New Tris(pyrazolyl)triazine and Pyrazolylpyridine Gold(I) and Palladium(II) Derivatives Based on the 3,5-Bis(4-butoxyphenyl)pyrazole Group – Architectures with Different Types of Bonding Interactions

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The 3,5-bis(4-butoxyphenyl)pyrazolyl group (Pz^{bp2}) has been used as a building block for mono- and polymetallic derivatives of 2,4,6-tris[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]-1,3,5-triazine ($TPz^{bp2}Tz$, **1**), 2-[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]pyridine ($Pz^{bp2}Py$, **2**), and 3,5-bis(4-butoxyphenyl)pyrazole (HPz^{bp2}, **3**) ligands. The synthesis and characterisation of the new hexadentate ligand **1** are described, together with the chemistry of its metal complexes containing $[Pd(\eta^3\text{-}C_3H_5)]^+$ and $[Au(PPh_3)]^+$ fragments. The related complexes containing $Pz^{bp2}Py$ (**2**) were also studied and their structural characteristics were compared to those of the $TPz^{bp2}Tz$ species. The role of the counter-ion on the supramolecular assembly of complexes containing the HPz^{bp2} ligand **3** was made clear by the X-ray structures of $[Pd(\eta^3\text{-}C_3H_5)(HPz^{bp2})_2](BF_4)$ and $[Au(HPz^{bp2})(PPh_3)](NO_3)$. Hydrogen bonds and/or bonding interactions are responsible for pseudohelical one-dimensional polymers or supramolecular columnar arrays, respectively.

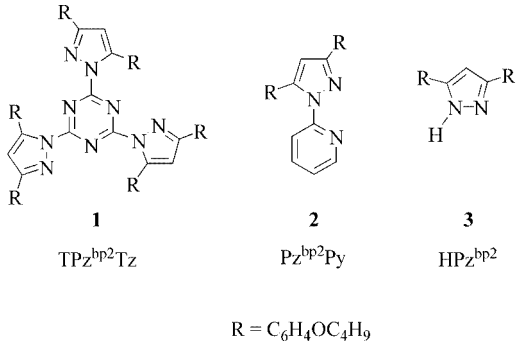
Introduction

Research into the self-assembly of transition metal complexes is of increasing interest for the design of supramolecular structures.[1–7] Of the strategies currently in use to control molecular aggregates, non-covalent interactions such as metal coordination and hydrogen bonding have been of much use in recent years.[8,9]

Our group has acquired some expertise in studying metal complexes containing long chain-substituted pyrazole groups. The coordinative ability of 3,5-bis(4-butoxyphenyl)-pyrazolate towards gold(I) derivatives, for example, yielded complexes such as $[Au(Pz^{bp2})(PPh_3)]$, with supramolecular aurophilic Au···Au interactions,[10a,11,12] and $[(PPh_3)Au(\mu\text{-}Pz^{bp2})Au(PPh_3)]^+$, presenting intramolecular Au···Au contacts and molecular entities controlled by interactions through the corresponding counter-ions.[10b] Similar effects have also been described for related silver(I) derivatives.[5] On the other hand, π-allyl palladium(II) fragments are useful to provide stable complexes containing *N*,*N*′-bidentate ligands,[13] making these metal groups suitable for our coordinative purposes.

In addition, 1,3,5-triazine ligands have also been shown to be versatile for the preparation of metal complexes with a large variety of structural architectures.[14]

To extend these results, we decided to study new metal derivatives of a polydentate ligand, 2,4,6-tris[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]-1,3,5-triazine ($TPz^{bp2}Tz$, **1**), containing three pyrazole groups in addition to the three nitrogen atoms of the triazine core (Scheme 1). Their coordination capability towards $[Pd(\eta^3\text{-}C_3H_5)]^+$ and $[Au(PPh_3)]^+$ fragments is analysed in a search for polymetallic complexes. The nature of the counter-ion and the effect of the



1 $TPz^{bp2}Tz$ **2** $Pz^{bp2}Py$ **3** HPz^{bp2}

Scheme 1

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OR substituents on the pyrazole groups are also considered as elements for potential supramolecular architectures.

The chemistry of the new complexes is described and compared to that observed on treatment of the same metal fragments with bidentate 2-[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]pyridine (**2**) and monodentate 3,5-bis(4-butoxyphenyl)pyrazole (**3**) ligands, regarded as building blocks presenting coordinative positions related to those of the new ligand $TPz^{bp2}Tz$ (**1**) (Scheme 1).

Results and Discussion

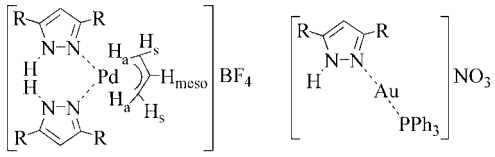
Synthesis and Structural Characterisation of the 2,4,6-Tris[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]-1,3,5-triazine Ligand ($TPz^{bp2}Tz$, 1)

We treated 3,5-bis(4-butoxyphenyl)pyrazole (**3**) with 2,4,6-trichlorotriazine (stoichiometry 3:1) in dry THF under argon atmosphere, by the procedure that we have already described for several 2,4,6-tris(pyrazol-1-yl)-2,4,6-triazines,[15] to obtain the 2,4,6-tris[3,5-bis(4-butoxyphenyl)-pyrazol-1-yl]-1,3,5-triazine ligand (**1**, $TPz^{bp2}Tz$) in a 30% yield.

This ligand was fully characterized by spectroscopic techniques and its main properties in relation to the gold(I) and palladium(II) complexes are commented on in the following sections.

Treatment of $[Pd(\eta^3\text{-}C_3H_5)]^+$ and $[Au(PPh_3)]^+$ with 3,5-Bis(4-butoxyphenyl)pyrazole. Formation of $[Pd(\eta^3\text{-}C_3H_5)(HPz^{bp2})_2](BF_4)$ (4) and $[Au(HPz^{bp2})(PPh_3)](NO_3)$ (5)

Both pyrazole derivatives **4** and **5** (Scheme 2) were isolated as stable, white solids, soluble in dichloromethane and acetone. Elemental analysis, IR and ^1H NMR spectroscopy data agree with the proposed formulations.



4 **5**

R = $C_6H_4OC_4H_9$

Scheme 2

Compound **4** was synthesised by treatment of the cationic complex $[Pd(\eta^3\text{-}C_3H_5)(S)_2]^+$ (S = solvent), prepared in situ, with **3** in the same solvent in a 1:2 molar ratio. The IR spectrum of **4** displays characteristic bands of the pyrazole ligand. Between them, a ν(NH) absorption band at 3307 cm^{-1} was observed. This band was slightly shifted to higher frequencies in relation to that of the free ligand (3229 cm^{-1}), which has been shown to have a strong hydrogen bond.[16] Related, but weaker, hydrogen bond interactions are therefore suggested for **4** (it has been reported that HPz-type ligands with free NH bonds present a ν(NH) absorption band at 3400 cm^{-1}).[17] Two ν(BF) absorption bands at 1067 and 1039 cm^{-1}, from the BF_4^- group, were also observed and support the presence of interactions towards that counter-ion (two bands agree with a distorted tetrahedral geometry in contrast to the broad single band at 1070 cm^{-1} for the tetrahedral free anion).[18]

On the other hand, the ^1H NMR results indicate the presence of an η^3-allyl group, together with two equivalent coordinated pyrazole ligands, each of these showing non-equivalence in the two butoxyphenyl substituents. The allylic part of the spectrum can be interpreted in terms of a symmetrical η^3-allyl group, so there are three different proton environments: H_{meso} in the central carbon, H_s (*syn*) and H_a (*anti*). The signal at highest field (δ = 3.18 ppm), and with the largest coupling constant (J = 12.7), is assigned to the H_a protons nearest to the metal, with the other doublet signal at δ = 3.92 ppm (J = 6.8) being assigned to the H_s protons. The H_{meso} signal appears a as multiplet at lower field (δ = 5.70 ppm).

Compound **5** was prepared by addition of one equivalent of **3** to a dichloromethane solution of $[Au(NO_3)(PPh_3)]$, previously obtained by treatment of $[AuCl(PPh_3)]$ with $AgNO_3$.[19] A ν(NH) absorption band at 3250 cm^{-1} in the IR spectrum of **5** suggests the presence of hydrogen bond interactions, analogously to what was observed in **4**. A band for the ionic NO_3^- group at 1384 cm^{-1} [18,19] agrees with the formation of a cationic complex $[Au(HPz^{bp2})(PPh_3)]^+$.

On the other hand, a 1:1 PPh_3/HPz ratio is established from the ^1H NMR spectrum (clearly observed from the 15:1

Table 1. Selected bond lengths [Å] and angles [°] for **4** with e.s.d.s. in parentheses, including the hydrogen bond geometries

	A	B	C	
Pd–N1	2.10(2)	2.12(1)	2.12(1)	
Pd–N3	2.11(1)	2.12(1)	2.10(1)	
Pd–C9	2.10(1)	2.10(1)	2.10(1)	
Pd–C10	2.13(2)	2.10(1)	2.10(1)	
Pd–C11	2.15(2)	2.12(2)	2.12(2)	
C9–C10	1.382(5)	1.384(5)	1.384(5)	
C10–C11	1.377(5)	1.384(5)	1.386(5)	
N1–Pd–N3	91.1(3)	93.4(4)	93.3(4)	
N1–Pd–C9	98.8(6)	97.9(4)	100.0(4)	
N1–Pd–C10	132.8(6)	130.3(4)	131.1(4)	
N1–Pd–C11	167.1(6)	167.2(4)	169.3(4)	
N3–Pd–C11	100.8(6)	99.3(4)	97.1(4)	
N3–Pd–C9	170.0(6)	168.3(3)	166.1(4)	
N3–Pd–C10	132.9(6)	132.7(4)	131.2(4)	
C9–Pd–C10	38.2(3)	38.3(2)	38.7(2)	
C9–Pd–C11	69.3(5)	69.3(3)	69.8(3)	
C10–Pd–C11	37.6(3)	38.3(2)	38.4(2)	
Hydrogen bond geometries				
D–H···A	D···A	D–H	H···A	D–H···A
N2A–H2A···F9′ [a]	2.81(2)	0.86	1.97	167.9
N4A–H4A···F2	2.89(1)	0.86	2.06	162.9
N2B–H2B···F7	3.02(1)	0.86	2.19	161.7
N4B–H4B···F1	2.81(1)	0.86	1.99	174.0
N2C–H2C···F11	2.81(1)	0.86	1.91	163.8
N4C–H4C···F5	2.81(1)	0.86	2.01	175.1

[a] The atomic numbering as in Scheme 5.

ratio between the integrated signals of aromatic PPh_3 and H4 pyrazole protons). In contrast to the behaviour observed for palladium derivative **4**, complex **5** features two equivalent butoxyphenyl substituents, suggesting the presence of a metallotropic equilibrium as previously found for related complexes.[20]

Crystal and Molecular Structures of 4 and 5

Single crystals of **4** and **5** suitable for single-crystal X-ray analysis were obtained after recrystallisation from dichloromethane/diethyl ether and dichloromethane/hexane, respectively. Selected bond lengths and angles with their estimated standard deviations are listed in Tables 1 and 2.

Table 2. Selected bond lengths [Å] and angles [°] for **5** with e.s.d.s. in parentheses, including the hydrogen bond geometries

N3−O5	1.236(9)			
N3−O3	1.245(8)			
N3−O4	1.213(8)			
Au1−N1	2.077(5)			
Au1−P1	2.239(2)			
P1−C32	1.800(8)			
P1−C26	1.826(8)			
P1−C38	1.822(7)			
Au1···O1′ [a]	3.540(6)			
N1−Au1−P1	178.1(2)			
O5−N3−O3	117.9(8)			
O5−N3−O4	121.0(8)			
O3−N3−O4	121.2(7)			
Hydrogen bond geometries				
D−H···A	D···A	D−H	H···A	D−H···A
N2−H2···O3	2.764(9)	0.95(6)	1.82(7)	171(6)
C4−H4A···O4′′	3.382(9)	0.93	2.63	137.3
C40−H40A···O5′′′	3.31(1)	0.93	2.88	115.1

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

The palladium derivative **4** crystallises in the monoclinic system, space group $P2_1/n$, as three $[Pd(\eta^3\text{-}C_3H_5)(HPz^{bp2})_2]^+$ species (A, B, and C, showing different dihedral angles between phenyl and pyrazole groups) associated through BF_4^- groups in the asymmetric unit (Figure 1, top). Each BF_4^- group was bonded through strong N−H···F hydrogen bonds (Table 1) with two N−H pyrazole groups bridging two neighbouring complexes. The geometry of each palladium(II) atom in A, B, and C can be described as approximately square-planar. Two pyrazole ligands coordinate to each palladium(II) centre through the corresponding unsubstituted pyrazole atoms N1 and N3, with bond lengths in the 2.10−2.12 Å range. The maximum deviation of the allylic terminal atoms in these units A, B, and C, if we define the coordination plane as that containing the palladium and the two nitrogen atoms mentioned, is 0.17(1) Å for C9 in molecule A. The central allyl carbon C10 also deviates, by 0.51(9), 0.53(1), and 0.59(1) Å in A, B, and C, respectively. The dihedral angles between the allyl planes C11C10C9 and C11PdC9 in each of the A, B, and C molecules are 63.8(9), 67.4(8), and 66.6(8)°. The Pd−allyl distances are in the range expected for complexes containing *N*,*N*′-ligands coordinated *trans* to palladium-allyl fragment.[13c,21]

The crystal structure of **4** could be defined as a pseudohelical polymer, consisting of $[Pd(\eta^3\text{-}C_3H_5)(HPz^{bp2})_2]^+$ units bonding through BF_4^- anions as shown in Figure 1 (bottom). The F12 moiety of the third unit (C) is hydrogen-bonded to the N−H pyrazole group of the neighbouring A′ molecule from the new asymmetric unit (symmetry operation *x*, *y*, *z* + 1). The $[Pd(\eta^3\text{-}C_3H_5)(HPz^{bp2})_2]^+$ moiety is thus arranged pseudohelically along the *c* axis, with the pitch of the pseudohelix (i.e., the

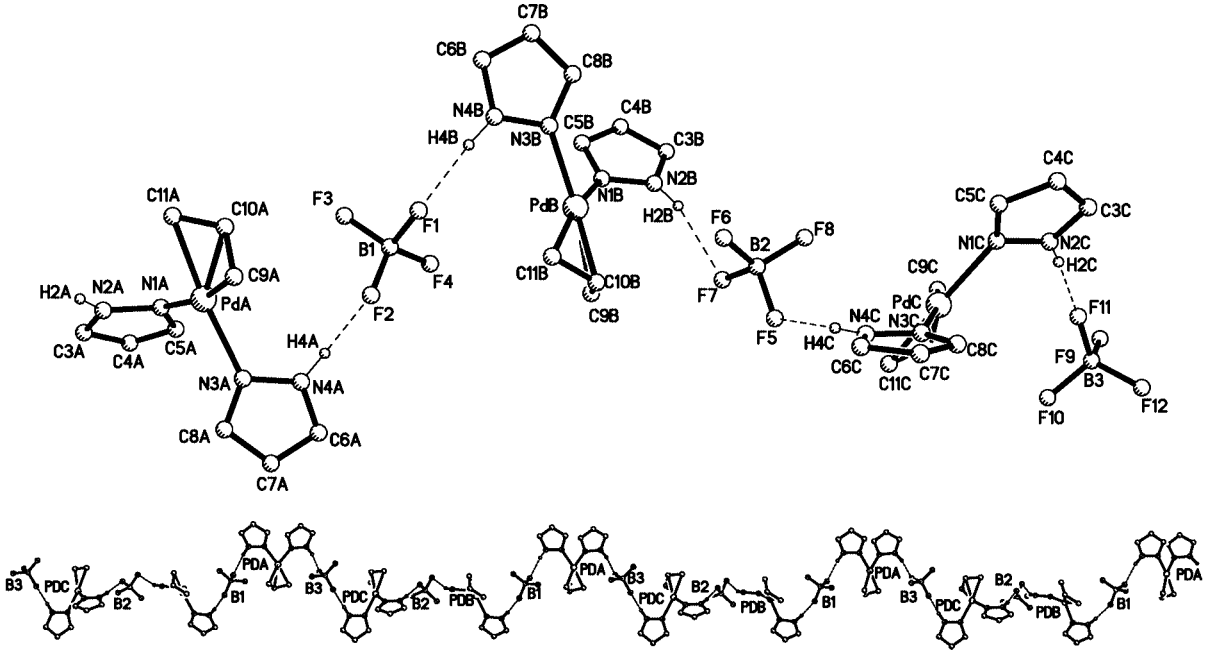


Figure 1. (top) Asymmetric unit of **4** with the atomic numbering scheme; (bottom) View of the helical distribution of **4** along *c* axis; substituents on pyrazole in both pictures are omitted for clarity

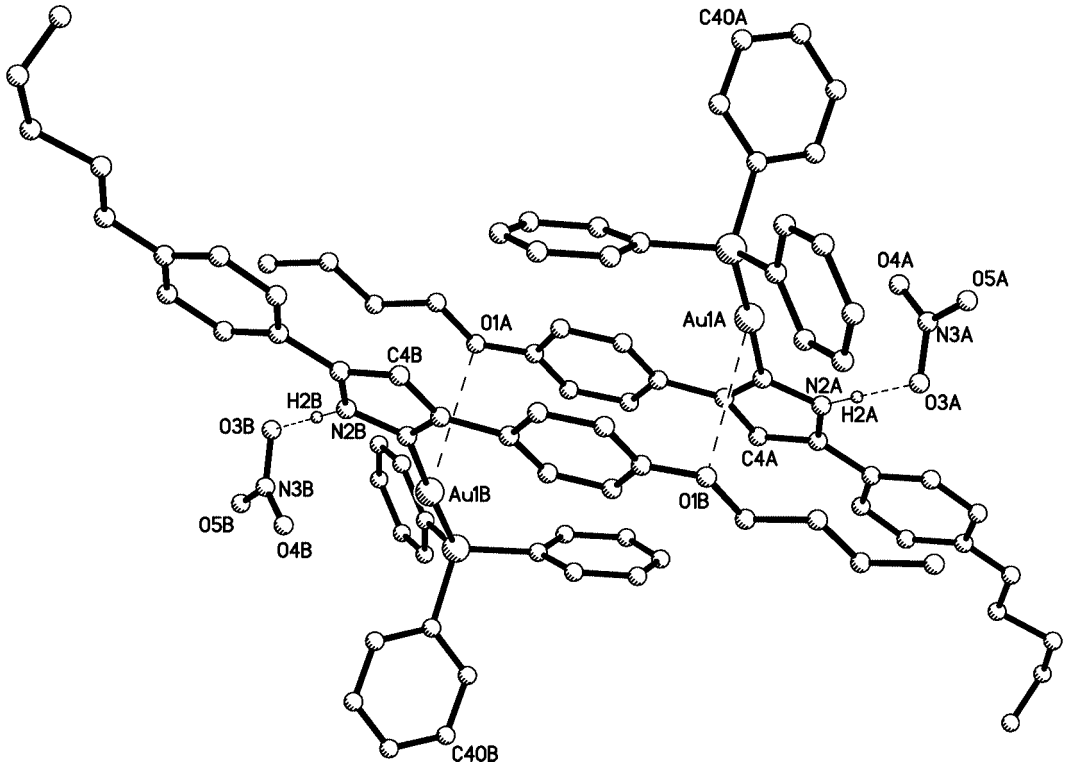


Figure 2. Molecular structure of **5** showing the dimeric unit through Au···O intermolecular bonds

distance between palladium(II) atoms of each four units) corresponding to the *c* axis. The molecular packing could be described as a columnar distribution of pseudohelical chains lying along the *c* axis. The formation of this polymer in the solid state demonstrates the important role played by intermolecular interactions through counter-ions in the supramolecular arrangements.

The crystal structure of **5** (Figure 2) consists of a mononuclear gold(I) cationic complex and a nitrate counter-ion. Both were bonded by a strong hydrogen bond (N2−H2···O3, with a N2···O3 distance of 2.764(9) Å; Table 2). The geometry around the gold(I) can be described as almost linear, the P1−Au1−N1 angle being 178.1(2)°. The Au1−N1 and Au1−P1 bond lengths are similar to

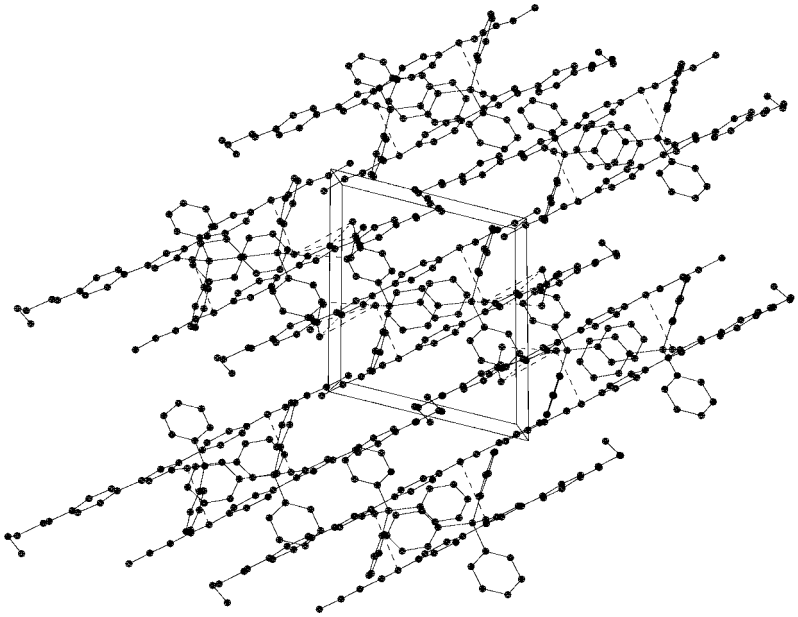


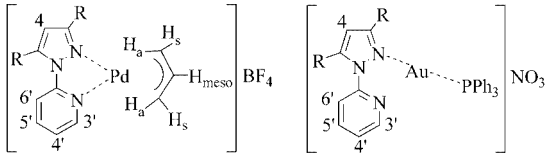
Figure 3. Molecular packing of **5** through *c* axis

those reported for some neutral complexes of the [Au(L)(PPh_3)] type (HL = 1-methylthymine, 6-methylpyridone, 7-azaindole).[22] The most interesting feature in **5** was the presence of a very weak intermolecular coordinative interaction [Au···O, at 3.540(6) Å, ca. 0.30 Å longer than the sum of Van der Waals radii] between two neighbouring molecules. This interaction occurs through the oxygen atom of the $C_6H_4OC_4H_9$ substituent at the 5-position of the pyrazole ligand and the metal centre of the adjacent molecule and appears to be responsible for the formation of "dimers" in an antiparallel head-to-tail disposition (Figure 2). The adjacent aromatic rings of opposite substituents of each molecule of "dimers" are parallel, but are separated face-to-face by a distance of 4.4 Å. This distance suggests that π-π stacking interactions need not be considered, although they might be of help in adopting the observed dimeric arrangement.

The molecular packing could be described as a columnar distribution of these dimeric units along the *b* axis. Layers almost orthogonal to the columnar axis defined by the substituents on the pyrazole are also observed (Figure 3). New weak interactions through the O4 and O5 atoms of the NO_3^- group (not implicated in the hydrogen bond described above) between dimeric units from neighbouring columns are also present (Table 2). As a consequence, the effect of the counter-ion on the supramolecular assembly again seems to be determinant for the crystalline structure here.

Treatment of $[Pd(\eta^3\text{-}C_3H_5)]^+$ and $[Au(PPh_3)]^+$ with 2-[3,5-Bis(4-butoxyphenyl)pyrazol-1-yl]pyridine. Formation of $[Pd(\eta^3\text{-}C_3H_5)(Pz^{bp2}Py)](BF_4)$ (6) and $[Au(Pz^{bp2}Py)(PPh_3)](NO_3)$ (7)

Compounds **6** and **7** (Scheme 3) were both isolated as stable yellow solids, soluble in dichloromethane and acetone, as described in the Exp. Sect. Elemental analysis and IR and ^1H and ^{13}C NMR spectroscopy data agree with the proposed formulations. Conductivity measurements in acetone solution are consistent with 1:1 electrolytic behaviour in both cases.



6 **7**

$R = C_6H_4OC_4H_9$

Scheme 3

On addition of an equivalent of **2** to $[Pd(\eta^3\text{-}C_3H_5)(S)_2](BF_4)$, the ionic complex **6** is formed. The gold(I) complex **7** was prepared by starting from cleavage of the chloride in [AuCl(PPh_3)] by addition of $AgNO_3$, giving rise to [Au(NO_3)(PPh_3)], and the subsequent replacement of the NO_3^- group by the *N*,*N*′-bidentate ligand **2**. The ν(C=N) absorption bands in the IR spectra of both compounds were not significantly modified in relation to that of the free ligand, indicating that the metal coordination had almost no effect on this bond, behaviour also observed for related gold(I) derivatives containing *N*-heterocyclic ligands.[23] Characteristic bands of BF_4^- and NO_3^- anions were observed for **6** and **7**, respectively.

The ^1H NMR spectrum of **6** in $CDCl_3$ at room temperature, in the allylic region, consisted of three broad signals: a multiplet at δ = 5.68 ppm, a doublet at δ = 3.87 ppm (J = 6.5) − partially overlapping with that of the OCH_2 signal at δ = 4.06 ppm − and a doublet at δ = 3.21 ppm (J = 12.8) corresponding to the H_{meso}, H_s, and H_a protons (the last of these clearly assigned from the observed coupling constant). The broadness of the allyl signals suggests a fluxional behaviour based on the asymmetry of the *N*,*N*′-coordinated ligand and attributable to a rapid *syn-syn* and *anti-anti* interchange. The remaining signals in the ^1H NMR spectrum are assigned to the pyrazolylpyridine ligand.

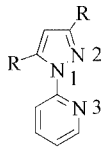
The ^1H NMR spectra of **7** was measured at room temperature in CD_2Cl_2. All the ligand proton signals were slightly modified by coordination. The general behaviour involves small shifts downfield for these signals, the largest shifts being observed for the 3′-H and 5′-H pyridine protons (Scheme 3). However, the position of 6′-H pyridine proton was almost unchanged (δ = 8.41 ppm for the free ligand and δ = 8.38 ppm for the complex), suggesting a very weak metal interaction towards the *N*-pyridine atom. On the other hand, the 4-H pyrazole proton shows a downfield coordination shift of δ = 0.12 ppm, and both downfield and upfield effects were observed for the phenyl substituents in positions 3 and 5. Related behaviour has also been observed for copper and ruthenium derivatives containing pyrazolylpyridine-type ligands.[24,25] The downfield shifts occurring for pyrazole protons and substituents on the 4- and 5-positions were attributed to ligand-metal coordination, whereas upfield shifts for substituents on the 3-position were attributed to ring current anisotropy effects. The above ^1H NMR results agree with a monodentate coordination of the ligand towards the pyrazole N atom, allowing the characteristic twofold coordination of gold metal centres. In this context it should be pointed out that tri- and tetracoordinate gold(I) derivatives with PPh_3 and *N*-donor ligands have also been described, although less frequently,[26] and so an interaction with the pyridine N atom should not be excluded for complex **7**. However, the well defined signals observed for all the protons suggest that exchange of gold(I) between the two nitrogen coordination sites does not occur at room temperature. This fact, probably due to steric effects of substituents on the pyrazole group, favours the linear complex.

On close examination of the ^{13}C NMR spectroscopic data and after complete assignment of all signals by means of NMR experiments with pulse field gradients — (^1H-^1H) COSY, (^1H-^{13}C) HMQC, and (^1H-^{13}C) HMBC — it can be concluded that the complexation chemical shift effects (CCSEs) in the palladium(II) and gold(I) complexes **6** and

7 are positive, save for the carbon adjacent to the pyridine nitrogen, which bonds the pyrazole group. Such increments are larger in the palladium complex **6** (around 4 ppm) than in the gold complex **7** (around 2 ppm).

In order to establish more conclusive results regarding the metal ligand coordination, ^{15}N NMR studies were carried out by means of (^{1}H-^{15}N) HMBC experiments on the ligand and the palladium(II) and gold(I) derivatives

Table 3. ^{15}N NMR spectroscopic data (in $CDCl_3$ at 298 K) for the free ligand **2**and its Pd(η^3-C_3H_5) (**6**) and Au(PPh_3) (**7**) derivatives



$R = C_6H_4OC_4H_9$

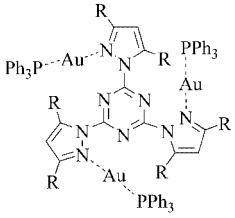
	Pyrazole N1	N2	Pyridine N3
2	−166.4	−84.9	−84.0
6	−167.9	−136.8	−151.0
7[a]	−168.0	−104.1	−88.0

[a] ^{15}N NMR data in CD_2Cl_2.

(Table 3). For the palladium complex **6** it was clearly observed that coordinative nitrogen atoms, N2 from pyrazole and N3 from pyridine, were significantly shifted upon coordination relative to the free ligand. For gold derivative **7**, in contrast, such an effect was only produced on the pyrazole nitrogen atom N2. Consequently, an *N*,*N*′-bidentate pyrazolylpyridine coordinative mode was proposed for the palladium derivative but only a monodentate coordination involving the pyrazole group for the gold complex **7**. Both results also agree with the expected tetracoordinate square-planar and two-coordinate linear environments around the palladium(II) and gold(I) metal centres, respectively.

Treatment of [Pd(η^3-C_3H_5)]$^+$ and [Au(PPh_3)]$^+$ with 2,4,6-Tris[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]-1,3,5-triazine. Formation of [Pd_2(η^3-C_3H_5)$_2$($BPz^{bp2}TzO$)](BF_4) (8) and [Au_3($TPz^{bp2}Tz$)(PPh_3)$_3$](NO_3)$_3$ (9)

Treatment of **1** with [Pd(η^3-C_3H_5)]$^+$ or [Au(PPh_3)]$^+$ fragments resulted in bimetallic and trimetallic complexes,



9

$R = C_6H_4OC_4H_9$

Scheme 4

respectively. The gold(I) derivative was isolated from treatment of three equivalents of [Au(NO_3)(PPh_3)] with one of **1** in dichloromethane solution as a yellow solid product, stable enough in solution for NMR purposes. It was characterized as the complex [Au_3($TPz^{bp2}Tz$)(PPh_3)$_3$](NO_3)$_3$ (**9**, Scheme 4) on the basis of its ^{1}H NMR spectroscopic and mass spectrometric data.

On the other hand, it was interesting to note that a side product, in the form of a microcrystalline white solid accompanying the main compound **9**, was also isolated from the reaction. Treatment of this mixture in dichloromethane/diethyl ether allowed crystals of this by-product to be separated, and these were identified as the pyrazolate complex [Au_2(μ-Pz^{bp2})(PPh_3)$_2$](NO_3).[10b]

The IR spectrum of **9** shows the main absorption bands of the $TPz^{bp2}Tz$ ligand. A very weak unexpected band was also observed at 1682 cm^{-1}, and was attributed to a ν(C=O) absorption arising from partial hydrolysis of the $TPz^{bp2}Tz$ ligand in the complex. This band increases after repeated attempts to purify the product confirming that the hydrolysis process is enhanced.

The structural ^{1}H NMR spectroscopic data, in relation to those obtained for [Au($Pz^{bp2}Py$)(PPh_3)](NO_3) (**7**), suggest monodentate *N*-pyrazole coordination towards the Au(PPh_3) fragment. The tris(pyrazoly)ltriazine ligand bridges three metal centres coordinated with three *N*-pyrazole atoms from the three asymmetric *N*,*N*′-chelating sites. The 15:1 relationship between the aromatic PPh_3 and the 4-H pyrazole protons agrees with the proposed formulation.

A relevant aspect of the molecular behaviour observed at room temperature is the effect that the metals induce on the pyrazole substituents, those in the proximity of Au(PPh_3) fragment (3-position) being different to those at the 5-position. The former thus show defined signals for all protons of the chains but the related signals for the latter are broad. This behaviour is consistent with the proposed monodentate coordination of gold(I) centres only towards the pyrazole groups. Rotation of the pyrazole group bonded to the Au(PPh_3) fragment around the pyrazole-triazine bonding axis is possible, and the environment of the substituents on the 3-position close to the Au(PPh_3) fragment is not modified, unlike that of 5-position substituents, which change in their spatial proximity to gold metal centres.

To confirm the proposed trimetallic formulation of **9**, a study by mass spectrometry (FAB and ESI) was carried out. Figure 4 displays a fragmentation scheme for this complex. The parent ion was not observed either by FAB or by ESI (dry acetonitrile and chloroform) mass spectra. In contrast, in all the cases mentioned above, two ion peaks at m/z = 2444.7 and 1277.2 were detected. The former (m/z = 2444.7) corresponds to the [$TPz^{bp2}Tz$ + B]$^+$ fragment (a_1) arising from the association of the $TPz^{bp2}Tz$ ligand with a metallic cluster B {B = [Au_2(PPh_3)NO_3($OH)_2$]}. From this fragment, the second ion peak (m/z = 1277.2) is formed by the loss of $TPz^{bp2}Tz$. On the other hand, the ESI spectrum (in dry acetonitrile) shows a new peak at m/z = 867.7 (0.3 mass units separated from their counterparts) for the tric-ation [{Au_3($TPz^{bp2}Tz$)(PPh_3)$_3$(NO_3)} − 2 H]$^{3+}$ (a_3) (calcd.

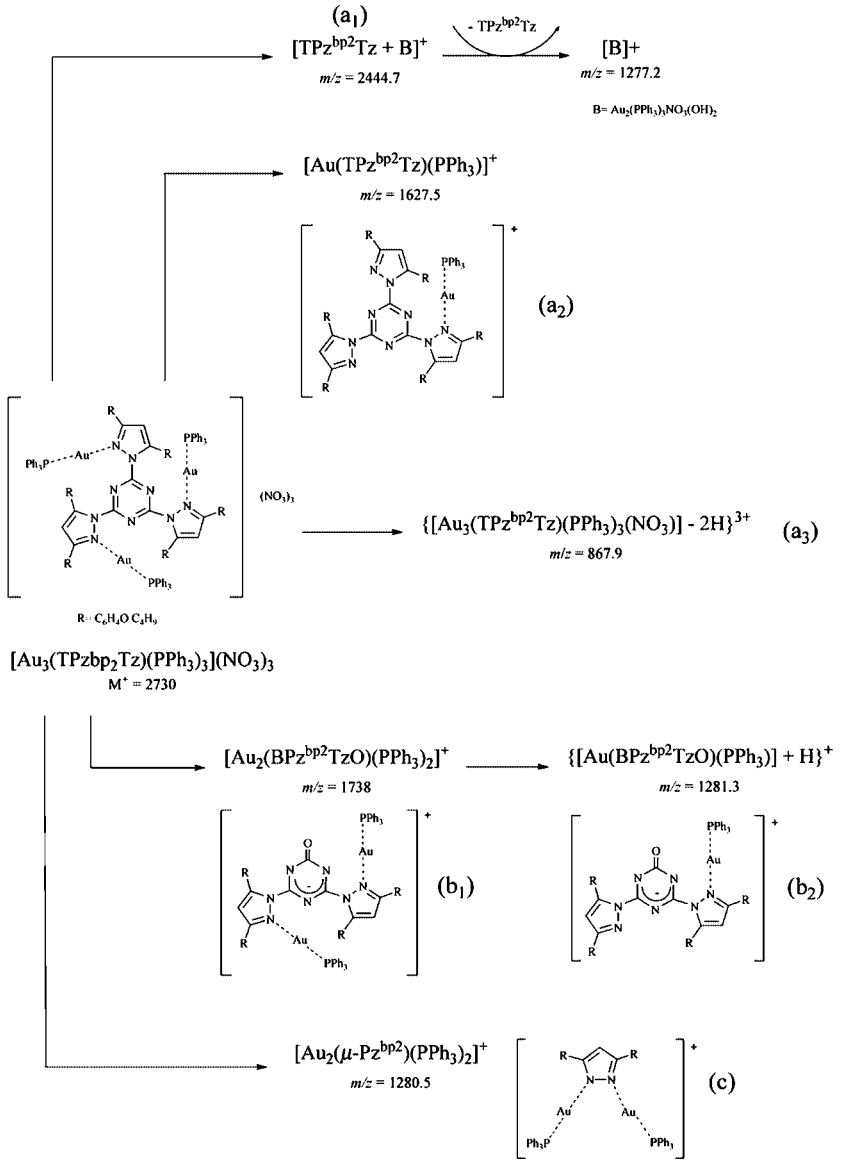


Figure 4. Fragmentation scheme for the complex $[Au_3(TPz^{bp2}Tz)(PPh_3)_3](NO_3)_3$ **9**; symbols (a), (b), and (c) indicate: (a) fragments containing the $TPz^{bp2}Tz$ ligand, (b) fragments containing the hydrolysed $TPz^{bp2}Tz$ ligand ($BPz^{bp2}TzO$), and (c) side product

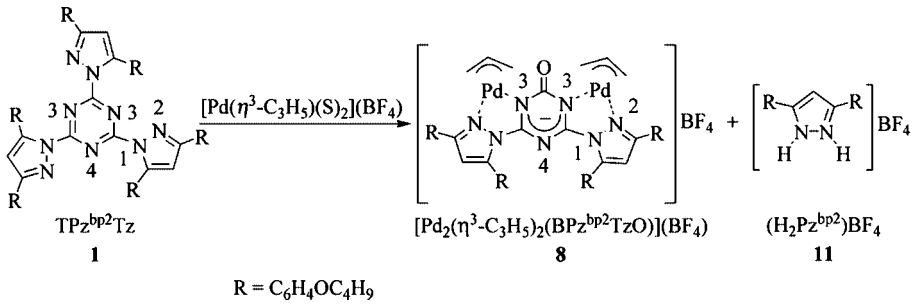
2605). Another fragment, observed in all spectra, at m/z = 1627.5 was related to the mononuclear species $[Au(TPz^{bp2}Tz)(PPh_3)]^+$ (a_2). The above results agree with the presence of a $TPz^{bp2}Tz$ ligand in a trimetallic species.

On the other hand, additional ion peaks at m/z = 1738.6 and 1281.3 were also observed and related to a hydrolysis process of the $TPz^{bp2}Tz$ ligand, producing binuclear $[Au_2(BPz^{bp2}TzO)(PPh_3)_2]^+$ (b_1) and mononuclear $[\{Au(BPz^{bp2}TzO)(PPh_3)\} + H]^+$ (b_2) species, respectively. These were the sole peaks observed when the ESI spectrum was recorded in solvents favouring hydrolysis, such as methanol. Finally, the presence of the side product formulated as $[(PPh_3)Au(\mu\text{-}Pz^{bp2})Au(PPh_3)]^+$ (c) at m/z = 1280.5 was also evidenced, in agreement with the isolation of that compound from the reaction.

Several attempts to crystallise **9** from different solvents were carried out, but hydrolysis products prevent the obtention of crystals suitable for X-ray purposes.

Similar results were also obtained for the related complex $[Au_3(TPz^{bp2}Tz)(PPh_3)_3](CF_3SO_3)_3$ (**10**), containing $CF_3SO_3^-$ as counter-ion.

The binuclear complex $[Pd_2(\eta^3\text{-}C_3H_5)_2(BPz^{bp2}TzO)](BF_4)$ (**8**) was obtained by treatment of **1** with $[Pd(\eta^3\text{-}C_3H_5)(S)_2]^+$ in a 1:3 molar ratio. The suggested molecular structure (Scheme 5) was defined by bonding two $[Pd(\eta^3\text{-}C_3H_5)]^+$ fragments bound in two bidentate positions of the hydrolysed tris(pyrazolyl)triazine ligand $BPz^{bp2}TzO$, which has lost a pyrazolyl group. A related hydrolysis product has precedent in the described cationic complex $[\{(\eta^3\text{-}2\text{-}Me{-}C_3H_4)Pd\}_2(Me{-}BPzTO)]^+$,[21] and also in the estab-



Scheme 5

lished nucleophilic displacement reactions of some 1,3,5-triazines.[27] This was the sole metal derivative isolated from the above reaction. It was interesting to note, though, that the first solid to separate from the reaction mixture was a white crystalline product, identified as the pyrazolium salt $[H_2Pz^{bp2}](BF_4)$ **11** (see Exp. Sect.).

The IR spectrum of **8** shows the characteristic bands due to the ν(C=O) absorption at 1696 cm^{-1} and the ^1H NMR spectrum present all the expected pyrazolyl signals as well as the 1:1 ratio of H4 pyrazole and H_{meso} allyl protons.

From the analysis of the ^{13}C NMR spectroscopic data and having assigned all signals by means of NMR experiments with pulse field gradients — (^1H-^1H) COSY, (^1H-^{13}C) HMQC and (^1H-^{13}C) HMBC — we observed that the CCSE signs for complexes **8** and **9** are similar, but that the absolute values of **9** are approximately half those of **8**. The appearance of the additional carbonyl signal in the spectrum of the palladium(II) complex **8** confirms the hydrolysis process.

The ^{15}N NMR spectroscopic data obtained from (^1H-^{15}N) HMBC correlation experiments for the free $TPz^{bp2}Tz$ ligand **1** and the palladium complex **8** are presented in Table 4. As in the previous $[Pd(\eta^3\text{-}C_3H_5)(Pz^{bp2}Py)](BF_4)$ complex **6**, the observed chemical shift effects on the palladium derivative in relation to the free ligand agree with a bidentate coordination by *N*-pyrazole and *N*-triazine coordinating nitrogen atoms and confirm the proposed formulation.

Table 4. ^{15}N NMR spectroscopic data in $CDCl_3$ at 298 K of the free ligand **1** and its $Pd(\eta^3\text{-}C_3H_5)$ derivative **8**

	Pyrazole[a]		Triazine[a]	
	N1	N2	N3	N4
1	−169.3	−86.0	−156.8	−156.8
8	−170.2	−138.8	−123.8	−197.4

[a] The atomic numbering as in Scheme 5.

Finally, the ESI mass spectrum (in chloroform) of **8** shows the molecular ion peak *m*/*z* = 1116.3 confirming the formation of the hydrolysis derivative $[Pd_2(\eta^3\text{-}C_3H_5)_2(BPz^{bp2}TzO)](BF_4)$.

Conclusion

The designed complexes $[Pd(\eta^3\text{-}C_3H_5)(HPz^{bp2})_2](BF_4)$ (**4**) and $[Au(HPz^{bp2})(PPh_3)](NO_3)$ (**5**) each show strong hydrogen bonding between each NH-pyrazole of one cationic unit and their corresponding counter-ions. In view of the molecular geometries around the metal centres − square-planar for the palladium derivative and linear for gold − as well as those of their counter-ions, tetrahedral BF_4^- and planar NO_3^-, these hydrogen bonds − N−H···F for **4** and N2−H2···O3, C4−H4A···O4′′ and C40−H40A···O5′′′ for **5** — are responsible for the observed supramolecular structures, of the pseudohelical type for **4** and with columnar features for **5**. In addition, **5** forms "dimers" produced by coordinative Au···O interactions between the pyrazole OR groups and the metal centres of two neighbouring molecules. We can therefore conclude that factors such as hydrogen bonding, the counter-ion effect, the presence of coordinating substituents on the ligand and a suitable molecular geometry are crucial for specific supramolecular assemblies.

Moreover, the following structural features should be pointed out:

i) The palladium complex of $TPz^{bp2}Tz$ is hydrolysed, giving rise to a bimetallic species $[Pd_2(\eta^3\text{-}C_3H_5)_2(BPz^{bp2}TzO)](BF_4)$ (**8**), containing two allyl-palladium moieties, which occupy two symmetrical *N*,*N*′-bidentate chelating positions of the ligand. The central carbon atom of the triazine core is now bonded to an oxygen, thus producing a C=O group instead of the initial C-Pz^{bp2} one, due to the nucleophilic displacement of the pyrazole group in the hydrolysis process.

ii) The formation of a trimetallic derivative $[Au_3(TPz^{bp2}Tz)(PPh_3)_3](NO_3)_3$ (**9**), containing three $Au(PPh_3)$ fragments coordinated in a monodentate fashion towards the *N*-pyrazole atoms of the $TPz^{bp2}Tz$ ligand, has been established.

The natures of the metal fragments determine the mono- or bidentate coordination of each *N*,*N*′-chelating position in the $TPz^{bp2}Tz$, analogously to what occurs in similar complexes of the related bidentate $Pz^{bp2}Py$ ligand. The presence of a square-planar or more flexible linear metal environments for **8** and **9**, respectively, appears to be correlated with the isolation of a binuclear palladium complex or a

trinuclear gold derivative. These results offer new insights into the attainment of polymetallic complexes with supramolecular organisations.

Experimental Section

Materials and Instrumentation: The commercial starting materials $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ and $[AuCl(PPh_3)]$ were used as supplied. Ligands 2-[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]pyridine (**2**, $Pz^{bp2}Py$)[24] and 3,5-bis(4-butoxyphenyl)pyrazole (**3**, HPz^{bp2})[16] were prepared as described in the literature. Commercial solvents were dried prior to use.

Melting points were determined on a microscope hot stage apparatus and are uncorrected.

Elemental analyses for carbon, hydrogen, and nitrogen were carried out by the Microanalytical Service of the Complutense University. IR spectra were performed on a FTIR Nicolet Magna-550 spectrophotometer in the 4000−400 cm^{-1} region with samples as KBr pellets.

^1H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker DRX-400 at 27 °C. Chemical shifts (δ) are given in ppm from TMS for ^1H and ^{13}C NMR spectroscopy. ^{15}N NMR chemical shifts were obtained by the Inverse Gated ^1H-Decoupling Technique and are referenced to external nitromethane. *J* coupling constants are in Hz. The assignments are based on NMR experiments with pulse field gradients: (^1H-^1H) COSY, (^1H-^{13}C) HMQC, (^1H-^{13}C) HMBC, and (^1H-^{15}N) HMBC.[28]

FAB-MS positive spectra were performed on a VG AutoSpec spectrometer. ESI-MS positive spectra were carried out by the Mass Spectrometry Service of the Complutense University with a LC-SQUIRE spectrometer, in dry acetonitrile, chloroform, or methanol as solvents. The ion peaks are given in *m*/*z*.

Synthesis of 2,4,6-Tris[3,5-bis(4-butoxyphenyl)pyrazol-1-yl]-1,3,5-triazine ($TPz^{bp2}Tz$, 1): NaH (95%, 44 mg, 1.74 mmol) was added to a solution of 3,5-bis(4-butoxyphenyl)pyrazole (**3**, 600 mg, 1.65 mmol) in freshly distilled dry THF (30 mL). After 1.5 h at 90 °C, the solution was allowed to cool down, and 2,4,6-trichlorotriazine (cyanuric chloride, 90%, 102 mg, 0.55 mmol) was added. The solution, which had turned from a yellow to a white colour, was heated for 11 h at 90 °C and for 15 h at 60 °C. The solvent was evaporated and the residue was chromatographed on 60 F_{254} silica gel with chloroform/acetonitrile (95:5) as eluent. R_f = 0.55, m.p. 158−160 °C. Yield: 193 mg, 30%. Exact mass: calcd. for $C_{72}H_{81}N_9O_6$: 1168.49; found 1168.63. IR (KBr): $\tilde{\nu}$ = 1613 cm^{-1} ν(C=N). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.76 ppm (d, ^3J = 6.9 Hz, 6 H, H_o), 7.24 (d, ^3J = 6.8 Hz, 6 H, H_o), 6.98 (d, ^3J = 6.9 Hz, 6 H, H_m), 6.85 (d, ^3J = 6.8 Hz, 6 H, H_m), 6.63 (s, 3 H, H4), 4.04 (t, ^3J = 6.5 Hz, 6 H, OCH_2), 3.87 (t, ^3J = 6.6 Hz, 6 H, OCH_2), 1.82 (m, ^3J = 6.7 Hz, 6 H, CH_2), 1.72 (m, ^3J = 6.8 Hz, 6 H, CH_2), 1.51 (m, ^3J = 7.4 Hz, 6 H, CH_2), 1.43 (m, ^3J = 7.5 Hz, 6 H, CH_2), 1.01 and 0.94 (t, ^3J = 7.4 Hz, 18 H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K): δ = 164.5 ppm (Tz), 159.9 (^3J = ^3J = 7.6 Hz, C_p), 159.2 (^3J = ^3J = 9.2 Hz, C_p), 154.3 (^2J = ^3J = ^3J = 3.7 Hz, C3), 147.8 (^2J = 8.1, ^3J = ^3J = 4.0 Hz, C5), 130.2 (^1J = 160.3, ^3J = 7.1 Hz, C_o), 127.7 (^1J = 159.5, ^3J = 7.0 Hz, C_o), 124.1 (^3J = ^3J = 7.6 Hz, C_{ipso}), 123.1 (^3J = ^3J = 8.0 Hz, C_{ipso}), 114.5 (^1J = 160.2, ^3J = 4.6 Hz, C_m), 113.9 (^1J = 160.5, ^3J = 4.2 Hz, C_m), 109.4 (^1J = 175.5 Hz, C4), 67.6 (^1J = 142.1, ^2J = 3.5 Hz, OCH_2), 31.3 and 31.2 (^1J = 126.3 Hz, CH_2), 19.2 and 19.1 (^1J = 127.2 Hz, CH_2), 13.79 and 13.77 (^1J = 125.3 Hz, CH_3).

Synthesis of $[Pd(\eta^3\text{-}C_3H_5)(HPz^{bp2})_2](BF_4)$ (4): $AgBF_4$ (35 mg, 0.18 mmol) was added under nitrogen to a solution of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (33 mg, 0.09 mmol) in freshly distilled acetone (15 mL). After stirring for 6 h in the darkness, the solution was filtered through a plug of Celite and cooled with an ice bath. Compound **3** (HPz^{bp2}, 131 mg, 0.36 mmol) was then added and the mixture was stirred for 5 h. The solvent was removed under vacuum and the white product was crystallised from dichloromethane/diethyl ether. Yield: 73 mg, 42%. $C_{49}H_{61}BF_4N_4O_4Pd$ (962.21): calcd. C 61.11, H 6.34, N 5.82; found C 60.96, H 6.11, N 5.66. IR (KBr): $\tilde{\nu}$ = 3307 cm^{-1} ν(N−H), 1613 ν(C=N), 1067 and 1039 ν(BF). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 11.87 ppm (s, 2 H, NH), 7.61 and 7.41 (d, ^3J = 8.5 Hz, 8 H, H_o), 6.96 and 6.78 (d, ^3J = 8.5 Hz, 8 H, H_m), 6.54 (s, 2 H, H4), 5.70 (m, ^3J_s = 6.8, ^3J_a = 12.7 Hz, 1 H, H_{meso}), 3.99 and 3.94 (t, ^3J = 6.6 Hz, 8 H, OCH_2), 3.92 (d, ^3J_s = 6.8 Hz, 2 H, H_s), 3.18 (d, ^3J_a = 12.7 Hz, 2 H, H_a), 1.87−1.70 (m, 8 H, CH_2), 1.64−1.40 (m, 8 H, CH_2), 1.00 and 0.98 (t, ^3J = 7.3 Hz, 12 H, CH_3).

Synthesis of $[Au(HPz^{bp2})(PPh_3)](NO_3)$ (5): $AgNO_3$ (34 mg, 0.20 mmol) was added under nitrogen to a solution of $[AuCl(PPh_3)]$ (100 mg, 0.20 mmol) in acetone (25 mL). After stirring for 2 h in darkness, the solution was filtered through a plug of Celite and the solvent was evaporated. Compound **3** (HPz^{bp2}, 73 mg, 0.20 mmol) was added to a solution of the obtained product in dry dichloromethane and the mixture was stirred for 5 h at room temperature. The solvent was removed under vacuum to provide a oil, from which a white solid was isolated by addition of dichloromethane and hexane. This solid was crystallised from dichloromethane/hexane. Yield: 90 mg, 51%. $C_{41}H_{43}N_3O_5AuP$ (884.94): calcd. C 55.60, H 4.86, N 4.75; found C 55.82, H 4.73, N 4.88. IR (KBr): $\tilde{\nu}$ = 3250 cm^{-1} ν(N−H), 1613 ν(C=N), 1384 $\nu_{as}(NO_3)$. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.78 ppm (d, ^3J = 8.8 Hz, 4 H, H_o), 7.57−7.40 (m, 15 H, PPh_3), 6.92 (d, ^3J = 8.8 Hz, 4 H, H_m), 6.71 (s, 1 H, H4), 3.97 (t, ^3J = 6.6 Hz, 4 H, OCH_2), 1.78 (m, 4 H, CH_2), 1.49 (m, 4 H, CH_2), 0.99 (t, ^3J = 7.3 Hz, 6 H, CH_3).

Synthesis of $[Pd(\eta^3\text{-}C_3H_5)(Pz^{bp2}Py)](BF_4)$ (6): This compound was prepared in a similar way to **4**, from $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (110 mg, 0.30 mmol), $AgBF_4$ (117 mg, 0.60 mmol), and **2** ($Pz^{bp2}Py$) (265 mg, 0.60 mmol). White crystals were obtained by crystallisation from dichloromethane/hexane. Yield: 215 mg, 53%. $C_{31}H_{36}BF_4N_3O_2Pd$ (675.21): calcd. C 55.09, H 5.33, N 6.22; found C 54.75, H 5.30, N 6.21. IR (KBr): $\tilde{\nu}$ = 1609 and 1571 cm^{-1} ν(C=N), 1069 and 1027 ν(BF). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.85 ppm (m, 1 H, H6′), 7.81 (ddd, ^3J = 8.6, ^3J = 7.3, ^4J = 1.6 Hz, 1 H, H4′), 7.58 (d, ^3J = 8.6 Hz, 2 H, H_o), 7.53 (m, 1 H, H5′), 7.39 (d, ^3J = 8.5 Hz, 2 H, H_o), 7.06 (d, ^3J = 8.5 Hz, 2 H, H_m), 7.04 (d, ^3J = 8.6 Hz, 2 H, H_m), 6.99 (d, ^3J = 8.6 Hz, 1 H, H3′), 6.70 (s, 1 H, H4), 5.68 (m, ^3J_s = 6.5, ^3J_a = 12.8 Hz, 1 H, H_{meso}), 4.06 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 3.87 (d, ^3J_s = 6.5 Hz, 2 H, H_s), 3.21 (d, ^3J_a = 12.8 Hz, 2 H, H_a), 1.82 (m, 4 H, CH_2), 1.54 (m, 4 H, CH_2), 1.01 (t, ^3J = 7.4 Hz, 6 H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K): δ = 161.3 and 161.2 ppm (C_p), 157.4 (^3J = ^3J = 4.6 Hz, C3), 153.8 (^1J = 187.7 Hz, C6′), 149.7 (C2′), 147.1 (^2J = 8.8, ^3J = ^3J = 5.0 Hz, C5), 141.2 (^1J = 167.6 Hz, C4′), 130.4 (^1J = 160.5, ^3J = 7.5 Hz, C_o), 130.1 (^1J = 160.2, ^3J = 7.3 Hz, C_o), 124.5 (^1J = 170.3 Hz, C5′), 122.9 (^3J = ^3J = 7.8 Hz, C_{ipso}), 119.7 (^3J = ^3J = 7.7 Hz, C_{ipso}), 117.4 (^1J = 164.6 Hz, CH allyl), 115.7 (^1J = 161.8, ^3J = 4.7 Hz, C_m), 114.7 (^1J = 161.2, ^3J = 4.5 Hz, C_m), 114.6 (C3′), 111.3 (^1J = 181.7 Hz, C4), 68.1 (^1J = 142.7 Hz, OCH_2), 63.6 (CH_2

allyl), 31.2 (^1J = 126.5 Hz, CH_2), 19.2 (^1J = 127.5 Hz, CH_2), 13.8 (^1J = 125.0 Hz, CH_3).

Synthesis of [Au(Pz^{bp2}Py)(PPh$_3$)](NO$_3$) (7): Compound **7** was prepared similarly to **5**, from [AuCl(PPh$_3$)] (80 mg, 0.16 mmol), $AgNO_3$ (27 mg, 0.16 mmol), and **2** (Pz^{bp2}Py) (71 mg, 0.16 mmol). The obtained yellow solid was purified by treatment with dichloromethane. Yield: 74 mg, 48%. $C_{46}H_{46}AuN_4O_5P$ (961.94): calcd. C 57.38, H 4.78, N 5.82; found C 57.48, H 4.90, N 5.62. IR (KBr): $\tilde{\nu}$ = 1611 and 1576 cm^{-1} ν(C=N), 1357 $\nu_{as}(NO_3)$. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 8.38 ppm (m, 1 H, H6′), 7.87 (d, ^3J = 8.8 Hz, 2 H, H_o), 7.82 (ddd, ^3J = 8.1, ^3J = 7.5, ^4J = 1.6 Hz, 1 H, H4′), 7.54−7.41 (m, 15 H, PPh_3), 7.40 (m, 1 H, H5′), 7.35 (d, ^3J = 8.1 Hz, 1 H, H3′), 7.25 (d, ^3J = 8.8 Hz, 2 H, H_o), 6.91 (d, ^3J = 8.8 Hz, 4 H, H_m), 6.83 (s, 1 H, H4), 4.00 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 1.78 (m, 4 H, CH_2), 1.51 (m, 4 H, CH_2), 1.00 (t, ^3J = 7.4 Hz, 6 H, CH_3). ^{13}C NMR (400 MHz, CD_2Cl_2, 298 K): δ = 161.1 and 161.0 ppm (C_p), 154.9 (^3J = ^3J = 4.1 Hz, C3), 151.7 (C2′), 149.8 (^1J = 182.9, ^3J = 7.2 Hz, C6′), 147.4 (^2J = 7.3, ^3J = ^3J = 3.7 Hz, C5), 140.1 (^1J = 166.1 Hz, C4′), 135−130 (PPh_3), 130.9 (^1J = 159.9, ^3J = 7.3 Hz, C_o), 129.1 (^1J = 159.4, ^3J = 7.4 Hz, C_o), 124.7 (^1J = 167.0 Hz, C5′), 124.4 (^3J = ^3J = 8.0 Hz or ^3J = ^3J = 7.7 Hz, C_{ipso}), 121.9 (^3J = ^3J = 8.0 Hz or ^3J = ^3J = 7.7 Hz, C_{ipso}), 120.9 (^1J = 175.2 Hz, C3′), 115.6 (^1J = 160.8 Hz or ^1J = 159.7, ^3J = 4.3 Hz, C_m), 115.5 (^1J = 160.8 Hz or ^1J = 159.7, ^3J = 4.3 Hz, C_m), 107.7 (^1J = 178.5 Hz, C4), 68.7 (^1J = 143.6 Hz, OCH_2), 32.0 (^1J = 125.3 Hz, CH_2), 20.0 (^1J = 126.2 Hz, CH_2), 14.4 (^1J = 124.7 Hz, CH_3).

Synthesis of [Pd$_2$(η^3-C$_3$H$_5$)$_2$(BPz^{bp2}TzO)](BF$_4$) (8): The synthetic procedure used for **8** was similar to that described for **4**, from [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ (21 mg, 0.06 mmol), $AgBF_4$ (23 mg, 0.12 mmol), and **1** (TPz^{bp2}Tz) (46 mg, 0.04 mmol). The resulting yellow solid was purified by crystallisation in dichloromethane/hexane. Yield: 36 mg, 75%. $C_{55}H_{64}BF_4N_7O_5Pd_2$ (1201.61): calcd. C 54.93, H 5.33, N 8.15; found C 55.00, H 5.66, N 8.00. IR (KBr): $\tilde{\nu}$ = 1696 cm^{-1} ν(C=O), 1611 ν(C=N), 1066 ν(BF). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.59 and 6.99 ppm (d, ^3J = 6.8 Hz, 8 H, H_o), 7.03 and 6.62 (d, ^3J = 6.8 Hz, 8 H, H_m), 6.52 (s, 2 H, H4), 5.44 (m, ^3J_s = 6.5, ^3J_a = 13.0 Hz, 2 H, H_{meso}), 4.05 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 3.99 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 3.79 (br., ^3J_s = 6.5 Hz, 4 H, H_s), 3.21 (br., ^3J_a = 13.0 Hz, 4 H, H_a), 1.80 (m, 8 H, CH_2), 1.53 (m, 8 H, CH_2), 1.00 and 0.99 (t, ^3J = 7.5 Hz, 12 H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, 298 K): δ = 163.1 ppm (Tz), 161.2 (^3J = ^3J = 8.9 Hz, C_p), 160.0 (^3J = ^3J = 8.8 Hz, C_p), 158.2 (^2J = ^3J = ^3J = 4.1 Hz, C3), 158.0 (CO), 149.2 (^2J = 6.5, ^3J = ^3J = 3.3 Hz, C5), 130.1 (^1J = 160.5, ^3J = 7.1 Hz, C_o), 129.9 (^1J = 160.3, ^3J = 7.0 Hz, C_o), 122.3 (^3J = ^3J = 7.8 Hz, C_{ipso}), 119.7 (^3J = ^3J = 8.0 Hz, C_{ipso}), 114.7 (^1J = 161.3, ^3J = 4.2 Hz, C_m), 114.2 (^1J = 160.8, ^3J = 4.6 Hz, C_m), 114.1 (^1J = 156.2 Hz, CH allyl), 111.9 (^1J = 181.7 Hz, C4), 68.18 (^1J = 142.2, ^2J = 4.0 Hz, OCH_2), 67.74 (^1J = 142.9, ^2J = 3.7 Hz, OCH_2), 63.8 (^1J = 162.8 Hz, CH_2 allyl), 31.26 and 31.17 (^1J = 124.7 Hz, CH_2), 19.17 and 19.15 (^1J = 125.4 Hz, CH_2), 13.8 (^1J = 124.9 Hz, CH_3).

Treatment of TPz^{bp2}Tz with [Au(NO$_3$)(PPh$_3$)]. Formation of [Au$_3$(TPz^{bp2}Tz)(PPh$_3$)$_3$](NO$_3$)$_3$ (9): This compound was prepared by a procedure analogous to that described for **5**, from [AuCl(PPh_3)] (74 mg, 0.15 mmol), $AgNO_3$ (26 mg, 0.15 mmol), and **1** (TPz^{bp2}Tz) (58 mg, 0.05 mmol). The obtained yellow solid was purified by treatment with dichloromethane/hexane. Yield: 82 mg, 60%. $C_{126}H_{126}Au_3N_{12}O_{15}P_3$ (2729.82): calcd. C 55.39, H 4.61, N 6.15; found C 55.00, H 4.39, N 6.01. IR (KBr): $\tilde{\nu}$ = 1611 cm^{-1} ν(C=N), 1384 $\nu_{as}(NO_3)$. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.83 ppm (d, ^3J = 6.8 Hz, 6 H, H_o), 7.60−7.40 (m, 45 H, PPh_3), 7.3−7.5 (br., 6 H, H_o), 7.02 (br., 6 H, H_m), 6.92 (d, ^3J = 6.8 Hz, 6 H, H_m), 6.83 (s, 3 H, H4), 4.00 (t, ^3J = 6.5 Hz, 6 H, OCH_2), 3.94 (br., 6 H, OCH_2), 1.80 (m, ^3J = 7.0 Hz, 6 H, CH_2), 1.75 (br., 6 H, CH_2), 1.54 (m, ^3J = 7.5 Hz, 6 H, CH_2), 1.49 (br., 6 H, CH_2), 1.01 (t, ^3J = 7.4 Hz, 9 H, CH_3), 0.98 (br., 9 H, CH_3). ^{13}C NMR (400 MHz, CD_2Cl_2, 298 K): δ = 162.1 ppm (br., Tz), 160.9 (C_p), 156.5 (br., C_p), 154.8 (C3), 149.1 (br., C5), 135−130 (PPh_3), 129.7 (C_o), 128.9 (br., C_o), 124.9 (C_{ipso}), 122.1 (br., C_{ipso}), 115.7 (C_m), 115.1 (br., C_m), 112.1 (br., C4), 68.7 (OCH_2), 32.00 and 31.98 (CH_2), 20.04 and 19.97 (CH_2), 14.4 (CH_3).

Treatment of TPz^{bp2}Tz with [Au(CF$_3$SO$_3$)(PPh$_3$)]. Formation of [Au$_3$(TPz^{bp2}Pz)(PPh$_3$)$_3$](CF$_3$SO$_3$)$_3$ (10): $AgCF_3SO_3$ (54 mg, 0.21 mmol) was added under nitrogen to a solution of [AuCl(PPh_3)] (102 mg, 0.21 mmol) in dry THF (25 mL). After stirring for 2 h in the darkness, the solution was filtered through a plug of Celite. Compound **1** (TPz^{bp2}Tz, 80 mg, 0.07 mmol) was then added and the mixture was stirred for 4 h at room temperature. The solvent was removed under vacuum to afford an oil, from which a yellow solid was isolated by addition of diethyl ether and hexane. This solid was purified by treatment with dichloromethane. Yield: 119 mg, 57%. $C_{129}H_{126}Au_3F_9N_9O_{15}P_3S_3$ (2990.82): calcd. C 51.76, H 4.21, N 4.21; found C 52.03, H 4.28, N 4.25.

Synthesis of [H$_2$Pz^{bp2}](BF$_4$) (11): HBF_4−diethyl ether complex (85%, 37 mg, 0.36 mmol) was added to a solution of **3** (HPz^{bp2}, 131 mg, 0.36 mmol) in diethyl ether (5 mL) and the mixture was stirred for 1 h at room temperature. A white crystalline precipitate was filtered off and washed with diethyl ether. Yield: 73 mg, 45%. IR (KBr): $\tilde{\nu}$ = 3238 and 3178 cm^{-1} ν(N−H), 1619 ν(C=N), 1067 ν(BF). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 13.2 ppm (br., 2 H, NH), 7.67 (d, ^3J = 8.5 Hz, 4 H, H_o), 7.03 (d, ^3J = 8.5 Hz, 4 H, H_m), 6.86 (s, 1 H, H4), 4.02 (t, ^3J = 6.6 Hz, 4 H, OCH_2), 1.80 (m, 4 H, CH_2), 1.51 (m, 4 H, CH_2), 0.99 (t, ^3J = 7.3 Hz, 6 H, CH_3).

X-ray Structure Determination

Prismatic single crystals of [Pd(η^3-C_3H_5)(HPz^{bp2})$_2$](BF$_4$) (**4**) were obtained by crystallisation from dichloromethane/diethyl ether. Single needle crystals of [Au(HPz^{bp2})(PPh$_3$)](NO$_3$) (**5**) were obtained by crystallisation from dichloromethane/hexane.

The data for both compounds were collected on a Smart Bruker CCD detector diffractometer. A summary of the fundamental crystal data and refinement parameters for the two crystals is given in Table 5.

The structure of **4** was solved by direct methods and conventional Fourier techniques. The refinement was carried out by blocked full-matrix, least-squares on F^2.[29] The F atoms of the BF_4^- groups and some carbon atoms (including the allyl group) were refined for only two cycles anisotropically and in the last cycles the thermal factors were fixed. These carbon atoms were refined with geometrical restraints and a variable common carbon-carbon distance. The rest of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding on the carbon bonded atom with common isotropic displacement parameters.

The molecular structure of **5** was solved by direct methods and conventional Fourier techniques and refined by full-matrix, least-squares on F^2.[29] All non-hydrogen atoms were refined anisotropically except for the oxygen atoms in the nitrate group and the last carbon atoms of the butoxy group, which were refined isotropically. The hydrogen atoms were calculated and refined as riding on the carbon-bonded atom with a common isotropic displacement parameter, except for the H2 bonded to N2, which was lo-

Table 5. Crystal and refinement data for **4** and **5**

	4	**5**
Empirical formula	$[C_{49}H_{61}N_4O_4Pd]_3[BF_4]_3$	$[C_{41}H_{43}N_2O_2PAu]NO_3$
Formula mass	2889.68	885.72
Temperature [K]	296(2)	296(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	21.811(1)	10.7447(9)
b [Å]	26.518(1)	11.937(1)
C [Å]	25.889(2)	15.560(1)
α [°]	90	102.475(1)
β [°]	90.783(1)	94.261(1)
γ [°]	90	102.699(2)
V [Å^3]	14973(1)	1890.5(3)
Z	4	2
F(000)	6024	888
Crystal size [mm^3]	0.22 × 0.22 × 0.14	0.30 × 0.15 × 0.07
$d_{calcd.}$ [gcm^{-3}]	1.284	1.556
μ [mm^{-1}	0.431	3.981
Scan technique	phi and omega	phi and omega
Data collected	(−19, −31, −27) to (25, 31, 30)	(−12, −14, −18) to (12, 11, 18)
θ [°]	3.82−25	1.35−25
Reflns. collected	58758	9902
Reflns. indep.	23261 (R_{int} = 0.098)	6578 (R_{int} = 0.0451)
Data/restraints/parameters	23261/45/1174	6578/0/421
Reflns.obsd. (I) > 2σ(I)	10954	4646
R_1 (reflns. obsd.)[a]	0.107	0.047
Rw_F[b]	0.336	0.098
Largest diff. peak [eA^{-3}]	1.83	1.30

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $Rw_F = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

cated as one of the first peaks in a Fourier synthesis, included and its positions refined.

CCDC−194445 (**4**) and −194446 (**5**) 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, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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