660249000	-4.303498000
H	2.657970000	-0.532555000	-3.530691000
C	1.769515000	-3.223918000	-3.703378000
H	2.822138000	-3.094452000	-4.032923000
H	1.129711000	-3.191549000	-4.610159000
H	1.688945000	-4.237048000	-3.259752000
C	1.493150000	-2.919604000	2.410877000
H	0.415985000	-3.073124000	2.207700000
C	1.597285000	-1.702064000	3.344185000
H	2.654122000	-1.455820000	3.581131000
H	1.071441000	-1.896857000	4.302139000
H	1.134917000	-0.815173000	2.869810000
C	2.046424000	-4.185528000	3.092880000
H	2.001502000	-5.067841000	2.423509000
H	1.466171000	-4.417700000	4.010574000

H	3.105861000	-4.052079000	3.397725000
N	0.000000000	2.648752000	-0.090608000
N	-0.000000000	-2.648752000	-0.090608000

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