Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 3648

www.rsc.org/dalton

PAPER

Unexpected isomerism in "[Pd(2,9-dimethylphenanthroline)X_2]" (X = Cl, Br, I) complexes: a neutral and an ionic form exist†

Martino Rimoldi,[a] Fabio Ragaini,*[a] Emma Gallo,[a] Francesco Ferretti,[a] Piero Macchi[b] and Nicola Casati‡[a,c]

Received 19th October 2011, Accepted 5th January 2012
DOI: 10.1039/c2dt11979j

Complexes of composition "[Pd(2,9-dimethylphenanthroline)X_2]" (X = Cl, Br, I) have long been known and they are used as precursors for the synthesis of other derivatives or as catalysts. In the previous literature, they have invariably been described as neutral square planar complexes, but we have found that a second ionic isomer also exists, having composition $[Pd(Neoc)_2X]_2[Pd_2X_6]$, and that the formation of this isomer occurs under a wider range of conditions than that of the neutral one. Retrospectively, the ionic isomer had surely been obtained in most previous reports even if formation of the neutral one was claimed.

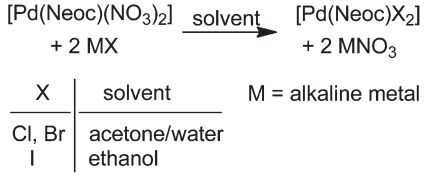
Introduction

Phenanthroline and substituted phenanthroline complexes have played a key role in the development of coordination[1] and organometallic chemistry and are actually finding increasing applications in homogeneous catalysis.[2–5] Among the members of this class of ligands, 2,9-dimethyl-1,10-phenanthroline (neocuproine, Neoc), its derivative 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (batocuproine), and the related 6,6′-dimethyl-2,2′-bipyridine have attracted special attention because the steric hindrance caused by the two methyl groups stabilises unusual coordination geometries and stabilises the formation of otherwise unstable adducts.[6–9] As a consequence, they have been shown to lead to higher catalytic activities with respect to unhindered phenanthrolines when employed as ligands for several palladium catalysed reactions, including the Heck reaction,[10] the oxidative Heck arylation of olefins by boronic acids,[11–14] the production of hydrogen peroxide,[15,16] the oxidative carbonylation of phenols,[17–19] and especially the alcohol oxidation by dioxygen.[20–31]

Palladium neocuproine halide complexes have been known for 40 years[32] and are often used as the starting material for the synthesis of more complex compounds or are proposed to be generated under catalytic conditions. Different synthetic approaches have been reported for their preparation, but the products are invariably formulated as $[Pd(Neoc)X_2]$ (X = Cl, Br, I). We have recently become interested in the use of palladium neocuproine complexes in the context of a mechanistic study of the palladium–phenanthroline catalysed carbonylation reaction of nitroarenes to carbamates.[33,34] While further investigating the reactivity of $[Pd(Neoc)Cl_2]$, we realised that even minor variations in the synthetic procedure led to products that displayed completely different solubility behaviour despite having the same elemental analysis, always in agreement with that calculated for the expected product.

A closer inspection of the literature shows that some inconsistencies in the reported solubility of $[Pd(Neoc)X_2]$ (X = Cl, Br, I) complexes are indeed present, which had been apparently overlooked by many scientists, including ourselves. Compounds of general formula $[Pd(Neoc)X_2]$ were reported for the first time in the literature in 1971,[32] obtained by stirring a suspension of $[Pd(Neoc)(NO_3)_2]$ in acetone–water (X = Cl, Br) or in ethanol (X = I) with a "large excess of alkali halide" for several hours (no more detail was given in the paper). The precipitated compounds were then recrystallised from chloroform, indicating that they are at least partially soluble in this solvent (Scheme 1).

The compounds thus synthesised were characterised by elemental analysis and UV spectroscopy. In a following paper,[35] compounds obtained in the same way were characterised by ^1H NMR ($CDCl_3$) spectroscopy, again implying they are soluble enough in chloroform.

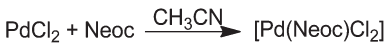


Scheme 1

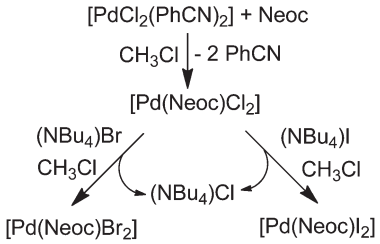
[a]*Università degli Studi di Milano, Dipartimento di Chimica Inorganica, Metallorganica e Analitica "Lamberto Malatesta" and ISTM-CNR, Via Venezian 21, 20133 Milano, Italy. E-mail: fabio.ragaini@unimi.it; Fax: + (39)0250314405; Tel: + (39)0250314405*
[b]*Department of Chemistry and Biochemistry, University of Bern Freiestrasse 3, CH3012 Bern, CH*
[c]*Università degli Studi di Milano, Dipartimento di Chimica Strutturale e Stereochimica Inorganica, via Venezian 21, 20133 Milano, Italy*

†Electronic supplementary information (ESI) available: ^1H NMR spectra of **1a**, **2a**, and **3a**. CCDC reference numbers 843108–843112. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt11979j

‡Present address: Diamond Light Source Ltd, Harwell Science and Innovation Campus, Chilton, OX110DE, UK.



Scheme 2



Scheme 3

Following works by Newkome[36,37] reported a different synthesis for [Pd(Neoc)Cl_2] (Scheme 2).

To a stirred acetonitrile solution of neocuproine, $PdCl_2$ dissolved in warm acetonitrile ([Pd$(CH_3CN)_2Cl_2$] is generated *in situ*) was added and the solution stirred for 2 h at room temperature. A crystalline precipitate was formed. In the same paper it was remarked that NMR characterisation was not possible because of the low solubility of the product in standard NMR solvents. This suggests that in fact the compound obtained was not the same as that in the previously mentioned works.

Later, Fanizzi obtained [Pd(Neoc)Cl_2] by treating a chloroform solution of [Pd$(PhCN)_2Cl_2$] with neocuproine.[38] The corresponding bromide and iodide complexes were obtained from [Pd(Neoc)Cl_2] by an exchange reaction with the corresponding tetrabutylammonium halides in the same solvent (Scheme 3).

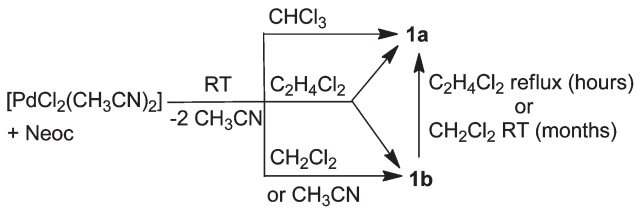
^{1}H NMR characterisation was possible only for X = Cl, Br, whereas the low solubility of [Pd(Neoc)I_2] did not allow the recording of the spectrum. However, elemental analysis confirmed the supposed composition.

Being interested in revealing the real identity of those products, we started a more careful investigation of these apparently trivial compounds and found that two structural isomers exist for each of the compounds in the series, one of which had escaped identification for more than 40 years, despite having previously been obtained in several cases. In recent years, it has emerged that the way palladium–phosphine complexes are prepared can change the final product and, especially, its catalytic activity.[39–41] In this paper, we demonstrate that a similar problem can also occur with a nitrogen ligand and we stress that more attention should be paid in correctly identifying the actual species employed or generated *in situ* than done in the past.

Results and discussion

Syntheses and molecular structures

Our initial observations originated by solubility differences obtained when [Pd(Neoc)Cl_2] was prepared by reaction of [Pd$(CH_3CN)_2Cl_2$] with neocuproine in either chloroform or methylene chloride. Whereas the product of the reaction in chloroform (**1a**) showed a good solubility in both $CHCl_3$ and CH_2Cl_2, that obtained from methylene chloride (**1b**), both at room and reflux temperature, was completely insoluble in both chlorinated solvents. However, elemental analyses of both **1a** and **1b** perfectly matched the expected composition. If the reaction was performed in 1,2-dichloroethane, the outcome depended on the temperature. If the reaction was run at reflux, only **1a** was obtained, whereas running it at RT resulted in a mixture of the two. Refluxing the so obtained mixture in $C_2H_4Cl_2$ for several hours resulted in the complete conversion of **1b** into **1a**. The same conversion also occurred in CH_2Cl_2 at RT, but it took several months to reach completion (Scheme 4). As mentioned in the introduction, Newkome reported the product of the reaction of [Pd$(CH_3CN)_2Cl_2$] with neocuproine in CH_3CN to be insoluble in standard NMR solvents.[36,37] However, since the reported yield was not quantitative, it may be doubted whether some "soluble" product was also formed and lost during the workup. We thus repeated this reaction and only insoluble **1b** was obtained (Scheme 4).



Scheme 4

These data strongly suggest that **1a** and **1b** are isomers and that the former is the thermodynamically favoured one, although formation of **1b** may be faster under some conditions. Since no geometric isomerism is possible for a square planar complex with a chelating ligand, the two compounds should be structural isomers.

The same series of reactions was performed starting from [Pd$(CH_3CN)_2Br_2$]. At variance from the chloride complex, in all cases only an insoluble compound, **2b**, was obtained, irrespective of the solvent and reaction temperature. In the case of the reaction run at RT in $CHCl_3$, the product contained less neocuproine than expected and was apparently contaminated by some $PdBr_2$. A small amount of a different soluble compound (see later) remained in solution. However, the soluble isomer **2a** was cleanly obtained by exchange of **1a** with tetrabutylammonium bromide in chloroform, in agreement with Fanizzi.[38]

We also investigated another approach to the synthesis of **2**, that is the direct reaction of palladium acetate, neocuproine and NaBr in methanol. This represents a slight modification of the procedure already used by Aresta *et al.* to prepare [Pd(Phen)I_2].[42] The procedure resulted in the formation of **2b** only if the reaction was run at RT, whereas formation of metallic palladium was observed in refluxing methanol.

As already reported in the literature,[43] [Pd$(CH_3CN)_2I_2$] is not stable and thus it could not be used as starting material to synthesise **3**. Both the reaction of palladium acetate with neocuproine and KI in methanol and the exchange reaction from **1a** afforded insoluble **3b**. Only by applying the original protocol, employing [Pd(Neoc)$(NO_3)_2$] as starting material, was some soluble **3a**, in mixture with **3b**, obtained.

Having a clearer picture of which conditions are suitable to obtain each isomer, we next started a series of attempts to grow crystals of the different compounds in order to unequivocally

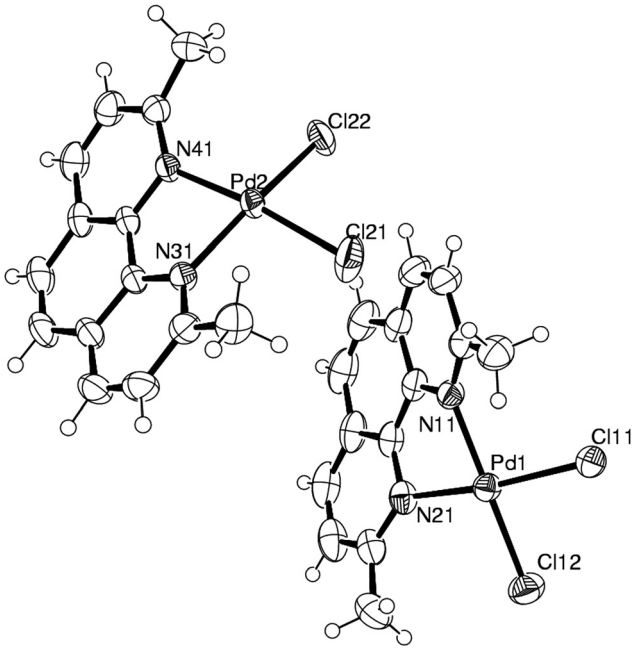


Fig. 1 Ortep view of the two independent molecules of **1a** in the crystal $[Pd(Neoc)Cl_2]\cdot\frac{1}{2}CH_2Cl_2$. The solvent was omitted for clarity. Ellipsoids are drawn at 50% probability level.

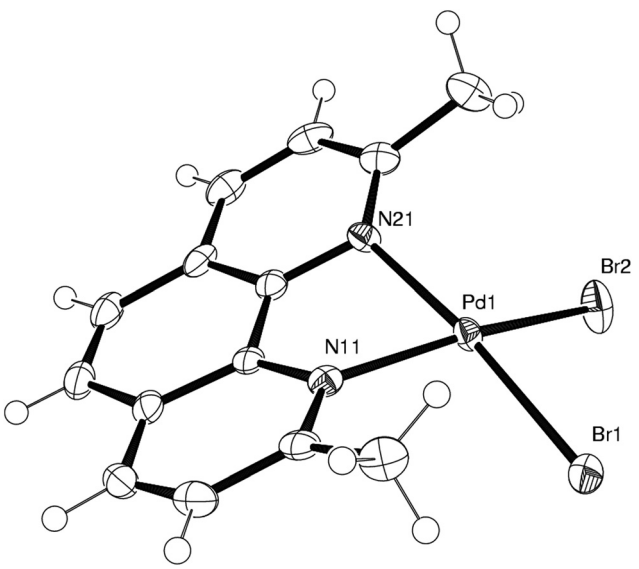


Fig. 2 Ortep view of the molecular structure of $[Pd(Neoc)Br_2]$, **2a**. Ellipsoids drawn at 50% probability level.

characterise at least a member of each series by X-ray diffraction.

Crystals of **1a** and **2a** could be successfully grown by slow diffusion of hexane into a CH_2Cl_2 solution of the corresponding complex at RT. Under these conditions, the chloride complex crystallised as a CH_2Cl_2 solvate (Fig. 1).

As shown in Fig. 1 and 2, compounds of type **a** are the expected mononuclear neutral complex.

All the structures of $[Pd(Phen)X_2]$ or $[Pt(Phen)X_2]$ (Phen = 1,10-phenanthroline) known to date are almost undistorted square planar and the phenanthroline plane coincides with the coordination plane of the metal. This also holds true for substituted phenanthrolines, but not those substituted in *ortho*, like neocuproine. In this case a huge distortion occurs, obviously due to a steric effect, so that the plane of Neoc and the square plane of the metal are quite inclined. This is evident in Fig. 1 and 2 for compounds **1a** and **2a**. The distortion implies a loss of planarity for Neoc and therefore a re-arrangement of the bonds within its skeleton.

A solid state form of compound **1a** has recently been reported,[44] but the form we obtained ($\mathbf{1a}\cdot\frac{1}{2}CH_2Cl_2$) is a *pseudo*-polymorph, having the crystallisation solvent co-crystallised (in a ratio 1 : 2). The space group type of **1a** and $\mathbf{1a}\cdot\frac{1}{2}CH_2Cl_2$ is incidentally the same ($P2_1/n$, keeping the same setting adopted in ref. 44) but the crystal lattice dimensions are quite different. Crystals of $\mathbf{1a}\cdot\frac{1}{2}CH_2Cl_2$ contains two molecules of **1a** in the asymmetric unit and the unit cell volume is of course more than 2 times larger (having CH_2Cl_2 inside also). The unprecedented structure of **2a** is instead isomorphic with **1a**, therefore with just one molecule in the asymmetric unit and no co-crystallised solvent. No traces of a $\mathbf{2a}\cdot\frac{1}{2}CH_2Cl_2$ polymorph were found. The molecular structures of **1a** (either with clathrated solvent or not) and **2a** are all very similar, characterised by the classical distortion of Neoc tetra-coordinated Pd or Pt complexes. The angles between the two planes (Neoc and N_2PdX_2) are *ca.* 40°. The Pd atom is always slightly shifted out of the average plane of the four coordinated atoms, making a slight distortion toward square pyramidal.

These molecular distortions make the Neoc coordination to Pd less efficient than the analogous phenanthroline. In $[Pd(Phen)Cl_2]$,[45] Pd–N distances are 2.036(2) Å (averaging the two distances), whereas in **1a** they are 2.06(1) Å (an average between the two crystalline forms; in parentheses standard deviation from the mean value are given, not the experimental uncertainties). For the Br derivative, the Pd–N distances are 2.053(6) for $[Pd(Phen)Br_2]$[46] and 2.08(1) Å for **2a**, respectively (averaging the two distances). Similar trends affect the Pd–X distances, which are longer for the Neoc derivatives.

These PdNeoc derivatives are quite similar to the corresponding PtNeoc ones,[38,47] where the same distortions are observed compared with the phenanthroline ligands. Interestingly, while $Pt(Neoc)Br_2$[47] is isomorphous to **2a**, $Pt(Neoc)Cl_2$ crystallises in a different form, orthorombic Pbca, without co-crystallised solvent.[38]

For both clathrated and solvent free crystalline forms of **1a**, the packing is characterised by antiparallel stacking of the Neoc ligands, perpendicular to the monoclinic axis in direction (1, 0, −1) for the clathrated form, along direction (1,1,1) for the solvent free one. This motif also characterises $Pt(Neoc)Cl_2$.

The very low solubility of type **b** compounds required growing single crystals in a different way, namely performing the reaction in a double layer: an acetonitrile solution of $[Pd(CH_3CN)_2Br_2]$ was layered over a dichloromethane solution of neocuproine allowing the diffusion to take place at −40 °C. As shown in Fig. 3, **2b** is a ionic compound of composition $[Pd(Neoc)_2Br][Pd_2Br_6]$. The CH_2Cl_2 solvent co-crystallised.

The structure of the cation is similar to that recently reported for the Cl derivative,[48] crystallised as the $(PF_6)^-$ salt. Despite apparent penta-coordination, the structure is in fact a highly

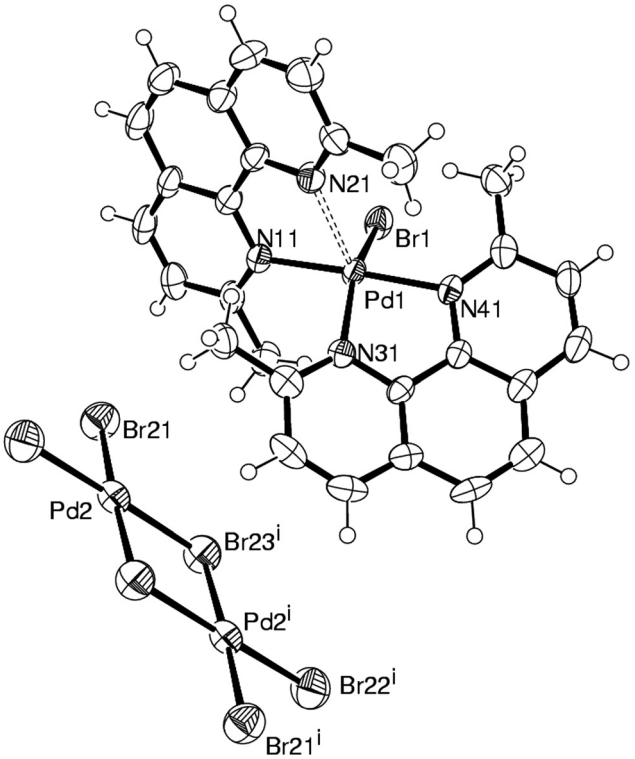


Fig. 3 Ortep view of the solid state form of [Pd(Neoc)$_2$Br]$_2$[Pd$_2$Br$_6$]·CH$_2$Cl$_2$ (**2b**·CH$_2$Cl$_2$); ellipsoids are drawn at 50% probability level. Solvent omitted for clarity.

distorted square planar with a fifth, very long Pd1–N21 coordination, 2.518(06) Å. Fig. 3 presents an orientation that highlights the distorted square planar. The three Pd–N bonds are not identical, with Pd–N31 being longer than the other two (N11–Pd1 2.045(6) Å; N31–Pd1 2.113(6) Å; N41–Pd1 2.031(5) Å).

Compound **2b**·CH$_2$Cl$_2$ crystallises as *triclinic* ($P\bar{1}$) and the crystal packing is also dominated by the stacking of Neoc ligands along (1,−1,0) direction. Anion–cation interactions are not strong and just limited to few C–H···Br. This solid state form is unambiguously different from both forms of **a**-type compounds, therefore an X-ray powder diffraction (XRPD) experiment on the bulk would immediately reveal the possible presence of both isomers.

However, XRPD on a sample obtained from the reaction of Pd(OAc)$_2$ with neocuproine and NaBr in methanol confirmed the presence of just a single solid state phase, with a diffractogram identical to that of **2b**·CH$_2$Cl$_2$, implying the presence of an isomorphic **2b**·CH$_3$OH. Therefore, no more than two compounds (**2a** and **2b**) are needed to explain the obtained results.

Compound **2b** has clearly the same composition as **1b** thus explaining why its existence had not been realised up to now (a slight difference in the amount of co-crystallised solvent may depend on the crystallisation conditions and would anyway be difficult to reliably assess by elemental analysis).

^{1}H NMR spectra of **1a–3a** in CDCl$_3$ all show the presence of a single set of signals attributable to a neocuproine ligand in a symmetrical environment. Except for this, it is not possible to draw any other conclusion from this data. On the other hand, no spectrum in CDCl$_3$ can be recorded for any compound of type **b**.

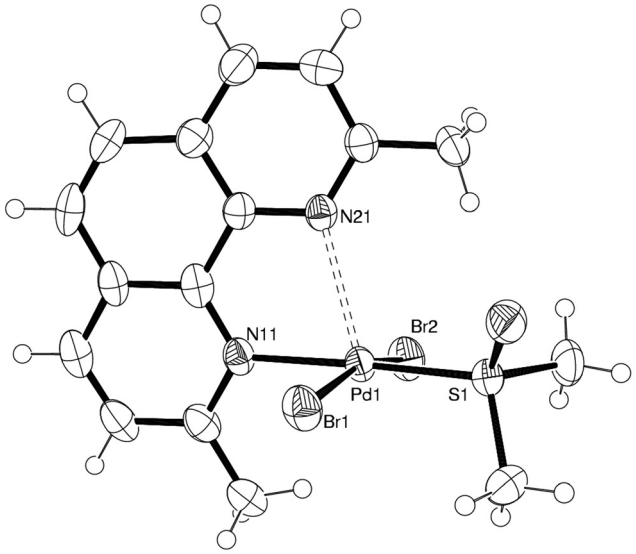


Fig. 4 The molecular structure of [Pd(Neoc)Br$_2$(DMSO)] (**2c**) in the solid state. Ellipsoids are drawn at 50% probability level.

Polar non-protic solvents, the only ones in which compounds **b** are at least partly soluble, should be considered with caution. Indeed, when **2b** was dissolved in DMSO and the solution was layered with THF, a new penta-coordinated palladium complex crystallised, identified as [Pd(Neoc)Br$_2$(DMSO)] (**2c**) with DMSO coordinated to Pd (Fig. 4). An analogous complex with platinum as metal and iodide as ligand is already known,[49] but the solid state form is different; **2c** is *monoclinic*, *C*2/*c*, whereas [Pt(Neoc)I$_2$(DMSO)] is *triclinic* $P\bar{1}$.

Compound **2c** is also a *pseudo*-pentacoordinate complex, where one of the two Neoc nitrogens is only weakly bound (Pd1–N21 2.571(5)). In a forthcoming paper,[50] we will discuss in more details this peculiar stereochemistry of penta-coordinated [Pd(Neoc)X$_2$L], which is quite a function of the nature of the X and L ligands. The structure of **2c** is somewhat analogous to that of [Pd(Neoc)Cl$_2$(CO)].[33]

The fact that **2c** is quickly obtained from **2b** supports the idea that the monomeric complexes are the thermodynamically favoured compounds and that the formation of compounds of type **b** is driven by their fast formation and their insolubility. If compounds of type **b** are given the possibility to dissolve, most times they will isomerise to type **a** compounds. Such isomerisation further explains why the existence of isomers **b** had not been appreciated before. We also incurred this misunderstanding. We have recently reported the synthesis and X-ray crystal structure determination of the full series of compounds [Pd(Neoc)X$_2$(CO)], obtained by carbonylating "[Pd(Neoc)X$_2$]" in CH$_2$Cl$_2$.[33,34] Some of the reactions were performed several times. In some cases the starting materials were insoluble in the solvent, but dissolved during the reaction and the same, soluble, carbonylated compound was obtained independent of the solubility of the starting material. Retrospectively, the crystals employed for the X-ray diffraction analysis of both the chloride and iodide members of the series had been grown from solutions of the corresponding compounds obtained employing samples of **1b** and **3b**, respectively. Only crystals of [Pd(Neoc)Br$_2$(CO)]

were obtained by a solution obtained by carbonylating a type **a** isomer.

While writing the present work, we became aware of a very recent paper[44]in which complex **1a** was obtained by reaction of $[PdCl_2(DMF)_2]$ and neocuproine in DMSO, followed by recrystallisation in DMF. Given the ability of DMSO to transform ionic **2b** into a neutral species, it is possible that this solvent also plays a role in addressing the reaction of $[PdCl_2(DMF)_2]$ and neocuproine towards neutral **1a**.

Although isomerisation of type **a** into type **b** species was observed under several experimental conditions, it must be remarked that, in our experience, this only holds if other anions are not added. On the other hand, when a suspension of species **1b** was treated with an excess of tetrabutylammonium chloride, the compound dissolved within 2 h, but reprecipitation with methanol again afforded the same insoluble isomer. When the reaction was performed in deuterated chloroform, the ^{1}H NMR spectrum of the solution evidenced the presence of free neocuproine and another series of signals attributable to a neocuproine ligand in a symmetrical environment. The former is probably due to neocuproine displacement associated with the formation in solution of species $[PdCl]_4^{2-}$ while the latter may be due to a compound such as $[(\eta^1\text{-Neoc})PdCl_3]^-$, although we have not investigated this aspect in more detail and the composition of the latter complex must be regarded as speculative. In analogy, it has been reported[38] that the use of an excess of tetraalkylammonium iodide when performing the ion exchange on compound **1a** leads to formation of $[NR_4]_2[Pd_2I_6]$ as a by-product.

As previously mentioned, treating $[Pd(CH_3CN)_2Br_2]$ with neocuproine in $CHCl_3$ afforded a precipitate of complex **2b**, apparently contaminated by palladium bromide (as indicated by elemental analysis), but small amounts of other soluble compounds were present in solution. It should first be noticed that we observed formation of palladium bromide even when a solution of $[Pd(CH_3CN)_2Br_2]$ in chloroform or methylene chloride was left to stand, but the decomposition is faster in $CHCl_3$. Moreover, when analytically pure $[Pd(CH_3CN)_2Br_2]$ was analysed by ^{1}H NMR in $CDCl_3$, an immediate decomposition was observed. Even after less than one minute from the solvent addition, the signal of free acetonitrile was largely dominant (*ca.* 95% of the total intensity in the CH_3 region) and only two very weak signals were observable at 2.42 and 2.37 ppm. This strongly suggests that aggregated units of the type $[Pd(CH_3CN)Br]_2(\mu_2\text{-}Br)_2$ are easily formed in these solvents, from which aggregation can further proceed to eventually produced insoluble oligomeric species containing little, if any, coordinated acetonitrile. It should be noted that the presence of free acetonitrile was also detected when recording a ^{1}H NMR spectrum of $[Pd(CH_3CN)_2Cl_2]$, but in much lower amounts.

Concerning the soluble fraction of the reaction between $[Pd(CH_3CN)_2Br_2]$ and neocuproine in $CHCl_3$, ^{1}H NMR spectroscopy showed the presence of three compounds, two of them (including **2a**) present in low amounts, each showing a symmetrical environment for the neocuproine ligand. By cooling this solution at −20 °C, crystals of one of those compounds were obtained and its X-ray structure solved. The compound was shown to be $[Pd(Neoc)_2Br]Br$ (**4**) (Fig. 5).

The cationic part of **4** is the same as in **2b**, but the anionic part does not contain palladium.

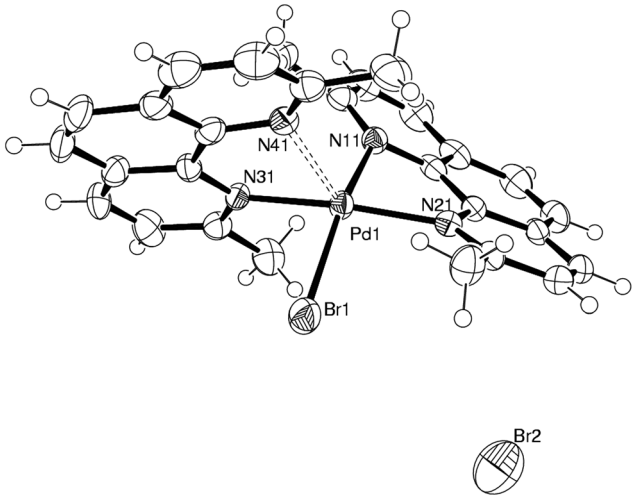


Fig. 5 Ortep drawing of $[Pd(Neoc)_2Br]Br{\cdot}2H_2O{\cdot}CHCl_3$ (**4**·$2H_2O$·$CHCl_3$).[51] Ellipsoids are drawn at 50% probability level.

Compound **4** has already been reported in the literature, obtained by reaction of **2a** with excess neocuproine, but no crystallographic characterisation was carried out.[32,35] Under our conditions, formation of **4** is clearly associated to the other reactions observed: loss of acetonitrile from $[PdBr_2(CH_3CN)_2]$ generates $PdBr_2$ oligomers that precipitate together with **2b**. The excess ligand that remains in solution results in the formation of **4**.

It should be noted that the ^{1}H NMR spectrum of **4** (and also that of the chloride analogue) has been reported[35] to show signals in accordance with an asymmetrical neocuproine. However, this is in contrast not only with our observation, but also with the fluxional nature of all other pentacoordinated neocuproine adducts we have analysed. Thus, the original report is probably partially erroneous and a mixture of complexes was likely obtained at the time.

Species **4** were obtained in crystal form, co-crystallised with H_2O and $CHCl_3$. As for **2b**, the cation can be rationalised as a distorted tetracoordinated square planar with a fifth loose coordination (Pd–N41 = 2.579(7) Å). The other three Pd–N bonds are more similar, instead (ranging from 2.048(7) to 2.081(7) Å). The crystal structure is *monoclinc*, $P2_1/c$ and the packing is again characterised by the stacking of Neoc ligands and weak C–H···Br^- interactions. Co-crystallised H_2O and $CHCl_3$ are also involved in hydrogen bond networks.

As previously mentioned, ^{1}H NMR characterisation of compounds **1–3** can be performed in $CDCl_3$ only for the soluble isomers **a**, whereas the use of coordinating solvents should be avoided. The observed signals for **1a** and **2a** are in very good agreement with those reported by Fanizzi,[38] whereas the agreement is less good with the only reported spectrum of the iodide complex.[35] This may be due to the low resolution of the instrument employed in that relatively old work. The spectra show a symmetrical coordination of the neocuproine ligand, in accord with the solid state structure.

UV spectra could also be recorded only for type a complexes. Our data agree quite well with those already reported in the literature[32] for the chlorine and bromine derivatives, although they are quite different from what was reported in the same reference for the iodine one.

Table 1 Polarity properties of the employed chlorinated solvents

	$CHCl_3$	CH_2Cl_2	$C_2H_4Cl_2$
Dielectric constant [52]	4.89	9.02	10.74
Dipole moment [52]	1.15	1.14	1.83
Acceptor number [53–55]	23.1	20.4	16.7

Reaction pathway to different isomers

We can now analyse which is the plausible pathway leading to the different isomers and the reasons why one is favoured over the other. We will first focus on the reactions employing [Pd$(CH_3CN)_2X_2$] type complexes as starting materials and in halogenated solvents, because these are the conditions in which different isomers can be obtained by slight variations of the experimental conditions.

Because **1b** isomerises to **1a** under some conditions, but the reverse was never observed, **1a** must be the thermodynamic product. Isomer **1b** is surely the kinetic product under some conditions, but the simplest general scenario implies that it may be always the kinetic product. Depending on the solvent and temperature, **1b** may or may not have the time to isomerise to **1a** before precipitating.

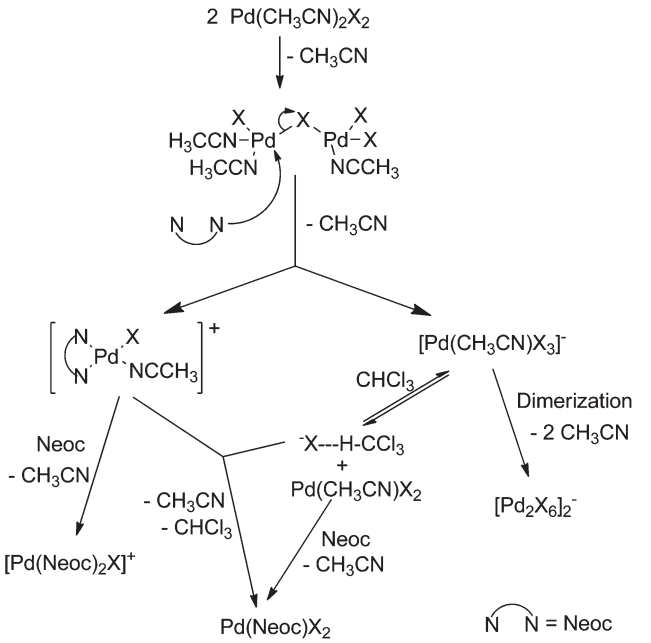
As far as the solvent influence is concerned, some properties of $CHCl_3$, $C_2H_4Cl_2$ and CH_2Cl_2, from which only **1a**, a mixture of **1a** and **1b,** and **1b** only are obtained at RT, are reported in Table 1.

A clear correlation between a single solvent property and the obtained results cannot be obtained, but chloroform has the highest acceptor number and forms the stronger hydrogen bonds. This implies that it should labilise coordinated chloride more efficiently than the other two solvents. Dichloroethane, on the other hand, is the most polar and should better solubilise the ionic isomer, retarding its precipitation and giving it the time to isomerise, a feature in accord with the observation that at reflux temperature only **1a** is obtained.

The reaction pathway shown in Scheme 5 accounts for all experimental observations.

Given the strong tendency of halides to assume a bridging position in palladium complexes, we propose that the starting point of the reaction with neocuproine is a dimeric complex formed from two [Pd$(CH_3CN)_2X_2$] units by acetonitrile loss. Observation of free acetonitrile in the ^{1}H NMR spectrum of both [Pd$(CH_3CN)_2Cl_2$] and [Pd$(CH_3CN)_2Br_2$] supports the presence of such type of complexes in solution.

The neocuproine attack should generate two intermediates, none expected to be stable under the reaction conditions. They will evolve to the two components of type **b** complexes, from which precipitation will occur. If the solvent can give strong enough hydrogen bonds, it may displace a halide from the anionic [Pd$(CH_3CN)X_3]^-$ giving an unsaturated intermediate that easily reacts with neocuproine to give a type **a** complex. The resulting free halide can coordinate to the cationic [Pd(Neoc)$(CH_3CN)X]^+$, affording additional **a** complex. When X = Br, the unsaturated [Pd$(CH_3CN)Br_2$] may also aggregate to insoluble $PdBr_2$ (actually a polymer with bridging bromides). The excess neocuproine and bromide left in solution can result in the precipitation of [Pd$(Neoc)_2Br]Br$ (**4**).



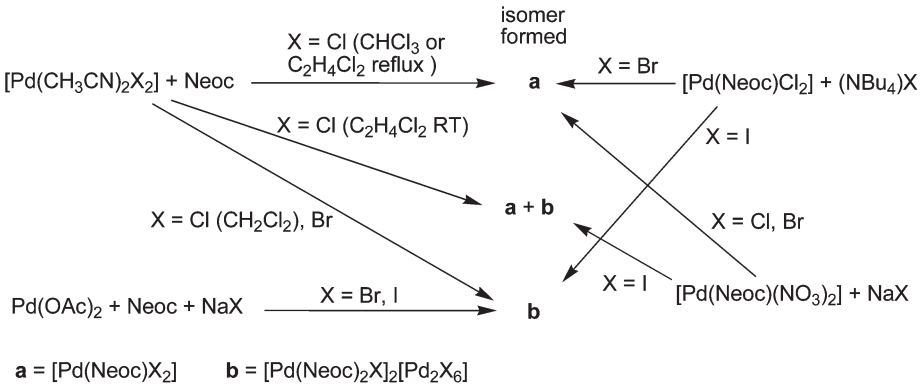
Scheme 5

The influence of the halide can now also be discussed. From an analysis of the data it emerges that it is increasingly more difficult to obtain the soluble isomer when descending the halogen group. There are two reasons that can justify this trend. The first is that several data in the literature indicates that in palladium complexes the tendency of halides to assume a bridging position increases in the order Cl < Br < I,[56] and bridging halides are present in isomer **b** complexes, but not in type **a** ones. The second, in cases where it is pertinent, is that chloride forms stronger hydrogen bonds than its heavier homologues, and this feature will facilitate halide abstraction from [Pd$(CH_3CN)X_3]^-$, orienting the reaction towards the formation of the neutral isomer **a**, as in Scheme 5.

Conclusions

A summary of the results obtained by different synthetic approaches is shown is Scheme 6. Out of the reported synthetic strategies, reaction of [Pd$(CH_3CN)_2X_2$] with neocuproine[33,34,36,37] led to either isomer **a** or **b** depending on the conditions in the case of the X = Cl, but only to isomer **b** in the case of the brominated compound. The exchange reaction of [Pd(Neoc)Cl_2] (**1a**)[38] led to isomer **a** in case of X = Br, but to isomer **b** for X = I. Reaction of palladium acetate with neocuproine and NaX (X = Br, I)[42] afforded in both cases isomer **b**, whereas the firstly reported strategy, metathesis of [Pd(Neoc)$(NO_3)_2$] with NaX,[32] gave isomer **a** for X = Cl, Br and a mixture of isomers **a** and **b** for X = I. This is the only procedure by which the neutral iodinated derivative could be obtained, even if in a mixture with the ionic one.

The ionic isomer can be converted into the neutral one under some conditions and dissolution of the ionic isomer in DMSO gives an adduct of the neutral compound, a behaviour that recalls that observed when reacting either ionic or neutral derivatives with CO.



Scheme 6

At this stage, a similar, if not the same, behaviour is to be expected with other sterically hindered phenanthrolines such as 2,9-dimethyl-4,7-diphenylphenanthroline (batocuproine) and, likely, related derivatives such as 6,6′-dimethylbipyridine. On the other hand, it is not experimentally determined if complexes of the type $[Pd(L)_2X]_2[Pd_2X_6]$ can also exist for other phenanthrolines lacking substituents in the 2 and 9 positions, or whether the same kind of isomers **a** and **b** can be also obtained for related platinum complexes. This will be the topic of a future study.

Experimental

General procedures

Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere employing standard Schlenk and cannula techniques. $CHCl_3$, CH_2Cl_2, $C_2H_4Cl_2$, CH_3CN (CaH_2) and MeOH ($Mg(OMe)_2$) were dried by distillation over the corresponding drying agent under dinitrogen immediately before use. All glassware was kept in an oven at 120 °C for at least 2 h and left to cool under vacuum before use. 2,9-Dimethyl-1,10-phenanthroline was purchased as the hydrate. It was dried by dissolving it in CH_2Cl_2, drying the resulting solution with Na_2SO_4, filtering the suspension under dinitrogen, and evaporating the filtered solution *in vacuo*. It was then stored under dinitrogen. It can be weighed in the air without problems, but must be stored in an inert atmosphere if water uptake is to be avoided. All other chemicals were purchased from Aldrich, Acros or Alfa Aesar and used as received. $CDCl_3$ was purified by passing it through a short column of basic alumina that had been previously dried by heating it *in vacuo* with a heating gun (to remove all acidic impurities and most of the water). The so purified solvent was degassed and stored over activated molecular sieves under dinitrogen and in the dark. DMSO-d_6 was distilled over CaH_2, degassed and stored over activated molecular sieves under dinitrogen. ^{1}H NMR spectra were recorded on a Bruker AC300 FT or on an Avance Bruker DPX300 spectrometer, working at 300 MHz. Signals are referred to $SiMe_4$ and *J* values are given in Hz. Elemental analyses were recorded on a Perkin-Elmer 2400 CHN Elemental Analyser.

Synthesis of PdX_2

Palladium bromide was prepared dissolving metallic palladium in a nitric acid (65%) and bromidic acid (48%) mixture according to the reported procedure.[43] Metallic palladium was completely dissolved by boiling the mixture; the volume of the solution was reduced and nitric acid was added three times, evaporating the solution almost to dryness every time to eliminate the HBr excess and decompose the $[PdBr_4]^{2-}$ ion. The solution was finally evaporated to dryness and a powdered brown precipitate was obtained.

Synthesis of $[Pd(CH_3CN)_2X_2]$ (X = Cl, Br)

$[Pd(CH_3CN)_2Cl_2]$. The procedure is adapted from that already described for the corresponding benzonitrile complexes.[57] Palladium chloride was suspended in acetonitrile (120 ml CH_3CN per gram of $PdCl_2$) and refluxed for 2 h allowing $PdCl_2$ to essentially dissolve completely. The hot solution was filtered through filtering paper with the aid of a cannula to remove very small amounts of undissolved impurities. The solution was then cooled at 0 °C to promote $[Pd(CH_3CN)_2Cl_2]$ precipitation. The yellow solid was recovered by filtration with a Buchner. The remaining solution was then evaporated *in vacuo* to afford additional complex (quantitative yield). Calcd for $C_4H_6N_2Cl_2Pd$: C, 18.52; H, 2.33; N, 10.80%. Found: C, 18.78, H, 2.26; N, 10.72%. δ_H ($CDCl_3$, RT, 300 MHz): 2,40 (s, CH_3). The spectrum also shows a signal at 2.03 ppm indicating free acetonitrile. A weak signal at 2.39 ppm is also observable. IR (nujol): 2335, 2304 cm^{-1} (in accord with the literature[58]) IR ($C_2H_4Cl_2$): 2337, 2306 cm^{-1}.

$[Pd(CH_3CN)_2Br_2]$. The same procedure described above was employed. Calcd for $C_4H_6N_2Br_2Pd$: C, 13.79; H, 1.74; N, 8.04%. Found: C, 13.61; H, 1.66; N, 7.78%. δ_H ($CDCl_3$, RT, 300 MHz): 2.41(s). Also observable is a singlet at δ 2.37, attributable to a dimeric species, and a much more intense signal (integrated intensity *ca.* 70 fold that of the other two signals) at δ 2.03 (s, free CH_3CN).

Synthesis of $[Pd(Neoc)(NO_3)_2]$

The synthesis was performed by adapting the procedure already reported for the corresponding phenanthroline complex.[59]

Palladium sponge was dissolved in 65% HNO_3. Then, solid neocuproine was added in small portions at half an hour intervals, until the brown solution became almost colourless. The orange precipitate was collected by filtration through a Buchner and washed with diluted HNO_3. After drying in the air and under vacuum, it was analytically pure and no recrystallisation was needed. Calcd for $C_{14}H_{12}N_4O_6Pd$: C, 38.33; H, 2.76; N, 12.77%. Found: C, 38.58; H, 2.57; N, 12.71%.

Synthesis of $[Pd(Neoc)Cl_2]$/$[Pd(Neoc)_2Cl]_2[Pd_2Cl_6]$ from $[PdCl_2(CH_3CN)_2]$

Reaction run in refluxing $C_2H_4Cl_2$. To a Schlenk flask equipped with a reflux condenser and under a dinitrogen atmosphere, $[Pd(CH_3CN)_2Cl_2]$ (115.2 mg, 0.444 mmol) and neocuproine (113.2 mg, 0.544 mmol) were added. $C_2H_4Cl_2$ (10 mL) was then added and the suspension was stirred and heated at reflux. The completeness of the reaction was checked after 2 h by assessing the absence of IR stretching bands at 2335 and 2304 cm^{-1} (in nujol, on a solution sample evaporated *in vacuo*) due to the reagent. The orange crystalline precipitate was collected by filtration on a Buchner (67% yield). Calcd for $C_{14}H_{12}N_2Cl_2Pd$: C, 43.61; H, 3.14; N, 7.27%. Found: C, 43.96; H, 3.54; N, 7.16%. δ_H ($CDCl_3$, 300 MHz, RT) 8.32 (d, 2H, J = 8.4); 7.86 (s, 2H); 7.57 (d, 2H, J = 8.4), 3.29 (s, 6H). λ_{max} (CH_2Cl_2)/nm 359, 395 (lit.,[32] 360, 390). Evaporation of the solution afforded an additional crop of a material with the same composition (33% yield, after washing out the excess neocuproine with toluene), although a small impurity must be present because the product appeared slightly darker. Both crops of product were completely soluble in $CHCl_3$.

Reaction run in $C_2H_4Cl_2$ at RT. The reaction was performed analogously to that described above, but at RT for 24 h, starting from $[Pd(CH_3CN)_2Cl_2]$ (220.0 mg, 0.850 mmol) and neocuproine (212.0 mg, 1.02 mmol), in $C_2H_4Cl_2$ (17 mL) The product recovered by filtration was formed by a mixture of **1a** (which was separated by dissolving it in $CHCl_3$ (17% yield) and **1b** (60% yield). Additional **1a** could be recovered by evaporating the filtered solution *in vacuo*.

Reaction run in refluxing CH_2Cl_2. The reaction was performed analogously to that described above, but at reflux for 15 h, starting from $[Pd(CH_3CN)_2Cl_2]$ (50.5 mg, 0.19 mmol) and neocuproine (48.0 mg, 0.23 mmol), in CH_2Cl_2 (7 mL). The brown-orange solid was completely insoluble in $CHCl_3$. Calcd for $C_{57}H_{50}Cl_{10}N_8Pd_4$ (corresponding to $[Pd(Neoc)Cl_2]\cdot 1/4CH_2Cl_2$): C, 42.07; H, 3.10; N, 6.89%. Found: C, 42.49; H, 3.13; N, 6.83%.

Reaction run in CH_2Cl_2 at RT. The reaction was performed analogously to the previous one, but at RT for 24 h, starting from $[Pd(CH_3CN)_2Cl_2]$ (52.0 mg, 0.20 mmol) and neocuproine (50.2 mg, 0.24 mmol), in CH_2Cl_2 (7 mL). The brown-orange solid was completely insoluble in $CHCl_3$. Calcd for $C_{57}H_{50}N_8Cl_{10}Pd_4$ (corresponding to $[Pd(Neoc)Cl_2]\cdot 1/4CH_2Cl_2$): C, 42.07; H, 3.10; N, 6.89%. Found: C, 42.31; H, 3.08; N, 6.86%.

Reaction run in $CHCl_3$ at RT. The reaction was performed analogously to the previous one, but at RT, starting from $[Pd(CH_3CN)_2Cl_2]$ (45.0 mg, 0.17 mmol) and neocuproine (48.0 mg, 0.23 mmol), in $CHCl_3$ (7 mL). The solution was stirred for 2 h and then the product was precipitated with diethyl ether. The solid was collected by filtration on a Buchner and dried *in vacuo* (85% yield). The solid is completely soluble in $CHCl_3$.

Reaction run in CH_3CN. $[Pd(CH_3CN)_2Cl_2]$ (105.2 mg, 0.405 mmol) was dissolved in warm (*ca.* 40 °C) acetonitrile (10 mL) and solid neocuproine (106.2 mg, 0.510 mmol) was added to the hot solution. An orange-brown precipitate was immediately formed. Stirring was continued for 2 h to complete the precipitation. The solid was collected by filtration on a Buchner and dried *in vacuo*. (152.6 mg, 98% yield). The solid is completely insoluble in $CHCl_3$. Calcd for $C_{14}H_{12}N_2Cl_2Pd$: C, 43.61; H, 3.14; N, 7.27%. Found: C, 43.95; H, 3.52; N, 7.57%.

Synthesis of $[Pd(Neoc)Br_2]$/$[Pd(Neoc)_2Br]_2[Pd_2Br_6]$ from $[PdBr_2(CH_3CN)_2]$

Reaction run in refluxing $C_2H_4Cl_2$. The reaction was performed analogously to that described for the corresponding reaction of the chlorinated derivative, but for 10.5 h, starting from $[Pd(CH_3CN)_2Br_2]$ (104.6 mg, 0.30 mmol) and neocuproine (75.0 mg, 0.36 mmol), in $C_2H_4Cl_2$ (8 mL). The precipitated product (90% yield) was collected by filtration on a Buchner. From the remaining solution, only a trace amount of a product that may be **2a** could be isolated. The precipitate product is completely insoluble in $CHCl_3$. Calcd for $C_{14}H_{12}Br_2N_2Pd$ ("$[Pd(Neoc)Br_2]$"): C, 35.44; H, 2.55; N, 5.90%. Found: C, 35.20; H, 2.48; N, 5.55%.

Reaction run in CH_2Cl_2 at RT. The reaction was performed analogously to the previous one, but at RT for 24 h, starting from $[Pd(CH_3CN)_2Br_2]$ (153.4 mg, 0.44 mmol) and neocuproine (110.0 mg, 0.53 mmol), in CH_2Cl_2 (12 mL). The brown precipitate (93% yield) was completely insoluble in $CHCl_3$. Calcd for $C_{57}H_{50}Br_8Cl_2N_8Pd_4$ (corresponding to $[Pd(Neoc)_2Br]_2[Pd_2Br_6]\cdot CH_2Cl_2$, in accord with the composition determined by X-ray diffraction): C, 34.53; H, 2.54; N, 5.65%. Found: C, 34.38; H, 2.20; N, 5.51%.

Reaction run in $CHCl_3$ at RT and preparation of single crystals of $[Pd(Neoc)_2Br]Br$ (4). The reaction was performed analogously to the previous one, but at RT for 3 h, starting from $[Pd(CH_3CN)_2Br_2]$ (23.8 mg, 0.068 mmol) and neocuproine (16.1 mg, 0.077 mmol), in $CHCl_3$ (15 mL). A larger solvent amount than usual was employed in this case, in the hope of facilitating the solubilisation of intermediate species. The brown precipitate (93% yield) was completely insoluble in $CHCl_3$. Calcd for $C_{57}H_{49}Br_8Cl_3N_8Pd_4$ (corresponding to $[Pd(Neoc)_2Br]_2[Pd_2Br_6]\cdot CHCl_3$): C, 33.94; H, 2.45; N, 5.27%. Found: C, 32.89; H, 2.27; N, 5.34%. The low values for all elements are attributed to contamination by $PdBr_2$, in accord with the easy decomposition of the starting complex in chloroform, as discussed before. The reaction solution was dried *in vacuo* and ^1H NMR ($CDCl_3$) analysis revealed that, besides very small amounts of **2a**, two more compounds are present in

solution. The NMR tube was placed in a refrigerator at −20 °C and a few single crystals of compound **4** formed over two days.

Reaction run in refluxing CH_3CN. $[Pd(CH_3CN)_2Br_2]$ (60.0 mg, 0.17 mmol) was dissolved in hot (70 °C) acetonitrile (10 mL) and solid neocuproine (40.4 mg, 0.19 mmol) was added to the hot solution. A dark brown precipitate was immediately formed. The solid was collected by filtration on a Buchner and dried in vacuum. The solid is completely insoluble in $CHCl_3$. Calcd for $C_{58}H_{51}Br_8N_9Pd_4$ (corresponding to $[Pd(Neoc)_2Br]_2[Pd_2Br_6]\cdot CH_3CN$): C, 35.93; H, 2.65; N, 6.50%. Found: C, 36.24; H, 2.41; N, 6.56%.

Syntheses by exchange reaction from $[Pd(Neoc)Cl_2]$ (1a)

$[Pd(Neoc)Br_2]$ (2a). The exchange reaction between $[Pd(Neoc)Cl_2]$ and twice the required molar amount of Bu_4NBr in chloroform was performed as reported in the literature.[38] The product was completely soluble in $CHCl_3$, in accord with the proposed neutral composition. However, in our hands, a single exchange reaction was not sufficient to remove all chloride. The ^1H NMR spectrum of the complex in $CDCl_3$ does not evidence the presence of the residual chloride because the signals of **1a** and **2a** are too close to each other. However, the elemental analysis of the product was out of range and when it was employed as a substrate for a carbonylation reaction to give $[Pd(Neoc)Br_2(CO)]$,[33] the presence of $[Pd(Neoc)Cl_2(CO)]$ could be also detected, since the signals of the chloride and bromide complexes are more separated in this case. The exchange procedure had to be repeated twice more with the same amounts to get a completely chloride-free and analytically pure compound. Calcd for $C_{14}H_{12}Br_2N_2Pd$: C, 35.44; H, 2.55; N, 5.90%. Found: C, 35.80; H, 2.64; N, 5.60%. δ_H ($CDCl_3$, 300 MHz, RT): 8.31 (d, 2H, J = 8.4 Hz); 7.85 (s, 2H); 7.58 (d, 2H, J = 8.4 Hz); 3.32 (s, 6H). λ_{max} (CH_2Cl_2)/nm 362, 412 (lit.,[32] 355, 410).

$[Pd(Neoc)_2I]_2[Pd_2I_6]$ (3b). The exchange reaction between $[Pd(Neoc)Cl_2]$ and twice the required molar amount of Bu_4NI in chloroform was performed as reported in the literature.[38] As reported, the black product precipitated out of the solution. After washing out the ammonium salts with methanol, it was completely insoluble in $CHCl_3$. This is in accord with the reported results, but contrasts with the attribution of the neutral composition (**3a**) to the obtained product, since **3a** should be soluble in this solvent. Calcd for $C_{56}H_{48}I_8N_8Pd_4$ ($[Pd(Neoc)_2I]_2[Pd_2I_6]$): C, 29.58; H, 2.13; N, 4.93%. Calcd for $C_{57}H_{49}I_8Cl_3N_9Pd_4$ (corresponding to $[Pd(Neoc)_2I]_2[Pd_2I_6]\cdot CHCl_3$): C, 28.61; H, 2.02; N, 4.68%. Found: C, 29.01; H, 2.31; N, 4.54%. Elemental analysis does not allow us to assess whether a crystallisation solvent molecule is present, as in the case of the chloride and bromide derivatives, or not, since the calculated values are very close to the experimental one in both cases.

Syntheses from $Pd(OAc)_2$, neocuproine and NaX

$[Pd(Neoc)_2Br]_2[Pd_2Br_6]$ (2b). $Pd(OAc)_2$ (124.2 mg, 0.553 mmol), neocuproine (149.6 mg, 0.718 mmol) and NaBr (136.6 mg, 1.328 mmol) were introduced into a Schlenk flask under dinitrogen and methanol (10 mL) was added. The suspension was stirred at room temperature for 1 h. The precipitated solid was collected by filtration on a Buchner, washed with a 1 : 1 MeOH–H_2O solution and dried *in vacuo* (80% yield). Calcd for $C_{56}H_{48}Br_8N_8Pd_4$ (corresponding to $[Pd(Neoc)_2Br]_2[Pd_2Br_6]$): C, 35.44; H, 2.55; N, 5.90%. Found: C, 36.32; H, 2.60; N, 6.13%. Despite the fact that the analysis for carbon is slightly out of range (which may be due to some clathrated solvent), the identity of the compound was confirmed by X-ray powder diffraction. The spectrum of the product was in good agreement with that simulated for **2b** based on the single crystal data. The same reaction was repeated at reflux temperature, but extensive formation of metallic palladium was observed.

$[Pd(Neoc)_2I]_2[Pd_2I_6]$ (3b). The synthesis was performed as the previous one, starting from $Pd(OAc)_2$ (53.0 mg, 0.236 mmol), neocuproine (63.2 mg, 0.35 mmol) and NaI (85.1 mg, 0.66 mmol), in methanol (5 mL). A black precipitate was formed (94% yield), which is completely insoluble in $CHCl_3$. Calcd for $C_{56}H_{48}I_8N_8Pd_4$ ($[Pd(Neoc)_2I]_2[Pd_2I_6]$): C, 29.58; H, 2.13; N, 4.93%. Found: C, 29.84; H, 2.20; N, 5.17%.

Syntheses of $[Pd(Neoc)I_2]$ (3a) by metathesis from $[Pd(Neoc)(NO_3)_2]$

$[Pd(Neoc)(NO_3)_2]$ (19.7 mg, 0.045 mmol) and NaI (35.6 mg, 0.237 mmol) were introduced in a Schlenk under a dinitrogen atmosphere and then ethanol (5 mL) was added under dinitrogen. The suspension was stirred at room temperature for 24 h. The solid was collected by filtration on a Buchner, washed with ethanol and dried in vacuum (94% yield). The same reaction has been also run in methanol. Calcd for $C_{14}H_{12}I_2N_2Pd$ ("$[Pd(Neoc)_2I_2]$"): C, 29.58; H, 2.13; N, 4.93%. Found: C, 30.02; H, 2.48; N, 5.03%. The precipitate was treated with $CHCl_3$ to yield a soluble fraction whose ^1H NMR spectrum is in full agreement with those observed for **1a** and **2a**, evidencing the formation of **3a** (some very small impurities are observable, however). δ_H ($CDCl_3$, 300 MHz, RT): 8.32 (d, 2H, J = 8.4 Hz); 7.85 (s, 2H); 7.58 (d, 2H, J = 8.4 Hz); 3.30 (s, 6H). λ_{max} (CH_2Cl_2)/nm 371 (lit.,[32] 445, 500 sh). The part that was not dissolved immediately in $CHCl_3$ was completely insoluble in this solvent, in accord with its formulation as **3b**.

Crystal structure determination

Compounds **1a**, **2a**, **2b**, **2c** and **4** were characterised by single crystal X-ray diffraction. All samples were mounted in air on a goniometer head and measured on a Bruker-APEX II CCD diffractometer, at room temperature, except **2a**, which was collected at T = 150 K (using an Oxford Cryosystem 600-cryostream device). Generator settings were 50 kV and 30 mA, radiation was Mo Kα, graphite monochromated. Frames were collected with 0.5° ω-scans. All structures were solved by direct methods and refined by least square refinement (using SHELX97,[60] under the wingx package[61]) Non-hydrogen atoms were refined including anisotropic thermal parameters. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model where each H was assigned a fixed isotropic displacement parameter. **2b**·0.5(CH_2Cl_2) is very close to a *monoclinic* lattice,

Table 2 Details of X-ray diffraction data collections on **1a**, **4**, **2a**, **2b**·CH_2Cl_2, and **2c**[a]

	1a	**4**	**2a**	**2b**·CH_2Cl_2	**2c**
Formula	$C_{29}H_{26}Cl_6N_4Pd_2$	$C_{29}H_{29}Br_2Cl_3N_4O_2Pd_2$	$C_{14}H_{12}Br_2N_2Pd$	$C_{57}H_{50}Br_8Cl_2N_8Pd_4$	$C_{16}H_{18}Br_2N_2OPdS$
T (K)	293(2)	293(2)	150(2)	293(2)	293(2)
λ	MoKα	MoKα	MoKα	MoKα	MoKα
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Triclinic*	*Monoclinic*
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$C2/c$
A (Å)	9.897(4)	17.348(5)	12.1525(7)	12.141(5)	20.1737(7)
b (Å)	21.440(8)	7.517(5)	7.8107(5)	8.103(5)	7.8067(3)
c (Å)	15.012(6)	24.825(5)	14.4621(8)	16.299(5)	23.4069(8)
α (°)	90	90	90	90.181(5)	90
β (°)	102.442(5)	99.147(5)	93.298(1)	109.819(5)	93.160(2)
γ (°)	90	90	90	89.497(5)	90
V (Å^3)	3111(2)	3196(2)	1370.5(1)	1508(1)	3680.8(2)
Z	4	4	4	2	8
Crystal size (mm^3)	0.2 × 0.16 × 0.12	0.23 × 0.15 × 0.13	0.2 × 0.1 × 0.05	0.15 × 0.12 × 0.08	0.2 × 0.18 × 0.1
θ range	0–31°	0–26.5°	2–29	1–25	1.7–28.7
Reflections	34 573	32 988	9451	10 597	12 802
Unique	9042	6580	2520	5098	4291
R_{int}	0.0226	0.0772	0.0405	0.0298	0.057
R_σ	0.0215	0.0671	0.0609	0.0469	0.075
Parameters	374	357	174	351	208
GoF	1.04	1.03	0.834	1.07	1.015
R_1 ($I/2\sigma(I)$)	0.0258	0.0746	0.0353	0.0426	0.0457
wR_2 ($I/2\sigma(I)$)	0.0604	0.1904	0.0488	0.1106	0.1017
Residuals (eÅ^{-3})	−0.47, +0.76	−1.8, +2.5	−0.37, +0.48	−1.42, +2.0	−1.0, +0.79

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$; $R_\sigma = \Sigma\sigma(F_o^2)/\Sigma F_o^2$ $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ GoF $= \{S/(n-p)\}^{1/2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$

Table 3 Metal–ligand distances in Pd Neoc complexes. Values are in Å

	1a[a]	**2a**	**2b**	**2c**	**4**
Pd–N11	2.055(2)	2.093(3)	2.045(6)	2.105(5)	2.081(7)
Pd–N21	2.067(2)	2.073(3)	2.518(6)	2.571(5)	2.061(7)
Pd–N31	2.067(2)		2.113(6)		2.048(7)
Pd–N41	2.042(2)		2.031(5)		2.579(7)
Pd–X1	2.297(1)	2.4148(4)	2.464(1)	2.4510(8)	2.435(2)
Pd–X2	2.2815(9)	2.4119(5)		2.4687(8)	
Pd–X3	2.2788(9)				
Pd–X4	2.2931(8)				
Pd–S				2.238(1)	

[a] Two molecules per asymmetric unit (X1–X4 are Cl11, Cl12, Cl13, Cl14, respectively).

however *triclinic* is more likely, because: a) cell angles deviate quite significantly from 90°; b) internal agreement for the 2/m Laue class is significantly higher; c) the structure is more likely centrosymmetric (based on reflection statistics) and in *monoclinic* this would imply two disordered orientations for Pd(Neoc)$_2$Br molecules (on the other hand the Pd_2Br_6 moieties are closes to 2/m symmetry, being mmm in isolation and lying about the −1 site in the *triclinic* structure).

Details of each data collection and results of each refinement are given in Table 2. Crystallographic information files are available as Supporting Information.† Metal–ligand distances are also reported in Table 3.

Acknowledgements

We thank the MiUR for financial support.

Notes and references

1 W. W. Brandt, F. P. Dwyer and E. D. Gyarfas, *Chem. Rev.*, 1954, **54**, 959–1017.
2 G. Chelucci and R. P. Thummel, *Chem. Rev.*, 2002, **102**, 3129–3170.
3 E. Schoffers, *Eur. J. Org. Chem.*, 2003, 1145–1152.
4 F. Fache, E. Schulz, M. L. Tommasino and M. Lemaire, *Chem. Rev.*, 2000, **100**, 2159–2232.
5 *Olefin Upgrading Catalysis by Nitrogen-Based Metal Complexes II: State-of-the-Art and Perspectives, Catal. Met. Complexes*, ed. G. Giambastiani and J. Campora, Springer, Dordrecht, The Netherlands, 2011, vol. 36.
6 V. G. Albano, G. Natile and A. Panunzi, *Coord. Chem. Rev.*, 1994, **133**, 67–114.
7 F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio and G. Pacchioni, *J. Chem. Soc., Chem. Commun.*, 1992, 333–335.
8 F. P. Fanizzi, N. Margiotta, M. Lanfranchi, A. Tiripicchio, G. Pacchioni and G. Natile, *Eur. J. Inorg. Chem.*, 2004, 1705–1713.
9 M. E. Cucciolito, V. De Felice, G. Roviello and F. Ruffo, *Eur. J. Inorg. Chem.*, 2011, 457–469.
10 W. Cabri, I. Candiani, A. Bedeschi and R. Santi, *J. Org. Chem.*, 1993, **58**, 7421–7426.
11 P. A. Enquist, J. Lindh, P. Nilsson and M. Larhed, *Green Chem.*, 2006, **8**, 338–343.
12 M. M. S. Andappan, P. Nilsson and M. Larhed, *Chem. Commun.*, 2004, 218–219.
13 M. M. S. Andappan, P. Nilsson, H. von Schenck and M. Larhed, *J. Org. Chem.*, 2004, **69**, 5212–5218.
14 P. A. Enquist, P. Nilsson, P. Sjoberg and M. Larhed, *J. Org. Chem.*, 2006, **71**, 8779–8786.
15 D. Bianchi, R. Bortolo, R. D'Aloisio and M. Ricci, *Angew. Chem., Int. Ed.*, 1999, **38**, 706–708.
16 C. Querci, R. D'Aloisio, R. Bortolo, M. Ricci and D. Bianchi, *J. Mol. Catal. A: Chem.*, 2001, **176**, 95–100.
17 H. Ishii, M. Goyal, M. Ueda, K. Takeuchi and M. Asai, *Appl. Catal., A*, 2000, **201**, 101–105.
18 A. Vavasori and L. Toniolo, *J. Mol. Catal. A: Chem.*, 2000, **151**, 37–45.
19 H. Yasuda, K. Watarai, J. C. Choi and T. Sakakura, *J. Mol. Catal. A: Chem.*, 2005, **236**, 149–155.
20 G.-J. ten Brink, I. W. C. E. Arends, M. Hoogenraad, G. Verspui and R. A. Sheldon, *Adv. Synth. Catal.*, 2003, **345**, 1341–1352.

21 I. W. C. E. Arends, G.-J. ten Brink and R. A. Sheldon, *J. Mol. Catal. A: Chem.*, 2006, **251**, 246–254.
22 G.-J. ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Adv. Synth. Catal.*, 2002, **344**, 355–369.
23 G.-J. ten Brink, I. Arends, M. Hoogenraad, G. Verspui and R. Sheldon, *Adv. Synth. Catal.*, 2003, **345**, 497–505.
24 G.-J. ten Brink, I. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636–1639.
25 B. V. Popp and S. S. Stahl, *J. Am. Chem. Soc.*, 2006, **128**, 2804–2805.
26 S. S. Stahl, *Angew. Chem., Int. Ed.*, 2004, **43**, 3400–3420.
27 S. S. Stahl, J. L. Thorman, R. C. Nelson and M. A. Kozee, *J. Am. Chem. Soc.*, 2001, **123**, 7188–7189.
28 W. R. Thiel, *Angew. Chem., Int. Ed.*, 1999, **38**, 3157–3158.
29 N. R. Conley, L. A. Labios, D. M. Pearson, C. C. L. McCrory and R. M. Waymouth, *Organometallics*, 2007, **26**, 5447–5453.
30 D. M. Pearson and R. M. Waymouth, *Organometallics*, 2009, **28**, 3896–3900.
31 D. M. Pearson, N. R. Conley and R. M. Waymouth, *Organometallics*, 2011, **30**, 1445–1453.
32 R. A. Plowman and L. F. Power, *Aust. J. Chem.*, 1971, **24**, 303–308.
33 F. Ragaini, M. Gasperini, S. Cenini, L. Arnera, A. Caselli, P. Macchi and N. Casati, *Chem.–Eur. J.*, 2009, **15**, 8064–8077.
34 F. Ragaini, H. Larici, M. Rimoldi, A. Caselli, F. Ferretti, P. Macchi and N. Casati, *Organometallics*, 2011, **30**, 2385–2393.
35 R. D. Gillard, L. A. P. Kane-Maguire and P. A. Williams, *Transition Met. Chem.*, 1977, **2**, 55–57.
36 G. R. Newkome, W. E. Puckett, G. E. Kiefer, V. K. Gupta, F. R. Fronczek, D. C. Pantaleo, G. L. McClure, J. B. Simpson and W. A. Deutsch, *Inorg. Chem.*, 1985, **24**, 811–826.
37 G. R. Newkome, V. K. Gupta, H. C. R. Taylor and F. R. Fronczek, *Organometallics*, 1984, **3**, 1549–1554.
38 F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, M. Lanfranchi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1991, 1007–1015.
39 C. Bianchini, A. Meli and W. Oberhauser, *Organometallics*, 2003, **22**, 4281–4285.
40 T. J. Mooibroek, E. Bouwman, M. Lutz, A. L. Spek and E. Drent, *Eur. J. Inorg. Chem.*, 2010, 298–310.
41 A. Marson, A. B. van Oort and W. P. Mul, *Eur. J. Inorg. Chem.*, 2002, 3028–3031.
42 M. Aresta, P. Giannoccaro, I. Tommasi, A. Dibenedetto, A. M. Manotti Lanfredi and F. Ugozzoli, *Organometallics*, 2000, **19**, 3879–3889.
43 S. Sakaki, H. Kanai and K. Tarama, *Can. J. Chem.*, 1974, **52**, 2857–2860.
44 V. N. Demidov, S. A. Simanova, A. I. Savinova, A. V. Zinchenko, T. B. Pakhomova and E. A. Aleksandrova, *J. Struct. Chem.*, 2010, **51**, 296–302.
45 K. Ha, *Acta Crystallogr. Sect. E.-Struct Rep., Online*, 2011, **66**, M38–U471.
46 K. Ha, *Acta Crystallogr. Sect. E.-Struct Rep., Online*, 2010, **66**, M7–U190.
47 R. J. H. Clark, F. P. Fanizzi, G. Natile, C. Pacifico, C. G. van Rooyen and D. A. Tocher, *Inorg. Chim. Acta*, 1995, **235**, 205–213.
48 S. Pratihar, J. Marek and S. Roy, *Inorg. Chim. Acta*, 2011, **372**, 362–366.
49 F. P. Fanizzi, N. Margiotta, M. Lanfranchi, A. Tiripicchio, G. Pacchioni and G. Natile, *Eur. J. Inorg. Chem.*, 2004, 1705–1713.
50 P. Macchi, N. Casati, A. Krawczuk-Pantula, F. Ragaini, A. Sironi, submitted.
51 The origin of the cocrystallised water is not obvious, since all reactions had been performed under dinitrogen and with dry solvents. Given the low amount of crystals obtained, it is possible that they have embedded most of the water present in trace amounts. However, it should also be recalled that the same compound has previously obtained in a "dry" form by letting it stay over P_2O_5, but quickly regained clathrated water when exposed to the air (ref. 32).
52 C. Laurence, P. Nicolet, M. T. Dalati, J.-L. M. Abboud and R. Notario, *J. Phys. Chem.*, 1994, **98**, 5807–5816.
53 V. Gutmann, *Coord. Chem. Rev.*, 1976, **18**, 225–255.
54 V. Gutmann, *Electrochim. Acta*, 1976, **21**, 661–670.
55 K. M. Kadish and J. E. Anderson, *et al.*, *Pure Appl. Chem.*, 1987, **59**, 711–714.
56 R. A. Widenhoefer and S. L. Buchwald, *Organometallics*, 1996, **15**, 2755–2763.
57 J. R. Doyle, P. E. Slade, H. B. Jonassen and R. N. Rhoda, in *Inorganic Synthesis*, John Wiley & Sons, Inc., 1960, pp. 216–219.
58 J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis Jr and A. S. Wilson, *Spectrochim. Acta, Part A*, 1967, **23**, 1121–1135.
59 G. Anderegg and H. Wanner, *Inorg. Chim. Acta*, 1986, **113**, 101–108.
60 G. M. Sheldrick, SHELX97-Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.
61 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.

