PERGAMON

Polyhedron 20 (2001) 3019–3025

POLYHEDRON
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Cyclometallation of 3-phenyl-6-*p*-toluidinopyridazine forming a six-membered auracycle and a five-membered palladacycle certified by X-ray analysis

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Received 2 May 2001; accepted 22 August 2001

Abstract

3-Phenyl-6-*p*-toluidinopyridazine (abbreviated as Hptp) was prepared as an ambidentate substrate of cyclometallation. Sodium tetrachloroaurate(III), gold(III) bromide, lithium tetrachloropalladate(II), and rhodium(III) chloride cyclometallated Hptp to give [Au(ptp)Cl_2], [Au(ptp)Br_2], [Pd(ptp)Cl], and [Rh$(ptp)_2$Cl], respectively. These complexes and [Pd(ptp)Cl(PBu_3)] (PBu_3 = tri-*n*-butylphosphine) were characterized spectroscopically. The square-planar structures of [Au(ptp)Br_2]·$(CH_3)_2SO$ and [Pd(ptp)Cl(PBu_3)]·CH_3OH were determined by X-ray analysis. Cycloauration preferred forming a six-membered metallacycle while cyclopalladation and cyclorhodation formed five-membered metallacycles. © 2001 Published by Elsevier Science Ltd.

Keywords: Cycloauration; Cyclopalladation; Cyclorhodation; 3-Phenyl-6-*p*-toluidinopyridazine

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1. Introduction

Cyclometallation is a procedure for activating directly the C–H bonds of organic molecules bearing suitable donor groups with appropriate metal compounds (metal = Pd, Rh, Pt, etc.) and in general, occurs preferably for substrates forming five-membered metallacycles [1]. Contrary to the well-developed area, direct cycloauration reported recently concerns, in many cases, six-membered metallacycles [2]. Such six-membered auracycles are, e.g. formed upon direct cycloauration of 2-benzylpyridine, 2-anilinopyridine, etc. while many five-membered auracycles have been obtained indirectly by transmetallation from the corresponding organomercury compounds: mercurated *N*,*N*-dimethylbenzylamine, azobenzene, etc. [3]. It looks as if cycloauration prefers forming a six-membered metallacycle. We are interested in this point and have prepared 3-phenyl-6-*p*-toluidinopyridazine (abbreviated as Hptp, Fig. 1) having two metallating sites 2′ (phenyl ring) and 2″ (*p*-tolyl group) which will result in forming a five- or a six-membered metallacycle, respectively (Fig. 2(A) and (B)). Double cyclometallation is also expected (Fig. 2(C)). Equimolar reactions of Hptp with sodium tetrachloroaurate(III) and lithium tetrachloropalladate(II) gave a six- and five-membered metallacycle, respectively (Fig. 2) but double cyclometallation was, so far, not achieved. To augment our knowledge, the reaction with Rh(III)Cl_3·$3H_2O$ was also carried out. Au(III) and Pd(II) have a d^8 electron configuration and are expected to form square-planar complexes but Rh(III) has a d^6 electron configuration and will form octahedral complexes.

2. Results and discussion

The reaction of 3-chloro-6-phenylpyridazine with *p*-toluidine in refluxing xylene gave 3-phenyl-6-*p*-toluidinopyridazine (Hptp: atom-labeling scheme for NMR spectra is given in Fig. 1) which was characterized by

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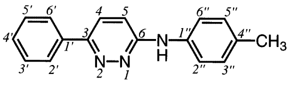
0277-5387/01/$ - see front matter
PII: S0277-5387(01)00912-3

the IR, ^1H and $^{13}C\{^1H\}$ NMR [in dimethylsulfoxide-d_6 (dmso-d_6)] spectra. Hptp reacted in an equimolar ratio with sodium tetrachloroaurate(III) and gold(III) bromide in a refluxing mixture of water and ethanol to give [Au(ptp)Cl_2] and [Au(ptp)Br_2], respectively, and with lithium tetrachloropalladate(II) in refluxing methanol [Pd(ptp)Cl]. Attempted double cyclometallation of Hptp with the two equivalent metal salts resulted in single cyclometallation: [Au(ptp)Cl_2] and $[Pd(ptp)Cl]_2$ $PdCl_2$ were obtained (the structure of the latter remains unexplained so far). Only monopalladation was reported for ligands potentially capable of undergoing double cyclopalladations, 3,6-diphenoxypyridazine and 4,6-diphenoxypyrimidine[4]. [Pd(ptp)Cl], the structure of which may be a Cl-bridged dimer as established generally for the related cyclopalladated complexes [1], did not give any suitable crystals for X-ray analysis and then the tri-*n*-butylphosphine (PBu_3) derivative, [Pd(ptp)Cl(PBu_3)], was prepared.

The ^1H NMR spectra of the complexes revealed that one aromatic proton was lost upon coordination and that the NH group was left intact. The ^1H chemical shifts of NH differed markedly between the Pd and Au complexes, suggesting the NH groups in different surroundings. The spectral pattern due to the aromatic ring protons also differed between the Pd and Au complexes. For Pd complexes the pattern of the *p*-tolyl group was retained but that of the phenyl group was altered, the latter being similar to those of the orthopalladated phenyl moieties reported in Ref. [4]. For Au complexes, the pattern of the phenyl group was retained but that of the *p*-tolyl group was altered appearing as two doublets and one singlet. In the $^{13}C\{^1H\}$ NMR spectra the number of peaks is consistent with the ^1H NMR results: six peaks were observed for the phenyl group and four for the *p*-tolyl in Pd complexes while vice versa in Au complexes. These facts suggest the modes of metallation shown in Fig. 2 ((A) for Au and (B) for Pd).



Hptp

Fig. 1. Structure of 3-phenyl-6-*p*-toluidinopyridazine (Hptp) and atom-labeling scheme for NMR spectra.

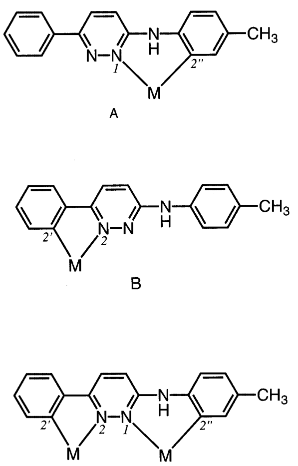


Fig. 2. Three modes of cyclometallation.

In the IR spectra (Nujol mulls) of the above complexes, the presence of ν(NH) bands indicates that the amino groups remain intact. In the ν(CN) region of the secondary aromatic amino groups, two medium-strong bands were observed for free Hptp (1324 and 1372 cm^{-1}) and similarly two for [Pd(ptp)Cl] (1355 and 1377 cm^{-1}). For [Au(ptp)X_2] (X = Cl, Br), however, only one band was observed (1377 (Cl) and 1378 (Br) cm^{-1}). The fact indicates different modes of coordination of the ligand towards the two metals. In the spectrum of [Pd(ptp)Cl] a characteristic band of five adjacent ring H atoms of free Hptp at 698 cm^{-1} was absent in the region of aromatic ring C–H out-of-plane deformation vibrations sensitive to ring substitution modes [5], while the band persisted in those of [Au(ptp)X_2]: 685 (Cl) and 694 (Br) cm^{-1}. These facts indicate that auration occurred at the *p*-tolyl group incorporating the amino group in a chelate ring and retaining the phenyl substituent intact (Fig. 2(A)) and that palladation occurred at the phenyl ring without the participation of the *p*-toluidino group (Fig. 2(B)) in agreement with the NMR results. The low energy bands of ν(M–X) are consistent with the structures where X is coordinated *trans* to the metallated carbon donor with a strong *trans* influence.

The square-planar structure of [Au(ptp)Br_2]·$(CH_3)_2SO$ in Fig. 3 is characterized with a six-membered auracycle and the overall structure is similar to that reported for [Au(anp)Cl_2] (Hanp = 2-anilinopyridine) [6,7]. The selected bond distances and bond angles are given in Table 1. One mole of dmso was included as a solvent of crystallization and the S atom was disordered. The O atom holds to N(3) through a hydrogen bond {N(3)–O(1) 2.75(1) Å}. The Au–Br lengths reflected the strong *trans* influence of the aurated carbon atom: the length *trans* to the carbon atom was approximately 0.12 Å longer than that *trans* to the nitrogen atom. The six-membered auracycle adopted a boat conformation and both Au(1) and N(3) are, respectively, 0.75(2) and 0.27(1) Å out of the mean plane defined by C(1), C(11), C(12) and N(1). The H(8) on C(13) is calculated to be close to Br(1) {2.81 Å} within the sum of the van der Waals radii (1.20 + 1.85 Å) and the unfavorable contact is relieved by the boat conformation, the aurated aromatic ring {C(11)–C(16)} making a dihedral angle of 36.4(3)° with the coordination plane {Au(1), Br(1), Br(2), C(12) and N(1)}. The angle 86.9(4)° at Au in the chelate ring is small as for

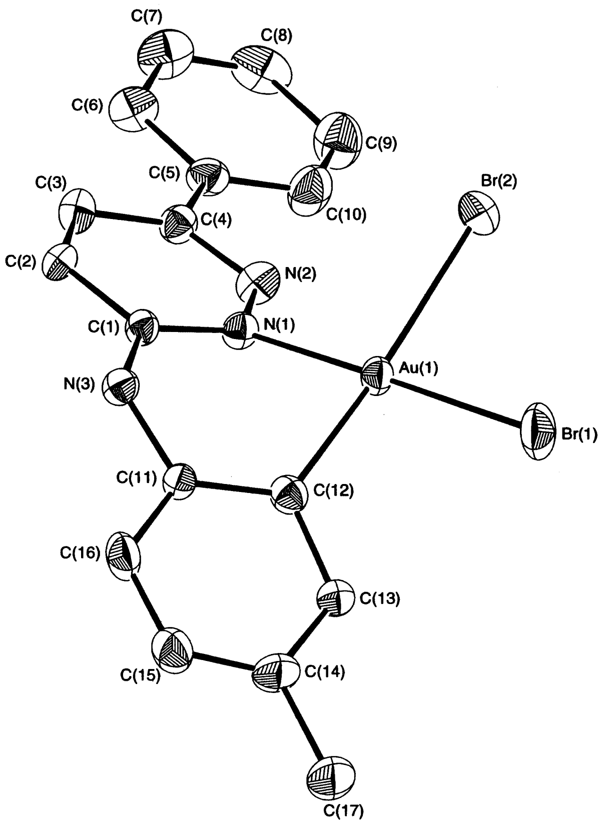


Fig. 3. ORTEP diagram for $[Au(ptp)Br_2]\cdot(CH_3)_2SO$ with atom labeling scheme. The hydrogen atoms and $(CH_3)_2SO$ are omitted for clarity.

the usual six-membered chelate rings and reflects the boat conformation. The N–C lengths around the aniline-like N(3) atom are asymmetric: 1.38(1) Å for C(1) of the heterocycle and 1.42(1) Å for C(11) of the phenyl ring. A similar trend was also found in the structures of $[Au(anp)Cl_2]$ and those of non-metallated 2-(1-naphthylamino)pyridine and 2-anilinopyridine [8]. The phenyl substituent of the pyridazine ring C(4) exerted no appreciable effect on the structure. The phenyl and pyridazine rings make only a small dihedral angle of 3.1(5)°. The large angle of 30.9(4)° between the aurated aromatic and pyridazine rings compared with that {9.2(4)°} of the corresponding fragment in $[PdCl(ptp)(PBu_3)]$ should result from the chelation of the fragment.

The structure of $[PdCl(ptp)(PBu_3)]\cdot CH_3OH$ was also square-planar (Fig. 4) but a five-membered palladacycle was formed in the complex. The selected bond distances and the bond angles are given in Table 1. One mole of methanol was contained as a solvent of crystallization and the O atom was involved in hydrogen bond with *H*N(3) {O(1)–N(3) 2.87(1) Å}. The tip parts of the Bu group of PBu_3 are considerably disordered. The palladacycle was nearly planar and the Cl atom was coordinated *trans* to the palladated carbon atom, as usually observed in related cyclopalladated complexes, [Pd(*C*–*N*)XP] (X = a halogen donor and P = a phosphorus donor) [1]. The coordination bond distances and bond angles around the Pd atom are normal for these type of complexes: the long Pd–Cl bond is due to the strong *trans* influence of the *trans* carbon donor C(6) [9], and the Pd–N(1) is longer than the Pd–N(pyridine-like) bonds in PdN_4-type complexes [10] reflecting the strong *trans* influence of the *trans* PBu_3 ligand. The acute N(1)–Pd(1)–C(6) angle of 80.9(4)° reflects a strained five-membered palladacycle. This complex also shows a similar asymmetric tendency as above between the two N–C bond distances of the aniline-like N(3) atom. The coordination plane is tetrahedrally distorted slightly {displacements form the mean plane: N(1) + 0.207(8), C(6) − 0.15(1), P(1) + 0.030(1), and Cl(1) and Pd(1) < 0.01 Å}. The palladated ring {C(5)–C(10)} makes a dihedral angle of 12.2(4)° with the coordination plane. The angle between the palladated and pyridazine rings is 6.4(5)°, slightly larger than the corresponding angle {3.1(5)°} of $[Au(ptp)Br_2]$, where the moiety is free.

Table 1
Selected bond lengths (Å) and bond angles (°)

$[Au(ptp)Br_2]\cdot(CH_3)_2SO$			
Bond lengths			
Au(1)–Br(1)	2.402(1)	Au(1)–Br(2)	2.518(1)
Au(1)–N(1)	2.001(7)	Au(1)–C(12)	1.990(9)
N(1)–C(1)	1.33(1)	C(1)–N(3)	1.38(1)
N(3)–C(11)	1.42(1)	C(11)–C(12)	1.39(1)
N(1)–N(2)	1.37(1)	N(2)–C(4)	1.34(1)
C(4)–C(5)	1.48(1)	C(5)–C(6)	1.41(1)
Bond angles			
Br(1)–Au(1)–Br(2)	89.24(4)	Br(1)–Au(1)–C(12)	91.9(3)
Br(2)–Au(1)–N(1)	91.8(2)	N(1)–Au(1)–C(12)	86.9(4)
Au(1)–C(12)–C(11)	121.8(6)	Au(1)–N(1)–C(1)	125.1(6)
C(12)–C(11)–N(3)	122.2(8)	C(11)–N(3)–C(1)	123.5(7)
N(3)–C(1)–N(1)	119.8(7)	N(2)–C(4)–C(5)	114.0(8)
C(6)–C(5)–C(4)	119.8(9)	C(4)–C(5)–C(10)	121.6(9)
C(6)–C(5)–C(10)	118.4(9)	C(12)–C(11)–C(16)	121.9(8)
$[Pd(ptp)Cl(Pbu_3)]\cdot CH_3OH$			
Bond lengths			
Pd(1)–Cl(1)	2.406(3)	Pd(1)–P(1)	2.277(3)
Pd(1)–N(1)	2.104(8)	Pd(1)–C(6)	2.02(1)
C(6)–C(5)	1.40(1)	N(1)–C(4)	1.34(1)
C(4)–C(5)	1.48(1)	N(1)–N(2)	1.34(1)
N(2)–C(1)	1.33(1)	C(1)–N(3)	1.37(1)
N(3)–C(11)	1.40(1)	C(11)–C(16)	1.41(1)
Bond angles			
Cl(1)–Pd(1)–P(1)	91.7(1)	Cl(1)–Pd(1)–N(1)	92.1(2)
P(1)–Pd(1)–C(6)	95.9(3)	N(1)–Pd(1)–C(6)	80.9(4)
Pd(1)–C(6)–C(5)	113.7(8)	Pd(1)–N(1)–C(4)	113.6(7)
C(6)–C(5)–C(4)	116(1)	N(1)–C(4)–C(5)	115(1)
N(3)–C(1)–N(2)	121.8(9)	C(11)–N(3)–C(1)	129.0(9)
C(12)–C(11)–N(3)	117(1)	C(16)–C(11)–N(3)	127(1)
C(6)–C(5)–C(10)	122(1)	C(12)–C(11)–C(16)	116(1)

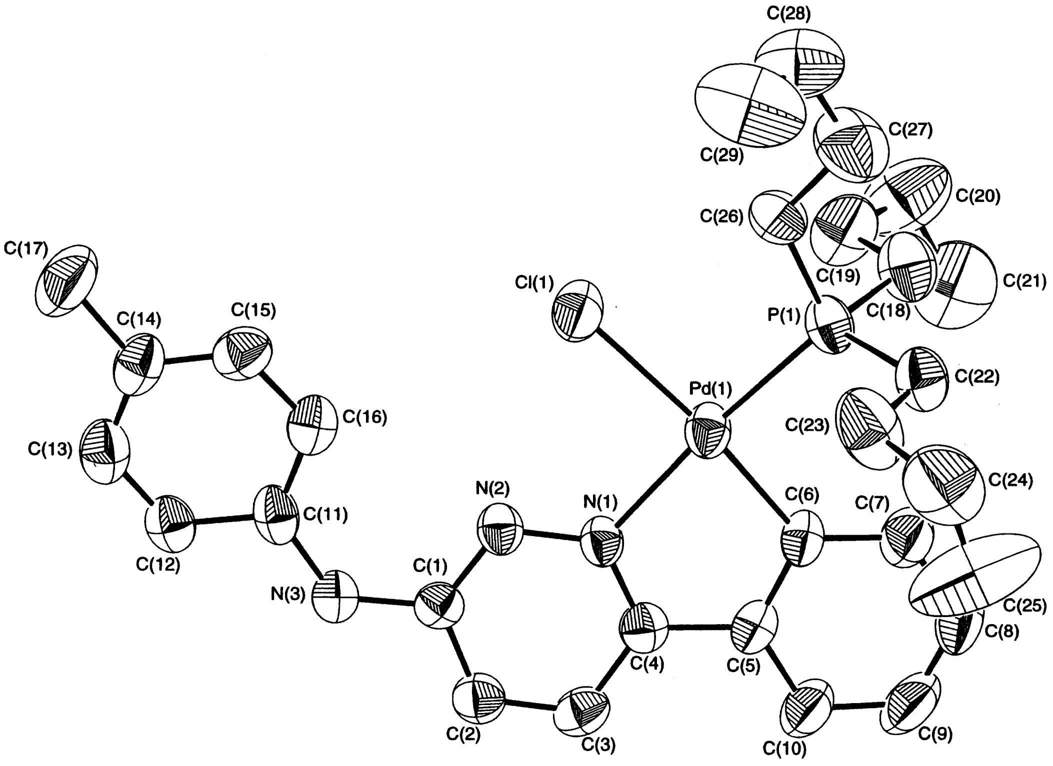


Fig. 4. ORTEP diagram for [Pd(ptp)Cl(PBu$_3$)]·CH$_3$OH with atom labeling scheme. The hydrogen atoms and CH$_3$OH are omitted for clarity.

Comparison of the structural parameters of the ptp ligands between the two structures reveals that bond distances differ only slightly while bond angles and conformations differ significantly (Table 1). Metallation deformed the benzene rings: the interior angle at the *ipso* carbon, C(5) (Pd) and C(11) (Au), became obtuse while that at the metallated carbon, C(6) (Pd) and C(12) (Au), became acute [from 120(1) to 115(1)° for Pd and from 122(1) to 115.8(8)° for Au] in the coordinated rings compared with the uncoordinated ones. The auration at C(12) {or C(16)} decreases the angle, C(1)–N(3)–C(11), and one of the external angles at C(11) compared with the corresponding angles in [Pd(ptp)Cl(PBu$_3$)], where the part is free from metallacycle, an analogous change is induced at C(5) upon palladation of C(6) {or C(10)}. The angle deformations should be accompanied by conformation changes: as indicated above, upon cyclometallation the dihedral angles between the benzene and pyridazine rings are altered compared with that when the part is free.

In addition to the above 1:1 complexes, the 1:2 complex formulated as [Rh(ptp)$_2$Cl]·1.5H$_2$O was obtained by the reaction of Hptp with RhCl$_3$·3H$_2$O in a 2:1 molar ratio. The 1:1 reaction product could not be, however, identified so far. The IR, ^{1}H and ^{13}C{^{1}H} NMR (in dmso-d_6) spectra of [Rh(ptp)$_2$Cl]·1.5H$_2$O were complicated compared with those discussed above. In the IR spectrum the region of NH vibrations was interfered by the presence of water and several peaks appeared. The characteristic band of the five adjacent aromatic ring H atoms of free Hptp at 689 cm^{-1} disappeared as in [PdCl(ptp)]. Two bands at 244 and 302 cm^{-1} may be assigned to ν(Rh–Cl). The ^{1}H and ^{13}C{^{1}H} NMR spectra can be interpreted as a superimposition of signals of the two ptp in slightly different environments, each sets of the signal patterns being assigned to the structure in Fig. 2(B) (the phenyl ring cyclometallation like the Pd complex). The complex should exist as [Rh(ptp)$_2$Cl(dmso-d_6)] in a dmso-d_6 solution, the two ptp ligands not being equivalent: e.g. δ(N*H*) at 10.72 and 10.31; δ(C*H*$_3$) at 2.24 and 2.31; and δ(*C*H$_3$) at 20.4 and 20.6 ppm. The rhodated carbon signals were observed as the two doublets at 162.9 {*J*(RhC) 35.0 Hz} and 164.7 {36.1} ppm. The structure in the solid state may be a Cl-bridged dimer with *cis-C* and *trans-N* disposition as generally found for cyclorhodated [Rh(*C–N*)$_2$(μ-Cl)]$_2$-type complexes [11,12]. Until now, several attempts failed to obtain crystals suitable for X-ray analysis.

The ambidentate substrate, Hptp, was cyclometallated with gold(III) to form a six-membered auracycle while with Pd(II) and Rh(III) a five-membered pallada- and rhoda-cycle, respectively. The factors causing the regioselectivity are not clear at present and further studies are in progress to solve the problem.

3. Experimental

3.1. Measurements

Measurements were carried out by the methods reported earlier [6]. Abbreviations: tl = *p*-tolyl, pd = pyridadinyl, and ph = phenyl; s = singlet, d = doublet, t = triplet, m = multiple, and br = broad. Signals of $^{13}C\{^1H\}$ NMR spectra were singlet unless otherwise indicated. The intensity of each signal was indicated in parentheses, if necessary.

3.2. Preparation

3.2.1. 3-Phenyl-6-*p*-toluidinopyridazine

A mixture of 5.00 g (26.2 mmol) of 3-chloro-6-phenylpyridazine and 2.81 g (26.2 mmol) of *p*-toluidine in 30 cm^3 of xylene was heated in an oil bath at 150 °C with continuous stirring for 6 h. The oil bath was removed and after the mixture was cooled briefly, 30 cm^3 of water was added cautiously with stirring followed by 4.00 g of solid sodium hydroxide. To the mixture cooled to room temperature (r.t.) 50 cm^3 of dichloromethane was added and the suspension was stirred until the brown lump was loosened to a yellow powder. The powder was filtered, washed with water and ethyl ether, dried in air, and recrystallized from hot acetone to give light yellow crystals. Yield: 4.92 g (72%). M.p. (dec.) 218–219 °C. Calc. for $C_{17}H_{15}N_3$: C, 78.13; H, 5.79; N, 16.08. *Anal.* Found: C, 77.80; H, 5.74; N, 16.41%. IR (Nujol, cm^{-1}): ν(NH) 3180, 3230. ^1H NMR (dmso-d_6, δ ppm): 2.33s (3H, CH_3); 7.20d (2H), 7.75d (2H) (tl); 7.26d, 8.02d (pd); 7.48t, 7.56t (2H), 8.11d (2H) (ph); 9.38s (NH). $^{13}C\{^1H\}$ NMR (δ ppm): 20.4 (CH_3), 118.9 (2C), 129.2 (2C), 130.3, 138.2 (tl); 116.6, 125.3, 151.3, 156.6 (pd); 125.7 (2C), 128.8, 128.9 (2C), 136.6 (ph).

3.2.2. [Au(ptp)Cl_2]

A mixture of 398 mg (1 mmol) of Na[$AuCl_4$]·$2H_2O$ and 261 mg (1 mmol) of Hptp in a mixture of 15 cm^3 of water and 15 cm^3 of ethanol was refluxed overnight with stirring. After cooling, the product was filtered, washed with water and ethanol, dried in air, and recrystallized from acetone to give 425 mg (80%) of a yellow powder. M.p. (dec.) 233–234 °C. Calc. for $C_{17}H_{14}N_3Cl_2Au$: C, 38.66; H, 2.67; N, 7.96. *Anal.* Found: C, 38.41; H, 2.60; N, 7.87%. IR (Nujol, cm^{-1}): ν(NH) 3212, 3230; ν(AuCl) 354, 283. ^1H NMR (dmso-d_6, δ ppm): 2.35s (3H, CH_3); 7.13d, 7.16d, 7.51s (tl); 7.84d, 8.38d (pd); 7.59m (3H), 8.15d (2H) (ph); 11.4s (NH). $^{13}C\{^1H\}$ NMR (343 K, δ ppm): 20.1 (CH_3); 120.1 (*C*–Au), 116.9, 129.3, 133.5 (tl); 123.8, 128.6, 146.8, 151.3 (pd); 126.5 (2C), 128.6 (2C), 130.0 (ph); 128.4, 133.6 133.7 (quaternary C of ph and tl).

3.2.3. [Au(ptp)Br_2]

Reaction of 473 mg (1 mmol) of $AuBr_3$·$2H_2O$ with 261 mg (1 mmol) of Hptp in similar conditions as above gave 97 mg (16%) of a yellow powder. M.p. (dec.) 207–209 °C. Gold mirror appeared on the reaction vessel and this might have lowered the yield. Calc. for $C_{17}H_{14}N_3Br_2Au$: C, 33.09; H, 2.29; N, 6.81. *Anal.* Found: C, 32.86; H, 2.28; N, 6.65%. IR (Nujol, cm^{-1}): ν(NH) 3290; ν(AuBr) 254, 193. ^1H NMR (dmso-d_6, δ ppm): 2.34s (3H, CH_3); 7.12d, 7.16d, 7.66s (tl); 7.83d, 8.39d (pd); 7.59m (3H), 8.18m (2H) (ph); 11.3s (NH). $^{13}C\{^1H\}$ NMR (δ ppm): 20.5 (CH_3); 122.3 (*C*–Au), 117.1, 129.7, 136.2 (tl); 124.0, 239.1, 147.4, 151.3 (pd); 126.8(2C), 129.0(2C), 130.5 (ph); 133.9 (2C), 128.2 (quaternary C of ph and tl). Recrystallization from hot dmso gave crystals suitable for X-ray analysis.

3.2.4. [Pd(ptp)Cl]

A mixture of 261 mg (1 mmol) of Hptp and $Li_2[PdCl_4]$, prepared in situ from 177 mg (1 mmol) of $PdCl_2$ and 85 mg (2 mmol) of LiCl in 30 cm^3 of methanol, was stirred overnight and then refluxed for 6 h. After cooling, the product was filtered, washed with methanol, and dried in air. The product was refluxed with 300 cm^3 of CH_2Cl_2 with stirring for 30 min and the undissolved material was collected, washed with CH_2Cl_2, and dried in air. Yield: 288 mg (72%). M.p. (dec.) 282 °C. Calc. for $C_{17}H_{14}N_3ClPd$: C, 50.77; H, 3.51; N, 10.45. *Anal.* Found: C, 50.81; H, 3.55; N, 10.42%. IR (Nujol, cm^{-1}): ν(NH) 3402, 3386; ν(PdCl) 250, 239. ^1H NMR (dmso-d_6, 373 K, δ ppm): 2.31s (3H, CH_3); 7.15d (2H), 7.70d (2H) (tl); 7.40d, 8.03d (pd); 6.97td, 7.09td, 7.44dd, 7.79d (ph); 9.25s (NH). $^{13}C\{^1H\}$ NMR (373 K, δ ppm): 19.7 (CH_3); 119.1 (2C), 128.6 (2C), 130.8, 136.9 (tl); 119.7, 125.1, 154,7, 159.0 (pd); 122.6, 123.8, 127.0, 135.2, 141.8, 149.7 (*C*–Pd) (ph).

3.2.5. Attempted double cyclometallation

The reaction of 261 mg (1 mmol) of Hptp and 796 mg (2 mmol) of Na[$AuCl_4$]·$2H_2O$ under the conditions used for the synthesis of [Au(ptp)Cl_2] precipitated a yellow powder analyzed as [Au(ptp)Cl_2]·C_2H_5OH (272 mg, 95%). Calc. for $C_{19}H_{20}N_3OCl_2Au$: C, 39.74; H, 3.51; N, 7.32. *Anal.* Found: C, 39.33; H, 3.31; N, 7.27%. Recrystallization of the powder from acetone gave the same complex as above.

The reaction of 261 mg (1 mmol) of Hptp and $Li_2[PdCl_4]$, prepared in situ from 355 mg (2 mmol) of $PdCl_2$ and 170 mg (4 mmol) of LiCl in 30 cm^3 of methanol, under the above conditions for the synthesis of [Pd(ptp)Cl] formed a brown powder of the composition $[Pd(ptp)Cl]_2$·$PdCl_2$ (209 mg, 85%). M.p. (dec.) 295 °C. Calc. for $C_{34}H_{28}N_6Pd_3Cl_4$: C, 41.60; H, 2.87; N, 8.56. *Anal.* Found: C, 41.79; H, 2.98; N, 8.31%. IR (Nujol, cm^{-1}): ν(NH) 3330, 3321; ν(PdCl) 354, 340, 263. The ^1H and $^{13}C\{^1H\}$ NMR spectra (dmso-d_6) were identical to those of [Pd(ptp)Cl].

3.2.6. [Pd(ptp)Cl(PBu$_3$)]

To a suspension of 1 mmol (402 mg) of [Pd(ptp)Cl] in 30 cm^3 of dichloromethane 1 mmol (202 mg) of PBu$_3$ was added and the mixture was stirred for 30 min at r.t. The solution was treated with Florisil and filtered. The filtrate was concentrated to a small volume and mixed with 20 cm^3 of hexane to precipitate the product. Yield: 276 mg (46%). M.p. (dec.) 191–192 °C. Calc. for $C_{29}H_{41}N_3ClPPd$: C, 57.62; H, 6.84; N, 6.95. *Anal.* Found: C, 57.68; H, 6.92; N, 6.88%. IR (Nujol, cm^{-1}): ν(NH) 3276; ν(PdCl) 255. ^{1}H NMR (CDCl$_3$, 298 K, δ ppm): 2.26s (3H, CH$_3$); 0.86t (9H), 1.41m (6H), 1.62m (6H), 2.07m (6H) (Bu); 7.04d (2H), 7,53d (2H) (tl); 7.08m (2H), 7.18dd (1H), 7.27m (1H) (ph); 7.37d (1H), 7.40d (1H) (pd); 7.58br (NH). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K, δ ppm): 20.3 (CH$_3$); 13.7, 24.1d (28.2), 24.2d (13.9), 29.6 (Bu); 120.9(2C), 129.7(2C), 132.7, 136.5 (tl); 123.6, 124.5, 128.6d (4.6), 135.7d (9.3), 144.4, 156.0d (5.7) (*C*–Pd) (ph); 118.2, 124.7, 154.7, 159.6d (1.2) (pd) ppm [figures in parentheses are *J*(P–C) in Hz]. Crystals for X-ray analysis were obtained by recrystallization from a mixture of dichloromethane and methanol.

3.2.7. [Rh(ptp)$_2$Cl]

To a solution of 1 mmol (263 mg) of RhCl$_3$·3H$_2$O in 30 cm^3 of 2-methoxyethanol, 2 mmol (523 mg) of Hptp was added and the mixture was refluxed for six days with stirring. After cooling to r.t., a yellow orange precipitate was filtered, washed with ethanol, and dried in air. The product was dissolved in 3 cm^3 of dmso on a hot plate at 128 °C, and the solution was filtered and allowed to cool to r.t. A precipitate was collected, washed with a small amount of dmso and then with methanol to afford 251 mg (37%) of a yellow–orange powder formulated as [Rh(ptp)$_2$Cl]·1.5H$_2$O. M.p. (dec.) 280 °C. Calc: for $C_{34}H_{31}N_6O_{1.5}ClRh$: C, 59.53; H, 4.55; N, 12.25. *Anal.* Found: C, 59.74; H, 4.62; N, 12.14%. ^{1}H NMR (dmso-d_6, δ ppm): 2.24s, 2.31s (CH$_3$); 5.77d, 6.96d, 7.17d, 7.68d (tl); 7.10d, 8.24d, 7.60d, 8.41d (pd), 6.33d, 6.38d, 6.48t, 6.89t, 6.90t, 6.96t, 7.65d, 7.70d (ph); 10.31s, 10.72s (NH). ^{13}C{^{1}H} NMR (dmso-d_6, δ ppm): 20.4, 20.6 (CH$_3$):119.2(2C), 122.5(2C), 129.1(2C), 129.8(2C) (tl); 118.0, 120.7, 122.3, 122.8, 124.1, 124.7, 127.2, 128.1, 128.7, 129.1, 131.8, 133.7 (*C*H); 132.6. 135.0, 134.0, 136.7, 140.2, 140.9, 155.3, 159.4, 158.6{2.9}, 159.7{3.0} (quaternary carbons); 162.9{35.0}, 164.7{36.1} (*C*–Rh). Figures in braces are *J*(Rh–C) in Hz. Several attempts to obtain crystals suitable for X-ray analysis failed.

Table 2
Crystal data and structure refinement parameters for [Au(ptp)Br$_2$]·(CH$_3$)$_2$SO and [Pd(ptp)Cl(PBu$_3$)]·CH$_3$OH

	[Au(ptp)Br$_2$]·(CH$_3$)$_2$SO	[Pd(ptp)Cl(PBu$_3$)]·CH$_3$OH
Empirical formula	$C_{19}H_{20}AuBr_2N_3OS$	$C_{30}H_{45}ClN_3OPPd$
Formula weight	695.22	636.53
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.9151(2)	10.5111(3)
b (Å)	12.6283(7)	20.1628(2)
c (Å)	9.9454(6)	15.8599(3)
α (°)	90.007(5)	
β (°)	115.602(5)	100.320(3)
γ (°)	65.908(4)	
V (Å^3)	1102.4(1)	3306.9(1)
Z	2	4
Absorption coefficient (cm^{-1})	103.56	7.15
Crystal color	red	yellow
D_{calc} (g cm^{-3})	2.094	1.278
2θ Range (°)	55	55
R	0.060	0.062
R_w	0.085	0.078
S, Goodness-of-fit on F^2	1.82	1.47

$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [\sigma_c^2(F_o)+(p^2/4)|F_o|^2]^{-1}$; $p = 0.0700$ for [Au(ptp)Br$_2$]·(CH$_3$)$_2$SO and 0.0600 for [Pd(ptp)Cl(PBu$_3$)]·CH$_3$OH; $S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$ (m = number of used reflections, n = number of refined parameters).

3.3. Crystallographic analysis

The crystallographic data for [Au(ptp)Br$_2$]·(CH$_3$)$_2$SO and [Pd(ptp)Cl(PBu$_3$)]·CH$_3$OH are given in Table 2. A prismatic red crystal of [Au(ptp)Br$_2$]·(CH$_3$)$_2$SO with dimensions of 0.20 × 0.25 × 0.33 mm was glued onto a glass fiber and coated with epoxy resin. A prismatic yellow crystal of [Pd(ptp)Cl(PBu$_3$)]·CH$_3$OH with dimensions of 0.10 × 0.20 × 0.30 mm was sealed in a glass capillary tube together with the mother liquor. X-ray diffraction data were collected at 25 °C on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). A total of 44 images was collected with two different goniometer settings ($2\theta_{max} = 55°$). Exposure time was 3 min per degree, and the readout was performed in 0.100 mm pixel mode. The diffraction data were processed by the PROCESS-AUTO program package. After the removal of the redundant data, a set of 4387 reflections [$I > 2\sigma(I)$] for [Au(ptp)Br$_2$]·(CH$_3$)$_2$SO and 2608 reflections [$I > 2\sigma(I)$] for [Pd(ptp)Cl(PBu$_3$)]·CH$_3$OH were used for the structure determination. A numerical absorption correction was applied to the data using the NUMABS program [13]. For each of the data sets the positions of the heavy atoms were found by the direct methods (SIR-92) [14], and subsequent cycles of full-matrix least-square refinement followed by difference Fourier syntheses (DIRDIF-94) [15] revealed the positions of the remaining non-hydrogen atoms. In the final refinement cycles all the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the refinement with idealized parameters. In each complex a hydrogen atom bound to the N(3) atom and those of the solvent of crystallization were not located. All calculations were performed using the TEXAN crystallographic software package [16] of the Molecular Structure Corporation.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 163482 and 163483 for $[Au(ptp)Br_2]\cdot(CH_3)_2SO$ and $[Pd(ptp)Cl(PBu_3)]\cdot CH_3OH$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank the Analytical Chemistry Laboratory, Faculty of Science, Nagoya University for allowing them to use the Bruker NMR spectrometer. The present work was partially supported by a Grant-in-Aid (Scientific Research No. 13640557) from the Ministry of Education, Science, and Culture.

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