

New Complexity for Aromatic Ring Agostic Interactions

M. Arif Sajjad,^a Kirsten E. Christensen,^b Nicholas H. Rees,^b Peter Schwerdtfeger,^c John A. Harrison^{a*} and Alastair J. Nielson^{a*}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Density functional theory (DFT) calculations reveal that for ligand directed aromatic ring C-H bond activation, the agostic donation can share the same antibonding acceptor orbitals as a previously unrecognised π -donation from the aromatic ring of the ligand. The recognition of carbon based orbitals assisting the agostic interaction has significant implication for C-H bond activation chemistry.

Transition metal catalyzed C-H bond functionalisations are now widely used in organic synthesis and are crucial to the development of pharmaceuticals, natural products and materials.¹ For these transformations, cyclometallation reactions involving d⁸ transition metals² are very useful as site selectivity can be controlled using pre-existing functional groups that position C-H groups for activation.³ The key activation step in these ligand-directed C-H bond functionalisations is the weakening of the C-H bond and this is achieved by the agostic interaction⁴ which is also found extensively in both early and late transition metal complexes.⁴

For transition metal alkyl β -agostic separations, the nature of the interactions involved have been found to be complex⁵ but for aromatic ring agostic interactions only C-H σ bond to metal and metal to C-H σ^* back donations have been identified.⁴ We report here that aromatic-ring C-H bond agostic interactions can have significantly more complexity than previously recognised.

Our early work on following the cyclometallation reaction of 1-tetralone oxime with Li₂PdCl₄ by ¹H NMR spectroscopy carried out at 60 MHz, suggested that a stable agostic intermediate could be observed.⁶ However, in a recent attempt to obtain more information about this intermediate, a search we made at 500 MHz

failed to identify the presence of any entities where time-averaged spectra gave a lowered ¹J(C-H) coupling constant characteristic of the agostic bond,⁴ even though a cyclometallated complex was recovered from the NMR solution and characterized by X-ray crystallography.⁷ We thus turned to a computed structure of the putative agostic intermediate to obtain metrics and then used NBO analyses⁸ and QTAIM atomic charges⁹ to uncover the characteristics of the agostic bonding situation.

The computed structure of the agostic complex [PdCl₂(1-tetralone oxime)] (**1**) in which the oxime ligand aromatic ring is not free to rotate, shows that the ligand coordinates to the metal with the C(8)-H bond electron density lying in the coordination plane, *trans* to the Cl(2) ligand and the (N)-OH hydrogen is involved in hydrogen bonding to the Cl(2) ligand [(N)-OH...Cl distance, 2.092 Å] (Fig. 1). The alicyclic ring portion of the ligand forms a boat-like conformation compared to the free ligand where a chair-like conformation is present. The C-H bond is positioned so that the H-atom sits more below the coordination plane than the C atom sits above it, giving Pd...C and Pd...H separations of 2.240 and 1.819 Å respectively (structural data are contained in table 1). Two features of the interaction are the lengthening of the C-H bond [1.152 Å in (**1**), 1.081 Å in the free ligand] which is well documented for agostic interactions and is related to the strength of the interaction^{4f} and also the deformation of the C(8)-H bond out of the plane of the aromatic ring, [H(7)-C(7)-C(8)-H(8) torsion angle -27.2°].^{10,11}

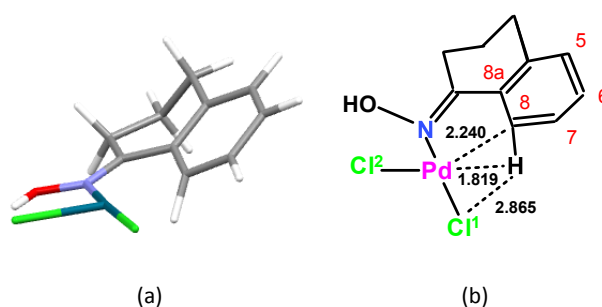


Fig. 1 (a) Computed structure of complex (**1**); (b) relevant separations (Å) and aromatic ring numbering.

^a Chemistry, Institute of Natural and Mathematical Sciences, Massey University Auckland, Private Bag 102904, North Shore Mail Centre, Auckland, New Zealand. E-mail: a.j.nielson@massey.ac.nz

^b Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK.

^c Centre for Theoretical and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, Private Bag 102904, North Shore Mail Centre, Auckland, New Zealand.

Electronic Supplementary Information (ESI) available: Cartesian coordinates, QTAIM properties, NBO donor/acceptor energies, occupancies and contour plots. See DOI: 10.1039/x0xx00000x

^d

Table 1 Selected structural data for complexes (1) to (5)

	(1)	(2)	(3)	(4)	(5)
Distances (Å)^a					
Pd····H	1.819	1.802	1.901	2.180	1.822
Pd····C	2.240	2.229	2.208	2.146	2.228
Cl(cis)····H	2.865	2.850	2.957	3.235	2.887
C-H	1.152	1.156	1.138	1.113	1.152
	(1.081)	(1.089)	(1.090)	(1.090)	(1.090)
Angles (°)					
Pd-N-C	119.9	120.2	120.0	119.8	120.8
Pd····C-H	54.0	53.7	59.4	76.8	54.6
Pd····H-C	95.2	95.3	89.6	73.4	94.4
Cl(trans)-Pd····H	157.7	159.0	153.4	146.3	157.2
Cl(trans)-Pd····C	166.3	165.3	167.8	167.3	166.2
Dihedrals (°)					
Cl(trans)-Pd-N-C	165.8	165.5	168.3	171.4	166.3
Ar-Plane/CP ^b	34.5	35.6	33.0	33.4	36.1
N-C-C-C	15.1	15.1	14.0	18.5	18.0
C-H deform (°)	-27.2	-27.6	-31.1	-43.7	-27.1

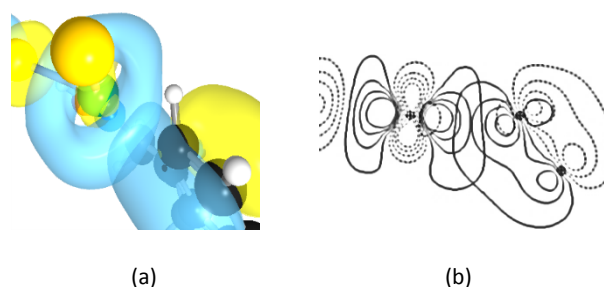
^a Free ligand values in brackets. ^b Angle between the aromatic ring plane and the coordination plane.

The description for the agostic situation in (1) provided by the NBO analysis shows that there are two C-H σ bond electron density donations to the metal and these do not involve purely metal d orbitals in this formally d⁸, Pd²⁺ system but instead utilise the *trans* and *cis*-related Pd-Cl antibonding orbitals [C-H σ to Pd-Cl $\sigma^*(trans)$ and Pd-Cl $\sigma^*(cis)$ *E*(2) values, 58.6 and 10.0 kcal mol⁻¹ respectively]. In addition there are two small energy back-donations from the metal to the C-H antibonding orbital [Pd to C-H σ^* *E*(2) values, 4.9 and 2.9 kcal mol⁻¹ (see supplementary Figure 2)].

The NBO analysis also indicates there are further bonding components present which have not been recognised previously. In addition to the C-H σ bond agostic donation, there is significant donation of π -electron density from the aromatic ring into the same antibonding orbitals on the metal that receives the agostic donation. These donations involve the C(7)-C(8) π -electron density [C(7)-C(8) π to Pd-Cl $\sigma^*(trans)$ and Pd-Cl $\sigma^*(cis)$ donations *E*(2) values, 20.3 and 6.5 kcal mol⁻¹ respectively] (Table 2). The other donation which is much smaller, involves the C(8)-C(8a) σ -electron density [C(8)-C(8a) σ to Pd-Cl $\sigma^*(trans)$ and Pd-Cl(2) $\sigma^*(cis)$ donations, *E*(2) values, 1.4 and 0.4 kcal mol⁻¹]. An NBO diagram along with a contour plot for the interaction of C(7)-C(8) π -electron density to Pd-Cl $\sigma^*(trans)$ [20.3 kcal mol⁻¹] is shown in Fig 2. (Similar diagrams and contour plots for the agostic contributions are found in the supplementary data). The sum of these values at 26.8 kcal mol⁻¹ for π -donation is approximately one third that of the agostic donation and compares with the N-OH····Cl hydrogen bonding component in

Table 2 NBO donations (kcal mol⁻¹) for complexes (1) to (5)

	(1)	(2)	(3)	(4)	(5)
C-Hσ to					
Pd-Cl $\sigma^*(trans)$	58.6	75.6	64.0	-	56.9
Pd-Cl $\sigma^*(cis)$	10.0	15.0	13.8	3.1	8.9
C(7)-C(8)π to					
Pd-Cl $\sigma^*(trans)$	20.3	27.6	41.9	-	0.1
Pd-Cl $\sigma^*(cis)$	6.5	10.5	13.8	-	-
C(8)-C(8a)σ to					
Pd-Cl $\sigma^*(trans)$	1.4	0.7	0.1	-	1.5
Pd-Cl $\sigma^*(cis)$	0.4	0.1	0.9	1.9	0.4
C(8)-C(8a)π to					
Pd-Cl $\sigma^*(trans)$	-	-	-	-	20.3
Pd-Cl $\sigma^*(cis)$	-	-	-	-	6.8

**Fig. 2** Aromatic ring C(7)-C(8) π -electron density donation to the Pd-Cl antibonding orbital in complex (1) (a), NBO orbital diagram; (b), NBO contour plot.

the complex of 23.8 kcal mol⁻¹.¹² Replacing the *cis*-Cl ligand with CH₃, whereby CH₄ would be eliminated in a cyclometallation reaction, shortens the Pd····H and Pd····C separations to 1.780 and 2.226 Å respectively. The C-H σ and C(7)-C(8) π to Pd-Cl $\sigma^*(trans)$ donations increase to 73.8 and 22.6 kcal mol⁻¹ compared to 58.6 and 20.3 kcal mol⁻¹ in (1). (see a full comparison of data in supplementary data Tables 6 and 7).

QTAIM atomic charges for the aromatic ring for (1) (see Table 1 of the supplementary data) show that with both agostic and aromatic ring π -donations present, the C(8)-carbon becomes much more negative than in the free ligand [*q*(C) values, -0.084e and 0.001e respectively]. In this case, the charges of the other ring carbons all become more positive than the free ligand by essentially the same amount (values range from 0.012e to 0.014e more positive) except for the C(7)-carbon (more positive by +0.026e). This would indicate that there is very little classic Wheland character¹³ at this stage as more positive charge would be expected to build up at the positions *ortho* and *para* to the C(8)-H bond. The agostic hydrogen becomes only slightly more positive [*q*(H8) increases by +0.016e], the hydrogen in the *ortho*-position much more positive [*q*(H7) increases by +0.065e] and the *meta* and *para*-hydrogens, much less [*q*(H6) and *q*(H5) increase by only +0.024e and +0.020e respectively].

In recognising this new complexity, substituent effects were introduced in an attempt to manipulate the electronic environment. This was carried out using the strongest electron donating or withdrawing groups available to influence either the σ or π -systems of the aromatic ring but not both at the same time. *Para*-substituents were utilised as the effects are more pronounced for these groups than at the *meta*-position¹⁴ and the *ortho*-position can involve a combination of steric and electronic effects.¹⁵

Replacing the C(5)-hydrogen in (1) with the strong σ -electron withdrawing SO₂Cl group (F value 1.16; R value -0.05¹⁴), complex (2), the Pd····H separation decreases [1.802 and 1.819 Å for (2) and (1) respectively] as does the Pd····C separation [2.229 and 2.240 Å for (2) and (1) respectively] [compare values for (2) with (1) in Fig. 3 and Fig. 1]. This occurs when the dihedrals and C-H bond deformation are very similar in both complexes [compare values for both complexes in Table 1]. In this case, the NBO analysis shows a significant increase in the agostic donations [C-H σ to Pd-Cl $\sigma^*(trans)$ and Pd-Cl $\sigma^*(cis)$, *E*(2) values, 75.6 and 15 kcal mol⁻¹ respectively, c.f.

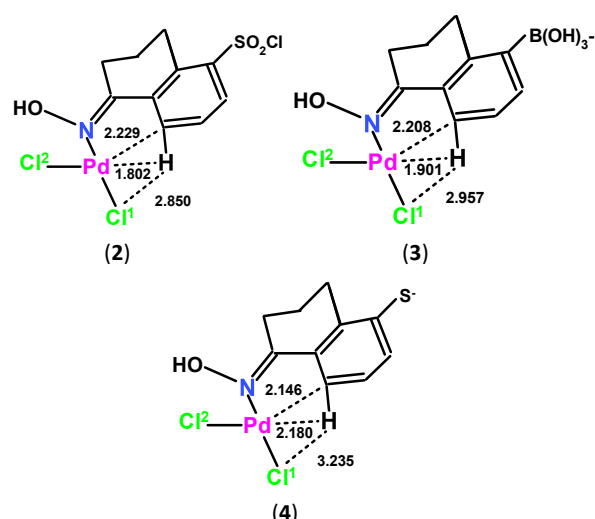


Fig. 3 Relevant separation metrics (Å) for C(5)-substituted [PdCl₂(1-tetralone oxime)] complexes. (2) SO₂Cl; (3) B(OH)₃⁻; (4) S⁻.

58.6 and 10.0 kcal mol⁻¹ for H at C(5)] and the aromatic ring C(7)-C(8)π-donation [C(7)-C(8)π to Pd-Clσ*(*trans*) and Pd-Clσ*(*cis*) donations, *E*(2) values, 27.6 and 10.5 kcal mol⁻¹ respectively for SO₂Cl, 20.3 and 6.5 kcal mol⁻¹ respectively for H at C(5) in (1)].¹⁶

The strongest π-electron withdrawing group available is the N=NPO(OCH₂CH₃)₂ substituent (F value -0.05; R value 0.79¹⁴) but this caused a conformational change to the alicyclic ring of the ligand related to the substituent size¹⁷ and was not included further in this study (see the optimised structure in supplementary Figure 3). However, no such conformational change occurred with the σ-electron donating B(OH)₃⁻ group (F value -0.42; R value -0.02¹⁴) and in the agostic complex (3), the Pd...H separation increased significantly [1.901 and 1.819 Å for (3) and (1) respectively] and the Pd...C separation became much shorter [2.208 and 2.240 Å for (3) and (1) respectively]. This occurs when the Cl(*trans*)-Pd-N=C dihedral angles increases slightly in magnitude [168.3 and 165.8° in (3) and (1) respectively] and the C-H deformation becomes slightly larger [-31.1 and -27.2° respectively].

The NBO analysis now shows that the agostic donation is only slightly higher than for H at C(5) in (1) [C-Hσ to Pd-Clσ*(*trans*) and Pd-Clσ*(*cis*), *E*(2) values, 64.0 and 13.8 kcal mol⁻¹ respectively, 58.6 and 10.0 kcal mol⁻¹ for H at C(5) in (1)] but with the closer Pd...C separation, there is a significant increase in the aromatic ring C(7)-C(8) π-donation [C(7)-C(8)π to Pd-Clσ*(*trans*) and Pd-Clσ*(*cis*) donations, *E*(2) values, 41.9 and 13.8 kcal mol⁻¹ respectively for B(OH)₃⁻ (3); 20.3 and 6.5 kcal mol⁻¹ respectively for H at C(5) in (1)].

In seeking to significantly enhance the π-electron density of the aromatic ring with the expectation of increasing the C(7)-C(8)π donation even further than in (3), the C(5)-hydrogen was replaced with the strong π-electron donating S⁻ group (F value -0.03; R value -1.24¹⁴), complex (4). The H-atom now moves even further away from the metal centre [Pd...H separations 2.180 and 1.819 Å in (4) and (1) respectively] and the Pd...C separation becomes very close [2.146 and 2.240 Å for (4) and (1) respectively]. The angle between the plane the aromatic ring makes with the coordination plane is essentially unchanged (angles between the planes, 33.4° and 34.5° respectively). The NBO analysis in this case shows that the agostic

donation has decreased to nearly zero [C-Hσ to Pd-Clσ*(*trans*) and Pd-Clσ*(*cis*), *E*(2) values, 0.0 and 3.1 kcal mol⁻¹ respectively, c.f. 58.6 and 10.0 kcal mol⁻¹ for H at C(5) in (1)] but there is now strong lone pair donation from the metal indicating significant Pd-C bond covalency (see Table 3 of the supplementary data). In this case, the Pd...C separation is well within the bond distance for η¹-complexes of palladium¹⁸.

With the extra complexity to the agostic interaction in the 1-tetralone oxime complex (1) identified, a rotatable aromatic ring analogue was computed to ascertain if the aromatic ring π-donation was not just a consequence of a constrained aromatic ring system. [PdCl₂(acetophenone oxime)] complex (5) (Fig. 4) in which there is no alicyclic ring, shows a similar Pd...H separation to (1), [1.822 and 1.819 Å respectively] but a slightly shorter Pd...C separation [2.228 and 2.240 Å respectively]. The angles associated with the separations are essentially the same in (5) and (1) (compare values in Table 1) as are the C-H bond deformation angles and the NBO analysis shows that the agostic donations are also very similar [C-H σ to Pd-Clσ*(*trans*) and Pd-Clσ*(*cis*) *E*(2) values 56.9, 8.9 kcal mol⁻¹ and 58.6, 10.0 kcal mol⁻¹ for (5) and (1) respectively]. The aromatic ring π-donation NBO *E*(2) values are also very similar [20.3, 6.8; and 20.3, 6.5 kcal mol⁻¹ for (5) and (1) respectively] but with the non-constrained aromatic ring in (5), the donation changes to the inner π-orbital system [ie the C(8)-C(8a)-orbital system of tetralone oxime complex (1)]. Associated with this move are small donations from the metal d-orbitals and bonding Pd-Cl orbitals in to the C=Cπ-antibonding orbital (see Table 3 of the supplementary data).¹⁹

It is worthwhile to note that the magnitude of *E*(2) is influenced by both the spatial overlap of the donor/acceptor NBO's as well as by the inverse of the difference between the NBO orbital energies. In the case of all the compounds discussed above it is the spatial overlap that is driving the strength of the interaction as the orbitals are not strongly resonant with one another, as indicated by the orbital energy values (see supplementary data Tables 4 and 5).

As C-C bond formation arising from cyclometallated sp³ carbon is of significant interest and some complexity other than the forward and back-donations in transition metal alkyl agostic complexes has been demonstrated,⁵ the agostic structure of [PdCl₂(8-methylquinoline)] (6), expected for the well-known cyclometallation reaction of 8-methylquinoline with PdCl₄²⁻²⁰ was computed (see Fig. 5). In this case, two hydrogens form close approaches to the metal²¹ one of which is longer than the other in this gas-phase, 0 K structure, [Pd...H separations of 1.888 and 2.187 Å; Pd...C separation 2.352 Å]. The rotation of the C-C bond involving the benzylic position is such that the C-H electron density of the upper

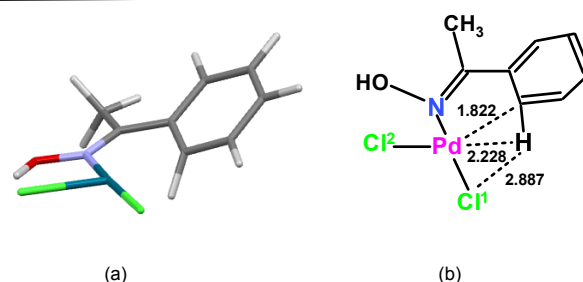


Fig. 4 (a) Computed structure of complex (5); (b) relevant separations (Å).

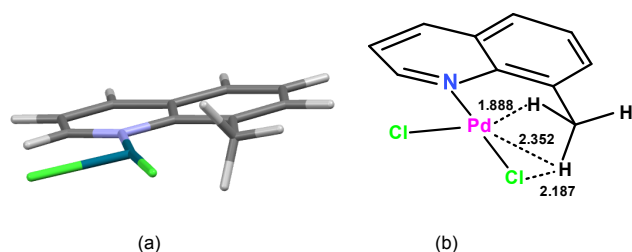


Fig. 5 (a) Computed structure of complex (6); (b) relevant separations (Å).

hydrogen forms the stronger agostic interaction, as shown by the length of the C-H bonds [1.144 and 1.112 Å; 1.097 Å for the C-H bond pointing away from the metal]. The NBO donations for (6) show that the upper agostic interaction has C-H σ to Pd-Cl σ^* (*trans*) and Pd-Cl σ^* (*cis*) *E*(2) values of 44.0 and 9.1 kcal mol⁻¹ and the lower one *E*(2) values of 16.6 and 3.7 kcal mol⁻¹ compared with the 3rd non-interacting hydrogen of 1.5 and 0.4 kcal mol⁻¹. The similarity in [PdCl₂(oxime)] complexes (1) and (6), is that the donations are into the same Pd-Cl antibonding orbital and if summed together, the two particular donations in (6) have similar *E*(2) magnitude as the single agostic interaction in (1). There is also Pd to C-H σ^* back donation involved for the upper agostic approach [*E*(2) value 6.0 kcal mol⁻¹] but no other donations that can be regarded as significant are involved in the interaction.

This work shows that the agostic interaction involved in aromatic-ring cyclometallation reactions for the type of ligands described, have more complexity than previously recognised in that there can be significant aromatic ring π -donation to the metal. Importantly, this donation can be manipulated by increasing or decreasing the electron density in the aromatic ring so that the ratio of agostic to aromatic ring π -donation can be significantly modified. With strong donation into the ring by an S⁻ substituent, the agostic interaction can be essentially turned off and sigma-bond covalency is developed. The origin of the π -donation from the aromatic ring can also be changed depending on whether the ring can rotate. In keeping with the Greek origin of the term agostic^{4b} we propose that augmentations other than the pure agostic donation, be given the term 'syndetic' from the Greek word syndetikos or sundeo (συνδέω) meaning 'serving to unite' 'to connect' or 'bind together'. The agostic donation for the aromatic ring systems presented here, is not an isolated interaction and as such introduces significant implication for C-H bond activation chemistry particularly in terms of the intimate involvement of orbitals associated with the carbon to be activated by metallation. Further computational work is in progress to identify the extent of the syndetic donation in complexes and reaction mechanism transition states that involve aromatic-ring C-H agostic interactions.

Notes and references

- (a) E. M. Beck and M. J. Gaunt in *Topics in Current Chemistry: C-H Activation*, Vol. 292. (Eds. J. Q. Yu, Z. J. Shi), Springer-Verlag: Berlin, Heidelberg, 2010, pp. 85-121; (b) J. Yamaguchi, A. D. Yamaguchi and K. Itami, *Angew. Chem., Int. Ed.*, 2012, **51**, 8960–9009; (c) J. Wencel-Delord, T. Dröge, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, **40**, 4740–4761.
- (a) I. Omae, *Coord. Chem. Rev.*, 2004, **248**, 995–1023; (b) J. Dupont, C. S. Consorti and J. Spencer, *Chem. Rev.*, 2005, **105**, 2527–2571; (c) M. Albrecht, *Chem. Rev.*, 2010, **110**, 576–623.
- (a) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147–1169; (b) O. Baudoin, *Chem. Soc. Rev.*, 2011, **40**, 4902–4911; (c) K. M. Engle, T.-S. Mei, M. Wasa and J.-U. Qu, *Acc. Chem. Res.*, 2012, **45**, 788–802. (d) A. F. M. Noisier and M. A. Brimble, *Chem. Rev.*, 2014, **114**, 8775–8806.
- (a) M. Lein, *Coord. Chem. Rev.*, 2009, **253**, 625–634; (b) M. Brookhart, M. L. H. Green and G. Parkin, *Proc. Natl. Acad. Sci. U.S.A.*, 2007, **104**, 6908–6914; (c) W. Scherer and G. S. McGrady, *Angew. Chem. Int. Ed.*, 2004, **43**, 1782–1806 (d) J. J. Schneider, *Angew. Chem. Int. Ed.*, 1996, **35**, 1068–1076; (e) R. H. Crabtree, *Angew. Chem. Int. Ed.*, 1993, **32**, 789–805; (f) M. Brookhart and M. L. H. Green, *J. Organometallic Chem.*, 1983, **250**, 395–408.
- (a) W. Scherer, V. Herz, A. Bruck, C. Hauf, F. Reiner, S. Altmannshofer, D. Leusser, and D. Stalke, *Angew. Chem. Int. Ed.*, 2011, **50**, 2845–2849; (b) W. Scherer, P. Sirsch, D. Shorokhov, M. Tafipolsky, G. S. McGrady and E. Gullo, *Chem. Eur. J.*, 2003, **9**, 6057–6070; (c) A. Haaland, W. Scherer, K. Ruud, G. S. McGrady, A. J. Downs and O. Swang, *J. Am. Chem. Soc.*, 1998, **120**, 3762–3772.
- A. J. Nielson, *J. Chem. Soc. Dalton Trans.*, 1981, 205–211.
- K. E. Chistensen, A. J. Nielson and N. H. Rees, unpublished results.
- F. Weinhold, C. Landis in *Valency and bonding: A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, England, 2005.
- (a) R. F. W. Bader in *Atoms in Molecules: A Quantum Theory*, The Clarendon Press, Oxford, 1990; (b) R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928; (c) P. Popelier in *Atoms in Molecules: An Introduction*, Prentice Hall, Pearson Education Ltd, 2000.
- W. Yao, O. Eisenstein and R. H. Crabtree, *Inorg. Chim. Acta*, 1997, **254**, 105–111.
- See references pertaining to agostic C-H bond deformation in pincer ligand complexes: S. Murugesan, B. Stoger, E. Pittenauer, G. Allmaier, L. F. Veiras and K. Kirchner, *Angew. Chem. Int. Ed.*, 2016, **55**, 3045–3048.
- As a result of the manner in which NBO energies are obtained, they should not be compared with other energies but are themselves directly comparable.
- (a) Z. Ke, T. R. Cundari, *Organometallics*, 2010, **29**, 821–834; (b) A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403–424; (c) A. D. Ryabov, I. K. Sakodinskaya, and A. K. Yatsimirsky, *J. Chem. Soc. Dalton Trans.*, 1985, 2629–2638; (d) A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, 1968, **90**, 909–913.
- C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **97**, 165–195.
- M. B. Smith in *March's Advanced Organic Chemistry: Reactions, Mechanism and Structure*, 7th Ed, Wiley, 2013.
- QTAIM analysis of the C(8)-H electron density in the C(5)-SO₂Cl substituted free ligand shows that $\rho(\text{bcp})$ is greater than in the C(5)-H free ligand.
- J. A. Harrison, A. J. Nielson, M. A. Sajjad, G. C. Saunders and P. Schwerdtfeger, *Eur. J. Inorg. Chem.*, 2016, 64–77.
- See references in: D. Saha, R. Verma, D. Kumar, S. Pathak, S. Bhunya, A. Sarkar, *Organometallics*, 2014, **33**, 3243–3246.
- Initial results of work at present in progress suggest that the origin of the π -donation can be similarly changed in the tetralone oxime complex by adding steric effects at C(7).
- D. W. Evans, G. R. Baker and G. R. Newkome, *Coord. Chem. Rev.*, 1989, **93**, 155–183.
- S. H. Crosby, G. J. Clarkson and J. P. Rourke, *J. Am. Chem. Soc.*, 2009, **131**, 14142–14143.