Supporting Information
for
The electronic structure of carbones revealed: Insights from Valence Bond theory

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Contents

Table S1. Cartesian coordinates (BP86/TZ2P) of **1** ($D_{\infty h}$) (atomic units).

Atom	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	2.411066
C	0.000000	0.000000	-2.411066
O	0.000000	0.000000	4.623402
O	0.000000	0.000000	-4.623402

Table S2. Cartesian coordinates (BP86/TZ2P) of **2** (atomic units).

Atom	X	Y	Z
C	0.000125	-1.285154	-0.000584
P	2.775656	0.132079	0.000059
P	-2.775145	0.132168	-0.000325
H	-3.593158	1.741838	2.045754
H	-3.601385	1.733140	-2.048253
H	-4.822169	-1.603769	0.010488
H	3.581338	1.764213	-2.031571
H	3.604844	1.714415	2.061641
H	4.822113	-1.602617	-0.030570

Table S3. Cartesian coordinates (BP86/TZ2P) of **3** (atomic units).

Atom	X	Y	Z
C	0.000312	-1.851573	0.003165
C	-2.297365	-0.710958	-0.056965
N	-3.156161	1.614062	0.945029
C	-5.786529	1.791728	0.831035
C	-6.632879	-0.284844	-0.408611
N	-4.536972	-1.747602	-1.008410
H	-2.057434	2.638222	2.125426
H	-6.820173	3.390468	1.577956
H	-8.533687	-0.808177	-0.948951
H	-4.552092	-3.520766	-1.720122
C	2.297883	-0.710781	0.060616
N	3.154012	1.615216	-0.941106
C	5.784473	1.793121	-0.833378
C	6.634018	-0.284316	0.402381
N	4.539544	-1.747185	1.007383
H	2.052045	2.640866	-2.117273
H	6.816029	3.392554	-1.581763
H	8.536200	-0.807829	0.937726
H	4.556681	-3.521035	1.717267

Table S4. Cartesian coordinates (BP86/TZ2P) of **4** (D_{2d}) (atomic units).

Atom	X	Y	Z
C	-2.468448	0.000663	0.000536
C	-0.000012	-0.002195	-0.002150
C	2.468345	0.000530	0.000366
H	-3.539393	-1.231091	1.261069
H	-3.540279	1.231700	-1.259438
H	3.534672	1.264001	1.233281
H	3.545688	-1.258602	-1.227426

Table S5. Cartesian coordinates (BP86/TZ2P) of **5** ($D_{\infty h}$) (atomic units).

Atom	X	Y	Z
Au	0.000000	0.000000	0.000000
C	0.000000	0.000000	3.688316
O	0.000000	0.000000	5.816373
C	0.000000	0.000000	-3.688316
O	0.000000	0.000000	-5.816373

Justification for the use of fragment restricted orbitals

To justify the use of the restrictions applied to the orbitals during the VBSCF calculations, we also performed VBSCF calculations without these restrictions for **1**. No symmetry restrictions were applied, which allows the formation of 'bent' bonds.[1,2] The disadvantage for the interpretation is that the ionic structures **E** are single excitations (Brillouin structures) with respect to the structures **A**, **C** and **D**, thus the effect of these structures is reflected in delocalisation of the orbitals to the other fragments (and in the weight of the structures).

The final VBSCF orbitals are displayed in Figure S1, together with the Mulliken population analysis to indicate the delocalisation of the orbitals. The orbitals remain predominantly localised on each fragment, and resemble the orbitals obtained using the restrictions to remain localised on certain fragments. The weights of the structures (excluding the weights of the ionic structures **E**) are shown in Table S6 (for convenience, the weights obtained with the strictly atomic orbitals are also shown). The GN weights for the delocal model for the neutral structures qualitatively agree with the restricted model; the ionic structures **E** are important in the restricted model, but they are 'absorbed' in the delocal model in the weights of **A**, **C**, and **E**, and in the orbitals in the delocal model, hampering the interpretation of the wavefunction using the delocal model. However, the agreement between the restricted and delocal model for the importance of the most relevant structures is such that the more easily interpretable restricted model is preferable to acquire insight into the bonding between the ligand and the central C atom.

Table S6. Gallup and Norbeck (GN) and Chirgwin-Coulson (CC) weights for the structures obtained using the delocal VBSCF model for **1** and **4**.

Model	$\mathbf{W_{covalent}}$ **(A)**	$\mathbf{W_{carbone}}$ **(B)**	$\mathbf{W_{carbene}}$ **(C)**	$\mathbf{W_{ionic}}$ **(D)**
1 (GN)	0.606	0.002	0.171	0.220
1 (CC)	0.738	0.037	0.554	-0.329
4 (GN)	0.805	0.010	0.171	0.015
4 (CC)	0.652	0.049	0.351	-0.052

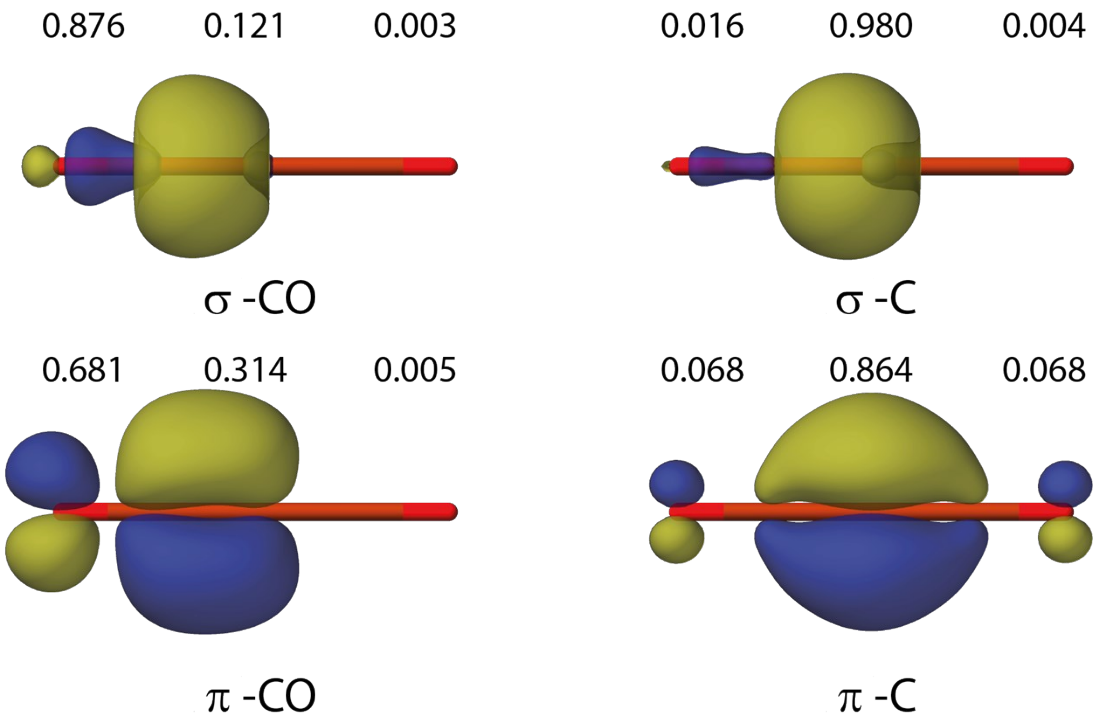

Figure S1. The VBSCF orbitals without the fragment restrictions. Indicated are the Mulliken populations per fragment (OC/C/CO).

Table S7. Total VB and CASSCF energies for compounds **1-5** (in au).

	VB-neutral	**VB-ionic**	**VB-delocal**	**CASSCF**
1	-263.282331	-263.308578	-263.385981	-263.435732
2	-722.458950	-722.609289	--	-722.761135
3	-487.424338	-487.447427	--	-487.539215
4	-115.856569	-115.859852	-115.964470	-115.983667
5	-359.983494	-360.060457	--	-360.134695

Table S8. EDA analysis for compounds **1-5** (all in kcal/mol).

Open shell fragments					
	1	**2**	**3**	**4**	**5**
$\Delta E_{\mathrm{Pauli}}$	363.63	331.61	443.16	449.53	170.25
$\Delta E_{\mathrm{electrostatic}}$	-304.66	-291.39	-389.50	-376.61	-124.38
ΔE_{orb}	-609.91	-508.84	-531.65	-514.27	-609.71
$\Delta E_{\mathrm{bonding}}$	-550.95	-468.62	-477.99	-441.34	-563.83
		Closed shell fragments			
$\Delta E_{\mathrm{Pauli}}$	181.02	271.66	360.96	256.29	127.63
$\Delta E_{\mathrm{electrostatic}}$	-181.56	-269.75	-405.59	-350.97	-92.30
ΔE_{orb}	-603.80	-537.26	-566.94	-697.34	-108.70
$\Delta E_{\mathrm{bonding}}$	-604.35	-535.36	-611.56	-792.02	-73.37

Table S9. The combined CC weights of the different types of valence bond structures in the two sets of calculations: first, the weights are listed when only the neutral structures are considered, second, the weights of the structures when the ionic structures are included as well (indicated with an asterisk).

Compound	**$W_{covalent}$ (A)**	**$W_{carbone}$ (B)**	**$W_{carbene}$ (C)**	**W_{ionic} (D)**	**W_{ionic} (E)**
1	0.462	0.056	0.482		
1*	0.310	0.066	0.249	0.017	0.358
2	--	0.261	0.739		
2*	--	0.107	0.145	0.235	0.512
3	0.590	0.053	0.358		
3*	0.382	0.061	0.222	0.053	0.281
4	0.756	0.017	0.227		
4*	0.696	0.018	0.180	0.005	0.100
5	0.014	0.675	0.311		
5*	0.006	0.348	0.130	0.378	0.138

Table S10. Orbital overlaps between the σ and π orbitals.

Compound	**$S_{\sigma\text{-}\sigma}$**	**$S_{\pi\text{-}\pi}$**
1	0.777	0.349
2	0.672	0.399
3	0.746	0.284
4	0.767	0.385
5	0.655	0.164

References

[1] Palke, W.E., Double Bonds Are Bent Equivalent Hybrid (Banana) Bonds, *J. Am. Chem. Soc.* **1986**, *108*, 6543-6544.

[2] Karadakov, P.B.; Gerratt, J.; Cooper, D.L.; Raimondi, M., Bent versus σ-π bonds in ethene and ethyne: the spin-coupled point of view, *J. Am. Chem. Soc.* **1993**, *115*, 6863-6869.