Chasing the agostic interaction in ligand assisted cyclometallation reactions of palladium (II)[†]

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

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A 500MHz NMR study of the reaction between 1-tetralone oxime and PdCl₄²⁻ in CD₃OD shows resonances attributable to a potential agostic intermediate prior to the formation of the insoluble cyclopalladated product which itself was characterised by X-ray crystallography. Calculated structural, spectroscopic, QTAIM, NBO and NCI analysis results obtained from density functional theory (DFT) calculations give a full description of the putative agostic intermediate [PdCl₂(1-tetralone oxime)] (**1**) which is shown to include a previously unrecognised π -electron density donation from the aromatic ring to the metal in close proximity to the agostic carbon atom. Changing the (N)–OH donor to (N)–OMe does not effect the magnitude of these interactions. (N)–OH and (N)–OMe acetophenone imines in which the aromatic ring has the potential to rotate show similar agostic and π -electron donation to the alicyclic ring counterparts. 1-Tetralone which coordinates to the metal by a Pd–O bond that is much weaker than the Pd–N complexes has a slightly stronger agostic component and slightly weaker π -electron donation than the oxime counterpart.

Introduction

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 In this regard, cyclopalladation reactions² are very useful as site selectivity can be controlled using pre-existing functional groups that position C–H groups for activation.³ Up until recently these functional groups have involved strongly coordinating ligand groups such as nitrogen donors which lead to cyclopalladated complexes in which the metal-carbon bond is less prone to subsequent functionalization due to the thermodynamic stability imparted by the formation of the cyclometallate ring system.⁴ However, it is now recognised that weakly coordinating donor groups such as carboxylic acids or ketones form less-stable cyclometallates in which the metal-carbon bond is more reactive⁴ and this advance has allowed the activation and post functionalisation to be made catalytic.⁵

Whereas most C–H functionalization methodologies are based on one-pot approaches that bypass isolation or even detection of reaction intermediates, there are potentially significant benefits in

intercepting them and investigating the main factors influencing their formation, stability, and reactivity. Any knowledge gained from such studies should improve understanding of the important steps involved in catalytic C–H functionalization processes and help develop more efficient methodologies.⁶

The key activation step in these ligand-directed C–H bond functionalizations is the weakening of the C–H bond and this is achieved by forming an agostic interaction⁷ which lengthens the bond by donation of σ -bond electron density to the metal. Removal of the hydrogen can then be assisted by the presence of a proton accepting ligand such as in the case of Pd(OAc)₂⁸ or having a base present such as NaOAc.⁹ Associated with the agostic interaction is the anagostic interaction in which no perturbation of the C–H bond occurs.¹⁰

With the increased use of cyclometallates in the synthesis of organic compounds, understanding the nature of the C–H bond activation process is of prime importance. We present here, the results of a high-field NMR study for a cyclopalladation reaction where we search for the agostic intermediate and then carry out DFT studies which gives a complete description of the agostic interaction and uncovers unexpected complexity for it. A preliminary account of some of this work has been communicated.¹¹

Results and discussion

NMR spectral study of the reaction of 1-tetralone oxime and PdCl₄²⁻

The 1-tetralone oxime ligand was used in the reaction with Li₂PdCl₄ as in earlier work on cyclopalladation reactions using this ligand as a model system for the modification of steroidal precursors, we were

^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.

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Scheme 1. Postulated intermediates identified by ^1H NMR spectroscopy at 60 MHz in the reaction of Li_2PdCl_4 and 1-tetralone oxime in CD_3OD .⁹

able to monitor by ^1H NMR spectroscopy when anagostic, agostic and soluble cyclopalladated intermediates appeared to be present⁹ (scheme 1). At the apparent agostic stage, an intermediate of the form $[\text{PdCl}_2(\text{1-tetralone oxime})]$ was isolated but the complex was unstable towards cyclopalladation even in the solid state so that no metrics could be obtained by X-ray crystallography. In addition, this type of complex was utilised in the study as it was expected to provide a 'pure' agostic interaction that did not include acetate as a co-ligand which could influence the nature of the interaction by providing a Lewis base close by that could lengthen the C–H bond.⁸

The original investigation of the reaction between 1-tetralone oxime and Li_2PdCl_4 was carried out in CD_3OD by ^1H NMR at 60 MHz using a single scan spectrometer where the resolution was insufficient to obtain well defined peaks.⁹ In the present ^1H NMR investigation, spectra were obtained at 500 MHz in an attempt to gain more detailed information about the apparent agostic intermediate that was identified in the earlier study by an upfield shift of the H8 proton to the vicinity of the free-ligand H8 resonance.⁹

The 500 MHz ^1H NMR spectrum and ^{13}C NMR spectrum obtained at 0°C after mixing the components at 0°C showed that there was only one major component present (see figs. 1–4 in the ESI[†]) as found in the earlier study. The ^1H NMR spectrum at 500 MHz shows the reported downfield shift for the C8-hydrogen of 2.60 ppm relative to the free ligand which is indicative of an anagostic interaction whereby the nitrogen atom is coordinated to the metal and H8 lies above the coordination plane.¹⁰ With analogy to other anagostic complexes arising from the use of PdCl_4^{2-} , the complex would be formulated as the anion $[\text{PdCl}_3(\text{1-tetralone oxime})]^-$.¹² In the ^{13}C NMR spectrum, the C8 resonance shifts from 125.0 ppm in the free ligand to 128.6 ppm when coordination of the ligand to Pd is indicated by a shift in the C1 (C=N bond carbon) resonance position from 155.5 to 164.0 ppm. A further indication of the

anagostic interaction that was not available in the earlier work is that the $^1\text{J}_{\text{C-H}}$ coupling constant is little changed from the free ligand ($^1\text{J}_{\text{C-H}}$ values 160.4 and 160.1 Hz respectively).

The spectral characteristics of the anagostic interaction for H8 remain the main event when the temperature is kept at 0°C but there is slow formation of small amounts of an intermediate identified by an upfield shift of H8 as well as a soluble cyclopalladated complex where H8 is not present. Warming the solution to 35°C increases the proportion of these two species at the expense of the anagostic intermediate and the very insoluble chloro-bridged cyclopalladated complex that is the isolated product of the reaction, crystallises out in the NMR tube. The ^{13}C NMR spectrum is consistent with the 3-component system indicated by the ^1H NMR spectrum.

The 35°C ^1H NMR spectrum is broad, but recooling to 0°C gives much better peak resolution (fig. 1) and also slows the transformation of the components. Based on the reported evidence that agostic hydrogens which lie in or about the coordination plane show an upfield shift in the ^1H NMR spectra compared to anagostic hydrogens which lie above the coordination plane,⁷ the H8-doublet in the spectrum at $\delta = 7.91$ might be assignable to an agostic hydrogen. Although the resonance lies in a similar position to the free ligand H8 resonance ($\delta = 7.87$), the other resonances for the ligand are not those of the free ligand (compare figs. 5 and 6 with fig. 1 in the ESI[†]) and the ^{13}C NMR characteristics are different. This region of the ^1H NMR spectrum corresponds to the poorly resolved region for the upfield shifted H8 in the earlier work.⁹ However, the $^1\text{J}_{\text{C-H}}$ coupling constant obtained from the CLIP-HSQC¹³ 500 MHz spectrum is similar to the free ligand value, and does not show the lowering found for complexes containing agostic hydrogens that are in fixed in-plane positions.⁷ This suggests that the agostic C–H bond if present, may move about the coordination plane to some degree and that the H8 position in the spectrum could be a result of time averaging whereby it experiences diminishing regions of equatorial current density.¹⁴

Cooling the 0° solution down to -60°C does not change the $^1\text{J}_{\text{C-H}}$ coupling constant to any meaningful extent indicating that the apparent time-averaging is still present at this lower temperature. However, the intensity of the H8-resonance at $\delta = 7.91$ attributed

Fig. 1 Aromatic region of the ^1H NMR spectrum for the reaction between PdCl_4^{2-} and 1-tetralone oxime in CD_3OD mixed at 0°C , warmed to 25°C and re-cooled to 0°C .

to the agostic H8 does decrease and two small peaks that are present around $\delta = 9.5$ in the 0°C spectrum (see fig. 1) increase in size. A DEPT 135 ^{13}C NMR spectrum shows there are 8 aromatic C–H carbons present for these two species in addition to those found for the anagostic, agostic and soluble cyclopalladated intermediates.

Restoring the temperature to 0°C then gives the original spectral characteristics for these peaks at this temperature and the same features were produced on cooling and reheating the solution several times to the same temperatures. The position of the $\delta = 9.5$ resonances for H8 is well downfield compared to H8 for the free ligand suggesting that hydrogen is again experiencing an above-plane, anagostic environment that is different to that found for H8 after mixing the components. The low-temperature study would then suggest that there is some form of equilibria between the apparent agostic component and the two $\delta = 9.5$ anagostic components but we have not investigated this aspect further at this stage.

X-ray crystal structure determination of the insoluble cyclometallated complex

In our earlier work on the reaction of Li_2PdCl_4 and 1-tetralone oxime the cyclopalladated product of the reaction was characterised by analytical data, NMR and IR spectroscopy but we were unable to obtain a crystalline sample. In the present investigation, the NMR tube was not used in a spinning mode and under these conditions, the product that formed in the tube was found to be crystalline.

An X-ray crystal structure shows the molecule is an asymmetric chloro-bridged dimer with C,N-cyclopalladated 1-tetralone oxime ligands at either end of the molecule in a mirrored coordination mode and a regular square planar coordination geometry about each palladium centre (fig. 2). On both sides of the molecule, the plane made up by the aromatic rings lie slightly out of this coordination plane by 10.7 and 4.8° for the left and right hand sides respectively. The alicyclic ring on the left-hand side of the molecule

Fig. 2 X-ray crystal structure of the insoluble cyclometallated complex retrieved from the NMR monitored reaction. Thermal ellipsoids represent 50% probability. Selected bond lengths, separations ($\text{\AA}$) and angles ($^\circ$): Pd(13)–N(11) 2.012(5), Pd(13)–C(9) 1.983(6), Pd(13)–Cl(14) 2.474(2), Pd(13)–Cl(34) 2.329(1), C(1)–N(11) 1.286(8), N(11)–O(12) 1.382(7), Cl(14)···H–O(32) 2.60, Cl(14)···H–O(12) 3.20, Cl(34)···H–C(8) 2.82, Cl(34)···H–C(28) 2.84; N(11)–Pd(13)–Cl(34) $173.8(2)$, N(11)–Pd(13)–Cl(14) $95.5(2)$, C(9)–Pd(13)–Cl(14) $174.8(2)$, C(9)–Pd(13)–N(11) $80.3(2)$, C(9)–Pd(13)–N(11) $95.5(2)$, Pd(13)–Cl(34)–Pd(33) $93.7(5)$, Pd(13)–Cl(14)–Pd(33) $86.7(5)$, Cl(14)–Pd(13)–Cl(34) $88.4(5)$, Pd(13)–N(11)–O(12) $125.3(4)$.

forms a distorted boat-like configuration whereas on the right-hand side there are two boat-like configurations arising from positional differences at C22 and C23 occurring from disorder at these positions. The Pd–Cl bonds are asymmetric with the bond lying *trans* to C9 being longer than the one lying *trans* to nitrogen [bond lengths 2.474(2) and 2.329(1) $\text{\AA}$ respectively]. The Pd–C and Pd–N bond lengths are similar to a range of other C,N-cyclometallates in general and the bond angles associated with the atoms in the coordination plane are also unspectacular.

Coordination of the Pd centres to the two Cl ligands results in an overall ‘butterfly’ arrangement for the molecule (fig. 7 of the ESI[†]) and in this case, there are several weak hydrogen bonds potentially present for some of the hydrogen atom placements. The (N)–OH group hydrogens and the adjacent Cl14 ligand have H···Cl separations of 3.199 and 2.595 $\text{\AA}$ with the latter representing a well-developed interaction and on the other side of the molecule, the aromatic ring C8 and C26-hydrogens have H···Cl separations of 2.820 and 2.840 $\text{\AA}$.

DFT description of the agostic interaction in [PdCl₂(1-tetralone oxime)] (1)

To obtain information about a putative agostic interaction in the reaction of 1-tetralone oxime and PdCl_4^{2-} , a full computational characterisation of the agostic complex [PdCl₂(1-tetralone oxime)] (1) was carried out. The dispersion-corrected PBE-D3 functional was used in the calculations as the inclusion of dispersion for weak interactions is regarded as important.¹⁵ In previous computational work on anagostic complexes of rhodium using a variety of 1-tetralone derivatives,¹⁰ we carried out some functional testing and settled on the PBE-D3 functional after finding that it performed as well as BP86¹⁶ which conforms to the uniform electron gas (UEG) limit¹⁷ and is known to perform well for agostic interactions¹⁸ as well as anagostic interactions.¹⁹ Keeping these points in mind, and to give comparability to studies we have carried out on anagostic interactions, we have continued to employ PBE-D3 for the agostic interactions in this work.

As a strategy for uncovering the nature of the interactions in the present study, we have computed the structures of the various agostic complexes and then compared the structural features in terms of the important metrics. Then, in relationship to bench synthesis protocol, we have computed spectroscopic data to give an initial indication of the change in properties and followed on with in-depth analysis of the interactions using QTAIM and NBO analysis. We are not aware of a previous complete computational study like this for an aromatic ring agostic interaction involved in a cyclometallation reaction. This type of approach to understanding underlying fundamentals greatly reduces the need for bench syntheses.^{10,20}

The computed structure of [PdCl₂(1-tetralone oxime)] (1) (fig. 3; selected metrics in table 1) shows that the oxime ligand coordinates to the metal with the C8–H bond electron density lying *trans* to the Cl2 ligand. This orientation arises when the ligand is rotated about the Pd–N bond so that the (N)–OH hydrogen forms a close approach to the Cl2 ligand [(N)–OH···Cl distance, 2.092 $\text{\AA}$] which is representative of a weak hydrogen bond. At the same time, the alicyclic ring portion of the ligand has a boat-like conformation

Fig. 3 (a) The energy minimised structure of [PdCl₂(1-tetralone oxime)] (**1**); (b) Aromatic ring numbering and important separations (Å) for **1**; (c) ball and stick diagram showing the NPdCl₂ coordination plane extended (red line) into the C(8)–H bond.

which is very similar to that found in the free ligand (fig. 8 of the ESI†). A similar ring conformation was found by computation for the anagostic approach in [RhCl(CO)₂(1-tetralone oxime)].¹⁰ With this conformation and the (N)–OH⁺⋯Cl hydrogen bonding component in the present agostic complex, the Pd–N–C bond rotation angle is very flat at just 14.4° and the benzene ring then lies at a plane angle of 34.5° to the palladium coordination plane (Ar/CP angle in table 1).

Table 1 Selected metrics and spectroscopic data for complexes **1–5**

	1	2	3	4	5
Bond Length (Å)^a					
Pd–N	2.015	2.053	2.011	2.047	2.088 ^c
Pd–Cl(<i>cis</i>)	2.272	2.279	2.272	2.278	2.260
Pd–Cl(<i>trans</i>)	2.293	2.280	2.294	2.280	2.252
C–H ^b	1.152	1.151	1.152	1.148	1.164
	1.081	1.090	1.090	1.090	1.090
Separations (Å)^a					
Pd⋯H	1.819	1.841	1.822	1.853	1.786
Pd⋯C	2.240	2.224	2.228	2.217	2.206
Cl⋯H	2.865	2.899	2.887	2.931	2.846
Angles (°)					
Pd–N–C	119.9	116.7	120.8	117.6	114.3
Pd⋯H–C	95.2	93.2	94.4	92.2	94.4
Pd⋯C–H	54.0	55.7	54.6	56.6	53.9
Dihedrals (°)					
Cl–Pd–N=C	14.3	37.2	13.7	37.7	27.3
Ar/CP angle	34.5	51.4	36.1	54.6	42.6
N–C–C–C torsion ^d	15.1	14.7	17.9	18.5	11.1
C–H deform	–27.2	–26.0	–27.1	–25.4	–28.0
Spectral Data					
<i>v</i> _{C–H} (cm ^{–1}) ^{b, e}	2462.8	2473.0	2468.5	2498.5	2346.8
	3133.3	3132.9	3134.8	3134.5	3119.9
	670.6	659.9	666.3	636.0	773.1
δ H ₈ (ppm) ^{b, e}	6.59	5.27	6.75	5.47	4.75
	8.13	8.22	8.04	8.18	8.33
	+1.54	+2.95	+1.29	+2.71	+3.58
¹ J _{C–H} (Hz) ^{b, e}	103.2	105.9	103.0	106.6	103.8
	139.4	139.5	139.0	140.2	141.1
	36.2	33.6	36.0	33.6	37.3

^a Values to 3 decimal places consistent with level of optimisation, SCF convergence and XC grids. ^b Values in bold are for the free ligand. ^c Pd–O bond length.

^d N–C1–C8a–C8 torsion angle ^e Values in italics indicate the difference between the complex and free ligand.

Fig. 4 Space-filled models for **1** looking (a) underneath the agostic interaction; (b) above the agostic interaction.

For the C8–H bond agostic approach in **1**, coordination of the ligand is such that the Pd⋯C and Pd⋯H separations are 2.240 and 1.819 Å respectively (fig. 3b) when the H atom sits more below the coordination plane than the C atom sits above it (figs. 3c and 4). A major feature of the interaction is the lengthening of the C–H bond to 1.152 Å compared with the free-ligand value of 1.081 Å. This lengthening is well documented for agostic C–H bonds and is determined by the strength of the interaction.^{4b,f} A second feature of the interaction is the deformation of the C8–H bond out of the plane of the aromatic ring, as shown by the H7–C7–C8–H8 torsion angle of –27.2°. It can be seen that if the H atom did not bend away from the metal, an unacceptable clash would develop and so if the nitrogen is to coordinate to the metal, the H atom has no alternative but to bend away. Both the lengthening and the deformation have been shown to occur by X-ray crystallographic determinations of complexes containing agostic interactions involving aromatic rings²¹ and both are features of Ru, Rh and Ir pincer complexes and more recently a Co pincer, containing aromatic C–H agostic bonds.²² A third feature seen in agostic complex **1** is that the C7–C8 and C8–C8a bonds lengthen in comparison to the individual adjacent C–C bonds whereas in the free ligand, the two bond lengths are shorter. However, the various C–C–C bond angles are all very similar [see the comparisons for the bond lengths and angles in fig. 9 of the ESI†].

Calculated spectroscopic data for **1** (table 1) indicate that in the ¹H NMR spectrum there is an up field shift of 1.54 ppm for the agostic H8 compared with the free ligand. This shift is known to arise from anisotropy associated with the metal centre²³ and was used to indicate the presence of an agostic interaction in the present cyclopalladation reaction⁹ but it has more recently been shown that the extent of the shift cannot be related to the interaction strength as the equatorial current density about the metal centre can vary.¹⁴ It should be noted that this calculated upfield shift of 1.54 ppm is for a static interaction in the gas phase at 0 K and does not relate to the position of H8 determined by the earlier experimental ¹H NMR study. Similarly, in the calculation, spectroscopic characteristics that relate to the interaction strength, are associated with C–H bond electron density depletion and for **1** there is a significant decrease in the ¹J_{C–H} coupling constant in comparison to the free ligand (103.2 and 139.4 Hz respectively) and the calculated C–H stretching frequency shifts to lower energy by 670 cm^{–1} (*v*_{C–H}, 2462.8 cm^{–1} in **1**, 3133.3 cm^{–1} for the free ligand).

QTAIM analysis (selected data in table 2) shows that a bond path and a bond critical point (bcp) occur for the metal and H8 and there is a centrally located ring critical point (rcp) (see fig. 5a) which are all features common to agostic interactions. Other features typical

Table 2 Selected QTAIM^a and NBO^b data for complexes 1–5

	1	2	3	4	5
Pd...X bond path					
$\rho(\text{bcp})$	0.0820	0.0820	0.0828	0.0822	0.0864
$\nabla^2\rho(\text{bcp})$	0.2631	0.2107	0.2569	0.2001	0.2636
C-H bcp					
$\rho(\text{bcp})$	0.2333	0.2346	0.2338	0.2361	0.2286
	0.2810	0.2810	0.2810	0.2810	0.2810
$\epsilon(\text{bcp})$	0.1059	0.1005	0.1076	0.0997	0.1024
	0.0126	0.0126	0.0132	0.0133	0.0096
H-Atomic basin					
Charge, $q(\text{H})$	0.056	0.044	0.057	0.044	0.050
Total Energy, $E(\text{H})$	-0.631	-0.633	-0.632	-0.629	-0.634
Dipolarisation, $M(\text{H})$	0.099	0.108	0.101	0.110	0.105
Volume, $V(\text{H})$	36.0	37.2	36.1	37.4	36.5
C-Atomic Basin					
Charge, $q(\text{C})$	-0.084	-0.070	-0.086	-0.072	-0.066
Pd-Atomic Basin					
Charge, $q(\text{Pd})$	0.641	0.627	0.642	0.629	0.659
NBO donations:					
C-Hσ to					
Pd-Cl $\sigma^*(\text{trans})$	58.6	57.7	56.9	53.7	64.4
Pd-Cl $\sigma^*(\text{cis})$	10.6	9.5	8.9	8.0	9.3
C(7)-C(8)π to					
Pd-Cl $\sigma^*(\text{trans})$	20.3	18.9	20.3 ^d	19.1 ^d	17.9
Pd-Cl $\sigma^*(\text{cis})$	6.5	6.0	6.8 ^d	6.5 ^d	5.4
C(8)-C(8a)σ to					
Pd-Cl $\sigma^*(\text{trans})$	1.4	1.7	1.4	1.7	1.3
Pd-Cl $\sigma^*(\text{cis})$	0.4	0.5	0.4	0.5	0.4

^a Atomic units: $\rho(\text{bcp}) = e/\text{Bohr}^3$; $\nabla^2\rho(\text{bcp}) = e/\text{Bohr}^5$; ϵ , dimensionless; $q = e$. $E = \text{Hartree}$; $M = e^*\text{bohr}$, $V = 1/\text{bohr}^3$

^b 2nd order perturbation energy $E(2)$ values in kcal mol⁻¹.

^c Values in bold are for the free ligand. ^d Values for the C8-8art donations.

of agostic interactions are the positive values for the electron density [$\rho(\text{bcp})$, 0.0820] and Laplacian of the electron density [$\nabla^2\rho(\text{bcp})$, 0.2631] which would indicate a purely electrostatic interaction but the negative energy density [$H(\text{bcp})$ value -0.0210] and a value above 1 for $|V|/G$ ($|V|$ = absolute potential energy density, G = kinetic energy density) which are more reliable indicators than the Laplacian,²⁴ indicate partial covalency. A 2D contour plot of the Laplacian of the electron density (fig. 5b) shows this partial covalency as an area of accumulated charge density along the C–H bond in the direction of the Pd to C–H bond vector. In addition, the C–H σ bond electron density is depleted with respect to the free ligand [$\rho(\text{bcp})$ values 0.2333 and 0.2810 respectively] and the ellipticity is very large in the direction of the bond path [$\epsilon(\text{bcp})$ value, 5.3365]. It has been noted that bond ellipticities for agostic interactions at the M...H bcp are large and could provide a qualitative measure of the delocalization within the QTAIM framework.²⁵ However, it has been shown that the agostic carbon can successfully compete for the bond path to the metal with the reason so far being indeterminated²⁶ so that direct comparisons are not always possible (see later).

Turning to the QTAIM atomic basin characteristics, with the agostic bond developed and electron density from the C–H bond donated towards the metal, the charge on H8 is slightly more positive than in the free ligand [$q(\text{H})$ values, 0.056e and 0.040e respectively] as might be expected when the C–H σ bond electron density is slightly depleted; the total energy becomes more negative [$E(\text{H})$ values, -0.631 and -0.609 respectively]; the dipolarisation becomes slightly less positive [$M(\text{H})$ values, 0.099 and 0.126 respectively] and the atomic volume decreases significantly [$V(\text{H})$ values, 36.0 and 46.5 respectively].

At this stage, it should be noted that care must be taken in not interpreting the changes in the H-atomic basin as being only due to development of the agostic approach (ie donation of the C–H σ bond electron density to the metal) particularly as other orbital

contributions within the molecule could also be affecting these parameters. Keeping this point in mind, and as a descriptive starting point for the later work presented, the C8 atomic charge becomes significantly more negative than in the free ligand [$q(\text{C})$ values, -0.084e and 0.001e respectively]; the total energy changes very little [$E(\text{C})$ values, -40.1 and -38.1 respectively]; the dipolarisation becomes larger [$M(\text{C})$ values, 0.142 and 0.115 respectively] and the atomic volume decreases significantly [$V(\text{C})$ values, 69.1 and 82.3 respectively]. However, one of the purposes of the present study is to try and ascertain what the agostic effect is on these parameters

Fig. 5 (a) QTAIM molecular graph showing bond paths between H₈...Pd and OH...Cl separations for 1. (b) 2D contour plot of the Laplacian of electron density for the C–H and metal interaction for 1.

and in particular to account for any electrostatic contribution to the agostic bonding component (see later). In this regard it is noted that the agostic interaction has been regarded as purely coulombic.²⁷

For the present complex, in terms of overall atomic basin charges, the agostic H-atom would form a weak repulsive interaction with the metal [$q(\text{H})$ and $q(\text{M})$ values, 0.056e and 0.641e] and the C-atom a weak attraction [$q(\text{C})$ value, -0.084e]. However, because of the anisotropic charge distribution about the C–H bond, the accumulation of electron density towards the metal will mean that consideration of the atomic basin charges alone would overestimate the repulsion between the metal and H so that multipole terms would need to be included. If the H atom did not bend away from the metal, not only would there be an unacceptable electrostatic situation but it would come much closer to the metal centre than the current 1.819 Å.

NBO analysis²⁸ gives a valence bond approach to bonding and can be used to give a quantitative measure of the C–H bond electron delocalisation in an agostic interaction.²⁵ Use of the second order perturbation energy, $E(2)$, derived from the Natural Bond Orbitals, then allows a quantitative assessment of the orbital nature of an agostic interaction that is not available from the molecular or atomic orbitals. It should be noted that the energies obtained from molecular orbitals are meaningless which has led to the description

of using atomic orbitals for analysis as 'illustrative' only.²⁸ It should also be noted that NBO energies cannot be compared with other energies but are themselves directly comparable. The difficulties associated with the determination of the strength of an agostic interaction have been recorded²⁹ with the actual strengths being estimated at between 1 and 20 kcal mol⁻¹.^{7c, 30}

The description of the agostic donation provided for **1** by the NBO analysis shows that there are two donations of the C–H electron density to the metal and these do not involve metal d orbitals in this formally d⁸, Pd²⁺ system but instead utilise the *trans* and *cis*-related Pd–Clσ* antibonding orbitals [C–Hσ to Pd–Clσ*(*trans*) and Pd–Clσ*(*cis*), *E*(2) values, 58.6 and 10.0 kcal mol⁻¹ respectively]. Fig. 6 shows contour plots and spatial images for these orbital contributions which account for the pure agostic donation in the complex. These images also indicate further that if the H8-hydrogen did not bend away from the metal, an unacceptable orbital overlap

Fig. 6 NBO orbital overlap 2D contour and 3D spatial overlap images for **1**. Top, C–Hσ to Pd–Clσ*(*trans*) donation [*E*(2) value, 58.6 kcal mol⁻¹]. Bottom, C–Hσ to Pd–Clσ*(*cis*) donation [*E*(2) value, 10.6 kcal mol⁻¹].

condition would most probably result, especially in the case of the C–Hσ to Pd–Clσ*(*trans*) orbital donation. The NBO analysis also shows there are two small-energy back donations from the metal to the C–H antibonding orbital [LP (lone pair) Pd to C–Hσ* *E*(2) values, 2.9 and 4.9 kcal mol⁻¹ respectively] which are known features associated with agostic interactions^{7b} and represent a type of weak hydrogen bond that is repulsive in terms of the electrostatics [*q*(H) and *q*(Pd) values 0.056e and 0.0641e respectively] but attractive in terms of the weak covalent back donation. There are also slight contributions to the C–H antibonding orbital from other lone pairs (LP's) on the metal, one on the *cis*-Cl ligand and Pd–Cl bonding (BD) components [*E*(2) values range from 0.15 to 0.68 kcal mol⁻¹ (see full details in data 3 of the ESI†)] The interaction involving the C–H NBO orbitals for the complex thus provides for much stronger donation to the metal than for back-donation from it. Other work has shown that back donation can become strong in some complexes and provide a dominant 'hydrogen bonding' situation.²⁵

A major feature of the the NBO analysis is that significant bonding components that do not involve C–H bond electron density are present which have not been recognised before. Two of the aromatic ring bonding molecular orbitals donate to the two Pd–Clσ* antibonding orbitals arising on the Cl atoms that lie *trans* and *cis* to the agostic approach and these are also the antibonding orbitals that the C–Hσ electron density donates into to form the agostic covalency. One aromatic ring donation involves the π-orbital that spans the agostic and 'outer' carbons [C7–C8π to Pd–Clσ*(*trans*) and Pd–Clσ*(*cis*) donations, *E*(2) values, 20.3 and 6.5 kcal mol⁻¹] and the other and more minor component, involves the σ-orbital that spans the agostic and 'inner' carbons [C8–C8σ to Pd–Clσ*(*trans*) and Pd–Clσ*(*cis*) donations, *E*(2) values, 1.4 and 0.4 kcal mol⁻¹]. Complexes in which C–Cσ bond electron density donates to metal centres have been termed 'C–C agostic interactions'.³¹ NBO orbital 2D contour plots and 3D spatial images diagrams for the two interactions involving the aromatic ring C7–C8π orbitals are shown in Fig. 7. These plots indicate that for both interactions, it is electron density in the vicinity of C8 that is involved in the donation to the metal so that there is intimate association in the agostic complex of the metal centre and the carbon atom that will eventually form the Pd–Cσ bond in any ensuing cyclometallation reaction. The two C7–C8π donation *E*(2) values of 20.3 and 6.5 kcal mol⁻¹ compare with the (N)–OH...Cl weak hydrogen bonding component (H...Cl separation 2.092 Å) in the complex of 23.8 kcal mol⁻¹.

In regard to the two donations, it should be noted that in aromatic ring systems, σ and π orbitals do not overlap and this is the case for the C8–Hσ and C7–C8π orbital systems so that even though the two donate to the same metal-based orbitals, there is no realistic synergic effect developed and the donations are separate entities. However, the NBO analysis shows there is a small overlap of the C7–C8π orbital with the C8–Hσ* orbital (carbon end) [*E*(2) value, 3.7 kcal mol⁻¹] so that synergy is not entirely lacking.

Fig. 7 NBO orbital overlap 2D contour and 3D spatial overlap images for **1**. Top, C7–C8π to Pd–Clσ*(*trans*) donation [*E*(2) value, 20.3 kcal mol⁻¹]. Bottom, C7–C8π to Pd–Clσ*(*cis*) donation [*E*(2) value, 1.4 kcal mol⁻¹].

Although the NBO energies of the π -donations are only about one third that of the agostic donations, they still provide a 'clip' that would appear to help anchor the agostic approach and there is also the electrostatic component, albeit weak in comparison [$q(C)$ and $q(M)$ values, $-0.084e$ and $0.641e$], to consider. For donations that increase the complexity but more importantly provide an assistance to the agostic interaction, we have previously introduced the term 'syndetic' from the Greek word *syndekos* meaning 'serving to unite', 'to connect' or 'bind together'.¹¹ The agostic interaction is thus not fixed by C–H bond electron density donation to the metal alone and it appears that it can be a more complex interaction for aromatic rings than previously thought. It can be seen that aromatic ring π -orbitals adjacent to the Pd centre, are intimately, albeit weakly, involved with the metal and this has consequence for the formation of the metal carbon bond in any ensuing cyclometallation reaction.

Although not necessary for the agostic interaction identification, we have included a non-covalent-interaction (NCI) analysis for **1** to give for the first time, the characteristics for this type of weak interaction. The use of the NCI approach is useful in weak interaction situations where QTAIM analysis does not give a bond path due to a bcp and ring critical point (rcp) coalescing³² but in the present case the bcp and rcp are well separated. This approach allows the nature of weakly interacting molecular regions to be resolved from 3D NCI iso-surface plots which are based on colour gradients where red indicates destabilising interactions, blue for stabilising interactions and green for the very weak delocalised but stabilising interactions. The depth of the particular colour is associated with how strong the interaction is.³³

The iso-plot for **1** (fig. 8) shows that the agostic interaction is indicated by an outer orange disc of depletion. This type of outer ring has been interpreted as a small area of steric crowding³⁴ and is also seen for the Pd–Cl bonds but not the Pd–N bond which contains the smaller N atom. A blue disc for the interaction and the Pd–Cl bonds does not appear in this plot. The N–OH $\cdots$ Cl interaction which the NBO analysis shows is weaker than the agostic interaction is also revealed as a lighter blue iso-surface.

Features of the NCI plot not revealed by bond paths and bcp's in the QTAIM analysis are the weak intramolecular interactions

Fig. 8 NCI isosurface plot of complex **1**. The sign of the second density Hessian eigenvalue (λ_2) times the electron density is shown by the colour map.

between the C7–H atom with the *cis*-Cl ligand (distance 3.048 Å) and the (N)–OH oxygen atom with an adjacent alicyclic ring hydrogen (distance 2.640 Å) both of which show light blue-green iso-surfaces indicating weak attractive interactions.

As a final feature of the complete analysis of the agostic interaction in **1** we include the QTAIM charges for the aromatic ring of the 1-tetralone oxime free ligand and the agostic complex so that a comparison can be made as to the effect of coordination in the agostic mode. For the aromatic ring, this is an important consideration as electrophilic aromatic substitution involving Wheland character has been proposed for the metallation process subsequent to the agostic approach.⁷ The Pd $\cdots$ C separation in **1** is also quite close (2.240 Å) and the NBO analysis showed there is an intimate association of the metal and a C– π orbital close to the C8 carbon atom (fig. 7). For the carbon atoms of the aromatic ring (fig. 9), the agostic carbon (C8) becomes much more negative than in the free ligand [$q(C)$ values, $-0.084e$ and $0.001e$ respectively] and the two carbons *ortho* to this position become more positive, particularly the C7 carbon which involves the syndetic C– π donation where $q(C)$ changes from $-0.014e$ to $0.014e$. The carbon *para* to C8 also becomes more positive, but to a much smaller degree than the two *ortho* positions and there are similar small increases in positive charge from both *meta* positions. These features would appear to be associated more with electron donation out of the aromatic ring when the agostic and syndetic donations take place than any Wheland-type character. The aromatic ring hydrogens reflect this situation, with H5 and H6 becoming slightly more positive compared to the free ligand, H7, which involves the syndetic C– π donation, becomes much more positive [$q(H)$ values, $0.079e$ and $0.014e$] and the agostic hydrogen with its charge the least effected [$q(H)$ values, $0.056e$ and $0.040e$]. The small increase for H8 may be a result of Pd to C–H σ^* back donation where the two major contributions have $E(2)$ values of 4.9 and 2.9 kcal mol⁻¹.

Fig. 9 QTAIM atomic charges for aromatic ring carbon atoms [$q(H)$ values in e]. (a) 1-tetralone oxime. (b) complex **1**.

The effect of structural changes made to the ligand.

(a) (N)-OMe complex **2**

A change was made to the nature of the ligand donor N-atom to remove the (N)–OH...Cl hydrogen bonding that is present in **1** and thus allow the ligand to be unconstrained by this component. In (N)–OMe complex **2** (scheme 2) where the H-bonding is removed, there would be an apparent clash of the OMe group with the coordination plane Cl2 atom with the result that the ligand rolls slightly upwards so that the plane made by the coordination atoms now drops down the C8–H bond [see the visualisation of this in fig. 8 in the ESI†]. This change can be seen in the metrics where the Pd–N bond becomes significantly longer than for (N)–OH complex **1** (2.053 and 2.015 Å respectively) and the Cl2–Pd–C=N dihedral increases to 37.2° (14.4° in **1**) even though the alicyclic ring section

Scheme 2. Structure and important separations (Å) for **2**.

of the ligand shows very little change (e.g. N–C1–C8a–C8 dihedral angles 14.7 and 15.1° for **2** and **1** respectively).

The plane the aromatic ring makes with the coordination plane (Ar/CP angle in table 1) now increases markedly from 34.5° in **1** to 51.4° in **2**. In this case, the Pd...H separation increases significantly to 1.841 Å (1.819 Å in **1**) and the Pd...C separation becomes smaller (2.224 and 2.240 Å for **2** and **1** respectively) so that the effect of the rolling action is to take the H atom away from the metal and push the C atom towards it. The C–H bond lengthening shows little change (1.151 and 1.152 Å in **2** and **1** respectively) as does the C–H bond deformation angle out of the arene ring plane (–26.0° in **2**, –27.2° in **1**).

The calculated spectroscopic data for **2** show an up field shift in the ¹H NMR spectrum of 2.95 ppm for H8 compared with the free ligand as the hydrogen moves further away from the metal centre and possibly into a new anisotropy region¹⁴ in comparison to **1** (1.54 ppm up field shift) and the ¹JC–H coupling constant is slightly larger (105.9 Hz for **2**, 103.2 Hz for **1**; the free ligand values are essentially the same at 139.5 and 139.4 Hz respectively) indicating that there is a very slight weakening of the agostic interaction in terms of the strength of the C–H bond. The calculated C–H stretching frequency reflects this situation with a smaller shift to lower energy (660 cm^{–1} compared to 670 cm^{–1} for **1**).

In terms of the QTAIM characteristics, there is a bcp with the same electron density value as for **1** [$\rho(\text{bcp})$, 0.0820] but the Laplacian of the electron density which gives a better representation at the flat surface at the bcp, has a lower value ($\nabla^2\rho(\text{bcp})$, 0.2107; 0.2631 for **1**) [in QTAIM methodology, when

$\nabla^2\rho(\text{bcp})$ is >0, the electron density, ρ is locally depleted³⁵]. The ellipticity is now lower [$\epsilon(\text{bcp})$ value, 2.2016, 5.3365 for **1**] and –V/G more negative (–1.3165; –1.2419 for **1**). For the C–H bond electron density, there is little change for the two complexes when the complexes and ligands are compared [$\rho(\text{bcp})$ differences, 0.0464 and 0.0477 for **2** and **1** respectively].

For the atomic basin properties, with the small decrease in the electron density at the bcp in comparing **2** with **1**, the H-atomic charge is now very similar to the free ligand and there are only small changes to the other parameters which would appear to be insignificant. For the C-atomic basin, where the free ligands of both complexes have similar atomic basin properties, for the complexes, the atomic charge becomes less negative [$q(\text{C})$ values, –0.070 and –0.084 for **2** and **1** respectively] and when this occurs the carbon moves slightly closer to the metal in **2** compared to **1** (2.224 and 2.240 Å respectively) which suggests that electrostatics do not play a major role for the positioning of this atom. The energies are the same, but the dipolarisation and the volume become smaller which would fit with the expected trends.

Turning to the NBO characteristics, as the Pd–N bond length has increased (2.053 and 2.015 Å in **2** and **1** respectively) there is little change in the strength of the donation from N to the *cis*-Pd–Cl antibonding orbital but for the *trans* case, significant lowering occurs [LP(1) N to BD* Pd–Cl2 values 96.3 and 105.4 kcal mol^{–1}]. In this situation, where the ligand has rolled up a little and where the Pd...H distance in the agostic interaction has lengthened (1.841 and 1.819 Å in **2** and **1** respectively) and the Pd...C distance has decreased (2.224 and 2.240 Å in **2** and **1** respectively), the C–H bond electron density donation to the metal NBO energetics becomes marginally smaller [C–Hσ to Pd–Cl σ*(*trans*) and Pd–Cl σ*(*cis*) $E(2)$ values 57.7 and 9.5 kcal mol^{–1} in **2**; 58.6 and 10.0 kcal mol^{–1} in **1**]. Also, the donations from the metal to the C–Hσ antibonding orbital show little change as do the syndetic aromatic ring π-orbital donations to the metal (see data 3 of the ESI†). This would indicate that the ligand positional change has little effect on the agostic interaction in terms of orbital overlaps.

(b) Acetophenone oxime complexes **3** and **4**

To gain further insight into the newly identified syndetic π-donations, we have looked at analogues of **1** and **2** in which the alicyclic ring is not present (scheme 3). In this situation, the aromatic ring is free to rotate which could potentially allow the metal greater access to the aromatic ring π-electron density. This

(**3**) R = H

(**4**) R = Me

Scheme 3. Structure of acetophenone oxime complexes **3** and **4**.

type of ligand is the more usual aromatic ring system on which cyclometallation reactions are carried out for directed C–H bond functionalisations.⁴

The computed structure for [PdCl₂(acetophenone oxime)] (**3**) is shown in fig. 10 where it is compared with the structure of **1**. Comparing the agostic bond metrics of **3** with alicyclic ring complex **1**, the Pd···H separation distance is very similar (1.822 and 1.819 Å respectively) but the Pd···C separation is slightly shorter (2.228 and 2.240 Å respectively). Inspection of the other structural details (table 1) shows that they are very similar, including the aromatic ring/coordination plane angles (Ar/CP angles, 36.1 and 34.5° respectively), the C–H bond deformations (–27.1 and –27.2° respectively) and the C–H bond length (1.152 Å in both complexes; 1.090 and 1.081 Å in the respective free ligands). Overall, the C–H bonds in the two agostic complexes position in an almost identical manner and this is not dependant on whether the aromatic ring has the potential to rotate. The calculated NMR and IR data shows that the agostic interaction is equally well developed in **3** than **1** with the ¹J_{C–H} coupling constant difference to the free ligand essentially unchanged (33.0 and 33.2 Hz respectively) as are the calculated C–H stretch shifts to lower energy in comparison to the free ligand values (666.3 and 670.6 cm^{–1}).

Inspection of the QTAIM data shows that at the Pd···C bcp the electron density is equally well developed [e.g. ρ(bcp) values are both 0.2810, *H*(bcp) values, –0.0311 and –0.0379; –V/G 1.4013 and 1.5150 respectively for **3** and **1** respectively] and there is similar electron density in the C8–H bonds and the ellipticities do not differ much (compare the ρ(bcp) and ε(bcp) values for **3** and **1** in table 2). In the NBO analysis, the agostic donation is slightly smaller [C–Hσ to

Pd–Clσ*(*trans*) and Pd–Clσ*(*cis*) *E*(2) values 56.9, 8.9 kcal mol^{–1} c.f. 58.6, 10.0 kcal mol^{–1} for **3** and **1** respectively and the aromatic ring syndetic π-donation NBO *E*(2) values are essentially the same (20.3, 6.8; and 20.3, 6.5 kcal mol^{–1} for **3** and **1** respectively). However, with the unconstrained aromatic ring in **3**, the donation changes to the inner π-orbital system which is the equivalent of the C8–C8π -orbital system of tetralone oxime complex **1** rather than the C7–C8π system.

In a further study of the effect of a rotatable aromatic ring without an (N)–OH···Cl 'lock', the structure of the (N)–OMe analogue, [PdCl₂(acetophenone methoxy-oxime)] complex **4** was also calculated. In this case, the Pd···H and Pd···C separations (1.853 and 2.217 Å) are very similar to those of [PdCl₂(1-tetralone methoxy-oxime)] complex **2** (1.841 and 2.224 Å) as are the relevant angles and dihedrals for the two complexes shown in table 1. Also similar are the QTAIM and NBO parameters shown in table 2. In particular, the NBO analysis indicates the agostic donation is slightly smaller in complex **4** than in **2** [C–Hσ to Pd–Clσ*(*trans*) and Pd–Clσ*(*cis*) *E*(2) values, 53.7 and 8.0; 57.7 and 9.5 respectively] and the syndetic aromatic ring π-donations which also switch to the inner π-orbital system, are very similar [C8–C8π to Pd–Clσ*(*trans*) and Pd–Clσ*(*cis*) *E*(2) values, 19.1, 6.5 and 18.9, 6.0 kcal mol^{–1} for **4** and **2** respectively].

(c) [PdCl₂(1-tetralone)] complex 5

As the approach to catalytic activation of aromatic C–H bonds involves a variety of ligand coordinated directing groups,³ in which less-stable cyclometallates lead to better postfunctionalisation,⁴ we have also looked at the non-derivatised 1-tetralone itself as a ligand. In complex **5** (scheme 4) the oxygen atom coordinates to the Pd centre with a significantly longer bond (Pd–O bond length 2.088 Å) than the oxime derivatives [Pd–N bond lengths 2.015 and 2.053 Å respectively for the (N)–OH and (N)–OMe derivatives **1** and **2**].

Fig. 10 Comparisons of the structures of [PdCl₂(acetophenone oxime)] (**3**), [PdCl₂(1-tetralone oxime)] (**1**), [PdCl₂(acetophenone methoxy-oxime)] (**4**) and [PdCl₂(1-tetralone)] (**5**).

Scheme 4. Structure of 1-tetralone oxime complex **5**.

With oxygen as the coordinating atom, the effect on the agostic interaction in **5** (fig. 10) is to bring H8 closer to the metal centre (Pd···H separation 1.786 Å) than for the oxime ligands [Pd···H separations 1.819 and 1.841 Å for the (N)–OH and (N)–OMe derivatives respectively]. This is also the case for the C8-carbon where the Pd···C distance closes to 2.206 Å in comparison to 2.240 and 2.224 Å for oxime complexes **1** and **2**. Overall, the C–Hσ bonding component lies more squarely over the coordination plane than for the nitrogen donor ligands (fig. 8 of the ESI†). The other important structural feature pertaining to the C8–H bond is the

deformation out of the plane of the aromatic ring, which at -28.0° is slightly larger than for the oxime complexes and equates to the closest Pd $\cdots$ H separation for all the ligands (1.786 Å). However, the deformation is not much different to (N)–OH ligand complex **1** where the Pd $\cdots$ H separation is 1.819 Å.

Inspection of the spectroscopic data shows that the agostic interaction is better developed with the ketone oxygen donor present. The $^1\text{J}_{\text{C-H}}$ coupling constant is the smallest of all the previous complexes and the calculated C–H stretch shifts to the lowest energy (compare the values in table 1). For the NBO analysis, it is seen that the agostic donation for **5** is slightly larger than for all the other ligands [C–H σ to Pd–Cl $\sigma^*(\text{trans})$ and Pd–Cl $\sigma^*(\text{cis})$ $E(2)$ values, 64.4 and 9.33 kcal mol $^{-1}$ (total 73.7 kcal mol $^{-1}$); 58.6 and 10.0 kcal mol $^{-1}$ (total 68.6 kcal mol $^{-1}$) for **1**, the next highest] and the aromatic ring C7–C8 π syndetic donation is slightly lower [C7–C8 π to Pd–Cl $\sigma^*(\text{trans})$ and Pd–Cl $\sigma^*(\text{cis})$ $E(2)$ values, 17.9, 5.4 kcal mol $^{-1}$ (total 23.3 kcal mol $^{-1}$); 20.3, 6.5 kcal mol $^{-1}$ (total 26.8 kcal mol $^{-1}$) for **1**. Interestingly, the back-donation from the metal to the C8–H σ^* orbital which can be expected to further weaken that bond, is the highest of all the complexes [LP Pd to C–H $\sigma^*E(2)$ value, 8.1 kcal mol $^{-1}$ for **5**, 5.0 kcal mol $^{-1}$ for **3**, the next highest]. The Pd–O bond is significantly weaker than the Pd–N bonds in the (N)–donor ligands [$E(2)$ values, 58.2 and 6.0 kcal mol $^{-1}$ (total 64.2 kcal mol $^{-1}$) in **5**; 105.4, 17.6 kcal mol $^{-1}$ (total 123.0 kcal mol $^{-1}$) for example, in **1**]. As already mentioned, this feature is of importance in the post-functionalisation of the cyclometallate where the metal-carbon bond for this type of ligand are found to be more reactive.^{4,5}

Conclusion

The results of the work presented here indicate that a possible agostic intermediate can be seen in the NMR spectra of the reaction of 1-tetralone oxime and PdCl $_4^{2-}$ in CD $_3$ OD solution which gives rise to a cyclometallated complex but importantly, this does not show the lowering of the $^1\text{J}_{\text{C-H}}$ coupling constant normally associated with agostic approaches. The computed structure of the agostic intermediate [PdCl $_2$ (1-tetralone oxime)] (**1**) shows features associated with the carbon atom making a close approach to the metal but the H-atom bends away from it. In this situation, the aromatic ring is inclined at an angle to the metal centre and an NBO analysis indicates that C–C π orbitals donate to the same Pd–Cl σ^* orbitals as does the C–H σ bond electron density. This shows that the agostic interaction in this type of system is more complex than previously recognised in that the C–C π orbital donation would appear to add assistance to the stability of the agostic interaction. The term ‘syndetic donation’ is used to reflect the assistance the C–C π orbital donation component provides. Although the two components donate to the same metal-based orbitals, there is little evidence for any meaningful synergy between them. The syndetic donation is also present where rotatable aromatic rings engage in the agostic interaction and this is also the case where a less stable oxygen donor provides the initial coordination of the ligand rather than the more usual N atom donor. This work presents a full computational study for an agostic interaction after recognition of the new complexity that is involved with the syndetic donation. The study reveals that there can be an intimate association of an aromatic ring π -orbital with the metal in conjunction with the

agostic donation and this changes the way in which the agostic interaction has been traditionally viewed and as such, has significant implication for C–H bond activation in ligand-assisted cyclometallation reactions leading to C–C bond functionalization. Further computational studies are underway to assess the relevance of syndetic donations in transition states in catalytic cycles involving aromatic ring agostic interactions and also in the increasing number of ligand coordinated directing groups that lead to metal-carbon bond formation.

Experimental

Materials and general methods

Lithium tetrachloropalladate was prepared by adding two equivalents of anhydrous lithium chloride in water to a suspension of palladium chloride in water and stirring the mixture until the solid dissolved and a dark red solution was obtained. The solution was filtered, the solvent removed under vacuum at 80°C until a dark red hygroscopic solid was obtained which was stored under nitrogen. 1-Tetralone oxime was prepared from 1-tetralone (Aldrich) by reaction with hydroxylamine hydrochloride and sodium hydroxide in ethanol. NMR spectra were obtained on a Bruker Avance III 500 MHz spectrometer. For the NMR reaction studies, sufficient CD $_3$ OD (Aldrich) was added to Li $_2$ PdCl $_4$ and 1-tetralone oxime in separate flasks to dissolve the components and the flasks were then cooled in dry-ice acetone baths to the required temperature. The contents were mixed at this temperature and quickly transferred to an NMR tube cooled to the particular temperature and the tube was then placed in the spectrometer also cooled to this temperature. All NMR spectra were run without spinning the NMR tube.

X-ray single crystal structure determination

Low temperature³⁶ single crystal X-ray diffraction data were collected using a (Rigaku) Oxford Diffraction SuperNova diffractometer ($\lambda=1.5418\text{ Å}$). Raw frame data were reduced using CrysAlisPro and the structures were solved using 'Superflip'³⁷ before refinement with CRYSTALS³⁸ as per data 1 (CIF) of the ESI $^+$. Full refinement details are also given in data 1 (CIF) of the ESI $^+$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1560179. Copies of the data can be obtained, free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

Computational details

DFT PBE-D3³⁹ functional based geometry optimizations and vibrational calculations for the complexes **1-6** were performed using Gaussian09 (G09).⁴⁰ A triple-zeta high quality basis set (aug-cc-pVTZ-PP)⁴¹ was employed for Pd; aug-cc-pVTZ⁴² for the attached ancillary ligands (Cl atoms), agostic hydrogen and nitrogen (attached to Pd) and a double-zeta quality basis set (aug-cc-pVDZ)⁴² was used for the remainder of the atoms. All the structures were energy-minimised and no imaginary frequencies were found in the vibrational analysis. For the QTAIM analysis, the input files (.wfx) were obtained from G09⁴⁰ and QTAIM calculations were performed with the AIMALL software package.⁴³ NBO calculations were

performed with the NBO6.0 package⁴⁴ and NBOView2.0⁴⁴ was used to visualize the contours and surfaces of donor-acceptor interactions. The same procedure was used for the ligand calculations.

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