

Five-membered cyclopalladated rings: Cambridge structural database analysis of geometrical parameters and 'aromatic' character†

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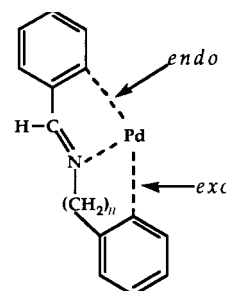
The relationship between the planarity of five-membered cyclopalladated rings and calculated aromaticity indices has been investigated. Geometrical parameters for 126 crystal structures containing the fragments $[\text{Pd}(\text{NXC}\text{Y})\text{A}_2]$ (X, Y = C or N; A = any ligand) were obtained from the Cambridge Structural Database. These were classified in terms of planarity by measuring the displacement of the N atom bonded to the Pd from the calculated mean plane formed by the other four atoms. The same classification was performed using the displacement of the Pd atom and the results compared. 'Aromaticity' indices for the five-membered cyclopalladated rings, V and HOMA, were also calculated based on experimental bond lengths and typically used in the analysis of five- or six-membered organic heterocycles. The correlation between calculated 'aromaticity' indices and planarity of the rings has been shown to be good. The stability and/or reactivity of the five-membered cyclopalladated rings suggested by the sequence of 'aromaticity' indices agrees well with the reactivity series of these compounds previously found for ligand-exchange reactions.

Organopalladium complexes have been widely studied in recent years¹ due to their use in organic and organometallic synthesis, catalysis and liquid-crystalline materials. They have also been used in mechanistic studies of oxidative addition, reductive elimination and alkyl exchange between metal centres.² Intramolecular C–H bond activation is one of the more obvious fields of interest and in the case of palladium often involves a cyclopalladated complex or indeed a cyclometallation reaction. N-Donors such as azobenzenes, imines, phenylpyridine and phenylpyrimidine, have been extensively used in cyclometallation reactions and have shown a strong tendency to form cyclopalladated five-membered rings containing square-planar Pd^{II}. For example, *N*-benzylidenamines have been used to prepare both *endo* and *exo* metalocycles,³ where the preference for *endo*-complex formation is delicately poised.

It has been suggested that since the five-membered ring of the *endo* complexes contains an N=C iminic double bond, the system is stabilized by partial electron delocalization within the ring, and therefore a certain level of 'aromaticity'.⁴ Hence, there has been some debate over the role of electron delocalization within the metalocycle as a driving force towards cyclization reactions. In addition, the electron delocalization of the Pd atom within the metalocycle could influence intermolecular interactions which are very important for mesogenic properties.

With this in mind, as the problem of aromatic character is of key importance and quite precise molecular geometries are now easily accessible (Cambridge Structural Data Base⁵), we have analysed the structures of a number of complexes containing a five-membered cyclopalladated ring. Computer structural databases can be efficiently exploited to obtain information about the relationships between various structural parameters.⁶

At the same time we have performed 'aromaticity index' calculations on the rings studied, in an attempt to correlate structural evidence of delocalization (planarity) with an accepted technique of calculating 'aromaticity' previously predominantly used in organic chemistry. If we can understand the relation between planarity and 'aromaticity' and the effect on both of the other ligands on the palladium atom, it may be possible



to begin to tailor the cyclopalladated ring to achieve the required stability or reactivity.

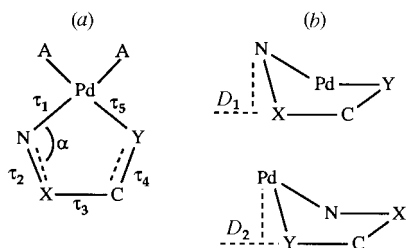
Experimental

Data retrieval

Crystal structures containing one of the submolecular fragments $[\text{Pd}(\text{NXCC})\text{A}_2]$ **1** (X = C or N) or $[\text{Pd}(\text{NCCN})\text{A}_2]$ **2** (A = any ligand) as shown in Fig. 1(a) were located from the Cambridge Structural Database (CSD). Version 5.10 (October 1995, 146272 entries) of the CSD system was used for the substructure search, geometry calculations and data analysis *via* the programs QUEST 3D⁵ and GSTAT.⁷ The search constraints were imposed by use of the CSD bit-screen mechanism⁷ to locate only those entries that had (i) error-free atomic coordinates following CSD check procedures, (ii) no reported disorder in the crystal structure and (iii) a crystallographic *R* factor ≤ 0.13 . For multiple determinations of the same structures only the most accurate have been retained. The final data files contained 138 fragments **1** from 93 structures and 36 fragments **2** from 33 structures (see SUP 57191).

In order to describe the geometric variations of the submolecular fragment **1** we analysed all the bond distances within the metalocycle and the bond angle $\alpha = \text{Pd-N-X}$ which gives information about the hybridization of the N atom. The planarity of the metalocycle ring has been studied in terms of the deviation D_1 of the N atom from the mean plane Pd–Y–C–X, or alternatively, of the Pd atom with respect to the

† Supplementary data available (No. SUP 57191, 16 pp.): refcodes, geometric parameters, aromaticities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.



- 1 X = C or N; Y = C
2 X = C, Y = N

Fig. 1 Molecular fragments located from the CSD and definitions of (a) torsion angles and (b) deviation from planarity parameters used

mean plane N-X-C-Y (D_2) [Fig. 1(b)]. In both cases the mean planes have been calculated as the least-squares best planes through the atoms.

Histograms of parameter distributions were inspected in order to assess the distribution of values. The presence of any correlation between two parameters was inspected visually using scatterplots of one parameter against the other and on a quantitative basis by the usual linear (Pearson's) correlation coefficient (ρ).⁸

The conformations of the metallocycle rings have been analysed by calculating the values of the torsion angles (τ_i , $i = 1-5$) for each fragment [Fig. 1(a)] and subsequently using a traditional approach to the conformational analysis of five-membered rings. Through a subroutine incorporated in the GSTAT package⁷ we have calculated phase and pucker parameters (ϕ and τ_{\max}) describing the conformations of the five-membered rings according to the formalism of Altona and co-workers.⁹

Calculations of aromaticity indices

The aromaticity indices chosen for this study, based on experimental bond lengths, are the ones typically used in the analysis of five- or six-membered organic heterocycles.¹⁰⁻¹²

The first index is the 'V' parameter, equation (1), also known

$$V = (100/N_0) [\sum(N - N_0)^2/n]^{1/2} \quad (1)$$

as the coefficient of variation for the bond orders of a particular heterocycle, where N_0 is the arithmetic mean of the various bond orders N and n is the number of bonds.¹⁰ For a fully delocalized heterocycle, $V = 0$. The bond orders N are given by $[(R^{-2} - R_2^{-2})/(R_2^{-2} - R_1^{-2})] + 2$,¹¹ where R is the bond length of any bond with bond order N and R_1 and R_2 are the single and the double bond lengths between the same atomic pair. In order to estimate the bond orders for the Pd-N and Pd-C bonds of the cyclopalladated rings we require ideal values for single and 'double' bond lengths. To find them we used the CSD to search for Pd-CH₃, Pd-NH₃, Pd-CO and Pd-NO₂ bonds. The average values found for the first two provide our ideal values for the single bond lengths. The Pd-CO and Pd-NO₂ bonds should provide our ideal values for the 'double' bond lengths. While there is clear evidence of strong π back bonding for the Pd-CO bond, the Pd-NO₂ is not the best example of a π interaction. However, the choice was determined by the absence of a suitable large number of structures containing more representative examples of Pd-N π back bonding. The value obtained for both the Pd-C and Pd-N single-bond lengths was 2.10 Å (ranging from 2.16 to 2.03 Å) and that for both the 'double'-bond lengths was 1.90 Å (ranging from 2.01 to 1.82 Å).

Another method for estimating the aromatic character of rings based on structural data is the HOMA index of aromaticity, equation (2).¹² It is important for our studies that the

$$\text{HOMA} = 1 - \left[\alpha \sum_i^N (R^{\text{opt}} - R_i)^2 / N \right] \quad (2)$$

Table 1 Values of R^{opt} and α for C-C, N-C, N-N and Pd-N, C bonds used for the calculation of HOMA

Bond	$R/\text{Å}$		$R^{\text{opt}}/\text{Å}$	α°
	Single	Double		
C-C ^a	1.524	1.334	1.397	98.89
C-N ^a	1.465	1.269	1.334	93.52
N-N ^a	1.420	1.254	1.309	130.33
Pd-N, C ^b	2.10	1.99	1.967	90.12

^a Ref. 12. ^b This paper.

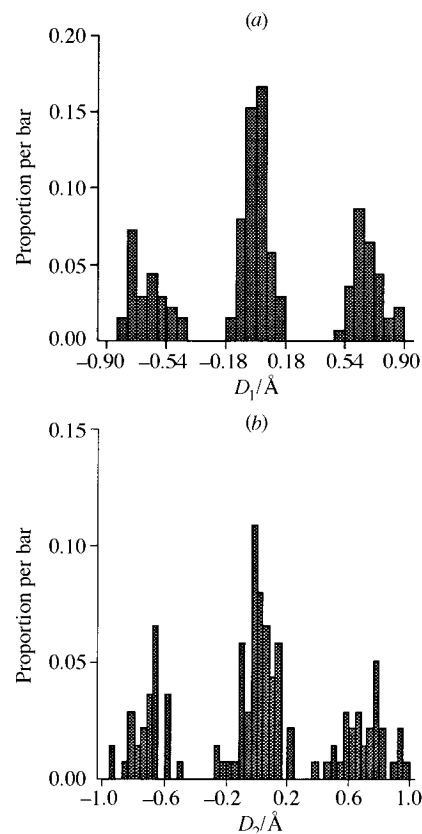


Fig. 2 Histograms of the deviation from planarity parameters (a) D_1 and (b) D_2

HOMA treatment is not limited to hydrocarbon systems only. Here R^{opt} is an empirically estimated optimum bond length, α is an empirical constant dependent upon the kind of bond, R_i is the bond length being considered and N is the number of bonds taken into consideration. Table 1 lists the R^{opt} and α values used in this work. The single- and 'double'-bond lengths of 2.10 and 1.90 Å for Pd-N and Pd-C used to calculate the V index allowed us to calculate the R^{opt} and α values reported in Table 1. The HOMA index is equal to 1 for benzene in which all R_i bonds would have optimum or close to optimum lengths, R^{opt} , and equal to 0 for a Kekulé structure with localized π electrons.

Results and Discussion

Five-membered cyclopalladated ring conformations

Bearing in mind that the aim of this work is to relate the structural evidence of aromaticity (planarity) in five-membered cyclopalladated rings to a quantitative analysis of aromaticity, we have investigated the relationships between various structural parameters.

The distributions of parameters D_1 and D_2 for the fragments [Pd(NXCC)A₂] **1** are shown in Fig. 2(a) and 2(b). In both cases the distribution is symmetrically centred around $D_{1,2} = 0$, where

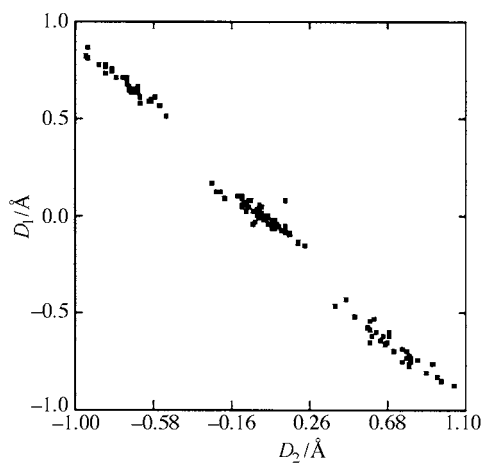


Fig. 3 Deviation from planarity parameters D_1 and D_2 for fragment **1** plotted one against the other

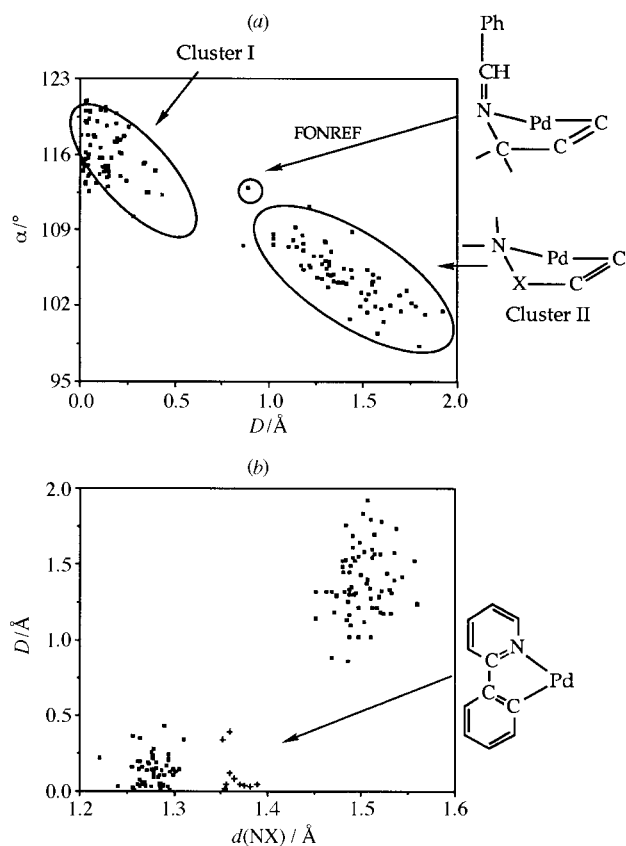


Fig. 4 Deviation from planarity parameter $D = |D_1| + |D_2|$ for fragment **1** plotted against (a) the bond angle α , (b) the bond distance $d(\text{NX})$

the $[\text{Pd}(\text{NXCC})\text{A}_2]$ fragment is essentially planar. The maximum deviations from planarity are represented by structures having $D_1 = 0.88, -0.83 \text{ \AA}$ and $D_2 = 1.04, -0.93 \text{ \AA}$, in which the N and the Pd atoms lie out of the mean planes through the PdCCX and NXCC units, respectively. As shown in Fig. 3 the parameters D_1 and D_2 are correlated indicating that they can both represent a measure of planarity. Given this correlation, we decided to use the parameter $D = |D_1| + |D_2|$ as our measure of planarity.

The planarity and the deviations from planarity in the metal-cycle rings are related to the hybridization of the N atom. Indeed, a strong negative correlation between the parameter D and the bond angle α is observed ($\rho = -0.95$). In the scatterplot Fig. 4(a) we can clearly distinguish between two clusters of

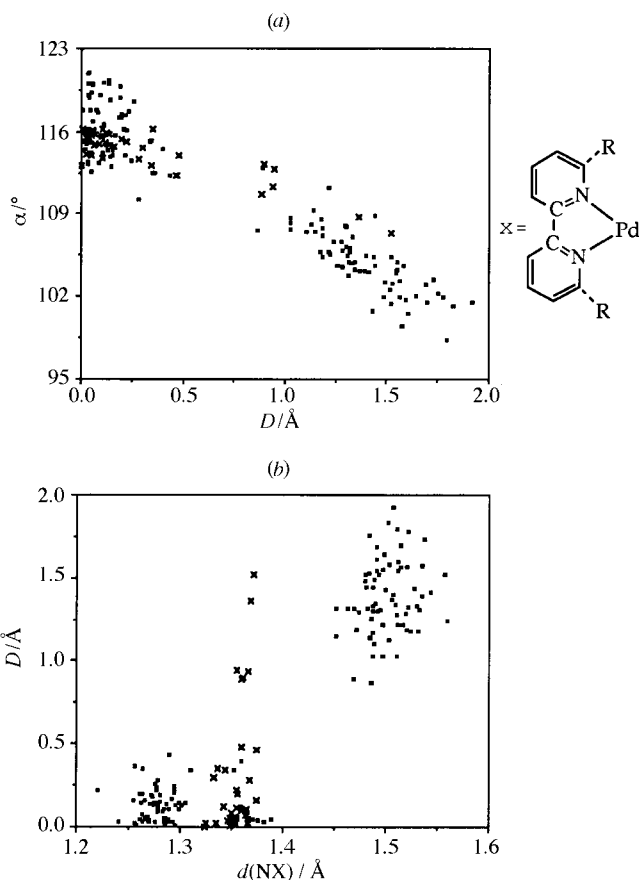


Fig. 5 Deviation from planarity parameter D for fragments **1** and **2** plotted against (a) the bond angle α , (b) the bond distance $d(\text{NX})$

data points: cluster I includes the structures of azobenzenes, imine and 2-phenylpyridine derivatives; II includes the structures of amine derivatives. The deviations from planarity increase when the value of α decreases from 120 [structures in cluster I, Fig. 4(a)] to 107.4° [structures in cluster II, Fig. 4(a)]. All the structures of the imine derivatives, found in cluster I, with near-planar metallocycle rings, contain five-membered *endo* complexes with a Pd-C_{aromatic} bond. It is well known that in systems where there is the possibility of a choice between several modes of metallation, five-membered *endo* compounds containing Pd-C_{aromatic} bonds are obtained.^{3,4} The only structure containing an exocyclic five-membered ring is $[\text{Pd}(\text{acac})(\text{C}_6\text{H}_4\text{CH}_2\text{N}=\text{CHC}_6\text{H}_5)]$ [CSD refcode FONREF, acac = acetylacetonate; see Fig. 4(a)].¹³ Although it possesses a Pd-C_{aromatic} bond and the N atom is sp^2 hybridized, the $d(\text{NC})$ bond distance within the five-membered cyclopalladated ring is typical of a single bond. The five-membered ring is not completely planar (as would have been expected for a ring containing an sp^2 N atom), D being 0.887 and 1.213 Å respectively for the two molecules in the asymmetric unit.

As shown in Fig. 4(b), the parameter D is positively correlated with the bond distance $d(\text{NX})$ ($\rho = 0.94$). The maximum deviation from planarity is associated with sp^3 -hybridized N atoms within the cyclopalladated ring and corresponds to $d(\text{NX})$ values typical for a single bond. The points marked '+' in Fig. 4(b) belong to structures of 2-phenylpyridine derivatives [cluster I, Fig. 4(a)] and the cyclopalladated ring is close to planar, a feature clearly imposed by the geometry of such a ligand. The $d(\text{NX})$, X = C, bond distances in these cases are typical values for an aromatic N=C bond.

Different distributions of points are obtained when the parameters of the submolecular fragment $[\text{Pd}(\text{NCCN})\text{A}_2]$ **2** [Fig. 5(a) and 5(b)] are included in this analysis. All the type **2** fragments contain 2,2'-bipyridine as the chelate ligand. As we

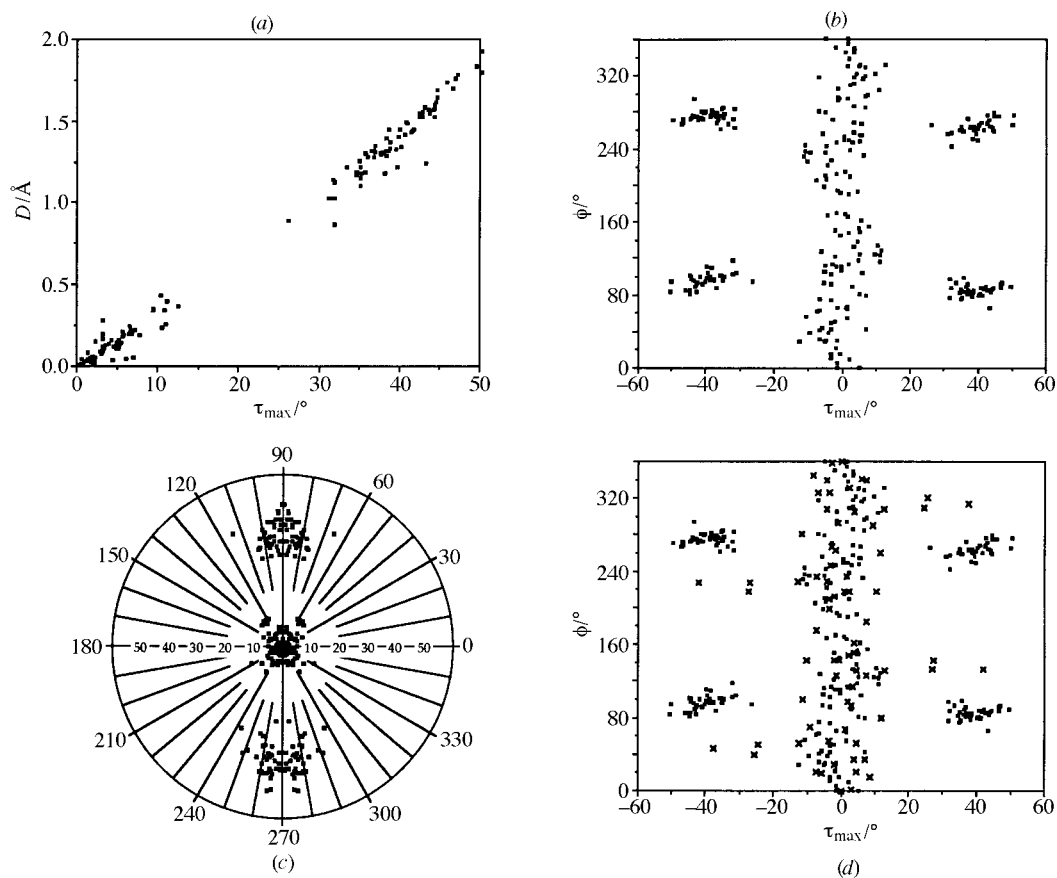


Fig. 6 Deviation from planarity parameter D for fragment **1** plotted against the maximum angle of torsion τ_{\max} in (a); plots of five-membered ring conformations for fragment **1**, (b) and (c), and for fragments **1** and **2**, (d)

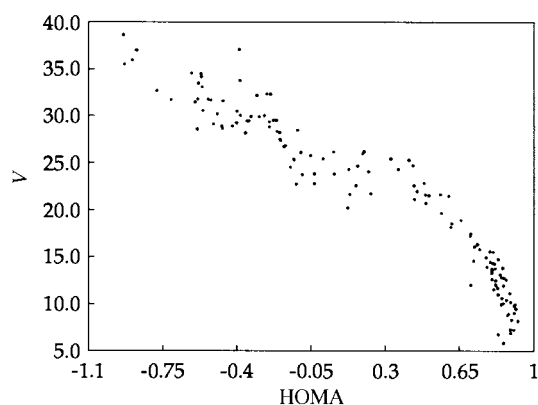


Fig. 7 Aromaticity indices (V and HOMA) plotted one against another

have seen in the case of 2-phenylpyridine derivatives, the five-membered ring in fragment **2** is expected to be planar. As shown in Fig. 5(a), few structures deviate from planarity and in all of these cases the bipyridine ligand is *ortho* substituted with respect to the N atoms. Any deviation from planarity observed in these cases may be attributed to steric effects and it is directly proportional to the bulkiness of the *ortho* bipyridine substituents. The $d(\text{NC})$ distances in fragment **2** are characteristic of an N–C aromatic bond distance; $d(\text{NC})$ was not found to be correlated to D , presumably because the deviation from planarity is caused by effects [see Fig. 5(b)] other than the hybridization of the N atom.

In order to analyse the five-membered cyclopalladated ring conformations in more detail we have used a description of puckering and conformation in terms of the maximum angle of torsion (τ_{\max}) and of the 'phase angle' (ϕ);⁹ τ_{\max} is another para-

meter which measures the planarity of the five-membered cyclopalladated rings and is correlated to the parameter D , as is shown in Fig. 6(a). For fragment $[\text{Pd}(\text{NXCC})\text{A}_2]$ **1**, Fig. 6(b) illustrates that 68 structures lie in the region where τ_{\max} is $0 \pm 18^\circ$, which implies that almost half the structures have a planar five-membered ring. On the other hand, 70 structures lie in the region where τ_{\max} is $37.5 \pm 13^\circ$. These clusters of points correspond to the regions $\phi = 90 \pm 18$ and $270 \pm 18^\circ$. The non-planar five-membered cyclopalladated rings of fragment **1** preferentially adopt envelope conformations defined by $\phi = 90$ and 270° . In our case, the values 90 ± 18 and $270 \pm 18^\circ$ of ϕ correspond to conformations close to the ideal envelope but include those distorted to the nearest asymmetric envelope along the pseudo-rotation pathway [Fig. 6(c)]. Finally, there are no structures at all with ideal twist five-membered cyclopalladated rings, a conformation which would correspond to ϕ values of 0 and 180° in these plots [Fig. 6(c)].

Fig. 6(d) illustrates the distribution of points when fragment **2** is included. Most of the structures are planar and thus they lie in the central region of the scatterplots. The few non-planar fragments show a very distorted envelope conformation.

Aromatic character of the five-membered cyclopalladated rings

Correlation between aromaticity indices and deviation from planarity (D). As we have already pointed out, the analysis of the submolecular fragments $[\text{Pd}(\text{NXCC})\text{A}_2]$ **1** ($X = \text{C}$ or N) includes structures in which two conjugated double bonds are present within the system $-\text{N}=\text{X}-\text{C}=\text{C}-$ as well as those in which the double bond $-\text{N}=\text{X}-$ is not present. In the former case the presence of the two double bonds and the filled palladium d orbitals of appropriate symmetry was proposed by Crociani *et al.*¹⁴ as a condition for the formation of five-membered

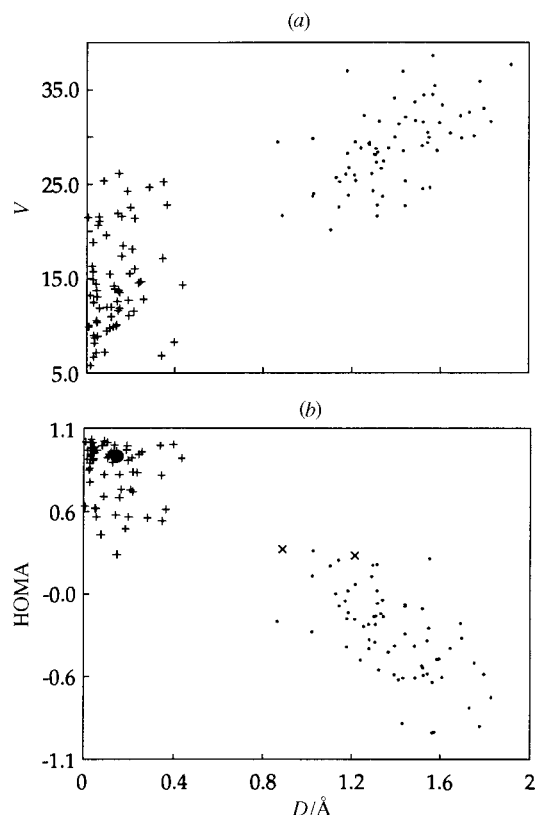


Fig. 8 Deviation from planarity parameter D for fragment **1** plotted against aromaticity index (a) V and (b) HOMA; ● and x denote the FONRAB and FONREF refcodes

aromatic rings. Therefore, given that there are cases in which aromaticity is expected and other cases in which there is little or no aromaticity (because of the absence of the two conjugated double bonds), we aimed to find a consistent method to quantify the degree of aromaticity (or non-aromaticity) of the five-membered cyclopalladated rings.

The aromaticity indices V and HOMA (see Experimental section) have been plotted one against the other providing evidence of the agreement between them (Fig. 7). Since these indices depend only on the bond lengths while the planarity measure does not, both V and HOMA have been plotted against the parameter D showing evidence of their possible correlation with the deviation from planarity of the five-membered cyclopalladated rings [Fig. 8(a) and 8(b)]. The results shown here are consistent with a loss of aromatic character resulting in increasing deviation from planarity. Each aromaticity index moves towards its indicative maximum when the parameter D approaches 0. Therefore, V is positively correlated to D while HOMA is negatively correlated to it. The points marked '+' in Fig. 8(a) and 8(b) belong to crystal structures containing an sp^2 -hybridized N atom and a planar or nearly planar five-membered cyclopalladated ring, that is cluster I [see Fig. 4(a)].

We would like to highlight at this point the difference between the aromatic character of *endo*- and *exo*-cyclopalladated rings. As shown in Fig. 8(b), for example, the HOMA values corresponding to the crystal structures of $[\text{Pd}(\text{acac})(\text{C}_6\text{H}_4\text{CH}=\text{NCH}_2\text{C}_6\text{H}_5)]$ and $[\text{Pd}(\text{acac})(\text{C}_6\text{H}_4\text{CH}_2\text{N}=\text{CHC}_6\text{H}_5)]$ (from CSD FONRAB and FONREF¹³) are very different. The HOMA value for the former compound (an endocyclic five-membered ring) is 0.825 indicating that the cyclopalladated ring could be considered as an 'aromatic system'. The exocyclic five-membered ring has HOMA values of 0.235 and 0.196 and thus shows much less aromatic character. Therefore, these results confirm that the aromatic character of the cyclopalladated rings in the *endo* adducts could be the main factor determining their preferred formation.

Since the delocalization within the five-membered cyclopalladated ring would be mainly reflected in the shortening of the Pd←N bond, we have plotted the $d(\text{PdN})$ distances against V and HOMA [Fig. 9(a) and Fig. 9(b)]. In both cases there is a correlation between them, where the shortest $d(\text{PdN})$ bond distance corresponds to the 'most aromatic' system.

Aromatic character and palladium π back-bonding ability.

The $d(\text{PdN})$ bond distance seems to control the level of aromaticity within the cyclopalladated five-membered rings. As shown in Fig. 9(a) and 9(b), an increase in the $d(\text{PdN})$ bond distance is associated with decreased aromatic character even in the cases of planar or nearly planar five-membered rings (cluster I). The $d(\text{PdN})$ bond distance is influenced by the nature of the *trans* A ligand. A systematic classification is not possible at this stage of the study, but we can deduce from the experimental evidence that the greater the π -acceptor ability of A the weaker is the Pd–N π bond. Most of the structures with a reduced aromatic character have Pd–P and Pd–S bonds *trans* to the Pd–N bond. In these cases we find the maximum $d(\text{PdN})$ bond distances, the average value of which is 2.10 Å.

This effect is more evident when we include the fragment $[\text{Pd}(\text{NCCN})\text{A}_2]$ **2** in this analysis, points x in Fig. 9(c) and 9(d). In this case all the structures have two conjugated double bonds –N=X–C=N– and therefore the possibility to form five-membered 'aromatic' rings. Indeed, we can see that in Fig. 9(c) and 9(d) the aromatic character decreases with increasing $d(\text{PdN})$ bond distance, or alternatively with decreasing ability of the Pd atom to back bond with the N atom.

The difference in aromatic character within the five-membered cyclopalladated ring is reflected in a different reactivity of the whole system. The sequence of increasing 'aromaticity' of the cyclopalladated compounds that our results suggest is the same as the decreasing reactivity sequence obtained from studies of ligand-exchange reactions,^{15,16} *i.e.* (a) the lower aromaticity indices of complexes containing the amine ligands {non-planar, non-aromatic $[\text{Pd}(\text{NXCC})\text{A}_2]$, X = C or N, fragments} correspond to greater reactivity in ligand-exchange reactions, (b) the higher aromaticity indices of the *endo*-palladacycles formed in the imine derivatives correspond to their preferred formation in cyclization reactions with respect to the *exo* adducts.

Conclusion

We began this study of structural parameters and 'aromaticity' in five-membered cyclopalladated systems with the intention of determining whether there existed a relationship between the two, and if so was it merely qualitative or could it in fact be quantified. We have shown that there is a clear relation between structural parameters and 'aromaticity' as determined using two methods of calculating aromaticity indices more usually applied to organic heterocycles.

The methodology used in this work is aimed at giving information about the stability and/or reactivity of cyclopalladated complexes with specific reference to the level of 'aromaticity' (as calculated by V and HOMA indices) in the five-membered cyclopalladated rings. It is noteworthy that the sequence of reactivity in terms of calculated aromatic character is confirmed by the studies of ligand-exchange reactions carried out by Sales and co-workers.¹⁵

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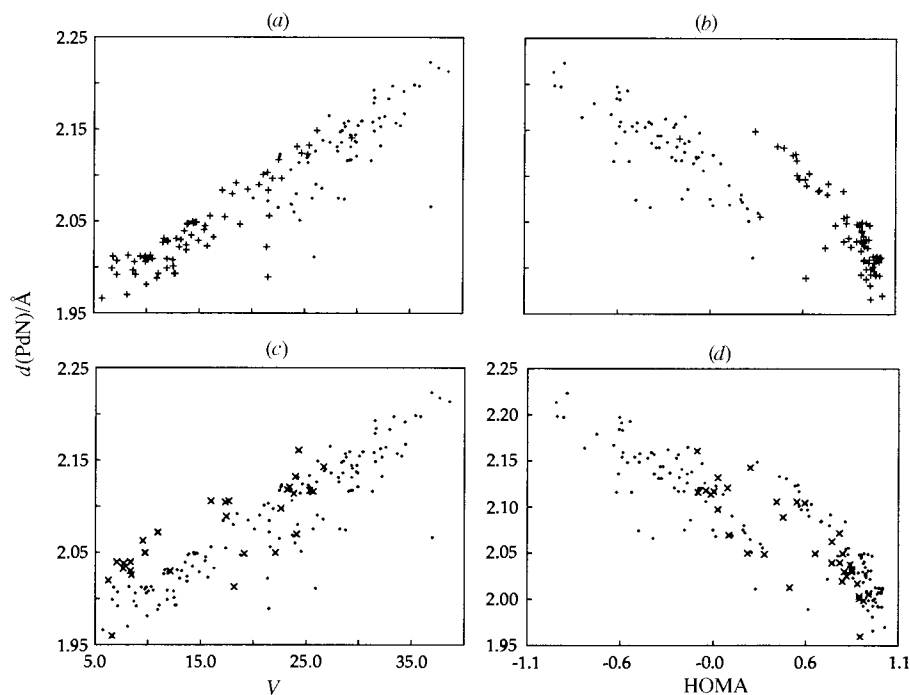


Fig. 9 The bond distance $d(NX)$ plotted against V and HOMA for fragment **1**, (a) and (b), where the sign '+' denotes structures containing an sp^2 -hybridized N atom; (c) and (d) for fragments **1** and **2** (points x)

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