What are the highest bond indices for main group and transition group elements?

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A bond index (BI) approximately measures the totals of the bond orders at any given atom in a molecule. Here I ponder what the maximum values might be for elements with filled valence shells.

Following Lewis in 1916[cite]10.1021/ja02261a002[/cite] who proposed that the full valence shell for main group elements should be 2 (for the first two elements) and 8 (the "*octet*"), Bohr (1922[cite]10.1007/BF01326955[/cite]), Langmuir (1919-1921[cite]10.1126/science.54.1386.59[/cite]) and Bury (1921[cite]10.1021/ja01440a023[/cite]) extended this rule to include 18 (the transition series) and 32 (the lanthanides and actinides). If we assume no contributions from higher Rydberg shells (thus 3s, 3p, 3d for carbon etc) and an electron pair model for orbital population (which amounts to the single-determinantal model), then the maximum bond index for hydrogen (and helium) would be 1, it would be 4 for main group elements, and then what?

For the special case of hydrogen, I have previously identified (for a hypothetical species) a bond index of 1.33, due mostly to a high Rydberg occupancy of 1.19e. The more normal BI is <1.0, as noted for this hexacoordinated hydride system. My current estimate for the maximum bond index for main group elements is <4.5. Thus for SF_6, it has the value of ~4.33 and that includes a modest occupancy of Rydberg shells of 0.36e = 0.18 BI. Exclude these and it is close to 4.

Move on from group 16 to group 6 and you get compounds such as $Me_4CrCrMe_4^{4-}$ or $ReMe_8^{2-}$ where the metal bond indices are ~6.5.‡ Compounds such as $Cr(Me)_6$ (BI = 5.6)** ** and W(Me)~6 ~(BI = 6.1) are rather lower. This is a long way from 18/2 = 9. The lanthanides and actinides[cite]10.1002/9781118688304.ch15[/cite] are unlikely to reveal many large BIs (32/2= 16 maximum value) since they are often ionic and the wavefunctions may be too complex to allow a simple index such as a BI to be safely computed.

So if we are hunting for record BIs, the transition elements are the place to hunt. Can a BI of 6.5 be beaten? Can it even approach 9, its maximum value? Does anyone know of candidate molecules?

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‡FAIR Data doi: 10.14469/hpc/3352.

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