Palladium(II) and Platinum(II) Dihalogeno-complexes containing the Polyfunctional Phosphine 7-Diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy). Crystal Structure of the Metallocycle *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$]·$2H_2O$†

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The co-ordination chemistry of the polyfunctional phosphine 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy) with some palladium(II) and platinum(II) dihalogeno-complexes has been investigated. It reacts with [Pd(cod)Cl_2] (cod = cycloocta-1,5-diene) in 1:1 molar ratio to give the metallocycle *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$] **1**, the molecular structure of which was unambiguously determined by an X-ray analysis. The structure consists of two *trans*-$PdCl_2$ moieties linked by two dpnapy molecules in a head-to-tail arrangement. In this way the two palladium atoms and two bridging dpnapy comprise a quasi-planar twelve-membered ring. Attempts to include a metal ion in the central cavity of the metallocycle failed. This result has been explained in terms of the geometric constraints of dpnapy, the structure of which was also determined. When [Pd(PhCN)$_2$$Cl_2$] was used as starting palladium source the reaction proceeded in a different way. Complexes of general formula [M(dpnapy)$_2$$Cl_2$] (M = Pd **2** or Pt **3**) containing two dangling dpnapy-*P* ligands were obtained from the reaction of dpnapy with [M(cod)Cl_2] (M = Pd or Pt), [Pd(PhCN)$_2$$Cl_2$] and [Pt(dmso)$_2$$Cl_2$] (dmso = dimethyl sulfoxide) when the ligand-to-metal molar ratio was 2:1. Complexes **2** and **3** have been used as starting materials for the synthesis of homo- and hetero-metallocycles. Unexpectedly, only homometallocycles have been isolated from these reactions, e.g. *trans*-[Pd(dpnapy)$_2$$Cl_2$] reacts with [{Rh(CO)$_2$Cl}$_2$] giving *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$] and *cis,cis*-[{Rh(CO)(μ-dpnapy)Cl}$_2$] the formation of which requires the transfer of a dpnapy ligand from the palladium to the rhodium complex. On the basis of IR and NMR findings, a mechanism is proposed for this and other related reactions.

The design and synthesis of polydentate ligands as building blocks for linear polymetallic systems are of current interest because of the unique chemical and physical properties that such systems can display.[1] In previous work [2] we reported the synthesis and NMR characterization of the polyfunctional phosphine 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy). This compound can be regarded as a combination of the well known binucleating short-bite compounds 1,8-naphthyridine[3] and 2-(diphenylphosphino)pyridine,[4] and is expected to act as the backbone of linear metal arrays as well as of metallocycles which are good precursors of linear trinuclear metal arrays.[5]

The co-ordination chemistry of dpnapy has been studied in relation to some rhodium(I),[2] iridium(I),[6] and Rh_2^{4+} [7] complexes displaying various geometries ranging from P-monodentate, P,N(1) bridging bidentate and P,N(8),N(1) binucleating tridentate. Formation of a metallocycle has been observed by using [{Rh(CO)$_2$Cl}$_2$] as starting material. In this case the twelve-membered metallocycle *cis,cis*-[{Rh(CO)(μ-dpnapy)Cl}$_2$], as confirmed by an X-ray diffraction analysis,[2] was obtained. Unfortunately this metallocycle does not possess the overall assembly to host metal ions in the central cavity. Inclusion of a metal ion in the cavity of a metallocycle requires a *trans* arrangement of the bridging ligands around the two metal centres. Only in this way, the lone pairs of two 'central' nitrogens can bind an incoming metal ion. As confirmation, the metallocycle [{Rh(CO)(μ-dppy)Cl}$_2$] [dppy = 2,6-bis(diphenylphosphino)pyridine], exhibiting a *trans* P–Rh–P configuration, easily co-ordinates a $SnCl^+$ ion in its cavity with formation of Sn–N and Sn–Rh bonds.[8]

In the present paper we report the results of an investigation which led to the synthesis of a series of mononuclear palladium(II) and platinum(II) dpnapy complexes. The synthesis and crystal structure of the metallocycle *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$]·$2H_2O$ as well as the structure of free dpnapy are also described.

Experimental

General Data.—The compound dpnapy was prepared as previously described.[2] The starting complexes [Pd(cod)Cl_2][9] (cod = cycloocta-1,5-diene), *trans*-[Pd(PhCN)$_2$$Cl_2$],[10] [Pt(cod)$Cl_2$],[11] and *cis*-[Pt(dmso)$_2$$Cl_2$][12] (dmso = dimethyl sulfoxide) were prepared according to the literature. All other chemicals were obtained from commercial sources and used as supplied. None of the compounds reported here is air sensitive, but all reactions were carried out under an atmosphere of dry nitrogen. Infrared spectra were recorded on KBr or CsI pellets with a Perkin-Elmer FT 1720X spectrometer, NMR spectra on a Bruker AMX 300 spectrometer using standard pulse

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

sequences. Molecular weights were determined with a Knauer vapour-pressure osmometer. Elemental analyses were performed by Malissa-Reuter Mikroanalytishes Laboratorium, Elbach, Germany, and REDOX snc Laboratorio di Microanalisi, Cologno Monzese (Milano), Italy.

Preparations.—trans,trans-[{Pd(μ-dpnapy)Cl_2}$_2$] **1**. *Procedure* (*a*). Solid dpnapy (0.120 g, 0.350 mmol) was added to a dichloromethane solution (50 cm^3) of [Pd(cod)Cl_2] (0.100 g, 0.350 mmol) and the resulting mixture left to stir for *ca*. 2 h. During this time it changed from yellow to orange, and a small amount of an unidentified light yellow solid was formed. This was filtered off and then, by addition of diethyl ether (40 cm^3) to the filtrate, complex **1** precipitated as an orange microcrystalline solid. Yield 0.136 g (75%) (Found: C, 50.25; H, 3.50; Cl, 13.30; N, 5.25. $C_{44}H_{38}Cl_4N_4P_2Pd_2$ requires C, 50.85; H, 3.65; Cl, 13.65; N, 5.40%). IR (Nujol mull, CsI): ν(Pd–Cl) 333 cm^{-1}. NMR (room temperature, CD_2Cl_2): ^1H, δ 3.53 (s, 3 H, 2-Me) and 2.53 (s, 3 H, 4-Me); ^{13}C, δ 29.13 (2-Me) and 18.61 (4-Me); ^{31}P, δ 21.69.

Procedure (*b*). The complex *trans*-[Pd(dpnapy)$_2$$Cl_2$] **2** (0.050 g, 0.058 mmol) was treated with the equivalent amount of *trans*-[Pd(PhCN)$_2$$Cl_2$] (0.022 g, 0.058 mmol) in dichloromethane (40 cm^3). The insoluble **2** dissolved progressively upon reaction while the solution became orange. Upon completion (*ca*. 5 min), hexane (40 cm^3) was added inducing the precipitation of complex **1** as orange microcrystals in nearly quantitative amount.

Procedure (*c*). Complex **2** (0.050 g, 0.058 mmol) was treated with the equivalent amount of [Pd(cod)Cl_2] (0.017 g, 0.058 mmol) in dichloromethane (40 cm^3). Complex **1** was obtained in high yield by following the procedure used previously.

Reaction of dpnapy with trans-[Pd(PhCN)$_2$$Cl_2$] *in* 1 : 1 *molar ratio*. Solid dpnapy (0.200 g, 0.584 mmol) was added to a CH_2Cl_2 solution (40 cm^3) of *trans*-[Pd(PhCN)$_2$$Cl_2$] (0.224 g, 0.584 mmol). The resulting mixture was stirred for 10 min and then left to stand for *ca*. 24 h. During this time a dark yellow crystalline solid precipitated. It was filtered off, washed with diethyl ether and dried under vacuum. Yield 0.176 g (58%) (Found: 50.80; H, 3.60; Cl, 13.60; N, 5.35. $C_{22}H_{19}Cl_2N_2PPd$ requires C, 50.85; H, 3.65; Cl, 13.65; N, 5.40%). IR (Nujol mull, CsI): ν(Pd–Cl) 342 and 291 cm^{-1}. The low solubility of the complex prevents an NMR solution characterization.

trans-[Pd(dpnapy)$_2$$Cl_2$] **2**. *Procedure* (*a*). Solid dpnapy (0.200 g, 0.584 mmol) was added to a dichloromethane solution (50 cm^3) of *trans*-[Pd(PhCN)$_2$$Cl_2$] (0.112 g, 0.292 mmol) and the resulting solution left to stir for 30 min. During this time compound **2** precipitated as a yellow solid. It was filtered off, washed with diethyl ether and dried. Yield 0.213 g (85%) (Found: C, 60.85; H, 4.35; Cl, 8.15; N, 6.45. $C_{44}H_{38}Cl_2N_4P_2Pd$ requires C, 61.3; H, 4.45; Cl, 8.20; N, 6.50%). IR (Nujol mull, CsI): ν(Pd–Cl) 366 cm^{-1}.

Procedure (*b*). Solid [Pd(cod)Cl_2] (0.100 g, 0.350 mmol) was added to a stirred dichloromethane (50 cm^3) solution containing dpnapy (0.240 g, 0.700 mmol). Immediately complex **2** precipitated in high yield.

cis-[Pt(dpnapy)$_2$$Cl_2$] **3**. Compound **3** was obtained by reaction of dpnapy with [Pt(cod)Cl_2] or *cis*-[Pt(dmso)$_2$$Cl_2$] by following the procedures used for **2**. Yield 80% (Found: C, 56.00; H, 4.05; Cl, 7.60; N, 6.00. $C_{44}H_{38}Cl_2N_4P_2Pt$ requires C, 55.60; H, 4.10; Cl, 7.45; N, 5.90%. IR (Nujol mull, CsI): ν(Pt–Cl) 296 and 317 cm^{-1}. NMR (room temperature, CD_2Cl_2): ^1H, δ 2.75 (s, 3 H, 2-Me) and 2.56 (s, 3 H, 4-Me); ^{13}C, δ 25.55 (2-Me) and 18.61 (4-Me); ^{31}P, δ 11.5 [^1J(Pt–P) = 3660 Hz]; ^{195}Pt ($CDCl_3$) δ −4433.53.

Reactions of trans-[Pd(dpnapy)$_2$$Cl_2$] **2**.—*With* [{Rh(CO)$_2$Cl}$_2$]. Complex **2** (0.100 g, 0.116 mmol) was treated with [{Rh(CO)$_2$Cl}$_2$] (0.023 g, 0.058 mmol) in dichloromethane (40 cm^3) and the resulting mixture left to stir for *ca*. 30 min. During this time an orange precipitate was formed. It was filtered off, washed four times with dichloromethane and then with diethyl ether and dried *in vacuo*. It was identified as *cis,cis*-[{Rh(CO)(μ-dpnapy)Cl}$_2$] by comparison of its spectroscopic data with those of an authentic sample.[2] Yield 0.054 g (92%). Addition of hexane to the mother-liquor gave *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$]. Yield 0.055 g (91%).

With cis-[Pt(dmso)$_2$$Cl_2$]. Solid *cis*-[Pt(dmso)$_2$$Cl_2$] (0.049 g, 0.116 mmol) was added to a dichloromethane mixture containing complex **2** (0.100 g, 0.116 mmol). The resulting mixture was left to stir for *ca*. 2 h, during which time the initial colourless solution became yellow-orange while a light brown solid precipitated. This was filtered off and to the filtrate hexane (20 cm^3) was added inducing the precipitation of *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$]. Yield 0.050 g (83%, based on palladium).

X-Ray Data Collection and Structure Refinement.—Diffraction data for dpnapy and *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$] **1** were collected at 298 K with a Siemens R3m/V automatic four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). To avoid loss of solvent, a 0.13 × 0.38 × 0.42 mm crystal of **1** was sealed in a Lindemann tube and then used for intensity data collection. Lattice parameters were obtained from least-squares refinement of the setting angles of 25 reflections in the range $15 \leqslant 2\theta \leqslant 30°$. Information concerning the conditions of crystallographic data collection and structure refinement is summarized in Table 3.

A total of 3635 (dpnapy) and 8674 (**1**) reflections were collected by the variable-speed ω–2θ scan method in the range 2θ $3 \leqslant 2\theta \leqslant 50°$ with *hkl* ranges 0–15, 0–12, −16 to 16 (dpnapy) and 0–15, 0–21, −22 to 22 (**1**); 3240 (dpnapy) and 7857 (**1**) were unique and, from these, 2017 (dpnapy) and 4983 (**1**) were assumed as observed [$I \geqslant 3\sigma(I)$] and used for the refinement of the structures. Examination of three standard reflections, monitored after every 150, showed no sign of crystal deterioration. Both data sets were corrected for Lorentz-polarization effects. ψ-Scan absorption corrections[13] were applied to the intensity data for **1** (maximum and minimum transmission factors 0.614 and 0.547).

The structure of dpnapy was solved by direct methods while that of complex **1** was solved by standard Patterson methods with the SHELXTL PLUS program[14] and subsequently completed by Fourier recycling. The full-matrix least-squares refinement was based on $|F_o|$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. The final full-matrix least-squares refinement, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + q(F_o)^2]$, where $q = 0.0010$ (dpnapy) and 0.0020 (**1**), converged at *R* and *R'* values of 0.0487 and 0.0568 for dpnapy and 0.0437 and 0.0462 for **1**. The corresponding ratios (observed reflections) : (refined parameters) were 8.9 and 9.7 : 1, respectively. Neutral-atom scattering factors and anomalous dispersion corrections were taken into account.[15] The last geometrical calculations were performed with the (locally modified) PARST program.[16] The final atomic co-ordinates for non-hydrogen atoms are given in Tables 4 and 5 and selected bond lengths and angles in Tables 1 and 2 for dpnapy and compound **1**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Synthesis, Characterization and Reactivity of the Metallocycle trans,trans-[{Pd(μ-dpnapy)Cl_2}$_2$] **1**.—The addition of an equivalent of dpnapy to a yellow dichloromethane solution of [Pd(cod)Cl_2] results in a dark orange solution from which the metallocycle *trans,trans*-[{Pd(μ-dpnapy)Cl_2}$_2$] **1** can be recovered. Compound **1** is an air-stable orange crystalline solid which dissolves easily in chlorinated solvents and sparingly in acetone and alcohols. It was characterized by IR and NMR spectroscopic methods as well as by an X-ray diffraction investigation which showed that **1** is composed of two *trans* Cl–Pd–Cl moieties joined by two dpnapy ligands in a head-to-tail arrangement. The NMR spectra indicate the solution geometry is the same as that in the crystal structure. The ^{31}P NMR spectrum shows a single resonance centred at δ 21.69, while the ^{1}H and ^{13}C spectra show the resonances due to the 2-Me protons and carbons at δ 3.53 and 29.13, respectively, significantly downfield with respect to the corresponding values exhibited by free dpnapy (δ 2.73 and 25.60). As we have previously pointed out,[2,6,7] when dpnapy co-ordinates to a metal through N(1) the 2-Me protons and carbons resonate much more downfield than those of the corresponding free dpnapy owing to the magnetic anisotropy of the metal.[17]

As evidenced by the ^{31}P NMR spectra, the addition of 1 equivalent of dpnapy to complex **1** in $CDCl_3$ at room temperature (r.t.) does not produce any change. On warming (60 °C, 24 h) rupture of the metallocycle and formation of *trans*-[Pd(dpnapy)$_2$Cl$_2$] **2** is observed.

Attempts to include species such as $HgCl_2$, $SnCl_2$ or AgX (X = BF_4 and CF_3CO_2) in the cavity of the palladium metallocycle failed. These results are in keeping with the X-ray diffraction findings which show that the constraints of the cavity preclude the inclusion of a metal ion.

The mechanism of the reaction between [Pd(cod)Cl$_2$] and dpnapy leading to the formation of complex **1** is unknown. The ^{31}P NMR spectra revealed that the reaction occurs through the formation of many, not isolated species which over a period of *ca.* 2 h rearrange giving **1** as the only final product.

Reaction of dpnapy and trans-[Pd(PhCN)$_2$Cl$_2$] *in* 1 : 1 *Molar Ratio.*—Unexpectedly, when *trans*-[Pd(PhCN)$_2$Cl$_2$] is used as starting palladium complex a different product is obtained. The addition of an equivalent of dpnapy to CH_2Cl_2 solution of *trans*-[Pd(PhCN)$_2$Cl$_2$] affords a dark yellow microcrystalline precipitate in good yield. Owing to its low solubility a satisfactory spectroscopic characterization is prevented. Its formulation is tentatively proposed on the basis of microanalysis and IR spectroscopic data. The microanalytical data yield the formulation Pd(dpnapy)Cl$_2$ while the solid IR spectrum, displaying two Pd–Cl stretches at 342 and 291 cm^{-1}, is indicative of a *cis* configuration of chlorines. Further information was obtained by monitoring the reaction by ^{1}H NMR spectroscopy ($CDCl_3$, r.t.) before precipitation of the complex occurs. This reveals the presence of a species exhibiting a resonance at δ 3.35 for the 2-Me protons, indicative of N(1) co-ordination. On the basis of these observations we suppose that this compound may be the *cis,cis* isomer of the metallocycle **1** displaying an overall geometry similar to that found in *cis,cis*-[{Rh(CO)(μ-dpnapy)Cl}$_2$],[2] although a formulation as a polynuclear species cannot be excluded.

Mixtures of unidentified compounds have been obtained from the reactions of dpnapy and [Pt(cod)Cl$_2$] or *cis*-[Pt(dmso)$_2$Cl$_2$] in 1 : 1 ligand-to-metal molar ratio.

Synthesis of the Complexes [M(dpnapy)$_2$Cl$_2$] (M = Pd **2** *or* Pt **3**).—Treatment of [Pd(cod)Cl$_2$] or *trans*-[Pd(PhCN)$_2$Cl$_2$] with 2 equivalents of dpnapy in dichloromethane solution affords the mononuclear complex *trans*-[Pd(dpnapy)$_2$Cl$_2$] **2**, in which dpnapy acts as a P-monodentate ligand. Complex **2** is a light yellow solid insoluble in the most common solvents. Its formulation is based on microanalytical data while the *trans* configuration, with two dangling dpnapy-*P*, is assigned on the basis of the single ν(Pd–Cl) absorption observed at 366 cm^{-1}. Steric demands[18] of dpnapy can account for the formation of the *trans* isomer, usually less stable than the *cis* for diphosphinepalladium dihalide complexes.[19]

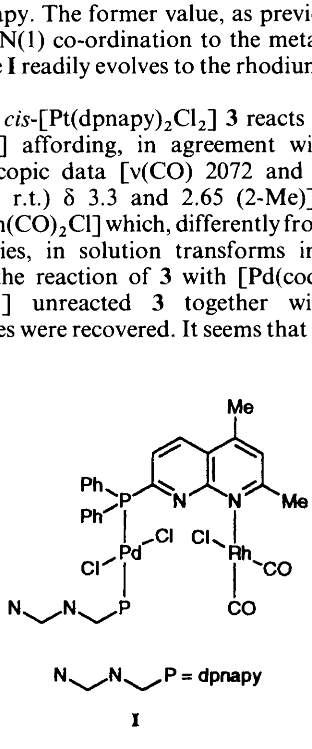
The *cis*-[Pt(dpnapy)$_2$Cl$_2$] **3** isomer is obtained from the reaction of *cis*-[Pt(dmso)$_2$Cl$_2$] or [Pt(cod)Cl$_2$] with 2 equivalents of dpnapy. It is a white crystalline solid soluble in chlorinated solvents. The solid-state IR spectrum shows two ν(Pt–Cl) absorptions at 296 and 317 cm^{-1}, while the ^{31}P NMR spectrum displays a sharp resonance at δ 11.5 with a coupling constant of 3660 Hz to ^{195}Pt satellites. The coupling constant is consistent with the presence of two phosphorus atoms in mutually *cis* positions.[20a,21] The ^{195}Pt NMR spectrum displays a sharp resonance at δ −4433.5.

Reactivity of the Complexes [M(dpnapy)$_2$Cl$_2$] (M = Pd **2** *or* Pt **3**).—Platinum(II) and palladium(II) complexes containing dangling bidentate ligands have been used in a number of instances to prepare homo- and hetero-binuclear complexes. In this context 1,2-bis(diphenylphosphino)methane and the hetero bidentate 2-(diphenylphosphino)pyridine and (diphenylarsino)(diphenylphosphino)methane have been very useful.[20b,c,22] Our attention then turned to the prospect of synthesizing homo- and hetero-bimetallic metallocycles by treating **2** and **3** with appropriate metal complexes.

The reaction of *trans*-[Pd(dpnapy)$_2$Cl$_2$] **2** with an equivalent of [Pd(cod)Cl$_2$] or [Pd(PhCN)$_2$Cl$_2$] readily produces the metallocycle *trans,trans*-[{Pd(μ-dpnapy)Cl$_2$}$_2$] in quantitative amount. Complex **1** is also the main product (83%, based on palladium), together with other unidentified Pt-containing species, of the reaction between **2** and *cis*-[Pt(dmso)$_2$Cl$_2$]. These reactions are very fast and no information on their mechanism was obtained by NMR spectroscopy even at low temperature. However it is evident that the reaction leading to **1** occurs with substantial ligand rearrangement. On the contrary, the resultant palladocycle would have dpnapy in a head-to-head rather than head-to-tail arrangement.

Complex **2** reacts with 1 equivalent of [{Rh(CO)$_2$Cl}$_2$] affording quantitatively the dpnapy metallocycles *cis,cis*-[{Rh(CO)(μ-dpnapy)Cl}$_2$] and *trans,trans*-[{Pd(μ-dpnapy)Cl$_2$}$_2$]. The formation of the metallocycles requires the transfer of a dpnapy molecule from palladium to rhodium with breaking of the Pd–P bond. Monitoring of the reaction by IR and proton NMR spectroscopy indicates that the first step involves attack of N(1) on rhodium with likely formation of the species [Cl$_2$(dpnapy)Pd(μ-dpnapy)Rh(CO)$_2$Cl] **I**. Consistent with the proposed structure two ν(CO) bands are observed in the IR spectrum (CH_2Cl_2) at 2070 and 2003 cm^{-1}, characteristic of a neutral *cis* dicarbonylrhodium species. The ^{1}H NMR spectrum ($CDCl_3$, r.t.) shows two signals at δ 3.2 and 2.75 for the 2-Me protons of dpnapy. The former value, as previously described, is indicative of N(1) co-ordination to the metal. Once formed the intermediate **I** readily evolves to the rhodium and palladium metallocycles.

The complex *cis*-[Pt(dpnapy)$_2$Cl$_2$] **3** reacts with 0.5 mol of [{Rh(CO)$_2$Cl}$_2$] affording, in agreement with the IR and NMR spectroscopic data [ν(CO) 2072 and 2005 cm^{-1}; ^{1}H NMR ($CDCl_3$, r.t.) δ 3.3 and 2.65 (2-Me)] [Cl$_2$(dpnapy)Pt(μ-dpnapy)Rh(CO)$_2$Cl] which, differently from the palladium analogous species, in solution transforms into unidentified species. From the reaction of **3** with [Pd(cod)Cl$_2$] or *trans*-[Pd(PhCN)$_2$Cl$_2$] unreacted **3** together with unidentified palladium species were recovered. It seems that platinum(II) like



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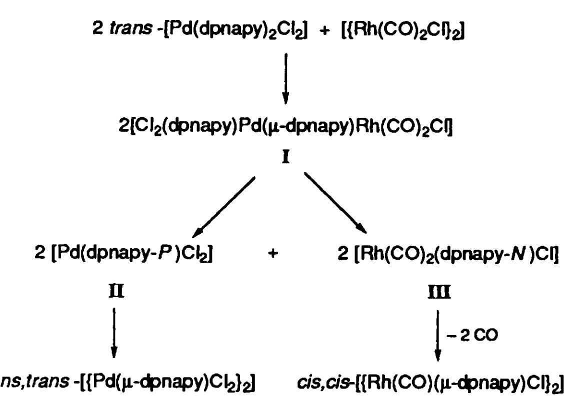


Scheme 1

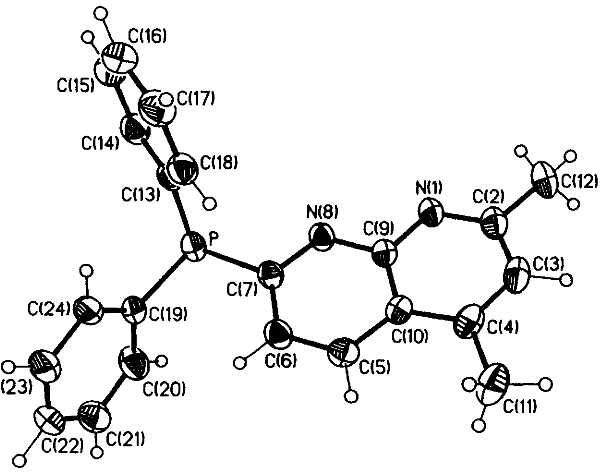


Fig. 1 Molecular structure and atomic numbering of dpnapy. Thermal ellipsoids are drawn at 50% probability while the hydrogen-atom size is arbitrary

iridium(I)[6] complexes have no tendency to form metallocycles with dpnapy.

The above results allow us to make some conclusions on the mechanism operating in these reactions which seems to proceed *via* transfer and ligand rearrangement. Transfer and successive reorientation of heterobifunctional phosphine ligands from one metal centre to another is not an unknown process. Usually it is assisted by another bridging ligand and accompanied by the formation of a metal–metal bond.[20b,c,4f] Furthermore Balch and co-workers[20b,c] have shown that the analagous reactions between $[M(NC_5H_4PPh_2)_2Cl_2]$ [M = Pd or Pt; $NC_5H_4PPh_2$ = 2-(diphenylphosphino)pyridine] and $[\{Rh(CO)_2Cl\}_2]$, leading to the head-to-tail binuclear complex $[MPd(\mu\text{-}NC_5H_4PPh_2)_2(CO)Cl_3]$, initially proceed *via* formation of the intermediate $[MRh(NC_5H_4PPh_2)_2Cl][Rh(CO)_2Cl_2]$ by transfer of a chloride from palladium or platinum to rhodium. We cannot invoke the same mechanism because there is no evidence for the formation of a similar ionic intermediate. On the contrary our results can reasonably be explained if the dissociation of one dpnapy molecule occurs. In this light the reaction between *trans*-$[Pd(dpnapy)_2Cl_2]$ and $[\{Rh(CO)_2Cl\}_2]$ could proceed initially, as mentioned before, *via* formation of the intermediate **I**. Subsequent breakage of a Pd–P bond, favoured by the *trans* effect exercised by the second dangling dpnapy-*P*, generates the two moieties *trans*-Pd(dpnapy-*P*)Cl_2 **II** and *cis*-$Rh(CO)_2$(dpnapy-*N*)Cl **III** which dimerize giving the homometallocycles *trans,trans*-$[\{Pd(\mu\text{-dpnapy})Cl_2\}_2]$ and *cis,cis*-$[\{Rh(CO)(\mu\text{-dpnapy})Cl\}_2]$, respectively (Scheme 1).

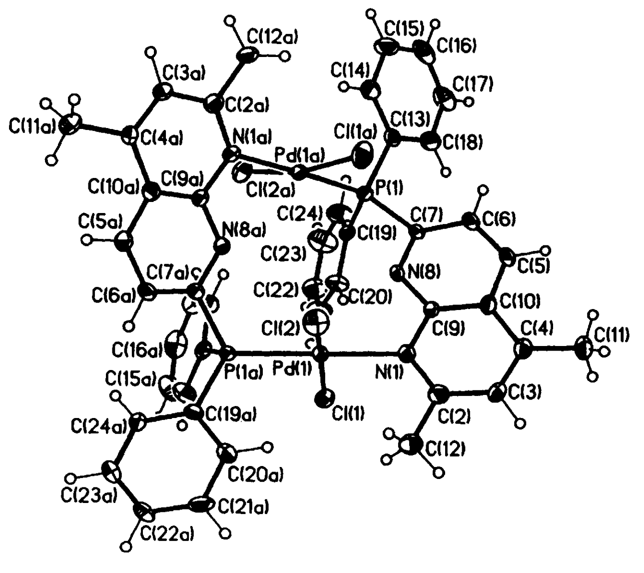


Fig. 2 Molecular structure and atomic numbering of complex **1**. The two water molecules are omitted for clarity. Other details as in Fig. 1

Table 1 Selected interatomic distances (Å) and angles (°) for dpnapy with estimated standard deviations (e.s.d.s) in parentheses

P–C(7)	1.846(3)	P–C(13)	1.823(4)
P–C(19)	1.830(3)	N(1)–C(2)	1.316(5)
N(1)–C(9)	1.369(4)	C(2)–C(3)	1.415(5)
C(2)–C(12)	1.488(5)	C(3)–C(4)	1.363(5)
C(4)–C(10)	1.419(5)	C(4)–C(11)	1.502(5)
C(10)–C(9)	1.416(4)	C(10)–C(5)	1.401(4)
C(9)–N(8)	1.353(4)	N(8)–C(7)	1.320(4)
C(7)–C(6)	1.405(4)	C(6)–C(5)	1.356(5)
C(7)–P–C(13)	102.2(1)	C(7)–P–C(19)	101.1(1)
C(13)–P–C(19)	102.7(1)	C(2)–N(1)–C(9)	117.5(3)
N(1)–C(2)–C(3)	122.5(3)	N(1)–C(2)–C(12)	117.4(3)
C(3)–C(2)–C(12)	120.1(3)	C(2)–C(3)–C(4)	121.5(3)
C(3)–C(4)–C(10)	117.1(3)	C(3)–C(4)–C(11)	122.0(3)
C(10)–C(4)–C(11)	120.9(3)	C(4)–C(10)–C(9)	118.1(3)
C(4)–C(10)–C(5)	124.9(3)	C(9)–C(10)–C(5)	116.9(3)
N(1)–C(9)–C(10)	123.1(3)	N(1)–C(9)–N(8)	114.6(3)
C(10)–C(9)–N(8)	122.3(3)	C(9)–N(8)–C(7)	118.6(3)
P–C(7)–N(8)	112.7(2)	P–C(7)–C(6)	124.4(2)
N(8)–C(7)–C(6)	122.8(3)	C(7)–C(6)–C(5)	118.9(3)
C(10)–C(5)–C(6)	120.4(3)	P–C(13)–C(14)	117.1(3)

The same mechanism may be operating in the reaction of complex **2** with $[Pd(cod)Cl_2]$ or *trans*-$[Pd(PhCN)_2Cl_2]$. In this case, after the initial attack of N(1) on the incoming palladium centre, the intermediates [Pd(dpnapy-*P*)Cl_2] and [Pd(dpnapy-*N*)(η^2-cod)Cl_2] or [Pd(dpnapy-*N*)(PhCN)Cl_2] are, respectively, formed. These readily dimerize giving the palladium metallocycle **1**.

The reactions of *cis*-$[Pt(dpnapy)_2Cl_2]$ with $[Pd(cod)Cl_2]$, *trans*-$[Pd(PhCN)Cl_2]$ or $[\{Rh(CO)_2Cl\}_2]$, which do not produce metallocycles, proceed in a different way very likely as a consequence of the inertness of the Pt^{II}–P bond compared with the Pd^{II}–P one and the different geometry of **3** from that of the palladium analogue.

Molecular Structure of dpnapy.—The molecule is constituted by a 2,4-dimethyl-1,8-naphthyridine moiety linked to a diphenylphosphine group in position 7, as illustrated in Fig. 1. The atoms of the two fused pyridine rings lie almost on a plane from which the maximum deviation is 0.058(4) Å for atom C(3). With respect to this mean plane the two phenyl rings of the phosphine, C(13)–C(18) and C(19)–C(24), form dihedral angles of 69.9(1) and 85.6(1)°, respectively. The phosphorus atom shows the expected very distorted tetrahedral geometry characterized by an average P–C bond distance of 1.833(3) Å

Table 2 Selected interatomic distances (Å) and angles (°) for complex **1** with e.s.d.s in parentheses

Pd(1)–P(1)	2.234(2)	Pd(1)–Cl(1)	2.298(2)	C(4)–C(11)	1.494(11)	C(5)–C(6)	1.360(10)
Pd(1)–Cl(2)	2.317(2)	Pd(1)–N(1)	2.118(5)	C(5)–C(10)	1.422(10)	C(6)–C(7)	1.398(9)
Pd(1a)–P(1a)	2.221(2)	Pd(1a)–Cl(2a)	2.303(2)	C(7)–N(8)	1.325(8)	N(8)–C(9)	1.356(8)
Pd(1a)–Cl(1a)	2.308(2)	Pd(1a)–N(1a)	2.095(6)	C(9)–C(10)	1.410(9)	N(1a)–C(2a)	1.313(9)
P(1)–C(7a)	1.850(7)	P(1)–C(13a)	1.824(7)	N(1a)–C(9a)	1.381(9)	C(2a)–C(3a)	1.432(10)
P(1)–C(19a)	1.803(7)	P(1a)–C(7)	1.845(7)	C(2a)–C(12a)	1.502(10)	C(3a)–C(4a)	1.358(10)
P(1a)–C(13)	1.821(7)	P(1a)–C(19)	1.808(7)	C(4a)–C(10a)	1.433(10)	C(4a)–C(11a)	1.489(11)
N(1)–C(2)	1.327(9)	N(1)–C(9)	1.373(8)	C(5a)–C(6a)	1.362(10)	C(5a)–C(10a)	1.405(10)
C(2)–C(3)	1.403(10)	C(2)–C(12)	1.489(11)	C(6a)–C(7a)	1.401(9)	C(7a)–N(8a)	1.330(8)
C(3)–C(4)	1.367(11)	C(4)–C(10)	1.428(10)	N(8a)–C(9a)	1.352(8)	C(9a)–C(10a)	1.397(9)
P(1)–Pd(1)–Cl(1)	89.8(1)	P(1)–Pd(1)–Cl(2)	90.8(1)	C(6)–C(5)–C(10)	119.9(6)	C(5)–C(6)–C(7)	118.8(6)
Cl(1)–Pd(1)–Cl(2)	168.4(1)	P(1)–Pd(1)–N(1)	177.6(2)	P(1a)–C(7)–C(6)	125.5(5)	P(1a)–C(7)–N(8)	110.8(5)
Cl(1)–Pd(1)–N(1)	88.4(2)	Cl(2)–Pd(1)–N(1)	91.3(2)	C(6)–C(7)–N(8)	123.6(6)	C(7)–N(8)–C(9)	117.7(6)
P(1a)–Pd(1a)–Cl(2a)	90.8(1)	P(1a)–Pd(1a)–Cl(1a)	89.6(1)	N(1)–C(9)–N(8)	114.3(6)	N(1)–C(9)–C(10)	122.5(6)
Cl(2a)–Pd(1a)–Cl(1a)	168.6(1)	P(1a)–Pd(1a)–N(1a)	178.1(2)	N(8)–C(9)–C(10)	123.2(6)	C(4)–C(10)–C(5)	125.1(6)
Cl(2a)–Pd(1a)–N(1a)	88.5(2)	Cl(1a)–Pd(1a)–N(1a)	91.5(2)	C(4)–C(10)–C(9)	118.5(6)	C(5)–C(10)–C(9)	116.4(6)
Pd(1)–P(1)–C(7a)	111.7(2)	Pd(1)–P(1)–C(13a)	115.9(2)	Pd(1a)–N(1a)–C(2a)	125.0(5)	Pd(1a)–N(1a)–C(9a)	116.2(4)
C(7a)–P(1)–C(13a)	102.3(3)	Pd(1)–P(1)–C(19a)	112.5(2)	C(2a)–N(1a)–C(9a)	118.7(6)	N(1a)–C(2a)–C(3a)	122.1(7)
C(7a)–P(1)–C(19a)	107.4(3)	C(13a)–P(1)–C(19a)	106.2(3)	N(1a)–C(2a)–C(12a)	119.4(7)	C(3a)–C(2a)–C(12a)	118.5(7)
Pd(1a)–P(1a)–C(7)	111.5(2)	Pd(1a)–P(1a)–C(13)	111.8(2)	C(2a)–C(3a)–C(4a)	120.6(7)	C(3a)–C(4a)–C(10a)	117.6(6)
C(7)–P(1a)–C(13)	110.2(3)	Pd(1a)–P(1a)–C(19)	115.2(2)	C(3a)–C(4a)–C(11a)	121.1(7)	C(10a)–C(4a)–C(11a)	121.4(6)
C(7)–P(1a)–C(19)	102.6(3)	C(13)–P(1a)–C(19)	104.9(3)	C(6a)–C(5a)–C(10a)	120.6(6)	C(5a)–C(6a)–C(7a)	118.8(6)
Pd(1)–N(1)–C(2)	124.6(5)	Pd(1)–N(1)–C(9)	116.9(4)	P(1)–C(7a)–C(6a)	123.7(5)	P(1)–C(7a)–N(8a)	113.3(5)
C(2)–N(1)–C(9)	118.4(6)	N(1)–C(2)–C(3)	121.3(7)	C(6a)–C(7a)–N(8a)	122.9(6)	C(7a)–N(8a)–C(9a)	117.3(6)
N(1)–C(2)–C(12)	117.6(6)	C(3)–C(2)–C(12)	121.1(7)	N(1a)–C(9a)–N(8a)	113.7(6)	N(1a)–C(9a)–C(10a)	122.0(6)
C(2)–C(3)–C(4)	122.8(7)	C(3)–C(4)–C(10)	116.4(6)	N(8a)–C(9a)–C(10a)	124.3(6)	C(4a)–C(10a)–C(5a)	125.1(6)
C(3)–C(4)–C(11)	121.7(7)	C(10)–C(4)–C(11)	122.0(7)	C(4a)–C(10a)–C(9a)	118.9(6)	C(5a)–C(10a)–C(9a)	116.0(6)

Table 3 Crystallographic data for dpnapy and complex **1** *

	dpnapy	**1**
Formula	$C_{22}H_{19}N_2P$	$C_{44}H_{42}Cl_4N_4O_2P_2Pd_2$
M	342.4	1075.4
a/Å	13.190(2)	12.810(2)
b/Å	10.262(2)	18.148(3)
c/Å	13.548(2)	19.076(3)
β/°	95.06(2)	91.59(2)
U/Å^3	1826.7(5)	4433(1)
D_c/g cm^{-3}	1.245	1.611
F(000)	720	2160
Crystal size/mm	0.45 × 0.32 × 0.38	0.13 × 0.38 × 0.42
μ(Mo-Kα)/cm^{-1}	1.56	11.66
R	0.0487	0.0437
R'	0.0568	0.0462
S	1.58	1.00
Maximum shift/error	0.031	0.174
Maximum difference peak, hole/e Å^{-3}	0.25, −0.30	1.01, −1.25

* Details in common: space group $P2_1/n$; monoclinic; $Z = 4$; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$, where N_o, N_p = numbers of observations and parameters.

Table 4 Final atomic coordinates (× 10^4) for dpnapy with e.s.d.s in parentheses

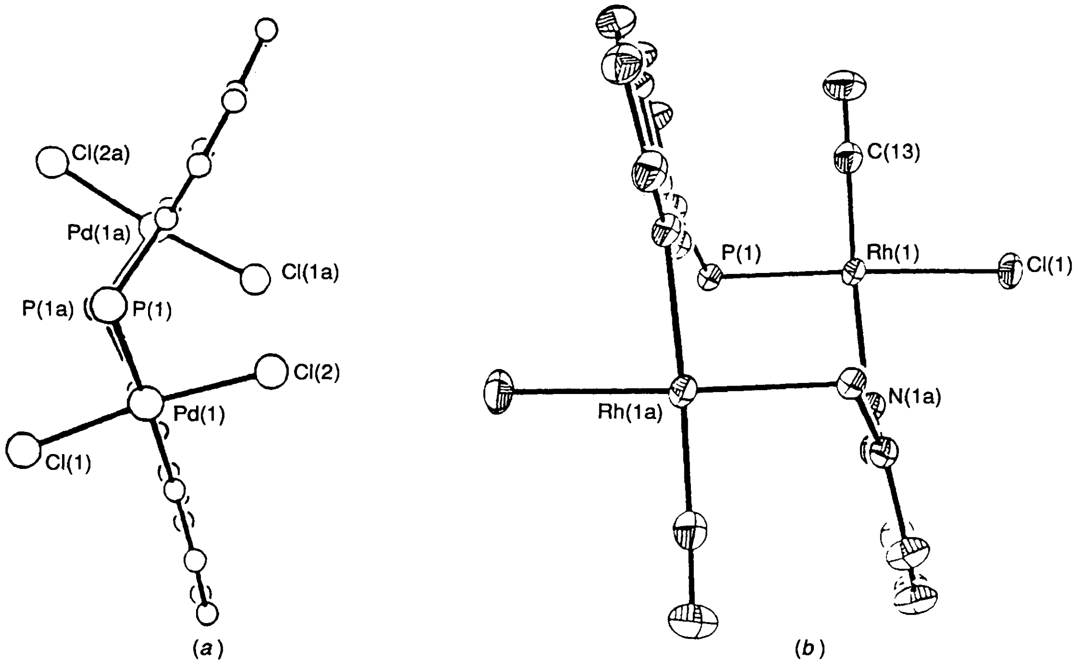
Atom	*x*	*y*	*z*
P	3028(1)	1541(1)	1099(1)
N(1)	2710(2)	4853(3)	−1535(2)
C(2)	2794(3)	6018(4)	−1925(3)
C(3)	3249(3)	7077(4)	−1383(3)
C(4)	3671(3)	6930(3)	−435(3)
C(10)	3614(2)	5673(3)	−5(2)
C(9)	3092(2)	4682(3)	−571(2)
N(8)	2934(2)	3483(3)	−198(2)
C(7)	3297(2)	3225(3)	720(2)
C(6)	3863(3)	4132(3)	1319(2)
C(5)	4016(3)	5340(3)	953(2)
C(11)	4169(3)	8042(4)	143(3)
C(12)	2391(3)	6196(4)	−2977(3)
C(13)	1686(3)	1631(3)	1315(2)
C(14)	1112(3)	515(4)	1139(2)
C(15)	107(4)	460(5)	1316(3)
C(16)	−357(3)	1536(6)	1663(3)
C(17)	185(3)	2664(5)	1829(3)
C(18)	1197(3)	2723(4)	1654(3)
C(19)	3660(3)	1511(3)	2356(2)
C(20)	4689(3)	1232(4)	2442(3)
C(21)	5255(3)	1255(4)	3337(3)
C(22)	4800(3)	1494(4)	4180(3)
C(23)	3778(3)	1744(4)	4121(3)
C(24)	3212(3)	1749(4)	3222(2)

and a mean bond angle 102.0(1)°, in agreement with values reported for similar compounds.

No distortion has been found in the naphthyridine plane caused by lone-pair repulsion, as found in free naphthyridine which appears to be slightly non-planar.[23] The authors explained its chelating action by co-ordination effects which, deforming the electron-density distribution of the two lone pairs and then decreasing their repulsion, allow the system to assume the observed planarity in the corresponding complexes.

The naphthyridine mean plane forms with the plane passing through C(7), C(13) and C(19) a dihedral angle of 134.2(1)° instead of the expected 90°. As a consequence the lone pair on P is directed away from the naphthyridine plane on which the two nitrogen lone pairs lie. The expected linear tridentate co-ordination might then be possible only if the diphenylphosphine group rotates around the P–C(7) bond until the above dihedral angle is close to 90°. In this way the three lone pairs are oriented in the same direction.

A rotation of the diphenylphosphine group of 180° with respect to this ideal trinucleating geometry still leaves the phosphorus lone pair on the naphthyridine plane but directed in the opposite direction with respect to that of the nitrogen atoms. Such an arrangement has been found in the binuclear complex [{Ir(cod)Cl}$_2$(μ-dpnapy)] where dpnapy co-ordinates two iridium centres on opposite sites, *via* the phosphorus and the 'terminal' N(1) atoms.[6]



(*a*) (*b*)

Fig. 3 Views of (*a*) *trans,trans*-[{Pd(μ-dpnapy)Cl$_2$}$_2$] and (*b*) *cis,cis*-[{Rh(CO)(μ-dpnapy)Cl}$_2$], evidencing the different arrangement of the ligands around the metal centres in the two metallocycles

Table 5 Final atomic coordinates (× 10^4) for complex **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	1329(1)	1337(1)	1693(1)	C(22)	−1480(7)	3297(5)	−303(4)
Pd(1a)	−731(1)	3169(1)	2725(1)	C(23)	−1777(8)	3913(6)	48(5)
P(1)	−112(1)	661(1)	1810(1)	C(24)	−1338(7)	4099(5)	679(5)
P(1a)	−68(1)	3848(1)	1877(1)	N(1a)	−1361(4)	2500(3)	3502(3)
Cl(1)	1050(2)	1346(1)	498(1)	C(2a)	−1820(6)	2742(4)	4064(4)
Cl(2)	1817(2)	1121(1)	2854(1)	C(3a)	−2318(6)	2256(4)	4543(4)
Cl(2a)	−2337(1)	3156(1)	2152(1)	C(4a)	−2309(6)	1515(4)	4438(4)
Cl(1a)	750(2)	3386(1)	3410(1)	C(5a)	−1634(6)	496(4)	3677(4)
N(1)	2662(4)	2006(3)	1550(3)	C(6a)	−1119(6)	295(4)	3092(4)
C(2)	3601(6)	1753(4)	1399(4)	C(7a)	−745(5)	847(3)	2651(3)
C(3)	4433(6)	2234(4)	1275(4)	N(8a)	−845(4)	1562(3)	2788(3)
C(4)	4344(5)	2983(4)	1326(4)	C(9a)	−1330(5)	1749(4)	3383(3)
C(5)	3111(6)	4014(4)	1633(4)	C(10a)	−1765(5)	1244(4)	3844(3)
C(6)	2116(6)	4219(4)	1771(4)	C(11a)	−2859(7)	1007(5)	4917(4)
C(7)	1342(5)	3677(3)	1791(3)	C(12a)	−1836(7)	3555(4)	4212(4)
N(8)	1533(4)	2963(3)	1733(3)	C(13a)	−1167(5)	837(4)	1171(4)
C(9)	2527(5)	2754(3)	1605(3)	C(14a)	−1353(7)	359(5)	618(4)
C(10)	3350(5)	3259(4)	1521(3)	C(15a)	−2143(8)	527(5)	129(5)
C(11)	5240(6)	3483(5)	1184(5)	C(16a)	−2716(7)	1164(6)	178(5)
C(12)	3734(6)	939(4)	1347(5)	C(17a)	−2519(7)	1640(5)	726(4)
C(13)	−307(5)	4827(3)	2010(4)	C(18a)	−1738(6)	1482(4)	1212(4)
C(14)	−900(6)	5021(4)	2576(4)	C(19a)	145(6)	−315(4)	1774(3)
C(15)	−1195(7)	5760(5)	2676(5)	C(20a)	1174(6)	−566(4)	1705(4)
C(16)	−864(8)	6286(5)	2222(6)	C(21a)	1386(6)	−1313(4)	1656(4)
C(17)	−280(8)	6087(4)	1657(6)	C(22a)	607(7)	−1812(4)	1697(4)
C(18)	20(7)	5362(4)	1552(4)	C(23a)	−411(7)	−1590(4)	1756(4)
C(19)	−584(5)	3656(3)	1005(3)	C(24a)	−642(6)	−843(4)	1797(4)
C(20)	−296(7)	3015(4)	651(4)	O(1)	4197(10)	6847(7)	679(6)
C(21)	−768(7)	2835(5)	12(4)	O(2)	4241(13)	5356(9)	445(8)

Molecular Structure of trans,trans-[{Pd(μ-dpnapy)Cl$_2$}$_2$]·2H$_2$O **1**.—The crystal packing of compound **1** consists of [{Pd(μ-dpnapy)Cl$_2$}$_2$] and water molecules of crystallization in 1:2 ratio with no significant interaction of the latter with the complex. The crystal structure can formally be described as built up of two *trans*-PdCl$_2$ fragments connected through two bridging dpnapy groups in a head-to-tail arrangement, as shown in Fig. 2. The bridging function of the ligand is realized through the phosphorus and N(1) atoms.

Each palladium centre atom is in a square-planar arrangement, being linked to two chlorine atoms and to the phosphorus and terminal nitrogen atoms of two different dpnapy molecules. The Pd–Cl, Pd–N and Pd–P distances are similar to those found in related compounds and do not require special comment. Atoms Pd(1) and Pd(1a) are out of the corresponding co-ordination planes [largest deviation 0.174(1) and 0.167(1) Å, respectively] which form a reciprocal dihedral angle of 15.5(1)°. The central cavity of the complex is almost a regular square: the Pd(1)···Pd(1a) distance is 4.710(1) Å while the separation between the central unco-ordinated N(8) and N(8a) atoms is 4.487(8) Å. Each fragment formed by naphthyridine, the phosphorus and the metal atom is almost planar and the dihedral angle between the two corresponding mean planes, intersecting at the two phosphorus atoms, is 51.8° [see Fig. 3(*a*)].

It is instructive to compare the structure of complex **1** with that of $[\{Pt(\mu\text{-dppy})I_2\}_2]$[24] as both compounds display a *trans* disposition of the two halides and of the two bridging ligands. The two metals and bridging ligands determine a quasi-planar twelve-membered metallocycle, in the cavity of which a metal atom may be located. As already stated the co-ordination of a metal ion in the cavity of a metallocycle requires the *trans* disposition of the two tridentate bridging ligands. For comparison in Fig. 3 are shown views of *trans,trans*-$[\{Pd(\mu\text{-dpnapy})Cl_2\}_2]$ and *cis,cis*-$[\{Rh(CO)(\mu\text{-dpnapy})Cl\}_2]$[2] from which the direction of the lone pairs of the central binding sites can be proposed. In agreement, the *trans,trans*-$[\{Rh(CO)(\mu\text{-dppy})Cl\}_2]$[8] metallocycle co-ordinates a $SnCl^+$ moiety in its cavity by formation of Sn–N and Sn–Rh bonds.

The dppy metallocycle shows a cavity larger than that in the dpnapy complex, mainly due to the longer phosphorus–metal bond length with respect to the nitrogen–metal interaction. Indeed the N ··· N distance in $[\{Pt(\mu\text{-dppy})I_2\}_2]$ is 5.057 Å (the reported value of 3.123 Å is wrong), which is significantly larger than the 4.487 Å as found in **1**. This difference seems to depend more on the bond distances than on the value of the dihedral angle between the pyridine planes in $[\{Pt(\mu\text{-dppy})I_2\}_2]$, which is larger than the angle between the naphthyridine planes in **1** (71.9 *vs.* 46°). In $[Cl_2(CO)Rh(\mu\text{-dppy})_2(\mu\text{-SnCl})Rh(CO)(SnCl_3)]$[6] the corresponding dihedral angle is 21.6° with a N ··· N distance of 5.038 Å. Nevertheless, the contraction of the cavity and the shortening of the N ··· N distance in complex **1** is not so large that insertion of a metal atom into the cavity is forbidden by simple steric hindrance effects.

In conclusion, as already mentioned, the failed attempts at inclusion of metal ions in the cavity of complex **1** may be explained in terms of (*i*) the asymmetry of dpnapy and (*ii*) the dihedral angle between the naphthyridine planes, which seems too large to allow bond interaction between N(8) and N(8a) with the incoming metal ion. For $[\{Pt(\mu\text{-dppy})I_2\}_2]$ displaying a dihedral angle of 71.9° no example of inclusion was reported.

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