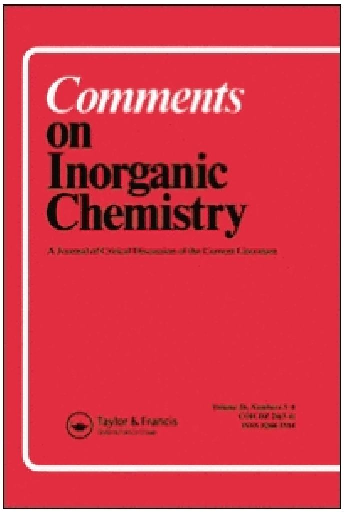


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Dinuclear Cyclopalladated Azobenzene Complexes: Crystal Structure Analysis of Homologous Series

Mauro Ghedini[a]; Alessandra Crispini[a]
[a] Dipartimento di Chimica, Universitd della Calabria, Italy

To cite this Article Ghedini, Mauro and Crispini, Alessandra(1999) 'Dinuclear Cyclopalladated Azobenzene Complexes: Crystal Structure Analysis of Homologous Series', Comments on Inorganic Chemistry, 21: 1, 53 — 68

To link to this Article: DOI: 10.1080/02603599908020415

URL: http://dx.doi.org/10.1080/02603599908020415

Dinuclear Cyclopalladated Azobenzene Complexes: Crystal Structure Analysis of Homologous Series

MAURO GHEDINI* and ALESSANDRA CRISPINI

Dipartimento di Chimica,
Universitá della Calabria,
I-87030 Arcavacata (CS), Italy

(Received 10 December, 1997)

Organometallic palladium(II) complexes obtained by cyclometallation reactions of azobenzene ligands or Schiff bases are of considerable interest in the context of practical applications such as lumunescent or liquid-crystalline materials. The shape and the dimensions of the molecules can play an important role in the physical properties of these new molecular materials. Various dinuclear cyclopalladated azobenzene complexes structurally characterised are reviewed with the intention to provide insights into the design of new dimeric metallomesogens with a suitable molecular shape.

Keywords: *metallomesogens, dinuclear cyclopalladated complexes, X-ray molecular structures, molecular fragment analysis*

INTRODUCTION

Cyclometallated compounds are organometallic species where an additional coordination of the metal to a donor atom of the same ligand sta-

---

* Correspondence Author.

Comments Inorg. Chem.
1999, Vol. 21, No. 1-3, pp. 53-68
Reprints available directly from the publisher
Photocopying permitted by license only

bilizes the carbon-metal σ bond. The stability of the resulting metal-containing ring is the reason which has motivated several investigations into the mechanisms of important catalytic processes, since it can be regarded as a possible intermediate in metal-catalyzed C-H bond activation.[1] However, the properties of the wide number of cyclometallated complexes described in these studies suggest that they can be useful, besides being model compounds, for certain practical applications such as luminescent[2] or liquid-crystalline materials.[3]

With reference to the latter topic the synthesis of thermotropic metal-containing liquid crystals (metallomesogens) is usually accomplished by reaction between a mesogenic ligand and the appropriate metal source. Accordingly, a large number of mesogenic organometallic palladium(II) complexes have been obtained by cyclometallation reactions of azobenzene ligands or Schiff bases. The products are dinuclear compounds whose molecular structures consist of two cyclopalladated halves connected by the anions formerly bonded to the palladium(II) precursor. The phase diagram of these materials has shown that the inclusion of the metal centre increases the transition temperatures by around 100°C and sometimes thermal decomposition takes place.[4] However, it has been proven that cyclopalladation of mesogenic azobenzenes induces a moderate luminescence[5] and, possibly, photorefractivity.[6] Therefore, a more thorough knowledge of the structural features of cyclopalladated species is of interest in the synthesis of new molecular materials.

The purpose of the present work is to analyse the molecular structures of a homologous series of dipalladium(II) complexes in order to provide an insight into the design of new compounds with a molecular shape suitable for dimeric metallomesogens safely processable with reference to thermal decomposition. The problems encountered in growing single crystals of mesogenic cyclopalladated complexes has resulted in the inclusion of species with any thermotropic behaviour but with a very similar geometric structure into the ensemble of compounds investigated. The objective is to rationalise the effects exerted on the global geometry of the molecule by the bridging ligands between the palladium(II) atoms and the different types of cyclopalladated ligands.

MOLECULAR FRAGMENT ANALYSIS OF DINUCLEAR CYCLOPALLADATED COMPLEXES

The dinuclear cyclopalladated complexes structurally analysed here contain certain molecular fragments which characterise the whole geometrical structure (Fig. 1a-c).

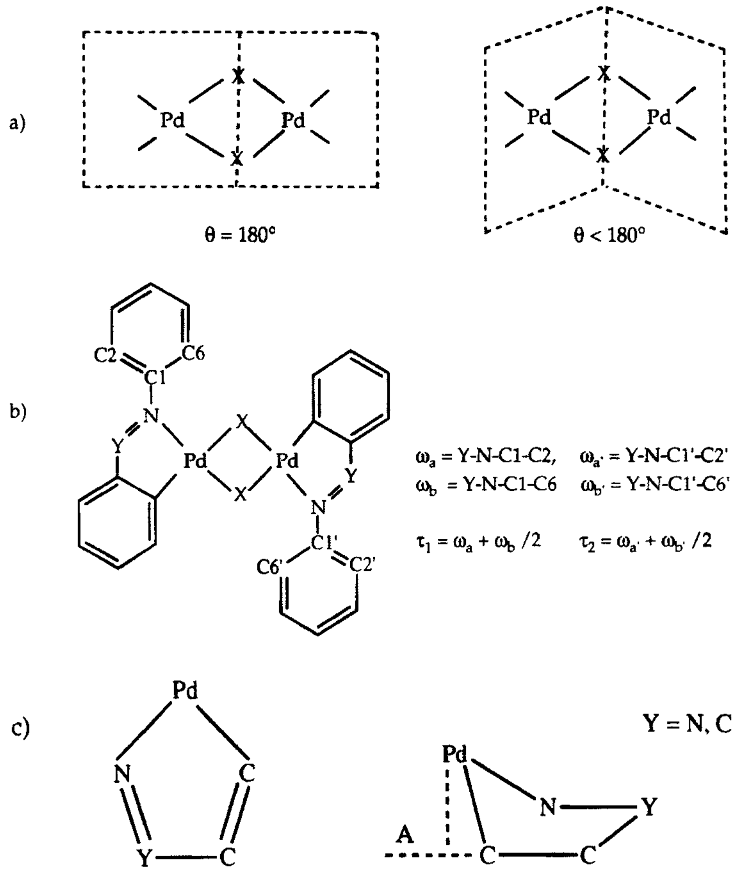


FIGURE 1 Molecular fragments and definitions of (a) dihedral angle θ, (b) Figure mean torsion angles τ_1 and τ_2 and (c) deviation from planarity in five-membered cyclopalladated ring

Since we are dealing with dinuclear complexes containing bridging ligands between metal centres, two possible structural arrangements emerge: the central Pd_2X_2 ring can be planar or hinged (Fig. 1a). The dihedral angle θ between the local coordination planes $Pd(1)X_2$ and $Pd(2)X_2$ of 180° gives rise to a global planar geometry; less than 180° leads to a hinged structure. The separation between the two PdX_2 units (the Pd-Pd intramolecular non-bonding distance, *d*), which is an important parameter in the calculation of the molecular dimensions, is related to the nature and type of the bridging ligands.

A further parameter which should be considered is the orientation of the two rotationally free phenyl rings of the azobenzene or imine ligands with respect to the planar core of the molecule described by the two mean torsion angles τ_1 and τ_2 (Fig. 1(b)). The coplanarity of the two phenyl rings with the central core depends mainly on the position of their substituents (if any)[7] and influences the molecular packing more than the crystal structure itself.

Finally, the five-membered cyclopalladated rings are expected to be planar in any cyclopalladated complex containing azobenzene or imine as the chelate ligands. The planarity of the five-membered cyclopalladated rings is described in terms of the deviation of the Pd atom with respect to the mean plane N-Y-C-C (*A*) (Fig. 1(c)).

1. Geometrical Influence of the Bridging Ligand

In order to evaluate the possible structural differences induced by the bridging ligand a systematic single-crystal X-ray study on a homologous series of $Pd_2(\mu\text{-}X)_2$ was required. For this purpose, dinuclear halo-bridged cyclopalladated complexes of the general formula $[(\text{Azo-6})Pd(\mu\text{-}X)]_2$ [H(Azo-6) = 4,4′–bis-hexyloxyazobenzene; X = Cl, (**1**), X = Br, (**2**), X = I, (**3**)] have been synthesized and structurally characterized.[8,9] The structure of the chloro-bridged derivative is shown in Fig. 2. Since the complexes **1**, **2** and **3** crystallize in the monoclinic space group $P2_1/c$ and are isomorphous, the only possible differences in geometrical parameters are observed within the Pd_2X_2 central core.

The size of the halogen bridging ligand influences the Pd-Pd intramolecular non-bonding distance *d*. In fact, the value of *d* increases in the order Cl < Br < I, being 3.528(1), 3.674(2) and 3.890(2) Å for X = Cl, Br, I. However, the geometry of the Pd_2X_2 ring is not related to the

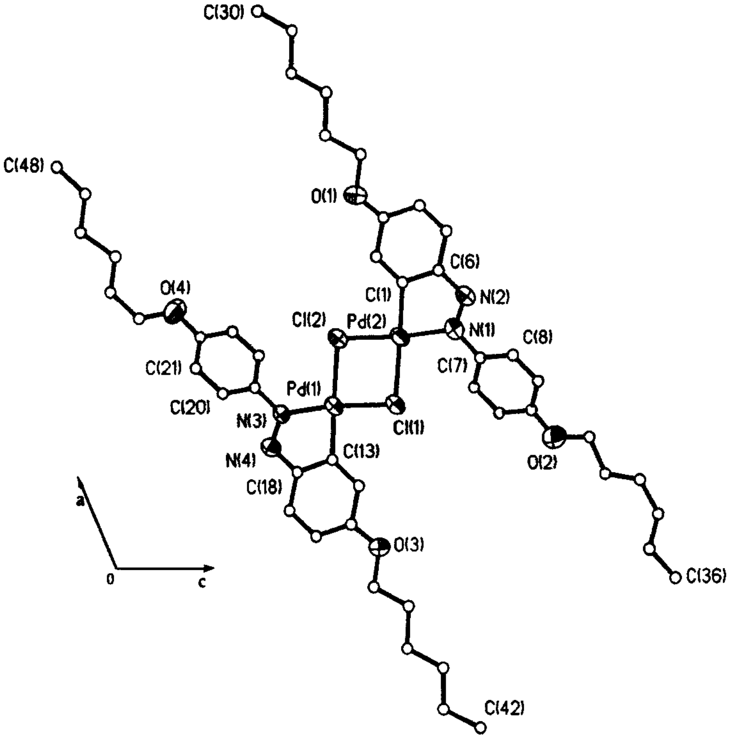
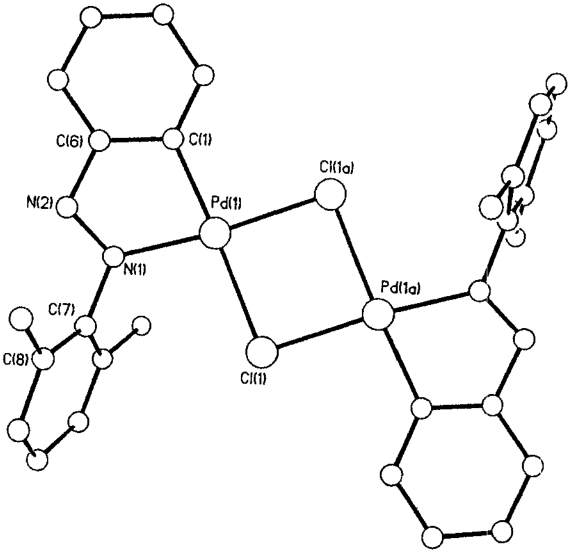
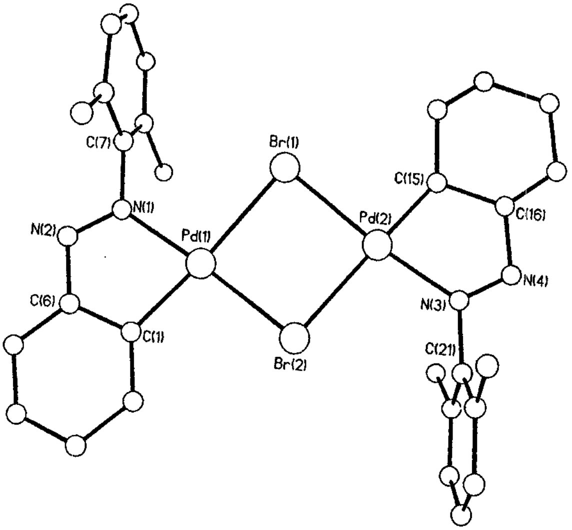


FIGURE 2 Molecular structure of complex $[(\text{Azo-6})\text{Pd}(\mu\text{-Cl})]_2$ (1) (from Ref. 8)

nature of the bridging ligand as the values of the dihedral angle θ have been found to be very similar in all three cases. The Pd_2X_2 rings exhibit a slight folding and the dihedral angles are 14.5° for complex **1**, 13.0° for complex **2** and 12.8°, for complex **3**.

In similar $[(L')Pd(\mu\text{-}X)]_2$ complexes [HL′ = 2, 6-dimethylazobenzene; X = Cl (**4**), Br (**5**), I (**6**)] only the chloro-bridged derivative has been found to have a global planar geometry with θ = 180° (Fig. 3(a)).[10] Both complexes **5** and **6** exhibit a hinged structure with dihedral angles of 15.1(1) and 19.8°, respectively (Fig. 3(b) and (c)).[11] The relationship between the *d* parameter and the nature of the halogen bridged ligand in complexes **4**, **5** and **6** confirms the relationship found in complexes **1**, **2** and **3**, as is shown in Fig. 4.


C(6)
C(1)
Cl(1a)
N(2)
Pd(1)
N(1)
Pd(1a)
C(7)
C(8)
Cl(1)


C(7)
Br(1)
N(1)
N(2)
Pd(1)
Pd(2)
C(15)
C(16)
N(4)
N(3)
C(6)
C(1)
C(21)
Br(2)

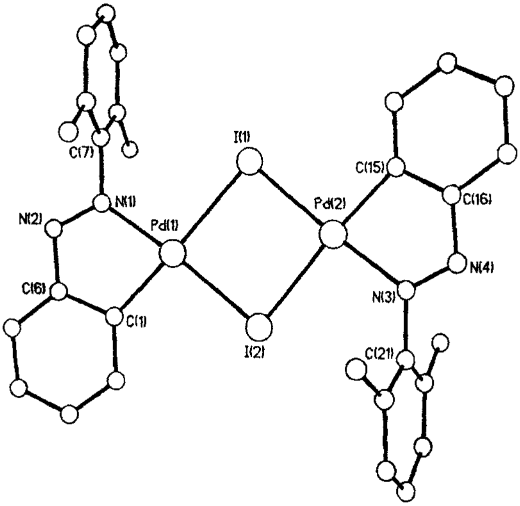


FIGURE 3 Molecular structure of complexes (a) $[(L')Pd(\mu\text{-}Cl)]_2$(**4**), (b) $[(L')Pd(\mu\text{-}Br)]_2$ (**5**) and (c) $[(L')Pd(\mu\text{-}I)]_2$ (**6**) (from Refs. 10 and 11)

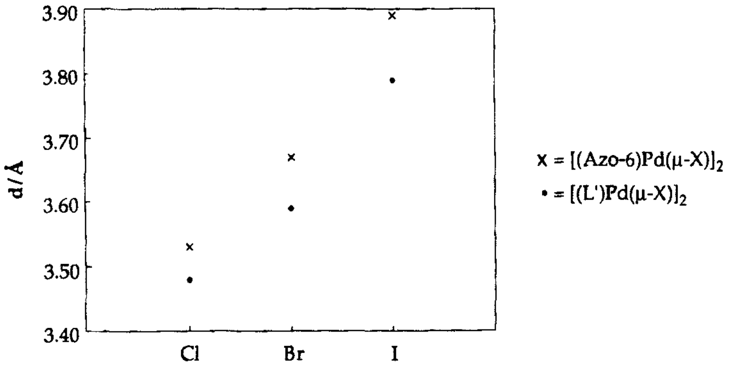


FIGURE 4 Pd-Pd intramolecular non-bonding distance *d* for complexes **1–6** plotted against the halogen bridged ligands

The geometry of the Pd_2X_2 central ring can be drastically changed by replacing the halogen atoms for bridging groups. The crystal structure of $[(L')Pd(\mu\text{-}X)]_2$ complexes where X is thiocyanate (**7**), azide (**8**) and acetato (**9**) have been resolved.[12] Substitution of bridging X^- by SCN^- is known to increase the metal-metal distance within $M\text{-}X_2\text{-}M$ groups when the SCN^- ion bridges the two metals through N and S atoms.[13] In fact, in complex $[(L')Pd(\mu\text{-}SCN)]_2$ (**7**) (Fig. 5) the two bridging thiocyanate ligands give a Pd-Pd intramolecular distance of 5.575(3) Å.

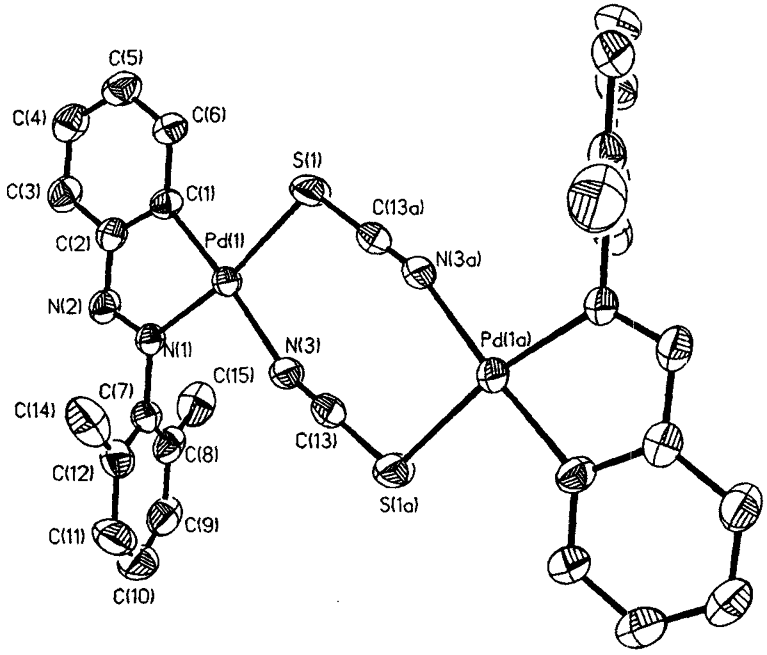


FIGURE 5 Molecular structure of complex $[(L')Pd(\mu\text{-}SCN)]_2$ (7)

The eight-membered $Pd_2(SCN)_2$ ring adopts a planar comformation as observed in other $M\text{-}SCN_2\text{-}M$ complexes.[14] Moreover the atoms of the $Pd_2(SCN)_2$ ring and the atoms of the five-membered cyclopalladated ring are approximately coplanar with a dihedral angle of 6.2(1)°. The bond lengths and angles have their expected values with a $Pd\text{-}N\equiv C$ angle of 160.6(6)°. The bond distances and angles within the cyclopalladated 2,6-dimethylazobenzene ligand are also found to be in good agreement with those observed for the previously described complexes.

Examples of decreased dinuclear centre dimensions are represented by complexes **8** and **9**. In binuclear complexes, where the azide group may function as a bridging group, the M-M intramolecular distance depends strongly whether the azide coordinates through the same nitrogen or the two end nitrogen atoms.[15] Complex $[(L')Pd(\mu^2\text{-}1,1\text{-}N_3)]_2$ (**8**) is one of the few examples of a dipalladium(II) compound containing an azide ligand bridged via a single nitrogen atom (Fig. 6). The Pd_2N_2 central ring is strictly planar and the Pd-Pd non-bonding separation of 3.283(1) Å is slightly smaller than the value of 3.478(1) Å observed in complex **4**.[10] The bond angles Pd(1)-N(3)-Pd(1a), Pd(1)-N(3)-N(4) and N(3)-N(4)-N(5) of 102.2(1), 130.6(3) and 179.1(6)° are comparable to those observed in other μ^2-1,1-N_3 dipalladium(II) complexes.[16]

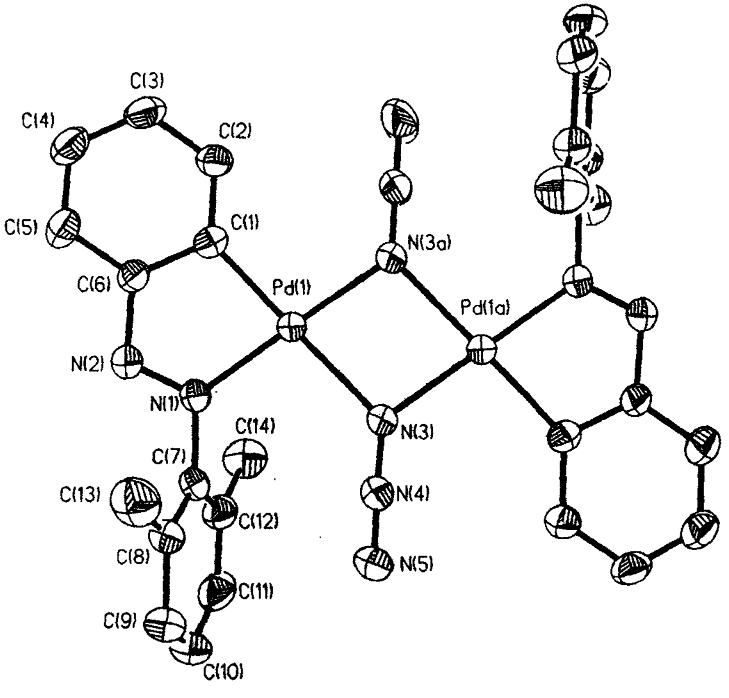


FIGURE 6 Molecular structure of complex $[(L')Pd(\mu^2\text{-}1,1\text{-}N_3)]_2$ (**8**)

A completly different global geometry is expected from the acetato-bridged dimer $[(L')Pd(\mu\text{-}OAc)]_2$ (**9**) (Fig. 7). In complex **9** each palladium atom has a slightly distorted square-planar coordination geometry comprised of two *cis* oxygen atoms from each of the two bridging acetates. The central part of the molecule has a boat conformation which is the geometry usually found in other acetato-bridged complexes.[17,18] The two mutually *cis* μ-acetate ligands force the cyclopalladated 2,6-dimethylazobenzene ligands to lie above one another in the dimeric molecule. However, the interligand repulsion in this case is stronger than the one found in other cyclopalladated μ-acetate complexes,[19] due to the presence of two methyl groups in *ortho* positions on the rotationally free phenyl rings. The coordination planes of the palladium atoms are tilted at an angle of 49.1(2)°. The non-bonding Pd-Pd distance of 3.196(3) Å is in the range observed for other μ-acetate palladium complexes in which the dihedral angle between the coordination planes is around 40°.[19,20]

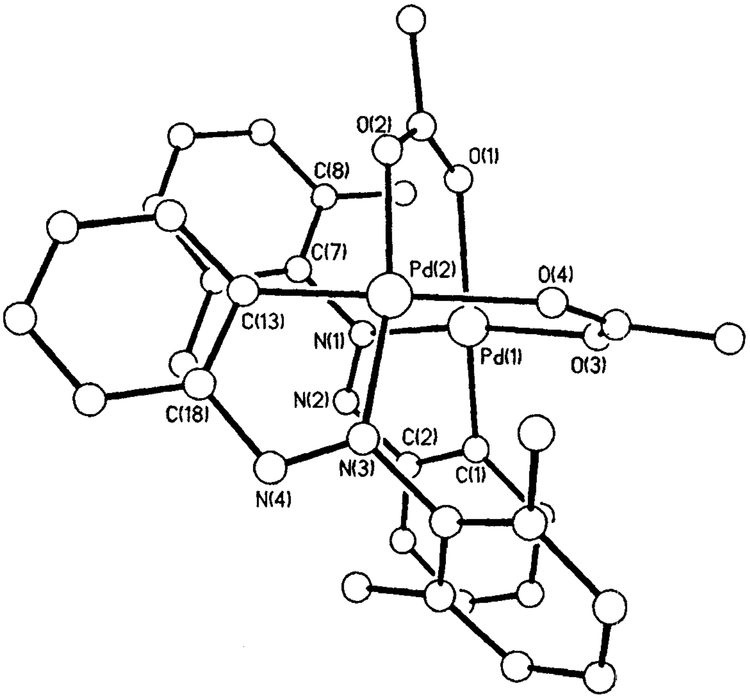


FIGURE 7 Molecular structure of complex $[(\mathrm{L}')\mathrm{Pd}(\mu\text{-OAc})]_2$ (9)

2. Geometrical Influence of the Cyclopalladated Ligand

N-donors such as azobenzenes and benzylideneamines are exstensively used in cyclopalladation reactions and they have a strong tendency to form cyclopalladated five-membered rings containing square-planar Pd(II).[21]

In the series of complexes $[(\text{Azo-6})\text{Pd}(\mu\text{-X})]_2$ the planarity of the whole molecule is broken by the twist of the two rotationally free phenyl rings, and the torsion angles τ_1 and τ_2 are found to be 35.3(1)° and 38.7(1)° in **1**, 36.8(2)° and 38.8(2)° in **2**, 40.8(3)° and 39.8(3)° in **3**. The values of τ_1 and τ_2 do not seem to be influenced by the nature of the halo-bridged ligand. Other examples of halo-bridged cyclopalladated complexes arising from azobenzenes not substituted in *ortho* positions are the μ-chloro 4-methyl-4'-hydroxyazobenzene derivative (complex **10**, Fig. 8(a)) [tilt angles of 28(1)° and 36(2)°] and the μ-chloro 4,4'-bis-hexylazobenzene derivative (complex **11**, Fig. 8(b)) [tilt angle of 55(3)°].[22]

The degree of twist of the rotationally free phenyl rings increases with the presence of non-hydrogen atoms at the *ortho* positions. In fact, for $[(\text{L}')\text{Pd}(\mu\text{-X})]_2$ complexes the presence of two methyl groups in *ortho* positions gives rise to a more pronounced loss of planarity. The values of τ_1 and τ_2 for complexes **4–9** are summarized in Table I.

TABLE I Values of τ_1 and τ_2 for $[(\text{L}')\text{Pd}(\mu\text{-X})]_2$ complexes

$[(L')Pd(\mu\text{-}X)]_2$	τ_1 (°)	τ_2 (°)
4	109.0, 79.7	75.1
5	84.5	99.6
6	86.1	95.1
7	74.4	74.4
8	69.8	69.8
9	65.5	72.0

The degree of planarity in terms of the geometry of the Pd_2X_2 central core and the twist of the rotationally free phenyl rings appears to influ-

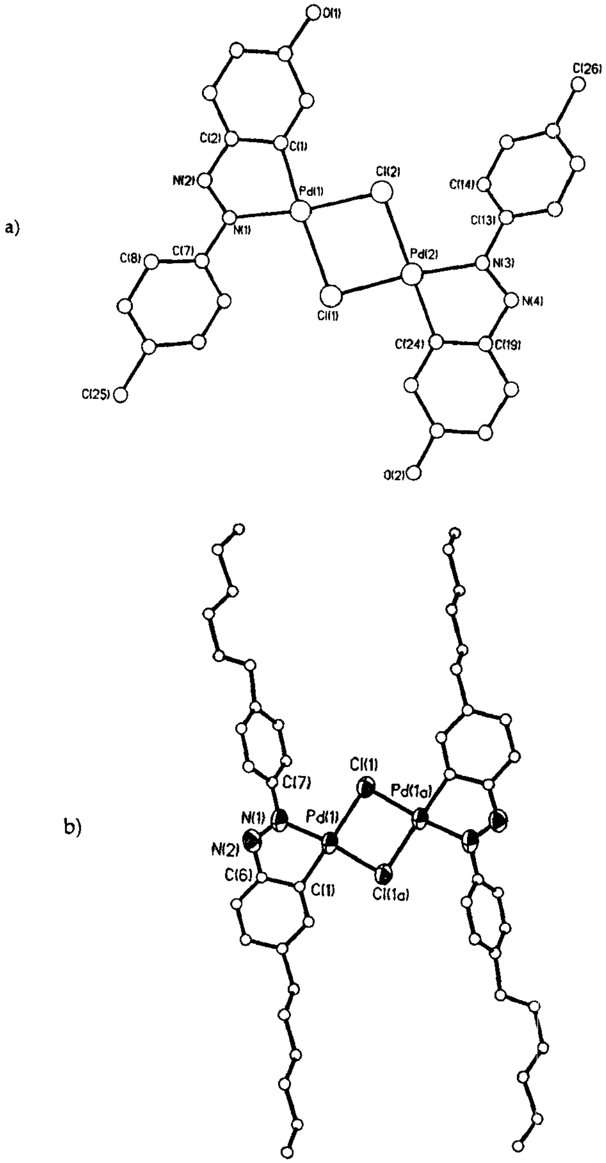


FIGURE 8 Molecular structure of complexes (a) **10** and (b) **11**

ence the molecular packing in these complexes: short intermolecular Pd-Pd contacts (D) are only found in complexes with a planar or nearly planar Pd_2X_2 central core and azobenzenes not substituted in *ortho* positions. For example, the value of D ranges from 3.668(1) Å in complex **1** to 3.758(3) Å in complex **3**. Short intermolecular contacts were not observed for any of the homologous $[(L')Pd(\mu\text{-}X)]_2$ complexes.

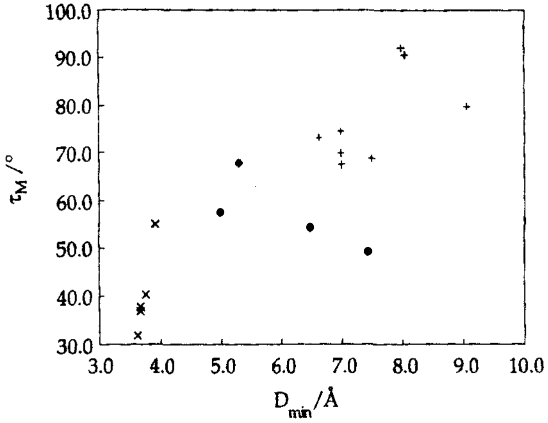


FIGURE 9 Shortest Pd-Pd intermolecular contact D_{min} for cyclopalladated complexes contaning azobenzene and benzylideneamine ligands plotted against the mean torsion angle τ_M ($\tau_M = \tau_1 + \tau_2/2$)

It is possible to quantitatively rationalise the correlation between planarity and molecular packing by plotting the mean torsion angle τ_M ($\tau_M = \tau_1 + \tau_2/2$) against the shortest Pd-Pd intermolecular contact, D_{min}. As shown in Fig. 9, a positive correlation between τ_M and D_{min} is observed. In the scatterplot of Fig. 9 we can distinguish between crystal structures of cyclopalladated complexes containing azobenzenes not substituted in *ortho* positions (points marked "x" in the low region of D_{min}) and crystal structures of $[(L')Pd(\mu\text{-}X)]_2$ complexes (points marked "+" in the region from 6.0 to 9.0 Å of D_{min}). The effect of the geometry of the Pd_2X_2 central ring on the molecular packing is evident if we include in the analysis crystal structures of cyclopalladated complexes containing benzylideneamines not substituted in *ortho* positions and containing a non-planar Pd_2X_2 central ring (points marked "♦", Fig. 9).[19b,23,24] In these cases the values of D_{min} lie in the middle region of the scatterplot (between 4.5 and 7.5 Å). Therefore, short intermolecular Pd-Pd contacts seem to depend both on the loss of planarity due to the geometry of the Pd_2X_2 central core and the degree of twist of the rotationally free phenyl rings. The crystal structure of $[(L'')Pd(\mu\text{-}Cl)]_2$ [HL'' = 2,6-dimethyl-N-(benzylidene)aniline] is also included in this analysis, and the values of τ_M and D_{min} of 67.4(1)° and 6.99 Å, respectively, are in the region of cyclopalladated complexes containing rotationally free phenyl rings *ortho* substituted with bulky methyl groups (Fig. 9). Moreover, in this complex the Pd_2Cl_2 central core is not planar and has shown a folding of 36.7(1)°.[25]

3. Five-Membered Cyclopalladated Rings

With reference to our recent study,[26] the planarity and the deviation from planarity in metallacycle rings are related to the hybridization of the N atom.

In particular, when the five-membered cyclopalladated ring belongs to complexes containing azobenzene or Schiff bases as chelate ligand, the presence of an sp^2-hybridized N atom within the ring assures the planarity of the molecular fragment. This geometric feature combined with the presence of two double bonds (-N=Y-C=C-, see Fig. 1(c)) and filled palladium d orbitals of appropriate symmetry are conditions for the formation of five-membered "aromatic" rings. In fact, we proved that planarity and level of "aromaticity" in terms of calculated "aromaticity" indices are positively correlated, indicating that the cyclopalladated ring under discussion could be considered an "aromatic" system.

CONCLUSIONS

The aim of this structural analysis is to investigate the role that different molecular fragments which are part of dinuclear cyclopalladated complexes play in thermotropic mesomorphism. As we have already pointed out, the palladium containing five-membered rings are essentially planar and the partial electron delocalization within the ring implies a certain level of "aromaticity."[26] Therefore, in the complexes under discussion each moiety consists of three aromatic rings of which two are coplanar, the five-membered ring and the palladated phenyl ring; the third phenyl ring is usually twisted about the C-N bond away from the bridging ligands. Moreover, the nature and type of the bridging ligands control the global geometry of the molecule and consequently its dimensions.

We are aware that the molecular geometries which result from room temperature single crystal X-ray analysis cannot be representative of the actual geometry which the compounds adopt in the high temperature mesophases. Then, speculations concerning the mutual geometry of molecular fragments should not be immediately correlated to the mesomorphic behaviour. However, the case of a system involving fused rings formed by the palladacycle and the palladated phenyl ring where the planarity and, to some extent, the electron delocalization can play an important role in mesomorphism is different. In particular, as far as rod-like thermotropic organic liquid crystals are concerned, a simple model requires that to produce a mesophase the length of the flexible tails (i.e., aliphatic chains) and the size of the rigid molecular core (i.e., conjugate aromatic rings) have to be appropriately balanced.[27] The role of these two being such that when the contribution of the flexible tail prevails, the transition temperature decreases, whereas if the contribution of the rigid core prevails, the transition temperature increases.[28] In fact, according to this approach, strong intermolecular core-core interactions have been invoked in order to explain both the increase of the transition temperatures or the lack of mesomorphism that the palladium complexes show with respect to the unmetalated ligands.[3]

Remarkably, the present investigation proves that in the case of rod-like liquid-crystalline cyclopalladated complexes, the presence of partially aromatic cyclopalladated rings increases the intermolecular π-π interactions and is responsible for increased transition temperatures. However, it has been shown that substituents in *ortho* positions of the unmetalated phenyl ring increase the intermolecular Pd-Pd separation. Moreover, provided that the whole molecule preserves a pro-mesogenic geometry, appropriate substituents with a moderate steric demand can reduce the intermolecular interactions and decrease the transition temperatures.

In conclusion, in the case of dinuclear cyclopalladated azobenzenes, the crystal structure analysis has the potential to be successfully combined with investigations on thermotropic mesomorphism in order to reliably relate molecular parameters and physical properties.

References

1. Ryabov A. D. *Chem. Rev.*, **1990**, *90*, 403.
2. Maestri M.; Balzani V.; Deuschel-Cornioley C.; Von Zelewsky A. *Adv. Photochem.*, **1992**, *17*, 1.
3. (a) Hudson S.A.; Maitlis P.M. *Chem. Rev.*, **1993**, *93*, 861; (b) Ghedini M.; Omenat A. *J. Chem. Soc., Chem. Commun.*, **1994**, 1309; (c) Rowe K.E.; Bruce D.W. *J. Chem. Soc., Dalton Trans.*, **1996**, 3913; (d) Neve F.; Ghedini M.; Crispini A. *J. Chem. Soc., Chem. Commun.*, **1996**, 2463; (e) Ghedini M.; Pucci D.; Neve F. *J. Chem. Soc., Chem. Commun.*, **1996**, 137.
4. Serrano J. L. "*Metallomesogens*," VCH, Weinheim, West Germany, **1996.**
5. Ghedini M.; Pucci D.; Calogero G.; Barigelletti F. *Chem. Phys. Lett.*, **1997**, *267*, 341.
6. Ghedini M.; Aiello I.; Roviello A. *Acta Polym.*, 1997, 48, 400.
7. Klebe G. *J. Mol. Struct. (Theochem)*, **1994,** *308*, 53.
8. Ghedini M.; Crispini A.; Morrone S.; Pucci D.; Francescangeli O. *Liq. Cryst.*, **1996,** *20*, 67.
9. Crispini A.; Ghedini M.; Pucci D.; Aiello I., in preparation.
10. Armentano S.; Crispini A.; De Munno G.; Ghedini M.; Neve F. *Acta Cryst., Sect. C*, **1991,** *47*, 966.
11. Ghedini M.; Crispini A.; Neve F. *J. Organomet. Chem.*, **1993**, *448*, 241.
12. Crispini A., results unpublished.
13. Dockum B.W.; Eisman G.A.; Witten E.H.; Reiff W.M. *Inorg. Chem.*, **1983**, *22*, 150.
14. Gregory U.A.; Jarvis J.A.J.; Kilbourn B.T.; Owston P. G. *J. Chem. Soc. A*, **1970,** 2770.
15. Dori Z.; Ziolo R.F.; *Chem. Rev.*, **1973**, *73*, 247.
16. Fehlhammer W.P.; Dahl L.F. *J. Am. Chem. Soc.*, **1972**, *94*, 3377.
17. (a) Wong-Ng W.; Cheng P.T.; Kocman V.; Luth H.; Nyburg S.C. *Inorg. Chem.*, **1979,** *18*, 2620;(b) Wehman E.; van Koten G.; Jastrzebski J.T.B.H.; Ossor H.; Pfeffer M. *J. Chem. Soc., Dalton Trans.*, **1988**, 2975.
18. Ghedini M.; Pucci D.; De Munno G.; Viterbo D.; Neve F.; Armentano S. *Chem. Mater.*, **1991**, *3*, 65.
19. (a) Churchill M.R.; Wasserman H.J.; Young G.J. *Inorg. Chem.*, **1980,** *19*, 762, (b) Navarro-Ranninger C.; Zamora F.; Lopez-Solera I.; Monge A.; Masaguer J.R. *J. Organomet. Chem.*, **1996,** *506*, 149.
20. (a) Gayoso M.; Alonso M.; Vila J.M.; Rivero E.B.; Hiller W.; Strahle J. Acta Cryst., *Sect. C*, **1988**, *44*, 929; (b) Garcia-Ruano J.L.; Lopez-Solera I.; Masaguer J.R.; Navarro-Ranninger C.; Rodriguez J.H.; Martinez-Carrera S. *Organometallics*, **1992,** *11*, 3013; (c) Blanco J.; Gayoso J.; Vila J.M.; Gayoso M.; Maichle-Mossmer C.; Strahle J. *Z. Naturforsch., Teil B*, **1993**, *48*, 903.
21. Albert J.; Ceder R.M.; Gomez M.; Granell J.; Sales J. *Organometallics*, **1992**, *11*, 1536.
22. Armentano S.; Crispini A.; De Munno G.; Ghedini M.; Neve F. *Acta Cryst., Sect. C*, **1991,** *47*, 2545.
23. Ghedini M.; Armentano S.; De Munno G.; Crispini A.; Neve F. *Liq. Cryst.*, **1990,** *8*, 739.
24. Albinati A.; Pregosin P.S.; Ruedi R. *Helv. Chim. Acta*, **1985**, *68*, 2046.
25. Crispini A.; De Munno G.; Ghedini M.; Neve F. *J. Organomet. Chem.*, **1992**, *427*, 409.
26. Crispini A.; Ghedini M. *J. Chem. Soc., Dalton Trans.*, **1997**, 75.
27. Vertogen G.; de Jeu, W.H. "*Thermotropic Liquid Crystals, Fundamentals*,"Springer Verlag, Heidelberg, Germany, **1988.**
28. Kelker, H.; Hatz R. "*Hanbook of Liquid Crystals*," Verlag Chemie, Weinheim, West Germany, **1980.**