Polynuclear Palladium Complexes with 3,5-Dimethylpyrazolate Exhibiting Three Different Coordination Modes

Juan Forniés,*[a] Antonio Martín,[a] Violeta Sicilia,[b] and L. Francisco Martín[a]

Abstract: The characterisation of dinuclear pyrazolato-bridged Pd^{II} complexes, $[\{Pd(\mu\text{-dmpz})Cl(Hdmpz)\}_2]$ (**1**) and $[\{Pd(\mu\text{-dmpz})(dmpz)(Hdmpz)\}_2]$ (**2**) (Hdmpz = dimethylpyrazole), has been carried out. An X-ray study of compound **2** reveals the existence of intramolecular $N{-}H\cdots N$ hydrogen bonds between neighbouring dmpz groups. Compound **2** has been deprotonated and both acidic hydrogen atoms substituted by two metal atoms of Cu^I, Ag^I or Au^I to give the tetranuclear compounds $[Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_6]$ (M = Cu, Ag, Au). The structure of these compounds resembles a box with a small cavity inside. There are also three π-electron-rich clefts between each of the three pairs of azolato rings, capable of further complexation. The reactions of $[Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_6]$ (M = Cu, Ag, Au) with $AgClO_4$ render compounds of the type $[\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}O_2ClO_2)\}_2]$ (M = Cu, Ag, Au). The X-ray structures of crystals obtained from a solution of compounds $[\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}O_2ClO_2)\}_2]$ (M = Ag, Au) in acetone reveals a $[\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag(OCMe_2)(OClO_3)Ag(\mu_2\text{-}O_2ClO_2)\}_2]$ stoichiometry, indicating that only two of the three π-electron-rich clefts have been used to accommodate Ag^+ ions. Each of the silver atoms are located in between two 3,5-dmpz rings and are η^1-bonded to the C^4 atom of each group.

Keywords: heterometallic complexes · palladium · pi interactions · pyrazolate complexes · structure elucidation

Introduction

Supramolecular chemistry, that is, the formation of new chemical structures by the assembly of molecular subunits bound together by noncovalent interactions, is having a major impact on current chemical research and will continue to do so in the future.[1] Early examples of supramolecular assemblies have been provided by "host–guest" chemistry, in which a "host" molecule includes a smaller "guest" within a cavity in its structure.[1, 2] The incorporation of transition-metal centres into such structures can confer new properties on these potential host molecules. The coordination geometry of the transition-metal atoms has been employed for the rational design and construction of highly-ordered supramolecular structures.[3–13]

The synthesis of shape-persistent macrocycles, which are potentially useful as molecular boxes, presents a new and interesting challenge.[2, 8] Pyrazolate ligands have a proven ability to hold metal atoms in close proximity, while permitting a wide range of intermetallic separations.[14–16] Pyrazoles are also known to favour the formation of trimeric metallacycles such as $[M^I(\mu\text{-pz*})]_3$ (M^I = Cu, Ag, Au; pz* = pyrazolate or substituted pyrazolate).[17–21] However, the homoleptic pyrazolate complexes of divalent metals $[\{M(\mu\text{-pz*})\}_n]$ (M = Cu, Zn, Cd, Hg, Pt) are typically open-chain polymers,[22–26] with the exception of the still intractable $[\{Pt(\mu\text{-pz})_2\}_3]$,[26] and the recently prepared $[\{Pd(\mu\text{-3-Ph-pz})_2\}_3]$,[27] characterised by X-ray diffraction. Recently, we have shown the ability of the π-electron-rich cleft between the two azolato rings to accommodate a silver cation, allowing the self-assembly of small molecules to obtain supramolecular structures.[28] In this paper we present the use of pyrazolate palladium compounds as precursors for the synthesis of new palladium-containing rings and the use of these rings as molecular subunits for supramolecular assemblies.

Although there has been a recent proliferation of new bonding modes for pyrazolate ligands,[29–31] as far as we know, only the complex $[Pd_2(C^\wedge P)_2(\mu\text{-dmpz})_2]$ [$C^\wedge P = CH_2\text{-}C_6H_4\text{-}P(o\text{-tolyl})_2\text{-}\kappa C,P$; dmpz = 3,5-dimethylpyrazolate)] has been shown to use the π-electron density of the dmpz groups to

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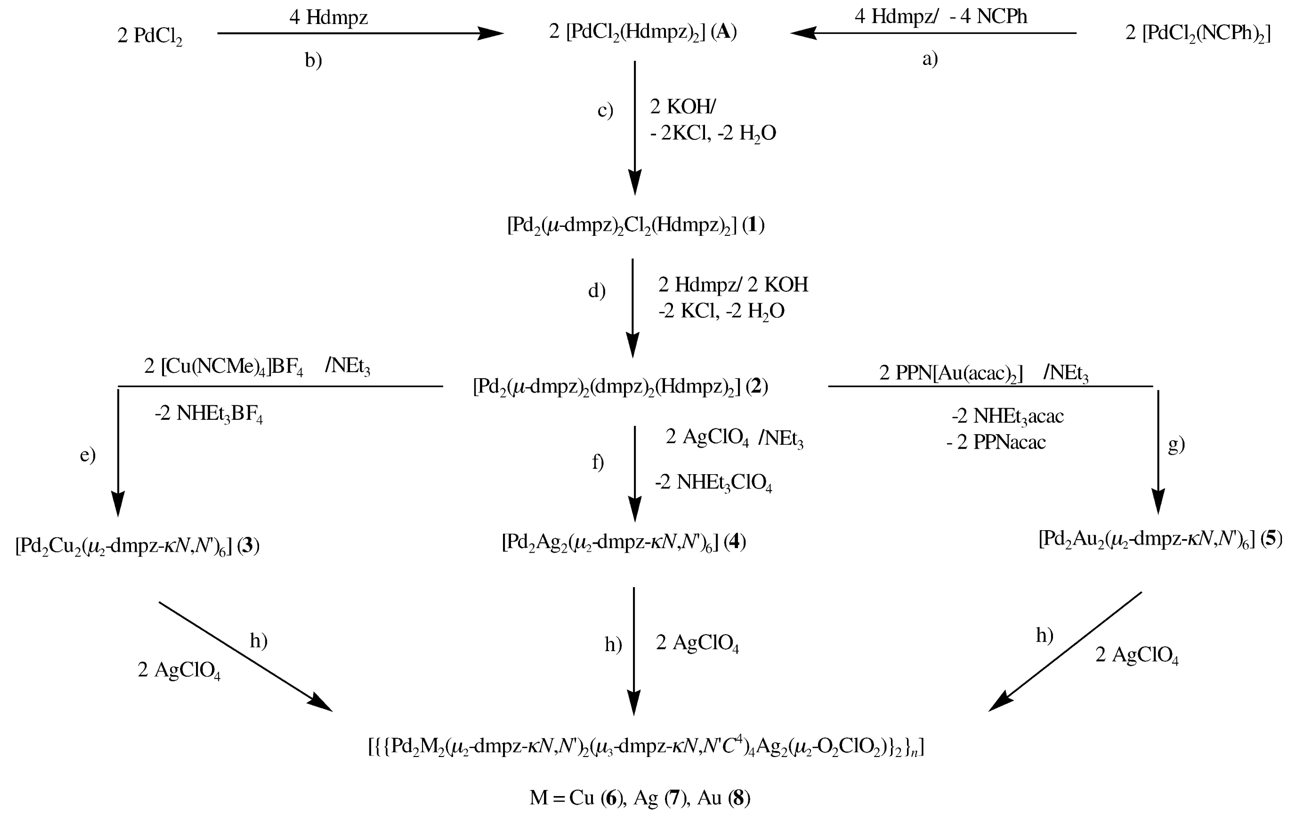


Scheme 1. Synthetic routes to $[\{\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}O_2ClO_2)\}_2\}_n]$.

Abstract in Spanish: *Se ha llevado a cabo la caracterización de dos nuevos complejos dinucleares de Pd^{II} con grupos pirazolato puente: $[\{Pd(\mu\text{-dmpz})Cl(Hdmpz)\}_2]$ (**1**) and $[\{Pd(\mu\text{-dmpz})(dmpz)(Hdmpz)\}_2]$ (**2**). El estudio por difracción de rayos X del compuesto **2** revela la existencia de enlaces de hidrógeno N–H···N intramoleculares entre grupos dmpz vecinos. El compuesto **2** ha sido desprotonado y ambos átomos de hidrógeno ácidos substituidos por dos átomos metálicos de Cu^I, Ag^I u Au^I para dar los compuestos tetranucleares $[Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_6]$ (M = Cu, Ag, Au). Estos compuestos presentan una estructura de caja con una pequeña cavidad en el interior. Hay además tres huecos ricos en densidad electrónica π entre cada uno de los tres pares de anillos pirazolato, disponibles para una posterior coordinación. Las reacciones de $[Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_6]$ (M = Cu, Ag, Au) con $AgClO_4$ dan lugar a los compuestos $[\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}O_2ClO_2)\}_2]$ (M = Cu, Ag, Au). La estructura determinada por difracción de rayos X de cristales obtenidos a partir de disoluciones de los compuestos $[\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}O_2ClO_2)\}_2]$ (M = Ag, Au) en acetona revela una estequiometría $[\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag(OCMe_2)(OClO_3)Ag(\mu_2\text{-}O_2ClO_2)\}_2]$, indicando que sólo dos de los tres huecos ricos en densidad electrónica π han sido utilizados para acomodar cationes Ag^+. Cada uno de estos dos átomos de plata están localizados entre dos anillos 3,5-dmpz y coordinados de forma η^1 al átomo de carbono C^4 de cada grupo.*

accommodate a transition-metal cation (Ag^+) yielding $[Pd_2(C^\wedge P)_2(\mu_3\text{-}3,5\text{-dmpz-}\kappa N,N',C^4)_2Ag(\eta^2\text{-}\mu\text{-}ClO_4)]$.[28] In this paper we report three new compounds $[\{\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}O_2ClO_2)\}_2\}_n]$ (M = Cu, Ag, Au) exhibiting the same kind of coordination of the 3,5-dmpz groups to Ag^+.

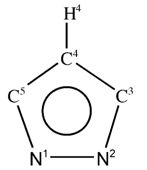
Results and Discussion

Synthesis and characterisation of $[$*trans*-$PdCl_2(Hdmpz)_2]$ (A) and $[\{Pd(\mu\text{-dmpz})Cl(Hdmpz)\}_2]$: The X-ray structure of compound [*trans*-$PdCl_2(Hdmpz)_2$] (**A**) has been described in a previous report.[32] However, as far as we know, no report of its synthesis or spectroscopic data has been published. In this paper we have prepared $[PdCl_2(Hdmpz)_2]$ (**A**) by two different methods and used it as starting material for the synthesis of new Pd^{II} compounds containing Hdmpz or $dmpz^-$ in different coordination modes.

The first method is similar to the one described for the synthesis of $[PdCl_2(Hpz)_2]$ (Hpz = pyrazole)[33] and consists of the reaction of $[PdCl_2(NCPh)_2]$ and 3,5-dimethylpyrazole (Hdmpz) in 1:2 molar ratio in dichloromethane for one hour (Scheme 1a).

The second method consists of the reaction of $PdCl_2$ and Hdmpz in 1:2 molar ratio (Scheme 1b). $PdCl_2$ is suspended in water, mixed with a dichloromethane solution of 3,5-dimethylpyrazole (Hdmpz) and reacted for three days. $[PdCl_2(Hdmpz)_2]$ (**A**) is obtained from the organic layer in a 90% yield.

The IR spectrum of **A** shows a broad absorption at 3200 cm^{-1} corresponding to ν_{st}(N–H).[34–37] The high value of the ν_{st}(N–H) frequencies indicate that the N–H···X hydrogen bonds observed in the X-ray structure of compound **A** must be quite weak. The ^{1}H NMR spectrum of **A** shows only one set of signals corresponding to both chemically equivalent Hdmpz groups (see Experimental Section).



Scheme 2. The atom numbering scheme used in the NMR analyses.

Treatment of **A** with the equimolar amount of potassium hydroxide produces the elimination of HCl, as KCl and H_2O, and the formation of the dinuclear compound $[Pd_2Cl_2(\mu\text{-dmpz})_2(Hdmpz)_2]$ (**1**) (Scheme 1c). The IR spectrum of **1** shows the characteristic signal for ν_{st}(N–H) at 3271 cm^{-1}. Its ^{1}H NMR spectrum (for the atom numbering see Scheme 2) shows two sets of signals; one relates to the bridging dmpz ($\delta = 2.19$ (CH$_3$), 2.42 (CH$_3$), 5.25 ppm (H^4)) and the other to the terminal Hdmpz groups ($\delta = 1.98$ (CH$_3$), 2.56 (CH$_3$), 5.83 (H^4), 11.18 ppm (N–H)). The assignment of the methyl signals has been carried out with the aid of a COSY experiment.[38, 39]

For this stoichiometry, three structures could be proposed (I, II, III, Scheme 3), but the spectroscopic data represent that expected for two of them (I and III). Taking into account the *trans* geometry of the starting material, structure III seems to be most probable.

Synthesis and characterisation of $[\{Pd(\mu\text{-dmpz})(dmpz)(Hdmpz)\}_2]$: In compound **1**, substitution of the Cl ligands by dmpz groups takes place by treating **1** with Kdmpz in a 1:2 molar ratio; the chloride anions being eliminated as KCl (Scheme 1d). The resulting neutral compound $[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$ (**2**) was characterised by IR and ^{1}H NMR spectroscopy as well as X-ray diffraction. Its molecular structure is shown in Figure 1. Selected bond lengths and angles are given in Table 1.

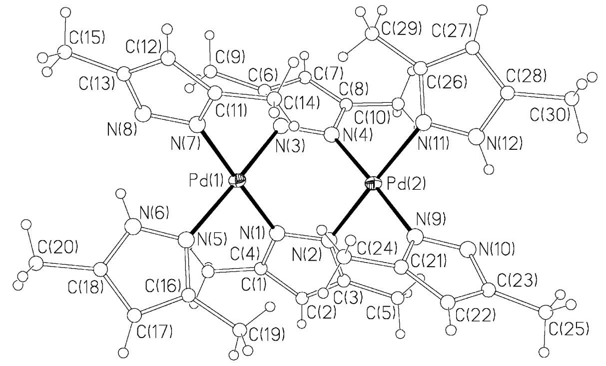
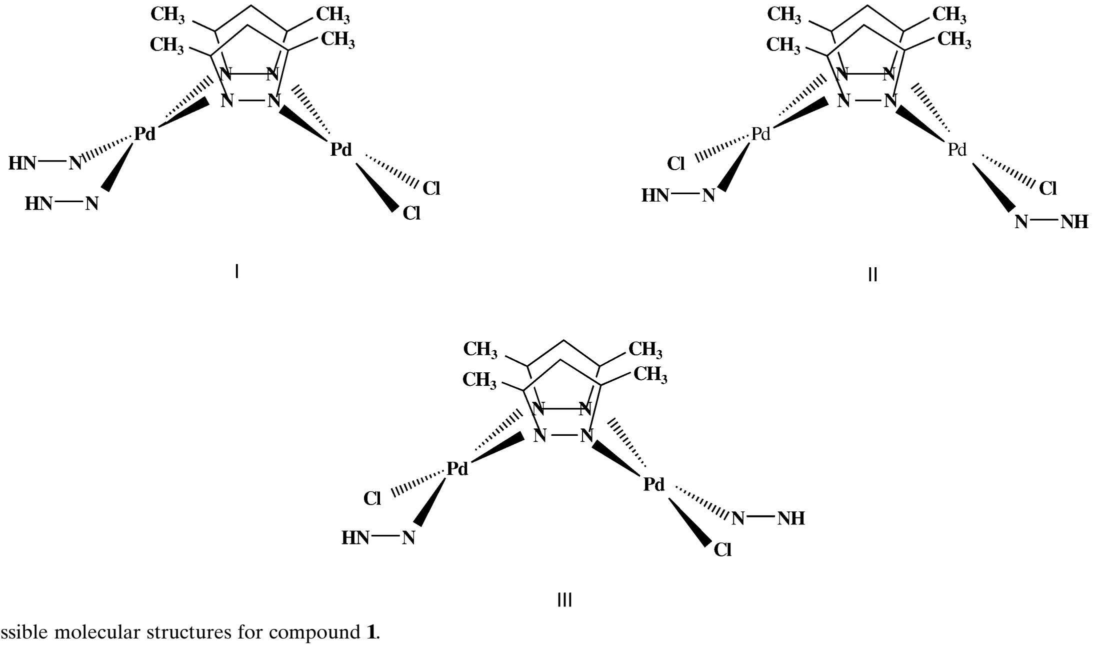


Figure 1. Molecular structure and numbering scheme for **2**.

Table 1. Selected bond lengths [Å] and angles [°] for complex **2**.

Pd(1)–N(1)	2.007 (9)	Pd(1)–N(3)	2.017 (9)
Pd(1)–N(5)	2.063 (9)	Pd(1)–N(7)	2.005 (9)
Pd(2)–N(2)	2.016 (9)	Pd(2)–N(4)	2.010 (9)
Pd(2)–N(9)	2.005 (9)	Pd(2)–N(11)	2.057 (9)
N(1)-Pd(1)-N(3)	87.1(3)	N(1)-Pd(1)-N(5)	91.6(3)
N(3)-Pd(1)-N(7)	92.9(4)	N(5)-Pd(1)-N(7)	88.6(4)
N(2)-Pd(2)-N(4)	86.1(4)	N(2)-Pd(2)-N(9)	92.6(4)
N(4)-Pd(2)-N(11)	93.1(4)	N(9)-Pd(2)-N(11)	88.4(4)
plane 1: N5, N6, C16–C20		plane 2: N7, N8, C11–C15	
plane 3: N9, N10, C21–C25		plane 4: N11, N12, C26–C30	

As can be seen, **2** is a dinuclear Pd^{II} complex that contains exclusively Hdmpz or dmpz as ligands. Two dmpz groups bridge the metal centres. The intermetallic distance is 3.4020 Å, which is longer than the analogous distances observed in other Pd^{II} complexes with the same kind of bridging system.[28, 40]. Each palladium atom is in an almost



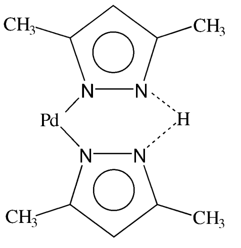
Scheme 3. Possible molecular structures for compound **1**.

square-planar coordination environment. The terminal ligands are an anionic dmpz and a neutral Hdmpz. The Pd−N bond lengths are in the range found in other Pd and Pt complexes with this kind of ligands.[28, 32, 40–45] The Pd_2N_4 six-membered ring reveals a boatlike conformation, the dihedral angle formed by the best least squares coordination planes of the metals being 89.2°. The angle between the planes containing the Pd-N-N-Pd fragments is 73.7°.[46] All of the dmpz and Hdmpz ligands are planar, within experimental error.

The dihedral angle between the terminal dmpz and Hdmpz groups bonded to the same metal centre are 68.4° (planes 1, 2) and 74.8° (planes 3, 4). The terminal groups are connected through intramolecular hydrogen bonds, the N−H ··· N distances being 2.753 (N6 ··· H ··· N8) and 2.759 Å (N12 ··· H ··· N10). The hydrogen atoms of the Hdmpz groups, fixed by the program, lie 2.015 (H ··· N10) and 2.016 Å (H ··· N8) from the nitrogen atom of the neighbouring dmpz group. All N−H ··· N and H ··· N separations are in the range of distances observed for N−H ··· N bond systems.[47–50]. The angles N−H ··· N—144.3° (N12-H-N10) and 143.1° (N6-H-N8)—are similar to those observed in complex $[\{Zn_2(\mu\text{-dmpz})_2(\text{dmpz})_2(\text{Hdmpz})_2\}]$ (N−H ··· N: 141°), in which the bridging hydrogen bonds are also intramolecular.[18] These angles are smaller than those observed for intermolecular N−H ··· N hydrogen bonds, which usually range between 160 and 180°.[47]

The IR spectrum of $[Pd_2(\mu\text{-dmpz})_2(\text{dmpz})_2(\text{Hdmpz})_2]$ (**2**) in KBr shows a band at 2800 cm^{-1} corresponding to the ν_{st}(N−H). The decrease in the frequency of the signal with respect to the starting material (**1**: 3271 cm^{-1} in Nujol) indicates the significant strength of the hydrogen bonds.[34–37]

The ^1H NMR spectrum of **2** at room temperature in $CDCl_3$ (see Experimental Section) shows six signals (6:6:6:1:2:1). A COSY experiment allows them to be gathered in two sets of signals, one for the bridging dmpz ($\delta = 2.19$ (CH_3), 5.47 ppm (H^4)) and another one for the terminal dmpz and Hdmpz groups ($\delta = 1.93$ (CH_3), 2.31 (CH_3), 5.73 (H^4), 11.00 ppm (N−H)). These spectroscopic data are consistent with C_{2v} symmetry. This symmetry is only possible if the dmpz and Hdmpz terminal groups, bonded to the same palladium centre, become chemically equivalent through a chelated proton structure (Scheme 4)[51] or if there is an intramolecular exchange of hydrogen between them.



Scheme 4. Cheated proton structure.

Synthesis and characterisation of $[Pd_2M_2(\mu\text{-dmpz})_6]$ (M = Cu, Ag, Au): $[Pd_2(\mu\text{-dmpz})_2(\text{dmpz})_2(\text{Hdmpz})_2]$ (**2**), which contains two acidic hydrogen atoms, can be deprotonated with a weak Lewis base and the resulting anionic compound is able to react with electrophilic species. Thus, the reactions of **2** with $Cu^{I,}$ Ag^I and Au^I salts in a 1:2 molar ratio in CH_2Cl_2 and in the presence of an excess NEt_3 result in the formation of the tetranuclear compounds $[Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_6]$ (M = Cu (**3**), Ag (**4**), Au (**5**)). In all cases, the protons are eliminated with formation of the corresponding triethylamonium salts ($[NHEt_3]BF_4$, $[NHEt_3]ClO_4$, $[NHEt_3]$acac) (Scheme 1e–g). These ammonium salts are soluble in the alcohols added to precipitate the complexes (see Experimental Section).

The instability of the Cu^I and Au^I precursors to air or moisture requires them to be manipulated in an inert atmosphere. However the resulting compounds (**3**–**5**) are stable and can be handled in air.

Complexes **3**–**5** have been characterised by elemental analyses and IR and ^1H NMR spectroscopy; these structural data seem to indicate that the three complexes display a similar structure (see Experimental Section). The IR data do not provide structural information and are not given in the experimental section. The assignment of the ^1H NMR signals to one kind of dmpz group or another was carried out with the aid of COSY experiments and literature data.[38, 39] The X-ray structure of **4** (M = Ag) has been studied. A selection of bond lengths and angles are indicated in Table 2 and the molecular structure of this compound is shown in Figure 2. Complex **4** is a cyclic tetranuclear compound that contains two palladium and two silver atoms with six dmpz groups acting as a bridge between each two metal atoms. The Pd_2N_4 fragment has a boatlike conformation. The dihedral angle formed by the best

Table 2. Selected bond lengths [Å] and angles [°] for complex **4**.

Pd(1)−N(1)	2.056 (6)	Pd(1)−N(3)	2.035 (6)
Pd(1)−N(9)	2.048 (6)	Pd(1)−N(11)	2.030 (5)
Pd(2)−N(5)	2.041 (6)	Pd(2)−N(7)	2.026 (6)
Pd(2)−N(10)	2.010 (6)	Pd(2)−N(12)	2.038 (6)
Ag(1)−N(2)	2.056 (6)	Ag(1)−N(6)	2.047 (6)
Ag(2)−N(4)	2.081 (6)	Ag(2)−N(8)	2.071 (6)
Pd1 ··· Pd2	3.513	Pd1 ··· Ag1	3.303
Pd1 ··· Ag2	3.185	Ag1 ··· Ag2	3.195
Pd2 ··· Ag2	3.382	Pd2 ··· Ag1	3.164
N(1)-Pd(1)-N(3)	85.9(3)	N(1)-Pd(1)-N(11)	92.9(9)
N(3)-Pd(1)-N(9)	92.8(2)	N(9)-Pd(1)-N(11)	88.1(2)
N(5)-Pd(2)-N(7)	87.7(2)	N(5)-Pd(2)-N(12)	93.4(2)
N(7)-Pd(2)-N(10)	92.3(2)	N(10)-Pd(2)-N(12)	86.4(2)
N(2)-Ag(1)-N(6)	167.4(3)	N(4)-Ag(2)-N(8)	169.6(2)
plane 1: N9, N10, C21–C25		plane 2: N11, N12, C26–C30	
plane 3: N1, N2, C1–C5		plane 4: N3, N4, C6–C10	
plane 5: N5, N6, C11–C15		plane 6: N7, N8, C16–C20	

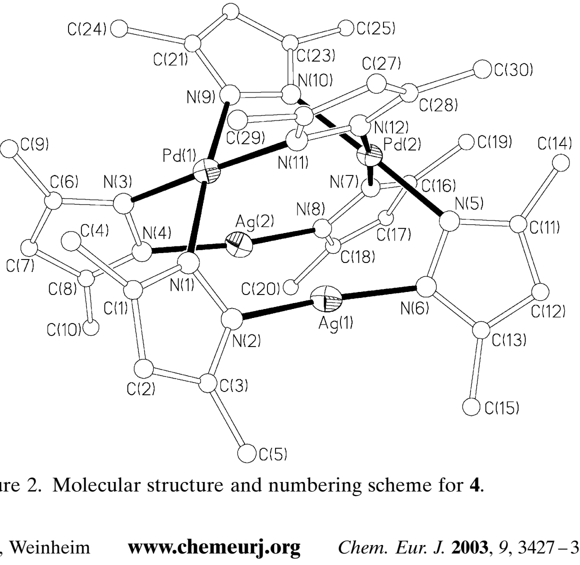


Figure 2. Molecular structure and numbering scheme for **4**.

least-squares coordination planes of the palladium atoms is 91.0° and the dihedral angle between the Pd-N-N-Pd planes is 70.8°.[46]

Each silver atom is bonded to two dmpz groups forming an almost linear environment (N2-Ag1-N6 = 167.4°, N4-Ag2-N8 = 169.6°), whereby each dmpz group acts as a bridge between one silver and one palladium atom. The N2-Ag1-N6 and N4-Ag2-N8 vectors are basically parallel to each other (torsion angle = 8.6°). The Ag atoms are located 3.1950 Å from each other, this distance being too great for a bond,[52] but short enough for a contact between the atoms to be considered. This distance is even shorter than the Ag···Ag contact length observed in [{Ag(pz)}$_n$] (Ag···Ag = 3.273 Å) and [{Ag(pz)}$_3$] (Ag···Ag = 3.43 Å) between silver atoms of different chains or trimers.[53]

The Pd–N[32, 40–45] and Ag–N[43, 53] bond lengths are in the range found in other related complexes.

The dmpz groups are planar within experimental error. The dihedral angle between each pair of dmpz groups bonded to a palladium atom in a *cis* disposition is 79.3° (planes 1 and 2), 63.4° (planes 3 and 4) and 76.4° (planes 5 and 6), similar to the ones observed in the starting compound. (84.7, 68.4 and 74.8°).[46] (See Table 2)

Despite the presence of bridging dmpz groups between the metal atoms, all intermetallic separations (3.164–3.513 Å) indicate that there are no metal–metal bonds. In this complex, the palladium atoms are separated 3.513 Å from each other, which is an even greater separation than in the starting compound (**2**: 3.402 Å).

Reactivity of [Pd$_2$M$_2$(μ-dmpz)$_6$] (M = Cu(3), Ag(4), Au(5)) towards AgClO$_4$: As we have recently shown, the π-electron-rich cleft between the two azolato rings in [Pd$_2$(C^P)$_2$(μ-dmpz)$_2$] [C^P = CH$_2$-C$_6$H$_4$-P(o-tolyl)$_2$-$\kappa C,P$; dmpz = 3,5-dimethylpyrazolate)] is able to accommodate a silver cation. Compounds [Pd$_2$M$_2$(μ-dmpz)$_6$] (M = Cu (**3**), Ag (**4**), Au (**5**)) contain three pairs of dmpz groups, signifying three π-electron-rich clefts that offer potentially interesting sites to complex Ag$^+$ ions. Therefore, we have studied their reactions with AgClO$_4$. Compounds **3**–**5** react with AgClO$_4$ in a 1:2 molar ratio in dried CH$_2$Cl$_2$/OEt$_2$, in an argon atmosphere and in the dark to give new compounds with the formula [Pd$_2$M$_2$(μ-dmpz)$_6$Ag$_2$(ClO$_4$)$_2$] (M = Cu (**6**), Ag (**7**), Au (**8**)). Even when using a large excess of AgClO$_4$, the final products are always **6**, **7** and **8** (Scheme 1h). The synthesis of **8** requires the addition of AgClO$_4$ in a 1:5 molar ratio to avoid the presence of starting material in the final solid.

Compounds **6**–**8** are only soluble in coordinating solvents such as acetone or tetrahydrofuran. For this reason single crystals were obtained from solutions of compounds **7** and **8** in acetone. The crystals have the stoichiometry [{Pd$_2$M$_2$(μ_2-dmpz-$\kappa N,N'$)$_2$(μ_3-dmpz-$\kappa N,N',C^4$)$_4$Ag(OCMe$_2$)(O-ClO$_3$)Ag(μ_2-O$_2$ClO$_2$)}$_2$] (M = Ag (**7'**), Au (**8'**); **7'** = **7** · OCMe$_2$, **8'** = **8** · OCMe$_2$)). Their molecular structures, which are quite similar, are shown in Figures 3 and 4. Tables 3 and 4 show selected bond lengths and angles.

As can be seen, both complexes are formed by two "Pd$_2$M$_2$(μ_2-dmpz-$\kappa N,N'$)$_2$(μ_3-dmpz-$\kappa N,N',C^4$)$_4$Ag$_2$(OCMe$_2$)-(OClO$_3$)(μ_2-O$_2$ClO$_2$)" fragments (M = Ag (**7'**), Au (**8'**)) in which the O$_2$ClO$_2$ anions are bridging. Both fragments are related by a centre of symmetry and each one contains two Ag atoms located in the clefts between each pair of azolato rings that are bridging silver (or gold) and palladium centres of the box.

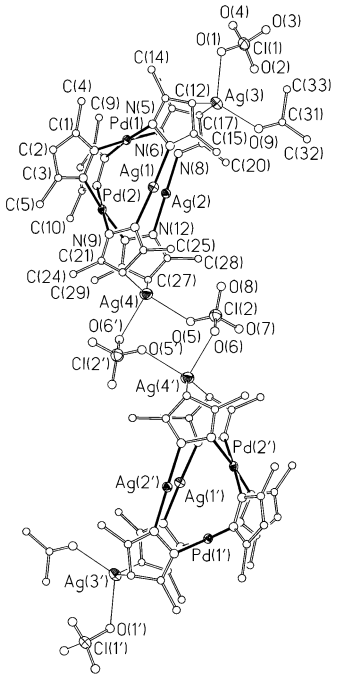


Figure 3. Molecular structure and numbering scheme for **7'**.

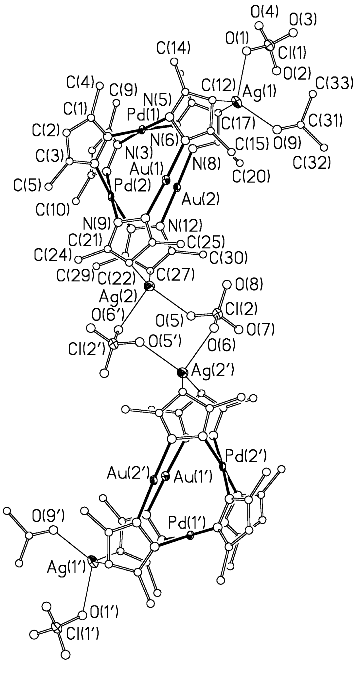


Figure 4. Molecular structure and numbering scheme for **8'**.

The structural parameters for the "Pd$_2$M$_2$(μ-dmpz-$\kappa N,N'$)$_6$" units (M = Ag (**7'**), Au (**8'**)) are very similar to the ones observed in complex [Pd$_2$Ag$_2$(μ_2-dmpz-$\kappa N,N'$)$_6$] (**4**). Each palladium centre displays an almost square-planar coordination environment formed by four N atoms of four dmpz groups with angles between *cis* ligands close to 90° (84.90–

Table 3. Selected bond lengths [Å] and angles [°] for complex **7′**.

Pd(1)−N(1)	2.006 (4)	Pd(1) −N(3)	2.009 (4)
Pd(1)−N(5)	2.049 (4)	Pd(1)−N(7)	2.036 (4)
Pd(2)−N(2)	2.009 (4)	Pd(2)−N(4)	2.007 (4)
Pd(2)−N(9)	2.036 (4)	Pd(2)−N(11)	2.067 (4)
Ag(1)−N(6)	2.059 (5)	Ag(1)−N(10)	2.060 (5)
Ag(2)−N(8)	2.064 (4)	Ag(2)−N(12)	2.063 (4)
Ag(3)−O(1)	2.455 (5)	Ag(3)−O(9)	2.369 (6)
Ag(4)−O(5)	2.451 (7)	Ag(4)−O(6′)	2.479 (8)
Ag(3)−C(12)	2.452 (6)	Ag(3)−C(17)	2.447 (6)
Ag(4)−C(22)	2.414 (6)	Ag(4)−C(27)	2.411 (6)
Pd1 ··· Pd2	3.484	Pd1 ··· Ag1	3.298
Pd1 ··· Ag2	3.251	Pd2 ··· Ag1	3.249
Ag1 ··· Ag2	3.029	Pd2 ··· Ag2	3.291
N(1)-Pd(1)-N(3)	86.73(17)	N(1)-Pd(1)-N(5)	94.93(17)
N(3)-Pd(1)-N(7)	93.02(18)	N(7)-Pd(1)-N(5)	85.05(18)
N(4)-Pd(2)-N(2)	86.57(18)	N(4)-Pd(2)-N(11)	95.16(18)
N(2)-Pd(2)-N(9)	93.11(18)	N(9)-Pd(2)-N(11)	84.94(18)
N(10)-Ag(1)-N(6)	172.38(17)	N(12)-Ag(2)-N(8)	170.55(17)
O(9)-Ag(3)-O(1)	117.2(2)	O(9)-Ag(3)-C(12)	99.6(2)
O(1)-Ag(3)-C(12)	101.39(18)	O(9)-Ag(3)-C(17)	112.9(3)
O(1)-Ag(3)-C(17)	95.63 (18)	C(12)-Ag(3)-C(17)	130.69(19)
O(5)-Ag(4)-O(6′)	88.8(3)	O(5)-Ag(4)-C(27)	94.0(2)
O(5)-Ag(4)-C(22)	129.7(2)	O(6′)-Ag(4)-C(27)	106.1(2)
O(6′)-Ag(4)-C(22)	93.8(4)	C(22)-Ag(4)-C(27)	131.2(2)

Table 4. Selected bond lengths [Å] and angles [°] for complex **8′**.

Pd(1)−N(1)	2.014 (7)	Pd(1)−N(3)	2.015 (7)
Pd(1)−N(5)	2.052 (7)	Pd(1)−N(7)	2.029 (7)
Pd(2)−N(2)	2.005 (7)	Pd(2)−N(4)	1.994 (7)
Pd(2)−N(9)	2.042 (7)	Pd(2)−N(11)	2.069 (7)
Au(1)−N(6)	2.003 (7)	Au(1)−N(10)	1.993 (7)
Au(2)−N(8)	2.007 (6)	Au(2)−N(12)	2.003 (7)
Ag(1)−O(1)	2.452 (7)	Ag(1)−O(9)	2.369 (8)
Ag(1)−C(12)	2.453 (9)	Ag(1)−C(17)	2.457 (9)
Ag(2)−O(5)	2.397 (8)	Ag(2)−O(6′)	2.482 (7)
Ag(2)−C(22)	2.391 (9)	Ag(2)−C(27)	2.422 (9)
Pd(1)−Au(1)	3.309(1)	Pd(1)−Au(2)	3.297(1)
Pd(2)−Au(1)	3.296(1)	Pd(2)−Au(2)	3.313(1)
Au(1)−Au(2)	3.119(1)		
N(1)-Pd(1)-N(3)	86.7(3)	N(1)-Pd(1)-N(5)	94.5(3)
N(3)-Pd(1)-N(7)	93.1(3)	N(7)-Pd(1)-N(5)	85.4(3)
N(4)-Pd(2)-N(2)	86.6(3)	N(4)-Pd(2)-N(11)	94.9(3)
N(2)-Pd(2)-N(9)	93.3(3)	N(9)-Pd(2)-N(11)	84.9(3)
N(10)-Au(1)-N(6)	174.3(3)	N(12)-Au(2)-N(8)	172.7(3)
O(9)-Ag(1)-O(1)	115.4(3)	O(9)-Ag(1)-C(12)	95.3(4)
O(1)-Ag(1)-C(12)	103.6(3)	O(9)-Ag(1)-C(17)	117.2(4)
O(1)-Ag(1)-C(17)	94.3(3)	C(12)-Ag(1)-C(17)	131.4(3)
O(5)-Ag(2)-O(6′)	89.6(3)	O(5)-Ag(2)-C(27)	95.3(3)
O(5)-Ag(2)-C(22)	128.4(3)	O(6′)-Ag(2)-C(27)	106.5(3)
O(6′)-Ag(2)-C(22)	96.7(3)	C(22)-Ag(2)-C(27)	130.6(3)

95.16°). The Pd_2N_4 six-membered metallocycle exhibits a boatlike conformation, the dihedral angle between the planes containing Pd-N-N-Pd being 72.3° for **7′** and 74.0° for **8′**.[46] Each silver (in **7′**) or gold (in **8′**) centre is bonded to two N atoms of two dmpz groups in an almost linear coordination environment (**7′**: N6-Ag1-N10 172.38°, N8-Ag2-N12 170.55°; **8′**: N6-Au1-N10 174.3°, N8-Au2-N12 172.7°), each pyrazolate ligand acting as a bridge between M (M = Ag (**7′**), Au (**8′**)) and one palladium atom. The N-M-N vectors are not parallel to each other (torsion angle = 38.7° (**7′**), 34.8° (**8′**)). The M−M separations are too great (Ag1 ··· Ag2 3.029 Å (**7′**), Au1 ··· Au2 3.119 Å (**8′**)) for a bond length,[52] but short enough for a contact between the atoms to be considered.[54–57]. The Ag ··· Ag separation (3.029 Å) is the shortest Ag ··· Ag contact length observed in this kind of compound: $[\{Ag(pz)\}_n]$ (Ag ··· Ag = 3.273 Å) and $[\{Ag(pz)\}_3]$ (Ag ··· Ag = 3.43 Å) between silver atoms of different chains or trimers.[53]

All Pd−N,[32, 40–45] Ag−N[43, 53] and Au−N[21, 58, 59] lengths are in the range of those found in other complexes with the same kind of ligands.

Each "$Pd_2M_2(\mu_2$-dmpz-$\kappa N,N')_6$" unit has two silver ions located in two of the π-electron-rich clefts between pairs of dmpz rings [the clefts formed by the dmpz ligands that are bridging palladium and M (M = Ag (**7**), Au (**8**)) centres]. Each silver cation (Ag3, Ag4 (**7′**) or Ag1, Ag2 (**8′**)) is approximately equidistant from the two dmpz rings; the distances from the C^4 atom of each 3,5-dmpz ring are close to 2.4 Å (**7′**: Ag3−C12: 2.452(6), Ag3−C17: 2.447(6), Ag4−C22: 2.414(6), Ag4−C27: 2.411(6) Å; **8′**: Ag1−C12: 2.453(9), Ag1−C17: 2.457(9), Ag2−C22: 2.391(9), Ag2−C27: 2.422(9) Å). The vectors between these silver centres and the C^4 atoms of each dmpz are nearly perpendicular to the corresponding dmpz ring (angles between the perpendicular to these planes and the Ag−C4 line in **7′** are: 3.7 (Ag3−C12), 1.0 (Ag3−C17), 3.4 (Ag4−C22) and 2.0° (Ag4−C27); and in **8′** are: 3.0 (Ag1−C12), 2.1 (Ag1−C17), 3.5 (Ag2−C22) and 2.8° (Ag2−C27). The Ag−C^4 distances are similar to the shortest values observed in complexes showing Ag-η^1-arene interactions (2.40–2.58 Å)[60–63] and clearly shorter than the Ag−C lengths observed in Ag-η^2-arene complexes (2.50–2.65 Å).[48–50, 64]

The Ag−η^1-dmpz interactions seem to be strong enough and responsible for the changes of the dihedral angles between each pair of dmpz groups bridging Pd and Ag or Pd and Au in the "$Pd_2M_2(\mu_2$-dmpz-$\kappa N,N')_6$" (M = Ag (**7′**), Au (**8′**)) units. These angles decrease from 63.4 and 76.4° in compound, **4**, to 45.8 and 45.2° in its derivative **7′**. In **8′** the corresponding dihedral angles are similar to those in **7′** (48.8 and 45.3°)[46]

The silver atoms involved in the Ag−η^1-dmpz interactions complete their coordination spheres with two oxygen atoms and display a distorted tetrahedral coordination environment. One Ag centre is bonded to an oxygen atom of a terminal $-OClO_3$ group and to that of an acetone molecule. The other one is bonded to two oxygen atoms, one from each of the two bridging O_2ClO_2 groups. All the Ag−O bond lengths are in the range of distances found in other complexes with the same kind of ligands.[65–70].

Finally, it must be mentioned that the bond lengths and angles within the rings of the dmpz groups that are η^1-coordinated to the silver centres are similar to those observed in the other dmpz ones, indicating that in spite of the η^1 interaction to Ag^+, the pyrazolato rings maintain their aromaticity.

As has been previously mentioned, compounds **6**–**8** are only soluble in coordinating solvents such as acetone or tetrahydrofuran, which would seem to indicate that the compounds prepared consist of infinite chains with bridging perchlorate groups (μ_2-O_2ClO_2) and that, in solution, the solvent produces partial breaking of the chains by coordination to the Ag centres η^1-coordinated to the pyrazolate ligands (see structures of **7′** and **8′**). It seems reasonable to suppose that the NMR data of compounds **6**–**8** in HDA correspond at least to species containing the $[\{Pd_2M_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag(OCMe_2)(OClO_3)Ag(\mu_2\text{-}O_2ClO_2)\}_2]$ (M = Cu (**6′**), Ag (**7′**), Au (**8′**)) fragment or an even smaller one (i.e. with a higher number of acetone molecules coordinated to Ag). All the ^1H NMR spectra of compounds **6**–**8** at room temperature in HDA show five signals (see Experimental Section) with a related integral of 6:6:6:1:2. COSY experiments allow these to be gathered into two sets of signals, one for the "$Pd_2(\mu\text{-dmpz})_2$" groups ($\delta \cong 2.70$ (s; Me), 5.55 ppm (H^4)) and the other for the "$Pd_2M_2(\mu\text{-dmpz})_4$" groups ($\delta \cong$ 2.29 (s; Me), 2.33 (s; Me), 5.90 ppm (H^4)). Some changes in the chemical shifts of all signals are observed when compared to those of the starting material. The low-field shift of the signal corresponding to the H^4 of the dmpz groups η^1 coordinated to Ag^+ (0.2–0.24 ppm) with respect to those in the starting material is especially significant.

Considering that the ^{13}C NMR data corresponding to the C atoms involved in the Ag–η^1 interactions would be especially informative (the C^4 atoms of the dmpz groups of "$Pd_2M_2(\mu\text{-dmpz})_4$"), we performed the ^{13}C NMR spectra of **6**–**8** in acetone [^2H]; unfortunately the low solubility of these compounds precluded obtaining good spectra.

Experimental Section

General procedures and materials: Elemental analyses were performed on a Perkin–Elmer 240-B microanalyser. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 200–4000 cm^{-1}). NMR spectra were recorded on a Varian Unity-300 spectrometer by using the standard references; 3,5-dimethylpyrazole (Hdmpz) was purchased from Aldrich. $[PdCl_2(PhCN)_2]$ was prepared as described elsewhere.[71, 72]

$[PdCl_2(Hdmpz)_2]$ (A)

Method A: 3,5-Dimethylpyrazole (0.1510 g, 1.571 mmol) was added to a red solution of $[PdCl_2(PhCN)_2]$ (0.300 g, 0.78 mmol) in CH_2Cl_2 (25 mL). The solution turned yellow. After one hour of stirring at room temperature, the solution was evaporated to dryness and Et_2O was added to the residue. The resulting yellow solid was filtered and air dried. Yield: 0.2610 g, 90%.

Method B: A solution of 3,5-dimethylpyrazole (1.9226 g, 20 mmol) in CH_2Cl_2 (200 mL) was added to a solution of $PdCl_2$ (1.7731 g, 10 mmol) in water (30 mL). The mixture was stirred for three days; then the organic phase was separated, evaporated to dryness and Et_2O (15 mL) was added to the residue. The resulting yellow solid was filtered and air dried. Yield: 3.1372 g, 94.2%; IR (Nujol): $\tilde{\nu} = 3200$ cm^{-1} (NH); ^1H NMR (300.13 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 1.89$ (s, 6H; Me), 2.67 (s, 6H; Me), 5.70 (s, 2H; H^4), 11.85 ppm (s, 2H; NH); elemental analysis calcd (%) for $PdC_{10}Cl_2H_{16}N_4$: C 32.50, H 4.36, N, 15.15; found: C, 32.90, H, 4.44, N, 15.69.

$[Pd_2Cl_2(\mu\text{-dmpz})_2(Hdmpz)_2]$ (1): Compound **A** (0.2429 g, 0.6576 mmol) was suspended in acetone (35 mL) and added to a solution of KOH (0.0370 g, 0.6594 mmol) in methanol (6 mL). The mixture was stirred at room temperature for 30 min. Evaporation of the solvent to one half of the volume afforded **1**. Yield: 0.1710 g, 78%; IR (Nujol): $\tilde{\nu} = 3271$ cm^{-1} (NH); ^1H NMR (300.13 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 1.98$ (s, 6H; Me (Hdmpz)), 2.19 (s, 6H; Me (μ-dmpz)), 2.42 (s, 6H; Me (μ-dmpz)) 2.56 (s, 6H; Me (Hdmpz)), 5.25 (s, 2H; H^4 (μ-dmpz)), 5.83 (s, 2H; H^4 (Hdmpz)), 11.18 (s, 2H; NH (Hdmpz)); elemental analysis calcd (%) for $Pd_2C_{20}Cl_2H_{30}N_8$: C 36.06, H 4.54, N 16.81; found: C 35.61, H 4.49, N 16.48.

$[Pd_2(\mu\text{-dmpz})_2(dmpz)_2(Hdmpz)_2]$ (2): A solution of KOH (0.2106 g, 3.7525 mmol) and 3,5-Hdmpz (0.3607 g, 3.7525 mmol) in methanol (45 mL) was added dropwise to a suspension of **1** (1.25 g, 1.8762 mmol) in CH_2Cl_2 (140 mL). The mixture was refluxed for 30 min and then stirred at room temperature for 60 min. Evaporation to dryness and addition of diethyl ether to the residue rendered a yellow solid, **2**, recrystallised from $CHCl_3/Et_2O$. Yield: 0.4640 g, 31%; IR (KBr): $\tilde{\nu} = 2800$ cm^{-1} (NH); ^1H NMR (300.13 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 1.93$ (s, 12H; Me), 2.19 (s, 12H; Me (μ-dmpz)), 2.31 (s, 12H; Me), 5.47 (s, 2H; H^4 (μ-dmpz)), 5.73 (s, 4H; H^4), 11.0 ppm (s, 2H; NH); elemental analysis calcd (%) for $Pd_2C_{30}H_{44}N_{12}$: C 45.37, H 5.64, N, 21.37; found: C 45.12, H, 6.08, N, 20.71. Single crystals of **2** for X-ray study were obtained by slow diffusion of Et_2O into a solution of **2** in CH_2Cl_2 at room temperature.

$[Pd_2Cu_2(\mu\text{-dmpz-}\kappa N,N')_6]$ (3): Compound **2** (0.2373 g, 0.3020 mmol) and NEt_3 (1.5 mL) was added to a colourless solution of $[Cu(CH_3CN)_4]BF_4$ (0.1905 g, 0.6056 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature for four hours and the resulting yellow solution evaporated to dryness. The addition of *i*PrOH (7 mL) to the residue rendered a green solid. Yield: 0.2273 g, 83%; ^1H NMR (300.13 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 2.28$ (s, 12H; Me, PdCu (μ-dmpz)), 2.30 (s, 12H; Me, PdCu(μ-dmpz)), 2.60 (s, 12H; Me, $Pd_2(\mu\text{-dmpz})$), 5.47 (s, 2H; H^4, $Pd_2(\mu\text{-dmpz})$), 5.66 ppm (s, 4H; H^4, PdCu (μ-dmpz)); elemental analysis calcd (%) for $Pd_2C_{30}Cu_2H_{48}N_{12}$: C 39.57, H 4.65, N 18.45; found: C 39.33, H 4.73, N 17.90.

$[Pd_2Ag_2(\mu\text{-dmpz-}\kappa N,N')_6]$ (4): $AgClO_4$ (0.5289 g, 2.5510 mmol) and NEt_3 (1.5 mL) were added to a solution of **2** (0.4008 g, 0.5102 mmol) in CH_2Cl_2/Et_2O (45/10 mL). The mixture was stirred at room temperature for 16 hours in the dark and the resulting yellow solution was evaporated to dryness. Addition of methanol (25 mL) to the residue rendered a yellow solid which was filtered off and washed with Et_2O (5 mL). Yield: 0.4366 g, 86%; ^1H NMR (300.13 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 2.22$ (s, 12H; Me, PdAg (μ-dmpz)), 2.27 (s, 12H; Me, PdAg(μ-dmpz)), 2.57 (s, 12H; Me, $Pd_2(\mu\text{-dmpz})$), 5.45 (s, 2H; H^4, $Pd_2(\mu\text{-dmpz})$), 5.68 ppm (s, 4H; H^4, PdAg (μ-dmpz)); elemental analysis calcd (%) for $Ag_2Pd_2C_{30}H_{48}N_{12}$: C 36.06, H 4.04, N 16.81; found: C 36.02, H 3.65, N 16.72. Single crystals of **4** for X-ray diffraction studies were obtained by slow diffusion of Et_2O into a solution of **4** in CH_2Cl_2 at room temperature.

$[Pd_2Au_2(\mu\text{-dmpz-}\kappa N,N')_6]$ (5): Compound **2** (0.1962 g, 0.2498 mmol) and NEt_3 (1.5 mL) were added to a purple solution of $PPN[Au(acac)_2]$ (PPN = $Ph_3P{=}N^+{=}PPh_3$) (0.4665 g, 0.4995 mmol) in CH_2Cl_2 (40 mL) under an argon atmosphere. The mixture was stirred for four hours and the resulting solution evaporated to dryness. Addition of dry methanol (30 mL) to the residue rendered a white solid, which was filtered off and washed with Et_2O (5 mL) Yield: 0.2055 g, 70%; ^1H NMR (300.13 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 2.26$ (s, 12H; Me, PdAu (μ-dmpz)), 2.32 (s, 12H; Me, PdAu(μ-dmpz)), 2.61 (s, 12H; Me, $Pd_2(\mu\text{-dmpz})$), 5.48 (s, 2H; H^4, $Pd_2(\mu\text{-dmpz})$), 5.74 ppm (s, 4H; H^4, PdAu (μ-dmpz)); elemental analysis calcd (%) for $Au_2Pd_2C_{30}H_{48}N_{12}$: C 30.80, H 3.60, N 14.27; found: C 31.20, H 3.57, N 14.02.

$[Pd_2Cu_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}ClO_4)_2]$ (6): $AgClO_4$ (0.1140 g, 0.550 mmol) was added to a solution of **3** (0.2505 g, 0.2750 mmol) in CH_2Cl_2/Et_2O (30/10 mL). The mixture was stirred at room temperature for 15 min under nitrogen and a yellow solid precipitated. The solid was filtered off and washed with Et_2O. Yield: 0.2566 g, 70%; ^1H NMR (300.13 MHz, [D_6]acetone, 20 °C, TMS): $\delta = 2.31$ (s, 12H; Me, PdCu (μ-dmpz)), 2.33 (s, 12H; Me, PdCu(μ-dmpz)), 2.72 (s, 12H; Me, $Pd_2(\mu\text{-dmpz})$), 5.54 (s, 2H; H^4, $Pd_2(\mu\text{-dmpz})$), 5.86 ppm (s, 4H; H^4, PdCu (μ-dmpz)); elemental analysis calcd (%) for $Ag_2C_{30}Cl_2Cu_2Pd_2O_8H_{48}N_{12}$: C 27.09, H 3.19, N 12.37; found: C 26.60, H 3.26, N 12.11.

$[Pd_2Ag_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}ClO_4)_2]$ (7): $AgClO_4$ (0.1245 g, 0.6005 mmol) was added to a solution of **4** (0.3000 g, 0.3002 mmol) in CH_2Cl_2/Et_2O (30/10 mL). The mixture was stirred for two hours under nitrogen. The resulting solution was evaporated to dryness and Et_2O (20 mL) was added to the residue. The resulting yellow solid was filtered off and recrystallised from acetone/hexane. Yield: 0.2146 g, 51%; ^1H NMR (300.13 MHz, [D_6]acetone, 20 °C, TMS): $\delta = 2.27$ (s, 12H; Me, PdAg (μ-dmpz)), 2.34 (s, 12H; Me, PdAg(μ-dmpz)), 2.71 (s, 12H; Me, $Pd_2(\mu\text{-dmpz})$), 5.56 (s, 2H, H^4, $Pd_2(\mu\text{-dmpz})$), 5.87 ppm (s, 4H, H^4, PdAg (μ-dmpz)); elemental analysis calcd (%) for $Ag_4C_{30}Cl_2Pd_2O_8H_{48}N_{12}$: C 25.48, H, 2.99, N 12.10; found: C 25.46, H 2.76, N,12.55. Small crystals of **7** for X-ray studies were grown by the slow diffusion of Et_2O into a solution of the complex in acetone under nitrogen at room temperature in the dark.

$[Pd_2Au_2(\mu_2\text{-dmpz-}\kappa N,N')_2(\mu_3\text{-dmpz-}\kappa N,N',C^4)_4Ag_2(\mu_2\text{-}ClO_4)_2]$ (8): $AgClO_4$ (0.1590 g, 0.7500 mmol) was added to a solution of **5** (0.1800 g, 0.1529 mmol) in CH_2Cl_2/Et_2O (25/15 mL). The mixture was stirred for two hours under nitrogen. The solvent was then evaporated to dryness and Et_2O (15 mL) was added to the residue. The resulting yellow solid was

Table 5. Crystal data and structure refinement for complexes **2**, **4**, **7′** and **8′**.

	2	**4**	**7′**	**8′**
formula	$C_{30}H_{44}N_{12}Pd_2$	$C_{30}H_{42}N_{12}Ag_2Pd_2$	$C_{66}H_{96}Ag_8Cl_4N_{24}O_{18}Pd_4 \cdot nC_6H_{14}$	$C_{66}H_{96}Ag_4Au_4Cl_4N_{24}O_{18}Pd_4 \cdot nC_6H_{14}$
a [Å]	9.5681(13)	12.269(2)	13.0699(13)	13.110(2)
b [Å]	12.720(2)	12.9463(18)	13.4069(12)	13.3927(17)
c [Å]	15.880(3)	13.024(3)	15.7827(16)	15.755(3)
α [°]	113.261(13)	118.941(9)	100.652(12)	101.524(17)
β [°]	107.472(16)	90.476(12)	111.788(9)	111.484(16)
γ [°]	90.025(18)	97.414(12)	104.087(10)	103.720(19)
V [Å^3]	1678.0(5)	1789.3(6)	2371.6(4)	2371.6(6)
Z	2	2	1	1
ρ_{calcd} [g cm^{-3}]	1.555	1.855	2.122	2.371
T [K]	150(1)	173(1)	150(1)	150(1)
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
dimensions [mm]	0.40 × 0.30 × 0.05	0.45 × 0.35 × 0.15	0.40 × 0.20 × 0.20	0.44 × 0.39 × 0.22
μ [mm^{-1}]	1.112	2.107	2.538	7.891
absorption correction	psi scans	psi scans	psi scans	psi scans
θ range [°]	2.25–24.98	1.80–25.00	2.28–24.98	2.30–24.96
reflections collected	6267	6222	8728	8704
independent reflections	5885 ($R_{int} = 0.0190$)	5920 ($R_{int} = 0.0436$)	8327 ($R_{int} = 0.0173$)	8305 ($R_{int} = 0.0322$)
final R indices [$I > 2\theta(I)$][a]	$R1 = 0.0800/wR2 = 0.2230$	$R1 = 0.0440/wR2 = 0.1092$	$R1 = 0.0347/wR2 = 0.0863$	$R1 = 0.0379/wR2 = 0.0899$
R indices (all data)	$R1 = 0.0830/wR2 = 0.2246$	$R1 = 0.0651/wR2 = 0.1218$	$R1 = 0.0385/wR2 = 0.0886$	$R1 = 0.0510/wR2 = 0.0959$
goodness-of-fit on F^2[b]	1.204	1.006	1.049	1.047
largest diff. peak/hole [e Å^{-3}]	2.76/−2.17	1.26/−0.93	1.49/−1.87	2.28/−2.09

[a] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{0.5}$; $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] Goodnes-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{0.5}$.

filtered off and vacuum dried. Yield: 0.1375 g, 56%; ^{1}H NMR (300.13 MHz, [D$_6$]acetone, 20 °C, TMS): $\delta = 2.28$ (s, 12H; Me, PdAu (μ-dmpz)), 2.33 (s, 12H; Me, PdAu(μ-dmpz)), 2.74 (s, 12H; Me, Pd$_2$(μ-dmpz)), 5.56 (s, 2H; H^4, Pd$_2$(μ-dmpz)), 5.98 ppm (s, 4H; H^4, PdAu (μ-dmpz)); elemental analysis calcd (%) for $Ag_2Au_2C_{30}Cl_2Pd_2O_8H_{48}N_{12}$: C 22.03, H 2.66, N 10.45; found: C 21.75, H 2.50, N 9.77. Single crystals of **8** for X-ray diffraction studies were obtained by slow diffusion of Et_2O into a solution of the complex in acetone at room temperature.

X-ray structure determinations: Crystal data and other details of the structure analyses are presented in Table 5. Suitable crystals of **2**, **4** ,**7′** and **8′** were obtained as indicated in each synthetic procedure. Crystals were mounted at the end of a quartz fibre. The radiation used in all cases was graphite monochromatic Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å).

Data for 2: All diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions were determined from 25 centred reflections in the range $22.3 < 2\theta < 30.5°$. An absorption correction was applied based on 548 azimuthal scan data. Maximum and minimum transmission coefficients were 0.947 and 0.665.

Data for 4: All diffraction measurements were made on a Siemens P4 four circle diffractometer. Unit cell dimensions were determined from 29 centred reflections in the range $19.47 < 2\theta < 28.88°$. An absorption correction was applied based on 390 azimuthal scan data. Maximum and minimum transmission coefficients were 0.594 and 0.527.

Data for 7′: All diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions were determined from 25 centred reflections in the range $23.5 < 2\theta < 32.3°$. An absorption correction was applied based on 566 azimuthal scan data. Maximum and minimum transmission coefficients were 0.923 and 0.812.

Data for 8′: All diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions were determined from 25 centred reflections in the range $24.6 < 2\theta < 31.6°$. An absorption correction was applied based on 496 azimuthal scan data. Maximum and minimum transmission coefficients were 0.969 and 0.682.

The structures were solved by Patterson and Fourier methods. All refinements were carried out by using the SHELXL-97 program.[73] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints except as noted below. All hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters that were 1.2 times the U_{iso} values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). In the structure of **7′**, the oxygen atoms (O(5) to O(8)) of one of the perchlorate groups were disordered over two positions refined with partial occupancy 0.7/0.3, and for the minor congener, a common set of thermal anisotropic parameters were used. Weak restraints (SADI and SAME instructions) were applied in the geometry of the perchlorate groups and n-hexane solvent molecule. For the latter, a common set of thermal anisotropic parameters were used. In the structure of **8′**, the methyl carbon atom of the acetone group was disordered over two positions refined with partial occupancy 0.5, and the geometry constrained (DFIX) to accepted values and refined with a common set of thermal anisotropic parameters. Weak restraints (SADI and SAME instructions) were applied in the geometry of the n-hexane solvent molecule. For the latter, a common set of thermal anisotropic parameters were used. Full-matrix least-squares refinement of this model against F^2 converged to the final residual indices given in Table 5. Lorentz and polarisation corrections were applied for all the structures.

CCDC-198898, CCDC-198899, CCDC-198900 and CCDC-198901 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; fax: (+44)1223-336033; or e-mail: deposit@ccdc.cam.ac.uk).

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