Organometallic Aromaticity

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Summary: Absolute hardness (HOMO–LUMO gap) has been used as a theoretical parameter to recognize aromaticity in organometallic compounds.

Aromaticity has been traditionally associated in organic molecules with electronic delocalization measured indirectly through Hückel's rule.[1] Recently, however, more systematic approaches have been devised to recognize the presence of aromaticity in different compounds: resonance energy for π electrons,[2,3] graphics theory,[4,5] back-bonding electron donation in metallocycles,[6] and molecular hardness.[7,8] Here we use the molecular hardness characterization of aromaticity, previously used in organic molecules, to investigate this property in organometallic compounds.

The absolute hardness[9] of a chemical species τ has been defined as the difference in energy between the HOMO and LUMO:

$$\tau = (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})/2$$

Absolute hardness is a measure of stability and can be used in accordance with the HSAB principle.[10] In this sense, the HSAB principle can be selective for reactivity among species when the chemical potentials (electronegativity) for the species are more or less the same.[11,12] Recently, Zhou and Parr[8] showed that it is directly related with aromaticity in organic compounds. Hence, with the knowledge of these energy levels, independent of the level of calculation, the aromaticity of different compounds can be evaluated. Table I shows absolute hardness for some metallacycles with four (W(C-t-BuCMeCMe)Cl_3, **1**),[13] five ($Cp_2Ti(C_4H_4)$, **2**;[6] [μ-ETOC=CHC(OC(O)Me)=](μ-^{t}BuS)-$Fe_2(CO)_6$, **3**;[14] $CpCo(PH_3)(C_4H_4)$, **4**),[6] and six (IrCHC(Me)-CHC(Me)CH)$(PEt_3)_3$, **5**)[15] atoms in the ring. Also listed are hardness values for group 15 heterobenzenes[16] (phosphabenzene, **6**; arsabenzene, **7**; stibabenzene, **8**) and heterocyclopentadienes (cyclosilapentadienide, **9**;[17] thiophene, **10**; selenophene, **11**). All the molecules have a planar ring with delocalized and multiple-bond character,[18] and except for one (**3** with two metallic atoms), the ring contains only carbon atoms and one heteroatom. Benzene, Cp^-, and cyclobutadiene calculations were done for comparison purposes.[19]

Table I. Absolute Hardness Values for Organometallic Molecules

compd	orbital energy (eV)		abs hardness (eV)
	LUMO	HOMO	
cyclopentadienide	−6.82	−11.96	2.56
benzene	−8.27	−12.81	2.27
cyclosilapentadienide	−6.42	−10.76	2.18
thiophene	−7.86	−12.20	2.17
selenophene	−8.15	−12.28	2.06
phosphabenzene	−9.43	−12.75	1.66
W (**1**)	−8.25	−11.40	1.57
arsabenzene	−9.28	−12.41	1.56
Co (**4**)	−9.40	−11.90	1.25
stibabenzene	−9.62	−11.95	1.16
Ti (**2**)	−10.10	−12.09	1.00
Fe (**3**)	−9.60	−11.41	0.91
Ir (**5**)	−9.66	−10.86	0.60
cyclobutadiene	−10.70	−10.70	0.00

Organometallic compounds with large values of hardness are expected to have high stability and hence to be aromatic. From Table I the dividing line between aromatic and nonaromatic species corresponds arbitrarily to 1.28 eV (half the value between cyclopentadienide (2.56 eV) and cyclobutadiene (0.00 eV)). Hence, from this parameter the species with lower values, in spite of the presence of delocalized bonds, cannot be considered as aromatic molecules.

The results agree with the known fact that aromaticity decreases in a family with the size of the heteroatom in all the rings:[16] Cp^- > cyclosilapentadienide, thiophene > selenophene, phosphabenzene > arsabenzene > stibabenzene. Also, there is qualitative agreement with the orbital criteria for maximizing delocalization.[6] For example, π conjugation can be observed around the entire ring, in accordance with metal back-bonding electron

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(18) Planarity is not necessarily a condition for aromaticity, as buckminsterfullerene indicates.[5]
(19) The experimental hardness of benzene is 5.3 eV (Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734). The values obtained here are relative and are for comparison purposes only, because experimental data for all the compounds are not available.

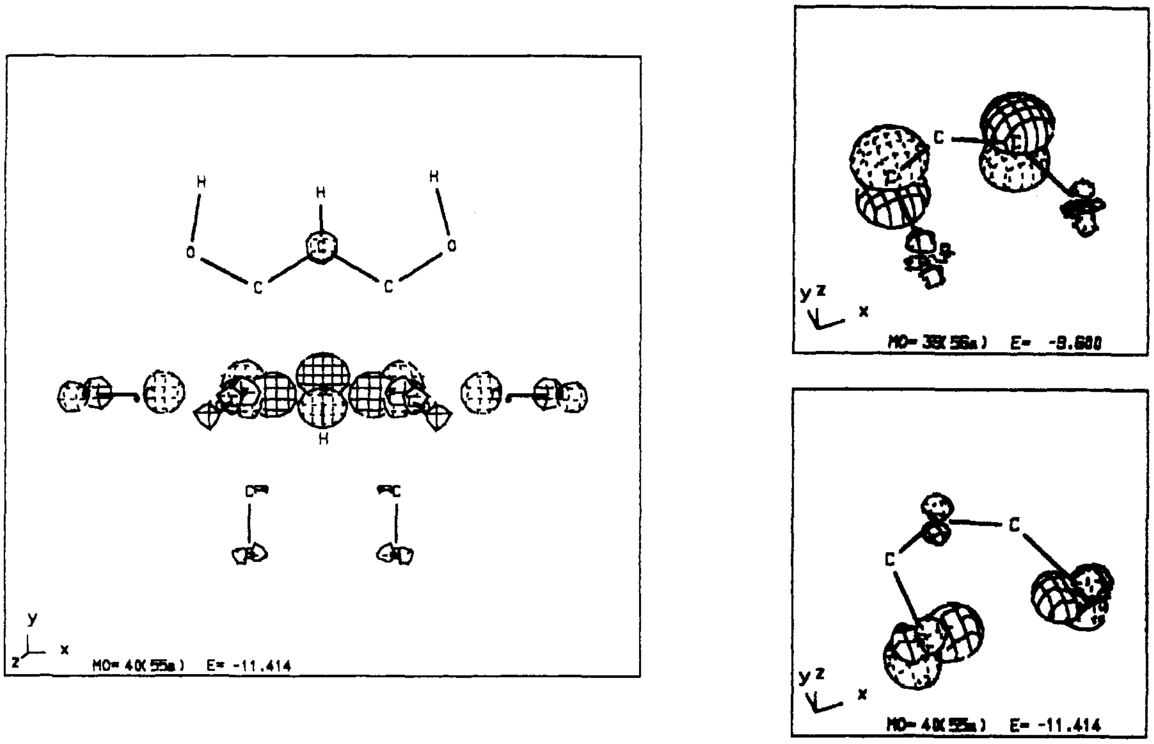
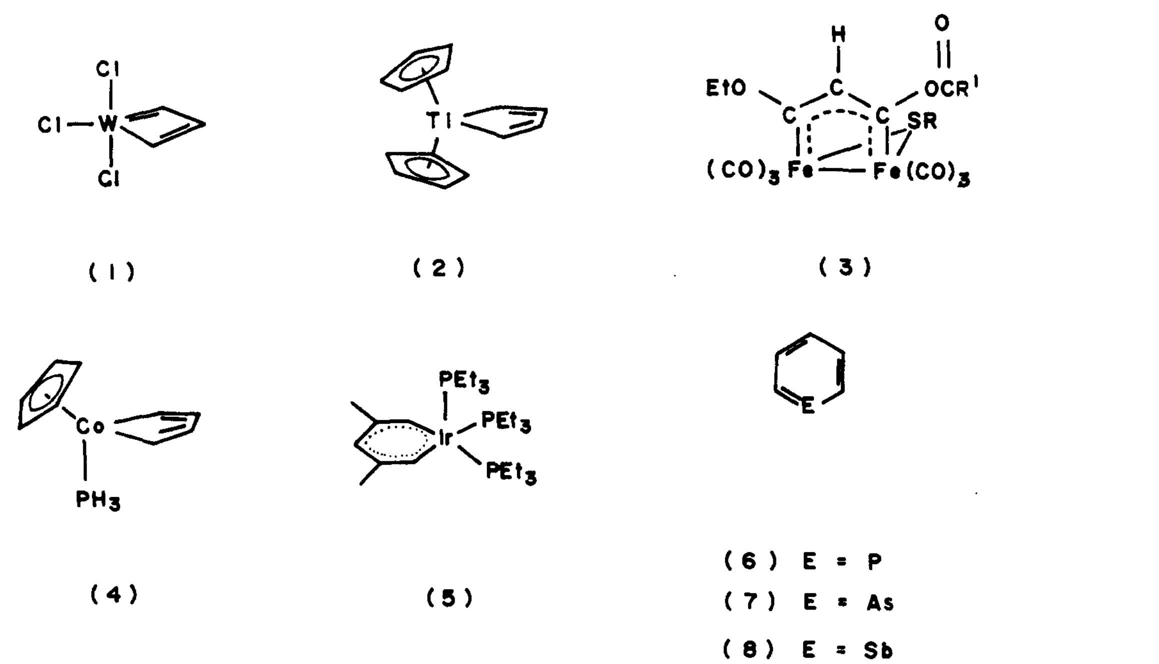


Figure 1. CACAO[29] drawings for (a, left) the complete HOMO, (b, top right) the partial LUMO, and (c, bottom right) partial HOMO of [μ-ETOC=CHC(OC(O)Me)=](μ-^{t}BuS)$Fe_2(CO)_6$ (3).

Chart I



donation to a empty π^* carbon fragment orbital in 1 but not in 3, where the HOMO is mainly a metal–metal bond orbital (Figure 1). An unexpected result, however, is that Cp^- is more aromatic than benzene.

From this work[20] the concept of absolute hardness (HOMO–LUMO gap) emerges as a simple parameter to recognize theoretically the presence of aromaticity in organometallic compounds.

(20) One of the reviewers pointed out that, for simple hydrocarbons such as the ones studied by Zhou and Parr, the HOMO–LUMO gap is a direct indication of reactivity but that for organometallic molecules where the chemical potential can be different, the HOMO–LUMO gap may still do the job but the theoretical basis is less secure.

Appendix

All calculations were performed by using the extended Hückel method[21] with the weighted H_{ii} formula.[22] The bond lengths reported by Hoffmann,[6] Schrock,[13] Seyferth,[14] Bleeke,[15] Ashe,[16] and Damewood[17] were used. Organic distances are well-known.[23] In 1, 3, and 5 organic

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Table II. Extended Hückel Parameters

atom	orbital	H_{ii} (eV)	ζ_1	ζ_2	C_1[a]	C_2[a]	atom	orbital	H_{ii} (eV)	ζ_1	ζ_2	C_1[a]	C_2[a]
Si	3s	−17.30	1.383				Co	4s	−9.21	2.000			
	3p	−9.20	1.383					4p	−5.29	2.000			
P	3s	−18.60	1.750					3d	−13.18	5.550	2.10	0.5680	0.6060
	3p	−14.00	1.300				Fe	4s	−9.17	1.900			
Cl	3s	−30.00	2.033					4p	−5.37	1.900			
	3p	−15.00	2.033					3d	−12.70	5.350	1.80	0.5366	0.6678
As	4s	−16.22	2.230				W	6s	−8.26	2.341			
	4p	−12.16	1.890					6p	−5.17	2.310			
Sb	5s	−18.80	2.323					5d	−10.37	4.980	2.068	0.6940	0.5631
	5p	−11.70	1.999				Ir	6s	−11.36	2.500			
Ti	4s	−8.97	1.075					6p	−4.50	2.200			
	4p	−5.44	0.675					5d	−12.17	5.800	2.557	0.63506	0.5556
	3d	−10.81	4.550	1.40	0.4206	0.7839							

[a] Contraction coefficient used in the double-ζ expansion.

groups were replaced by H to facilitate calculations. The values for the H_{ii} and orbital exponents are listed in Table II. The parameters of C, N, O, and H are the standard ones. The parameters of P,[24] Cl,[25] As,[26] Sb,[27] Ti,[6] Co,[6] Fe,[24] W,[25] and Ir[28] have been used in previous calculations.

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