

## COMMUNICATION

## Three-centre electron sharing indices (3c-ESI) as a tool to differentiate among (an)agostic interactions and hydrogen bonds in transition metal complexes

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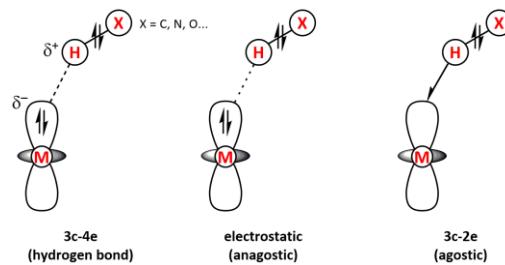
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The agostic bond plays an important role in chemistry, not only in transition metal chemistry but also in main group chemistry. In some complexes with  $M\cdots H\cdots X$  ( $X = C, N$ ) interactions, differentiation between agostic, anagostic, and hydrogen bond is challenging. Here we propose the use of three-centre electron sharing indices to classify  $M\cdots H\cdots X$  ( $X = C, N$ ) interactions.

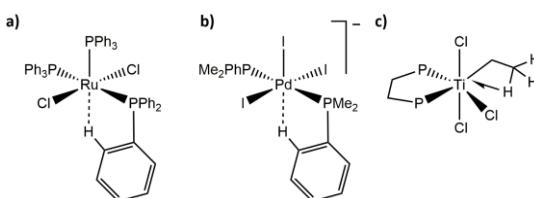
In 1965, La Placa and Ibers, and Bailey and coworkers synthesized the first transition metal complexes with a  $M\cdots H\cdots C$  interaction (Figure 1a-b, respectively).<sup>1, 2</sup> Lately, Prout *et al.*,<sup>3</sup> prepared and characterized a titanium compound presenting an unequivocal evidence of an attractive force between C-H and the metal centre (Figure 1c). However, it was not until 1983 that the term *agostic* was coined by Brookhart and coworkers.<sup>4, 5</sup> This term is used to explain the ability of the carbon-hydrogen bond –considered inert– to act as a ligand to a transition metal centre by forming a three-centre two-electron bond (3c-2e). The bond generally occurs between the  $\sigma_{C-H}$  electron pair and an empty d orbital of the metal and, as a result, the C-H bond is activated. In 1987, Brammer and coworkers<sup>6-9</sup> noticed that in some cases, such as  $(NPr^{\text{t}})_2[\text{PtCl}_4]\cdot[\text{PtCl}_2(\text{NH}_2\text{Me})_2]$  (FAZZAH10 complex in Table 1), the short intermolecular Pt-H interaction is better described as a 3c-4e interaction, *i.e.*, a hydrogen bond (H-bond). In this case, the metal brings an occupied d orbital. Three years later, Lippard *et al.*, considered the Pt-H interactions in  $cis$ - $[\text{Pt}(\text{NH}_3)_2(\text{N9-9-AA})\text{Cl}](\text{NO}_3)$  (KEHCEF) and  $cis$ - $[\text{Pt}(\text{NH}_3)_2(\text{N9-9-AA})_2](\text{NO}_3)_2$ , which did not carry out a reduction in the  $J_{\text{C}-\text{H}}$  values, as *anagostic*, a term that refers to the interactions that are neither agostic nor H-bond.<sup>10</sup> The anagostic bond is largely of electrostatic nature, with no electron sharing (see Scheme 1).

As a way to activate C-H or C-C bonds, agostic bonds play an



**Scheme 1** Orbital interactions for the different three-centre interactions.

important role in catalysis. However, currently there is no method to rigorously differentiate among agostic, anagostic, and H-bond  $M\cdots H\cdots X$  ( $X = C, N$ ) interactions. Many different methodologies such spectroscopic and diffraction techniques, structural as well as computational analysis have been used to discern which of these types of interactions occurs in a given transition metal complex.<sup>11, 12</sup> Agostic (anagostic) bonds are characterized by  $M\cdots H$  bond distances in the range 1.8–2.3 Å (2.3–2.9 Å) and  $\angle M\cdots H\cdots C$  angles in between 90–140° (110–170°).<sup>12, 13</sup> However, characterization based on simple geometrical rules presents limitations and, in some cases, may lead to a misassignment of the interaction type. On one hand, the difficulty of locating in X-Ray diffraction spectra a hydrogen



**Fig. 1** Some illustrative examples of (an)agostic interactions.

atom in the presence of a transition metal and the cost and long collection times required in neutron diffraction for large crystals, make the use of these techniques cumbersome.<sup>11, 14</sup> On the other hand, due to the weak or extremely weak interaction energy of these (an)agostic interactions or H-bonds, the use of  ${}^1\text{H}$  NMR spectroscopy (H atoms involved in agostic bonds

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appear upfield)<sup>13</sup> does not always help to discern the interaction type.<sup>9, 15, 16</sup> From a computational point of view, the most popular approaches to distinguish among these three-centre interactions are: *natural bonding orbitals* (NBO),<sup>17, 18</sup> the *electron localization function* (ELF),<sup>19–22</sup> and the topological analysis of the electron density within Bader's theory, the Quantum Theory of Atoms in Molecules (QTAIM).<sup>23–25</sup> Again, caution should be taken when using these approaches, which could lead to misidentification.<sup>11, 12, 26–29</sup> Despite the relevance of these kind of interactions in organometallic chemistry,<sup>4, 12, 30–32</sup> there is not yet a rigorous methodology capable to unambiguously identify them.

Some authors have shown that the sign of three-centre electron sharing indices (3c-ESI) computed at the HF or DFT levels allows to differentiate between 3c-2e and 3c-4e bonding: 3c-2e bonds yield positive values of the 3c-ESI, whereas 3c-4e bonds yield negative values. The differentiation of 3c-2e and 3c-4e interactions by the sign of 3c-ESI is valid only for single-determinant wavefunctions.<sup>33–36</sup> Finally, the absence of 3c-bonding is reflected by low values of the 3c-ESI<sup>37</sup> (see SI for more details).

With this in mind, herein, we propose the use of the computationally inexpensive 3c-ESI ( $\delta^{SD}(A_1, A_2, A_3)$ )<sup>34, 36, 38</sup> obtained from DFT approaches as a tool to discern among agostic, anagostic, and H-bond M···H–X interactions. At the DFT or HF level,  $\delta^{SD}(A_1, A_2, A_3)$  is computed from Eq. 1:

$$\delta^{SD}(A_1, A_2, A_3) = 4 \sum_{ijk} n_i n_j n_k S_{ij}(A_1) S_{jk}(A_2) S_{ki}(A_3), \quad (1)$$

where  $n_i$  is the occupancy of the corresponding molecular spin-orbital (with  $n_i = 0$  or 1 for HF/DFT calculations) and  $S_{ij}(A_1)$  is the overlap between spin-orbitals  $i$  and  $j$  in the basin of atom  $A_1$ . As said before, the sign of  $\delta^{SD}$  index depends on the number of electrons involved in the bonding. Thus, it is possible to distinguish between 3c-2e bonds, which have  $\delta^{SD} > 0$  from 3c-4e bonds with  $\delta^{SD} < 0$ . We also expect that for anagostic interactions this index will be close to zero. To check our hypothesis, we have computed 40 different organometallic systems possessing (an)agostic interactions or hydrogen bonds in their structures (see Supporting Information for structural and computational details).

In Table 1, we collect the main geometrical parameters used to discern among these types of interactions as well as the values obtained by applying the 3c-ESI computed at the BP86-D3BJ/6-31+G(d,p)~SDD+f(M)~SDD(I) level of theory with the ESI-3D program.<sup>39, 40</sup> In black, we represent the complexes that were correctly assigned whereas, in red, are those that initially were either misassigned or unidentified. In general, there is a good correspondence with previous assignments and current assignments based on 3c-ESI.

In our opinion, three regions can be identified in Figure 2. The first one corresponds to the 3c-4e bonds (i.e., H-bonds) and it is depicted by 3c-ESI values lower than 0.005. The second one corresponds to interactions considered anagostic, which have no 3c-bond. This section is delimited by 3c-ESI values between 0.005 and 0.040. Finally, all the complexes with indices higher than 0.040 can be considered 3c-2e bonds (i.e., agostic interactions). 3c-DIs calculated with different methods are quite similar among them (see Table S2).

**Table 1** The different transition metal complexes studied. Red compounds correspond to complexes with misassigned or ambiguous (an)agostic or H-bond interactions and the blue one to a 3c-3e interaction. Distances are given in Å and angles in degrees. Calculations were performed at the BP86-D3BJ/6-31+G(d,p)~SDD+f(M)~SDD(I) level.

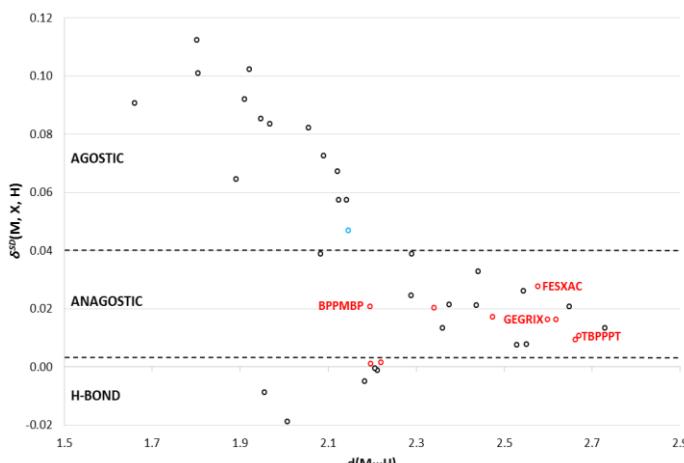
Ref.	CCDC - Metal	M···H	M···X	C–H	∠MXH	3c-ESI
41	CIPKOB – Ni(0)	2.006	3.114	1.108	179.73	-0.0186
42	ZIYJID – Au(I)	1.954	3.031	1.080	174.67	-0.0086
9	FAZZAH10 – Pt(II)	2.182	3.215	1.063	163.16	-0.0048
43	KEKZAB – Pt(II)	2.211	3.326	1.126	170.26	-0.0009
44	COCMOW – Pt(II)	2.205	3.210	1.042	161.51	-0.0002
44	COCMOW <sup>a</sup> – Pd(II)	2.196	3.197	1.038	161.50	0.0012
44	COCMOW <sup>a</sup> – Ni(II)	2.219	3.181	1.032	154.50	0.0017
45	WOCNIM – Ni(II)	2.527	3.266	1.104	123.33	0.0079
45	WOCMUX – Ni(II)	2.549	3.286	1.106	123.03	0.0080
46	TBPPPD – Pd(0)	2.660	3.389	1.099	123.19	0.0096
46	TBPPPT – Pt(0)	2.669	3.403	1.099	123.58	0.0109
1	RUCCLTP – Ru(II)	2.728	3.402	1.096	119.34	0.0135
47	JODFAM – Ni(II)	2.359	3.381	1.111	152.13	0.0137
29	GEGRIX <sup>b</sup> – Ag(III)	2.597	3.135	1.088	109.62	0.0165
48	BPPMBP <sup>a</sup> – Pd(II)	2.616	3.333	1.097	122.28	0.0166
49	YABXOS – Au(I)	2.472	3.376	1.107	137.9	0.0175
49	YACDIT – Au(I)	2.339	3.243	1.112	137.11	0.0206
48	BPPMBP <sup>a</sup> – Pd(II)	2.194	3.140	1.099	142.68	0.0209
50	FEKMOX – Pt(II)	2.646	2.776	1.101	84.98	0.0211
10	KEHCEF – Pt(II)	2.436	3.229	1.098	127.98	0.0215
51	VIGVIT <sup>a</sup> – Pt(0)	2.374	3.347	1.117	144.52	0.0217
51	VIGVIT <sup>a</sup> – Pt(0)	2.287	3.259	1.119	143.91	0.0248
3	BIXFUJ <sup>a</sup> – Hf(0)	2.543	2.818	1.121	92.18	0.0262
50	FESXAC – Pt(II)	2.575	2.751	1.114	86.95	0.0279
3	BIXFUJ <sup>a</sup> – Zr(0)	2.439	2.749	1.126	93.57	0.0331
3	BIXFUJ – Ti (0)	2.082	2.500	1.135	97.62	0.0390
52	KEHLAK <sup>a</sup> – Zr(IV)	2.289	2.616	1.126	93.68	0.0390
53	Cu(II)H33m <sup>c</sup>	2.144	2.154	1.110	75.52	0.0470
52	KEHLAK <sup>a</sup> – Zr(IV)	2.123	2.537	1.139	97.49	0.0575
52	KEHLAK <sup>a</sup> – Zr(IV)	2.140	2.531	1.143	96.08	0.0575
54	WODFOK – Ru(II)	1.889	2.465	1.142	106.20	0.0648
55	BIMHAH – Pt(II)	2.120	2.814	1.132	116.50	0.0673
56	IMOZIU – Pt(IV)	2.089	2.739	1.125	113.52	0.0729
57	PCAU(III)	2.054	2.682	1.152	110.33	0.0825
56	XAMPUY – Pt(II)	1.966	2.578	1.138	109.36	0.0838
58	MIJDOB – Mo(III)	1.946	2.463	1.165	101.73	0.0856
59	Cp*Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	1.659	2.150	1.205	95.98	0.0909
60	MULSAO – Pd(II)	1.909	2.580	1.157	112.26	0.0923
59	Cp*Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	1.803	2.313	1.210	98.36	0.1012
16	KILKOF – Pt(II)	1.919	2.394	1.195	97.80	0.1026
59	Cp*Ir(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	1.800	2.322	1.237	98.02	0.1125

<sup>a</sup> System with two or more different isomeric X-Ray structures.

<sup>b</sup> Non-optimized system. Geometrical values obtained from the X-Ray.

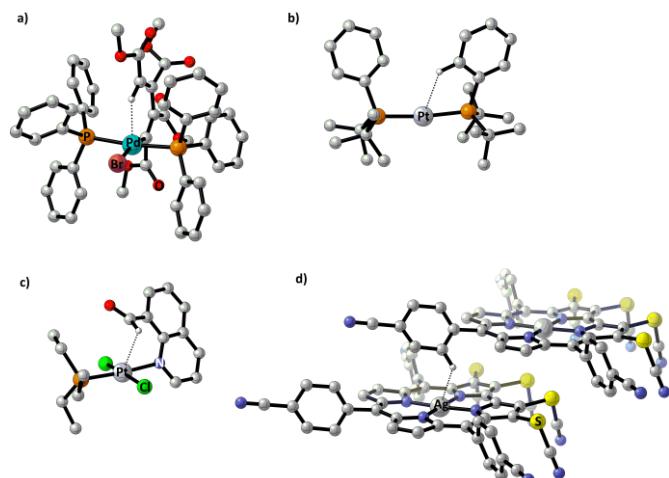
<sup>c</sup> Doublet system with a three-centre three-electrons interaction.

The suggested thresholds agree with those proposed by Chauvin et al. for the Rh(I)-η<sup>1</sup>-C interactions in P(CH)P pincer complexes.<sup>21</sup> These limits do not represent a hard boundary and the transition from one type of bond to another has to be considered somewhat fuzzy.



**Fig. 2** Representation of the three-centre electron sharing indices ( $\delta^{3D}(M,X,H)$ ) with respect to the M···H distance in Å. Blue dot refers to a Cu(II) radical system with a three-centre three-electrons interaction. Red dots refer to those complexes ambiguously characterized.

As can be seen in Figure 2, for the systems studied, agostic interactions have M···H distances in the range 1.7–2.1 Å, anagostic interactions in between 2.1–2.8 Å, and H-bonds in the range 1.9–2.2 Å. However, the geometric criterion is not enough to distinguish among the three possible interactions. Similarly, QTAIM criteria are not always applicable because many complexes do not present M-H bond critical points (see Table S1). The majority of misassigned complexes (initially described as agostic or hydrogen bonds) belong to the anagostic region. For example, in 1972, Maitlis et al. synthesized the compound **BPPMBP** (Scheme 2a) observing a distance between the δ-butadienyl hydrogen and the metal lower than the expected by the sum of their van der Waals radii. This result, quoting the authors: “*suggests that some interaction (hydrogen bonding?) is occurring*”.<sup>48</sup> However, the computed value of the 3c-ESI clearly assigns this interaction as anagostic ( $\delta^{3D}(Pd,H,C) = 0.0209$ ). Another example is found in complex **TBPPPT** (Scheme 2b), where the authors conclude that the short Pt(0)···H distance indicates that the metal is involved in an attractive interaction<sup>46</sup> with the H atom, without classifying it. Our methodology suggests the anagostic nature of the interaction with a 3c-ESI value of 0.0109. In the complex **FESXAC** (Scheme 2c), the interaction between the metal and the hydrogen was correctly described as “*different from that formulated as agostic covalent bond*”. The computed 3c-ESI of 0.0279 shows that this interaction belongs to the anagostic region. Recently, Sahu and coworkers observed an intermolecular interaction between two tetra(thiocyanato)corrolato-Ag(III) molecules (Scheme 2d, **GEGRIX**) which could not be correctly assigned due to the strong discrepancies obtained from the different computational techniques used.<sup>29</sup> According to the authors, this behaviour denoted the dual character of the interaction (*i.e.*, agostic and hydrogen bond). However, due to the nature of these interactions (see Scheme 1), it is not possible to have both of them in the same M···H-C moiety. Our 3c-ESI of 0.0165 indicates that the interaction between the two Ag(III) moieties belongs to the anagostic region.



**Scheme 2** Representative examples with misassigned or non-assigned three-centre interactions.

To sum up, we present a computational tool based on 3c-ESIs capable to distinguish among the different three-centre interactions, *i.e.*, agostic, anagostic, and H-bonds. We established some limits on the 3c-ESI values for the different regions; lower than 0.005 for hydrogen bonds, between 0.005 and 0.040 for anagostic interactions, and higher values than 0.040 for agostic interactions. This methodology has been used here to characterize the different interactions in diverse systems with misassigned or ambiguous three-centre interactions as well as to corroborate those assigned previously by other techniques. We hope that this study will encourage the use of this multicentre index as a tool to determine these interactions, which are of much interest in organometallic as well as in main group chemistry.

## Author Contributions

Y. G.-R.: investigation, formal analysis, writing – original draft, writing – review & editing. F. F. and E. M.: investigation, formal analysis, writing. M. S.: supervision, writing – review & editing, funding acquisition.

## Conflicts of interest

There are no conflicts of interest to declare.

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