Heterobimetallic pyrazolato complexes: the syntheses and crystal structures of *cis*-$(PPh_3)_2ClPt^{II}(3,5\text{-}Ph_2pz)$, *cis*-$(PPh_3)_2BrPt^{II}(\mu\text{-}3,5\text{-}Ph_2pz)Cu^ICl$, *cis*-$(PPh_3)_2ClPt^{II}(\mu\text{-}3,5\text{-}Ph_2pz)Ag^ICl$ and *cis*-$(PPh_3)_2BrPt^{II}(\mu\text{-}3,5\text{-}Ph_2\text{-}4\text{-}Br\text{-}pz)Au^IBr$ (pz = pyrazolato anion)

John P. Fackler, Jr.[*], Raphael G. Raptis[**,†] and H. H. Murray[††]

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843 (USA)

(Received November 12, 1991)

Abstract

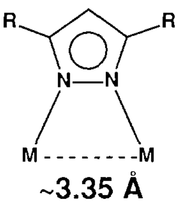
The mononuclear complex *cis*-$(PPh_3)_2ClPt(3,5\text{-}Ph_2pz)$, is formed from the reaction of *cis*-$(PPh_3)_2PtCl_2$ and Na[3,5-Ph_2pz]. This metalloligand can form adducts with all three Group 11 M^I halides. Three such heterobimetallic complexes, Pt/Cu, Pt/Ag and Pt/Au, as well as the Pt starting material, have been characterized by single crystal X-ray analysis. A rational synthesis for all complexes is given by *cis*-$(PPh_3)_2ClPt(3,5\text{-}Ph_2pz)\cdot Et_2O$ (**1**): $C_{55}H_{51}ClN_2OP_2Pt$, monoclinic, $P2_1/n$ (No. 14), $a=11.120(2)$, $b=24.438(6)$, $c=18.125(3)$ Å, $\beta=99.50(1)°$, $V=4858(2)$ Å^3, $Z=4$, $R=0.061$. For *cis*-$(PPh_3)_2BrPt(\mu\text{-}3,5\text{-}Ph_2pz)CuCl\cdot Et_2O$ (**2**): $C_{55}H_{51}BrClCuN_2P_2Pt$, orthorhombic, $Pc2_1n$ (No. 33), $a=10.721(3)$, $b=15.757(4)$, $c=30.263(8)$ Å, $V=5112(2)$ Å^3, $Z=4$, $R=0.051$. For *cis*-$(PPh_3)_2ClPt(\mu\text{-}3,5\text{-}Ph_2pz)AgCl\cdot Et_2O$ (**3**): $C_{55}H_{51}AgCl_2N_2OP_2Pt$, monoclinic, $P2_1/c$ (No. 14), $a=21.948(4)$, $b=11.946(3)$, $c=36.733(5)$ Å, $\beta=96.76(1)°$, $V=9564(1)$ Å^3, $Z=8$, $R=0.063$. For *cis*-$(PPh_3)_2BrPt(\mu\text{-}3,5\text{-}Ph_2\text{-}4\text{-}Br\text{-}pz)AuBr\cdot 2thf$ (**4**): $C_{59}H_{57}AuBr_3N_2O_2P_2Pt$, triclinic, $P\bar{1}$ (No. 2), $a=10.456(2)$, $b=12.301(3)$, $c=24.058(5)$ Å, $\alpha=77.66(2)°$, $\beta=89.18(2)°$, $\gamma=67.42(2)°$, $V=2783(1)$ Å^3, $Z=2$, $R=0.060$. The structures of the heterobimetallic units are bridged by single 3,5-diphenylpyrazolato ligands. The Pt···M^I distances average 3.37 Å.

Introduction[§]

Bimetallic complexes containing pyrazolato bridges constitute a large area of transition metal chemistry [1]. Rhodium and iridium dinuclear complexes containing two pyrazolato bridges [2] have exhibited a variety of interesting reactions including the formation of metal–metal bonds [3], small molecule activation and formation of 'A-frame' type species [4] and orthometallation reactions [5]. Mixed metal dinuclear and trinuclear pyrazolato complexes are known [6]. The synthesis of copper containing biomimetic molecules [7] is another research area involving pyrazoles.

Pyrazolato metal complexes are receiving attention for a variety of reasons; they bridge metal atoms separated by a distance of ~3.35 Å (Scheme 1) (the distance required [8] for O_2 activation), their donor and solubility properties can be modified [9] by varying the substitution of the 3-, 4- and 5-position without significantly affecting the environment around the metal atom, and they can mediate the transmission of electronic effects (i.e. antiferromagnetic coupling [10]) between the bridged metals [11].

In contrast to the doubly bridged systems, complexes containing a single pyrazolato bridge have received less



Scheme 1.

---

[*] Author to whom correspondence should be addressed.

[**] In part from the Ph.D. Dissertation of Raphael G. Raptis.

[†] Present address: The Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia.

[††] Present address: Corporate Research, Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, NJ 08801, USA.

[§] Abbreviations used: pz = pyrazolato anion; 3,5-Ph_2pz = 3,5-diphenylpyrazolato anion; 3,5-Ph_2pzH = 3,5-diphenylpyrazole; 3,5-R_2pz = 3,5-dialkylpyrazolato anion; dam = bis(diphenylarsino)methane; dppm = bis(diphenylphosphino)methane; dapm = (diphenylarsino)(diphenylphosphine)methane; thf = tetrahydrofuran; tht = tetrahydrothiophene.

0020-1693/92/$5.00

attention. Some rhodium–dam, dppm and dapm dimers with a bridging pyrazolato group have been reported [12]. A dirhodium and a diiridium pyrazolato bridged systems have been studied [11] with regard to redox chemistry; they show charge transfer through the conjugated pyrazolato bridge from one metal atom to the other upon oxidative addition to one of them, and deactivation of the other towards further oxidation. A heterobimetallic Ir(μ-pz)Au system [6e] derived from an Ir(pz) mononuclear starting material [13] has been described. In addition to the structure of the mononuclear iridium complex [13], Stobart and co-workers [14] have published the structure of a protonated 3,5-dimethylpyrazole coordinated to palladium(II). At ambient temperature the palladium complex is fluxional on a NMR time scale while the analogous platinum pyrazolate complexes [14] are static.

The usefulness of pyrazole and pyrazolato mononuclear complexes in the synthesis of dinuclear and trinuclear heterometallic species has been demonstrated [6, 15]. However, the ability of such metalloligands to bind to various metals such as the Cu, Ag and Au described here had not been recognized previously. Here we describe the synthesis of *cis*-$(PPh_3)_2ClPt^{II}$(3,5-Ph_2pz) (**1**), and the complete series of its Group 11 metal halide adducts, *cis*-$(PPh_3)_2XPt^{II}$(μ-3,5-Ph_2pz)-$Cu^{I}Cl$, (**2a**, X=Cl; **2b**, X=Br), *cis*-$(PPh_3)_2ClPt^{II}$-(μ-3,5-Ph_2pz)$Ag^{I}Cl$ (**3**), *cis*-$(PPh_3)ClPt^{II}$(μ-3,5-Ph_2pz)-$Au^{I}Cl$ (**4a**), *cis*-$(PPh_3)_2BrPt^{II}$(μ-3,5-Ph_2-4-Br-pz)$Au^{I}Br$ (**4b**), and the X-ray crystal structures of **1**, **2b**, **3** and **4b**.

Experimental

All reactions were carried out under an argon atmosphere using Schlenk techniques [16]. All solvents were dried and kept over molecular sieves prior to use. Sodium 3,5-diphenylpyrazolate was prepared by deprotonation of 3,5-diphenylpyrazole (Lancaster Ltd.) with sodium hydride in thf and precipitation with hexane. Literature procedures were followed for the synthesis of *cis*-$Pt(PPh_3)_2Cl_2$ [17], $CuBr_2$(3,5-Ph_2pzH) [18] and $AuBr_3$py [19] (a modification of the synthesis of $AuCl_3$py using HBr instead of HCl). All other reagents were purchased from commercial firms and used as received. Elemental analysis was performed by Desert Analytics, P.O. Box 41838, Tucson, AZ 85717. The fast atom bombardment mass spectra were obtained by the Texas A&M University Center for Chemical Characterization and Analysis, Mass Spectrometry Laboratory, using a VG Analytical 70S high resolution double-focusing magnetic sector mass spectrometer.

Synthesis of cis-$(PPh_3)_2ClPt$(3,5-Ph_2pz) (1)

To a solution of 30 mg (0.045 mmol) of *cis*-$Pt(PPh_3)_2Cl_2$ in 8 ml CH_2Cl_2 were added 11 mg (0.045 mmol) of Na[3,5-Ph_2pz]. After the reaction mixture was stirred for 24 h and allowed to settle, the colorless supernatant was transferred and the precipitate (NaCl) was washed with CH_2Cl_2. The CH_2Cl_2 solutions were combined, and removal of solvent *in vacuo* left a white solid. Slow Et_2O diffusion into a CH_2Cl_2 solution of this product gave colorless crystals of complex **1** (yield > 95%, m.p. (dec.) 207–209 °C) suitable for crystallographic work. The crystals of **1** lose their interstitial solvent upon prolonged exposure to air.

Synthesis of cis-$(PPh_3)_2ClPt$(μ-3,5-Ph_2pz)CuCl (2a)

To a solution of 50 mg (0.047 mmol) of complex **1** in 5 ml CH_2Cl_2 were added 9 mg (0.090 mmol) of CuCl and the mixture was stirred for 24 h. The colorless supernatant was filtered into another flask and **2a** was precipitated as a white solid by addition of Et_2O, m.p. (dec.) 244–246 °C. FAB-MS $(m/z)^+$: 455, 718, 755, 1001, 1037, 1073. *Anal.* Calc. for $C_{51}H_{41}Cl_2CuN_2P_2Pt$: C, 56.79; H, 3.76; N, 2.61. Found: C, 57.01; H, 3.81; N, 2.43%.

Synthesis of cis-$(PPh_3)_2BrPt$(μ-3,5-Ph_2pz)CuCl (2b)

To a solution of 42 mg (0.064 mmol) of $CuBr_2$(3,5-Ph_2pzH)$_2$ [18] in 5 ml thf was added a thf solution of NH(i-Pr)$_2$ (0.080 mmol). To the resulting brown solution were added 50 mg (0.063 mmol) of *cis*-$Pt(PPh_3)_2Cl_2$ and the reaction mixture turned yellow. The reaction was stirred for 12 h. Slow Et_2O diffusion into this solution afforded light yellow air-stable crystals with plate habit (yield > 50%).

Synthesis of cis-$(PPh_3)_2ClPt$(μ-3,5-Ph_2pz)AgCl (3)

To a solution of 26 mg (0.025 mmol) of complex **1** in 4 ml CH_2Cl_2 were added 5.5 mg (0.038 mmol) of AgCl and the mixture was stirred for 24 h. After the precipitate (excess AgCl) was allowed to settle, the colorless supernatant was filtered and Et_2O was allowed to slowly diffuse into it. Colorless crystals of complex **3**, m.p. (dec.) 201–203 °C, suitable for a crystallographic study were grown by this method (yield > 50%). FAB-MS $(m/z)^+$: 263, 455, 718, 755, 974, 1081, 1118.

Synthesis of cis-$(PPh_3)_2ClPt$(μ-3,5-Ph_2pz)AuCl (4a)

To a solution of 25 mg (0.032 mmol) of **1** in 5 ml CH_2Cl_2 were added 10 mg (0.032 mmol) Au(tht)Cl and the reaction was stirred for 24 h. Slow diffusion of Et_2O into this solution afforded colorless crystals (m.p. 218–220 °C) unsuitable for crystallographic work. FAB-MS $(m/z)^+$: 718, 755, 951, 1171, 1206.

Synthesis of cis-$(PPh_3)_2BrPt(\mu$-3,5-Ph_2-4-Br-pz)AuBr (4b)

Complex **4** was prepared from the reaction of a suspension of complex **1** in thf/toluene and a CH_2Cl_2 solution containing equimolar amounts of $AuBr_3py$ and Na[3,5-Ph_2pz]. Slow diffusion of Et_2O into this reaction mixture afforded, in good yield, orange crystals of **4**, suitable for a crystallographic study.

X-ray crystallography, data collection and refinement

The single crystal X-ray analyses of **1, 2b, 3** and **4b** were performed with a Nicolet R3m/E automated four-circle diffractometer and SHELXTL software implemented on an Eclipse S140 minicomputer. For **1** a single crystal was placed inside a glass capillary tube and sealed with epoxy glue, while for **2b, 3** and **4b** single crystals were mounted atop glass fibers for data collection. Initial cell parameters were determined by using orientation reflections obtained from photographic data and were confirmed by axial photographs and Delaunay reductions. Accurate unit cell parameters were calculated from the setting angles of high-angle reflections. On the basis of interaxial angles, monoclinic symmetry was suggested for **1** and **3**, orthorhombic for **2b**, and triclinic for **4b**. Intensity data were collected by the ω-scanning technique in bisecting geometry. The intensity data for **1** were collected using Wyckoff-ω scanning since it was known that the crystal decomposes upon loss of interstitial solvent. No symmetry equivalent reflections were measured. Because of the small size and inappropriate habit of the crystal of **2b** the high-angle reflections were very weak. Therefore, no data were collected beyond $2\theta = 40°$ for **2b**. The intensity data were corrected for Lorentz and polarization effects and standard decay. Empirical absorption corrections based on azimuthal scans of reflections spanning a range of 2θ values were applied. The systematically absent data uniquely determined the space groups of **1** and **3**, $P2_1/n$, while for **2b** there was a choice between the centrosymmetric *Pcmn* and the non-centrosymmetric $Pc2_1n$ space groups. The structure of **4** was successfully solved in $P\bar{1}$. Initial positional parameters for the platinum atoms of **1** and **2b** were determined by solving a sharpened Patterson map, while the initial positional parameter for the platinum atoms of **3** and the platinum and gold atoms of **4** were obtained from the direct methods program solution. All other non-hydrogen atoms were located in difference Fourier maps. The structure of **2b** could not be solved in the centrosymmetric space group *Pcmn*. At that point, a positive qualitative pyroelectricity test, conducted on a crystal from the same batch, indicated the presence of a polar axis in the solid material consistent with a non-centrosymmetric space group. The structure of **2b** was solved and refined successfully in the space group $Pc2_1n$. All phenyl groups were treated as rigid hexagons (C–C 1.395 Å, C–C–C 120°). Hydrogen atoms were included in the structures of **1, 3** and **4b** in calculated positions (C–H 0.96 Å). For **1, 3** and **4b**, all non-hydrogen atoms except phenyl group carbons were refined anisotropically, while for **2b** only the metal, halogen and phosphorus atoms were refined anisotropically. The 4-position of the pyrazolato ring of **2b** is partially chlorinated and the site occupancy factor for this chlorine atom refined to 0.25. Interstitial solvent molecules were found in all four structures. Complexes **1, 2b** and **3** cocrystallized with one molecule of Et_2O per molecule of complex, while **4b** cocrystallized with two molecules of thf. The Et_2O molecule of **1** and the thf molecules of **4b** were disordered and have not been modeled satisfactorily. When the refinement of the structure of **2b** had converged, the trial structure was converted to its enantiomer with a significant improvement in its refinement. The final difference Fourier maps for **1, 2b, 3** and **4b** contained peaks of residual electron density of 1.98 e/Å^3 at 1.09 Å from Pt, 0.76 e/Å^3 at 0.70 Å from Cl, 1.13 e/Å^3 at 1.16 Å from Pt(2), and 1.35 e/Å^3 at 0.88 Å from Pt, respectively. The small residual electron density next to the chlorine atom bonded to copper and the large thermal ellipsoid of the bromine atom bonded to platinum imply some halogen scrambling in the structure of **2b**. Parameters pertaining to data collection and structure refinement of **1, 2b, 3** and **4b** are listed in Table 1.

Structural description

As part of our efforts to explore the chemistry of heterobimetallic pyrazolato-bridged complexes of late transition metals, we have synthesized and structurally characterized the metalloligand *cis*-$(PPh_3)_2ClPt$(3,5-Ph_2pz), (**1**) and its Pt–Cu, Pt–Ag and Pt–Au derivatives *cis*-$(PPh_3)_2BrPt(\mu$-3,5-Ph_2pz) (**2b**), *cis*-$(PPh_3)_2ClPt(\mu$-3,5-Ph_2pz)AgCl (**3**) and *cis*-$(PPh_3)_2BrPt(\mu$-3,5-Ph_2-4-Br-pz)AuBr (**4b**). To the best of our knowledge, there is only one crystallographically characterized [13] complex containing a monodentate pyrazolato group and only one crystallographically characterized [6e] heterobimetallic complex containing a single pyrazolato bridge, although the protonated 3,5-dimethylpyrazole complex, *cis*-chlorobis(triethylphosphine)(3,5-dimethylpyrazole)palladium(II) tetrafluoroborate has also been described structurally [14].

Positional and isotropic equivalent thermal parameters for the platinum monomer **1**, the dinuclear Pt/Cu, Pt/Ag and Pt/Au complexes **2b, 3** and **4b** are given in Tables 2–5, respectively. Significant bond lengths and angles for **1–4b** are summarized in Table 6–9, respectively.

TABLE 1. Crystallographic data for **1**, **2b**, **3** and **4b**

	1	**2b**	**3**	**4b**
Formula	$C_{55}H_{51}ClN_2OP_2Pt$	$C_{55}H_{51}BrClCuN_2OP_2Pt$	$C_{55}H_{51}AgCl_2N_2OP_2Pt$	$C_{59}H_{57}AuBr_3N_2O_2P_2Pt$
Formula weight	1048.05	1191.97	1191.84	1519.75
Space group	$P2_1/n$ (No. 14)	$Pc2_1n$ (No. 33)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	11.120(2)	10.721(3)	21.948(4)	10.456(2)
b (Å)	24.438(6)	15.757(4)	11.946(3)	12.301(3)
c (Å)	18.125(3)	30.263(8)	36.733(5)	24.058(5)
α (°)	90	90	90	77.66(2)
β (°)	99.50(1)	90	96.76(1)	89.18(2)
γ (°)	90	90	90	67.42(2)
V (Å^3)	4858(2)	5112(2)	9564(1)	2783(1)
Z	4	4	8	2
D_{calc} (g/cm^3)	1.43	1.55	1.66	1.81
μ(Mo Kα) (cm^{-1})	31.9	42.6	36.9	74.0
Radiation γ (Å)	0.71069	0.71069	0.71069	0.71069
Temperature (°C)	22	22	22	22
Transmission factors, max., min.	0.550, 0.429	0.062, 0.041	0.375, 0.312	0.328, 0.237
R^a	0.061	0.051	0.063	0.060
R_w^b	0.061	0.052	0.060	0.066

$^aR=\Sigma||F_o|-|F_c||/\Sigma|F_o$. $^bR_w=[\Sigma\sqrt{w}(|F_o|-|F_c|)]/\Sigma\sqrt{w}|F_o|$; $w^{-1}=[\sigma^2(|F_o|)+|g|F_o^2]$.

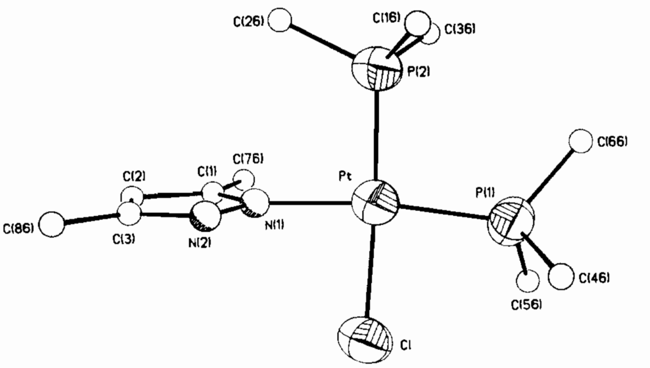


Fig. 1. A drawing of the structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Carbon and nitrogen atoms of arbitrary radii. Phenyl groups are represented by their *ipso* carbon atoms. Cocrystallized solvent molecule not shown.

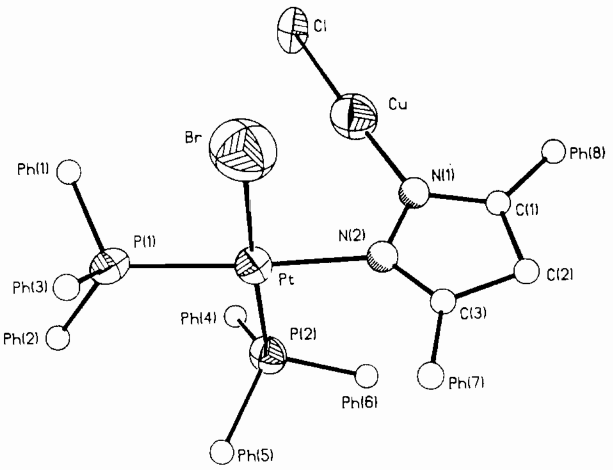


Fig. 2. A drawing of the structure of **2b**. Thermal ellipsoids are drawn at the 50% probability level. Carbon and nitrogen atoms of arbitrary radii. Phenyl groups are represented by their *ipso* carbon atoms. Cocrystallized solvent molecule not shown.

cis-$(PPh_3)_2ClPt(3,5\text{-}Ph_2pz)$ (*1*)

The monomeric complex **1** crystallizes in the monoclinic space group $P2_1/n$ with a whole molecule per asymmetric unit. Its structure (Fig. 1) shows small deviations from square-planar geometry about the Pt atom caused by repulsions between the bulky ligands. The plane of the pyrazolato ring forms a dihedral angle of 83.3° with the best-fit plane of platinum coordination, a result of the repulsions between the *cis*-PPh_3 and 3- and 5-phenyl substituents of the pyrazolato ligand. The $Pt–P_{cis}$ and $Pt–P_{trans}$ bond lengths show a statistically insignificant difference, 0.019(6) Å, possibly indicating a very weak *trans*-influence of the pyrazolato group. The Pt–N–N angle, 118.0(1)°, is almost ideal for the sp^2-hybridized nitrogen atom. The coordination structure of **1** is very similar to the coordination structure of the cation in *cis*-{$PdCl[P(C_2H_5)_3]_2$[3,5-dimethylpyrazole]}BF_4 reported by Bushnell *et al.* [14]. The metal–halide and metal–phosphorus distances vary by less than 0.02 Å between the two structures while the metal–nitrogen distance in the protonated palladium complex is about 0.05 Å shorter than the Pt–N distance in **1**. Both complexes show the heterocyclic ring to be essentially perpendicular to the coordination plane.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for *cis*-(PPh$_3$)$_2$ClPt(3,5-Ph$_2$pz) (**1**)

Atom	x	y	z	U_{iso}[a]
Pt	4749(1)	3329(1)	4418(1)	36(1)*
Cl	2816(4)	3257(2)	3662(2)	51(2)*
P(1)	3785(4)	3129(2)	5396(3)	42(2)*
P(2)	6638(4)	3428(2)	5078(3)	39(2)*
N(1)	5384(11)	3474(7)	3436(7)	40(6)*
N(2)	5277(14)	3972(8)	3154(9)	52(7)*
C(1)	5886(19)	3136(9)	3020(11)	63(9)*
C(2)	6163(16)	3409(10)	2393(11)	63(8)*
C(3)	5763(18)	3957(9)	2506(11)	58(8)*
C(11)	7880(10)	4157(5)	6141(8)	68(6)
C(12)	8005(10)	4640(5)	6556(8)	80(7)
C(13)	7030(10)	5004(5)	6510(8)	73(6)
C(14)	5928(10)	4885(5)	6048(8)	66(6)
C(15)	5803(10)	4402(5)	5633(8)	60(6)
C(16)	6778(10)	4038(5)	5679(8)	46(5)
C(21)	7800(9)	4047(4)	4115(7)	48(5)
C(22)	8706(9)	4166(4)	3691(7)	58(5)
C(23)	9674(9)	3803(4)	3685(7)	61(6)
C(24)	9736(9)	3322(4)	4104(7)	60(5)
C(25)	8830(9)	3203(4)	4528(7)	45(5)
C(26)	7862(9)	3566(4)	4534(7)	45(5)
C(31)	6951(11)	2328(5)	5205(6)	59(6)
C(32)	7374(11)	1833(5)	5535(5)	83(7)
C(33)	7989(11)	1825(5)	6271(5)	89(8)
C(34)	8180(11)	2311(5)	6677(5)	78(7)
C(35)	7757(11)	2805(5)	6347(5)	75(7)
C(36)	7142(11)	2814(5)	5611(5)	39(4)
C(41)	2470(11)	4097(5)	5103(6)	49(5)
C(42)	1644(11)	4498(5)	5242(6)	62(6)
C(43)	1065(11)	4456(5)	5866(6)	70(6)
C(44)	1312(11)	4013(5)	6352(6)	72(6)
C(45)	2137(11)	3611(5)	6213(6)	58(5)
C(46)	2716(11)	3653(5)	5588(6)	41(4)
C(51)	1714(11)	2451(5)	5331(7)	62(6)
C(52)	1065(11)	1968(5)	5142(7)	84(7)
C(53)	1602(11)	1541(5)	4803(7)	83(7)
C(54)	2787(11)	1596(5)	4653(7)	81(7)
C(55)	3435(11)	2078(5)	4842(7)	62(6)
C(56)	2899(11)	2506(5)	5181(7)	60(6)
C(61)	5042(11)	3434(4)	6787(7)	49(5)
C(62)	5700(11)	3348(4)	7502(7)	74(6)
C(63)	5919(11)	2816(4)	7771(7)	79(7)
C(64)	5479(11)	2371(4)	7325(7)	70(6)
C(65)	4821(11)	2457(4)	6610(7)	63(6)
C(66)	4602(11)	2989(4)	6341(7)	42(4)
C(71)	7255(11)	2319(6)	3098(8)	69(6)
C(72)	7484(11)	1764(6)	3239(8)	91(8)
C(73)	6561(11)	1425(6)	3413(8)	104(9)
C(74)	5409(11)	1640(6)	3446(8)	84(7)
C(75)	5180(11)	2195(6)	3305(8)	63(6)
C(76)	6103(11)	2534(6)	3131(8)	59(6)
C(81)	5877(14)	4392(5)	1302(8)	86(7)
C(82)	5980(14)	4853(5)	863(8)	104(9)
C(83)	6044(14)	5373(5)	1186(8)	90(8)
C(84)	6004(14)	5431(5)	1947(8)	103(9)
C(85)	5901(14)	4970(5)	2386(8)	87(7)
C(86)	5837(14)	4450(5)	2063(8)	59(6)
O*	5684(55)	204(23)	6395(30)	359(27)
C(1*)	4196(71)	488(31)	6660(42)	345(37)
C(2*)	4865(64)	908(31)	6499(42)	308(34)
C(3*)	6768(96)	324(39)	6209(54)	370(49)
C(4*)	7534(66)	−104(31)	6176(39)	307(34)

---

[a] Starred items: equivalent isotropic U defined as one-third of the orthogonalized U_{ij} tensor.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for *cis*-(PPh$_3$)$_2$BrPt(μ-3,5-Ph$_2$pz)CuCl (**2b**)

Atom	x	y	z	U_{iso}[a]
Pt	8858(1)	6426(3)	5944(1)	41(1)*
Cu	6023(4)	10551(4)	8411(1)	65(2)*
Br	10619(4)	6207(4)	5447(2)	103(2)*
Cl	11336(8)	4223(5)	6580(3)	55(3)*
Cl*	11652(25)	9161(19)	6777(8)	103(13)*
P(1)	7729(7)	5626(6)	5443(3)	44(3)*
P(2)	7304(7)	6611(7)	6440(2)	41(3)*
N(1)	5816(21)	11685(16)	8381(7)	55(8)
N(2)	10043(23)	7162(16)	6326(8)	49(7)
C(1)	6449(29)	12313(21)	8155(11)	64(10)
C(2)	11125(30)	8180(23)	6702(10)	54(9)
C(3)	10198(27)	7973(20)	6373(10)	48(8)
C(11)	9246(17)	4252(12)	5672(6)	37(9)
C(12)	9566(17)	3392(12)	5675(6)	67(10)
C(13)	8900(17)	2817(12)	5414(6)	78(11)
C(14)	7914(17)	3102(12)	5150(6)	76(11)
C(15)	7595(17)	3962(12)	5148(6)	65(10)
C(16)	8261(17)	4537(12)	5409(6)	54(9)
C(21)	5663(20)	4859(12)	5813(7)	70(11)
C(22)	4390(20)	4690(14)	5859(7)	69(11)
C(23)	3521(20)	5132(14)	5603(7)	91(13)
C(24)	3925(20)	5743(14)	5300(7)	73(10)
C(25)	5198(20)	5913(14)	5254(7)	50(9)
C(26)	6067(20)	5471(14)	5510(7)	50(8)
C(31)	8233(21)	5686(10)	4538(8)	59(9)
C(32)	8282(21)	6090(10)	4127(8)	79(13)
C(33)	7968(21)	6949(10)	4092(8)	79(13)
C(34)	7604(21)	7402(10)	4467(8)	88(12)
C(35)	7555(21)	6998(10)	4878(8)	50(10)
C(36)	7869(21)	6139(10)	4913(8)	55(10)
C(41)	5849(17)	5597(11)	7001(7)	53(9)
C(42)	5567(17)	4845(11)	7225(7)	80(11)
C(43)	6311(17)	4126(11)	7165(7)	72(10)
C(44)	7337(17)	4158(11)	6881(7)	76(11)
C(45)	7619(17)	4910(11)	6656(7)	48(8)
C(46)	6875(17)	5629(11)	6716(7)	44(8)
C(51)	4727(18)	6867(10)	6247(6)	59(9)
C(52)	3740(18)	7327(10)	6063(6)	64(10)
C(53)	3981(18)	8065(10)	5822(6)	66(10)
C(54)	5209(18)	8343(10)	5764(6)	73(11)
C(55)	6195(18)	7883(10)	5948(6)	70(10)
C(56)	5954(18)	7144(10)	6189(6)	46(8)
C(61)	7300(18)	8070(13)	6978(7)	67(10)
C(62)	7599(18)	8504(13)	7366(7)	70(11)
C(63)	8336(18)	8112(13)	7688(7)	87(12)
C(64)	8774(18)	7287(13)	7621(7)	77(11)
C(65)	8475(18)	6853(13)	7233(7)	59(9)
C(66)	7738(18)	7244(13)	6911(7)	54(9)
C(71)	9451(20)	8512(11)	5636(6)	65(12)
C(72)	8849(20)	9138(11)	5388(6)	72(10)
C(73)	8417(20)	9875(11)	5593(6)	79(11)
C(74)	8587(20)	9988(11)	6048(6)	74(11)
C(75)	9190(20)	9362(11)	6296(6)	71(11)
C(76)	9622(20)	8624(11)	6090(6)	41(8)
C(81)	12152(18)	6390(14)	7491(8)	90(10)
C(82)	13012(18)	6197(14)	7823(8)	102(14)
C(83)	14069(18)	6705(14)	7881(8)	102(14)
C(84)	14266(18)	7406(14)	7607(8)	76(11)

(*continued*)

TABLE 3. (*continued*)

Atom	x	y	z	U_{iso}[a]
C(85)	13406(18)	7599(14)	7274(8)	56(9)
C(86)	12349(18)	7091(14)	7217(8)	46(8)
O*	119(29)	6125(22)	8537(11)	135(12)
C(1*)	734(54)	7464(41)	8838(19)	151(21)
C(2*)	579(53)	6611(55)	8942(19)	173(23)
C(3*)	−258(74)	5258(54)	8573(27)	217(32)
C(4*)	−390(83)	4917(62)	8092(31)	276(41)

[a] Starred items: equivalent isotropic U defined as one-third of the orthogonalized U_{ij} tensor.

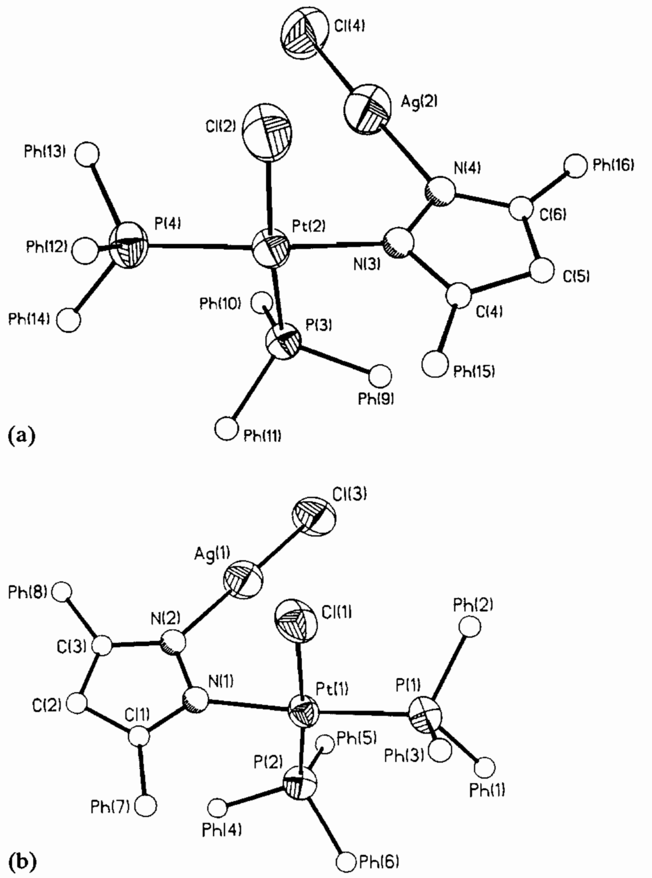


Fig. 3. A drawing of the structures of two enantiomers of **3**. Thermal ellipsoids are drawn at the 50% probability level. Carbon and nitrogen atoms of arbitrary radii. Phenyl groups are represented by their *ipso* carbon atoms. Cocrystallized solvent molecule not shown.

cis-$(PPh_3)_2BrPt(\mu$-3,5-$Ph_2pz)CuCl$ (*2b*), *cis*-$(PPh_3)_2ClPt(\mu$-3,5-$Ph_2pz)AgCl$ (*3*) and *cis*-$(PPh_3)_2BrPt(\mu$-3,5-Ph_2-4-Br-pz$)AuBr$ (*4b*)

The complexes **2b**, **3** and **4b** crystallize in the orthorhombic space group $Pc2_1n$, the monoclinic space group $P2_1/n$, and the triclinic space group $P\bar{1}$, respectively. While **2b** and **4b** contain one molecule per asymmetric unit, the asymmetric unit of **3** contains a pair of enantiomeric dinuclear Pt/Ag complexes. Their

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for *cis*-$(PPh_3)_2ClPt(\mu$-3,5-$Ph_2pz)AgCl$ (**3**)

Atom	x	y	z	U_{iso}[a]
Pt(1)	3262(1)	1521(1)	1178(1)	33(1)*
Pt(2)	8466(1)	2639(1)	1004(1)	42(1)*
Ag(1)	2827(1)	−1081(2)	1331(1)	62(1)*
Ag(2)	7966(1)	4044(2)	1707(1)	92(1)*
Cl(1)	2504(3)	1190(5)	682(2)	56(2)*
Cl(2)	7669(3)	3733(6)	715(2)	83(3)*
Cl(3)	3373(3)	7438(6)	1128(2)	75(3)*
Cl(4)	8363(4)	5763(7)	1903(3)	123(5)*
P(1)	3902(3)	1828(5)	740(2)	39(2)*
P(2)	3926(3)	1743(5)	1691(2)	40(2)*
P(3)	9201(3)	1631(5)	1338(2)	39(2)*
P(4)	9085(3)	3525(6)	633(2)	49(2)*
N(1)	2541(7)	1305(16)	1489(4)	35(7)*
N(2)	2348(8)	218(14)	1542(5)	39(7)*
N(3)	7799(7)	1906(14)	1277(4)	41(7)*
N(4)	7621(7)	2378(15)	1586(5)	46(7)*
C(1)	2174(9)	2020(17)	1636(5)	34(8)*
C(2)	1728(9)	1448(22)	1807(6)	43(9)*
C(3)	1852(9)	350(22)	1737(6)	48(10)*
C(4)	7522(9)	861(22)	1238(5)	44(9)*
C(5)	7145(10)	694(23)	1534(6)	60(11)*
C(6)	7255(10)	1651(22)	1742(7)	63(11)*
C(O11)	4977(7)	3162(11)	803(4)	61(7)
C(O12)	5609(7)	3320(11)	881(4)	85(9)
C(O13)	5985(7)	2427(11)	1008(4)	56(7)
C(O14)	5729(7)	1376(11)	1056(4)	49(6)
C(O15)	5098(7)	1218(11)	978(4)	41(6)
C(O16)	4722(7)	2111(11)	852(4)	48(7)
C(O21)	4225(7)	780(12)	104(5)	71(8)
C(O22)	4242(7)	−106(12)	−142(5)	81(9)
C(O23)	3967(7)	−1125(12)	−74(5)	89(10)
C(O24)	3675(7)	−1259(12)	241(5)	85(9)
C(O25)	3658(7)	−373(12)	487(5)	63(8)
C(O26)	3933(7)	646(12)	418(5)	51(7)
C(O31)	3569(7)	4070(15)	664(3)	60(7)
C(O32)	3325(7)	5020(15)	480(3)	63(8)
C(O33)	3091(7)	4951(15)	111(3)	77(9)
C(O34)	3101(7)	3933(15)	−74(3)	99(10)
C(O35)	3345(7)	2983(15)	110(3)	68(8)
C(O36)	3579(7)	3052(15)	479(3)	41(6)
C(O41)	3324(7)	924(10)	2254(4)	52(7)
C(O42)	3027(7)	982(10)	2569(4)	79(9)
C(O43)	2968(7)	2008(10)	2742(4)	81(9)
C(O44)	3205(7)	2977(10)	2600(4)	81(9)
C(O45)	3501(7)	2920(10)	2285(4)	55(7)
C(O46)	3561(7)	1893(10)	2112(4)	37(6)
C(O51)	4747(7)	426(12)	2149(4)	56(7)
C(O52)	5085(7)	−542(12)	2242(4)	73(8)
C(O53)	5072(7)	−1429(12)	1994(4)	74(8)
C(O54)	4722(7)	−1347(12)	1653(4)	62(7)
C(O55)	4384(7)	−379(12)	1559(4)	44(6)
C(O56)	4397(7)	508(12)	1807(4)	43(6)
C(O61)	5067(7)	2905(11)	1791(4)	61(7)
C(O62)	5420(7)	3879(11)	1808(4)	73(8)
C(O63)	5140(7)	4913(11)	1730(4)	77(9)
C(O64)	4506(7)	4973(11)	1635(4)	69(8)
C(O65)	4153(7)	3999(11)	1618(4)	51(7)
C(O66)	4434(7)	2965(11)	1696(4)	29(5)
C(O71)	2463(6)	3793(12)	1310(3)	43(6)
C(O72)	2530(6)	4954(12)	1307(3)	51(7)
C(O73)	2376(6)	5589(12)	1602(3)	75(8)

(*continued*)

TABLE 4. (*continued*)

Atom	x	y	z	U_{iso}[a]
C(O74)	2154(6)	5063(12)	1899(3)	118(12)
C(O75)	2087(6)	3902(12)	1901(3)	108(11)
C(O76)	2241(6)	3267(12)	1607(3)	34(6)
C(O81)	1296(8)	−713(14)	2173(5)	80(9)
C(O82)	968(8)	−1641(14)	2274(5)	89(9)
C(O83)	854(8)	−2538(14)	2032(5)	97(10)
C(O84)	1069(8)	−2506(14)	1689(5)	95(10)
C(O85)	1397(8)	−1578(14)	1589(5)	94(10)
C(O86)	1511(8)	−682(14)	1830(5)	64(8)
C(O91)	8678(7)	992(10)	1949(4)	49(7)
C(O92)	8428(7)	246(10)	2183(4)	66(8)
C(O93)	8443(7)	−902(10)	2116(4)	72(8)
C(O94)	8707(7)	−1305(10)	1814(4)	85(9)
C(O95)	8957(7)	−559(10)	1580(4)	72(8)
C(O96)	8942(7)	589(10)	1647(4)	46(6)
C(101)	9572(6)	3633(14)	1673(4)	58(7)
C(102)	9891(6)	4282(14)	1948(4)	90(10)
C(103)	10305(6)	3777(14)	2216(4)	85(9)
C(104)	10399(6)	2622(14)	2209(4)	70(8)
C(105)	10079(6)	1973(14)	1934(4)	52(7)
C(106)	9666(6)	2479(14)	1666(4)	47(6)
C(111)	9368(5)	341(13)	747(4)	57(7)
C(112)	9704(5)	−225(13)	504(4)	78(9)
C(113)	10342(5)	−280(13)	573(4)	77(9)
C(114)	10644(5)	232(13)	885(4)	68(8)
C(115)	10309(5)	798(13)	1127(4)	46(6)
C(116)	9671(5)	852(13)	1058(4)	34(6)
C(121)	8691(7)	4281(11)	−76(5)	69(8)
C(122)	8440(7)	4143(11)	−440(5)	88(9)
C(123)	8230(7)	3094(11)	−565(5)	59(7)
C(124)	8270(7)	2183(11)	−326(5)	63(7)
C(125)	8521(7)	2321(11)	38(5)	64(7)
C(126)	8731(7)	3370(11)	163(5)	49(6)
C(131)	9658(7)	5579(16)	574(4)	66(8)
C(132)	9819(7)	6661(16)	691(4)	95(10)
C(133)	9504(7)	7185(16)	953(4)	122(12)
C(134)	9029(7)	6626(16)	1097(4)	105(10)
C(135)	8868(7)	5544(16)	980(4)	76(8)
C(136)	9182(7)	5020(16)	718(4)	42(6)
C(141)	10316(8)	3464(13)	907(3)	63(7)
C(142)	10942(8)	3305(13)	889(3)	85(9)
C(143)	11142(8)	2819(13)	579(3)	82(9)
C(144)	10716(8)	2491(13)	286(3)	82(9)
C(145)	10090(8)	2650(13)	304(3)	63(7)
C(146)	9891(8)	3136(13)	614(3)	46(6)
C(151)	7576(7)	571(11)	565(5)	58(7)
C(152)	7677(7)	−138(11)	277(5)	69(8)
C(153)	7788(7)	−1275(11)	342(5)	90(10)
C(154)	7797(7)	−1701(11)	696(5)	93(10)
C(155)	7696(7)	−992(11)	985(5)	73(8)
C(156)	7585(7)	145(11)	919(5)	45(6)
C(161)	6484(7)	1424(12)	2180(4)	60(7)
C(162)	6260(7)	1645(12)	2513(4)	69(8)
C(163)	6577(7)	2374(12)	2765(4)	62(7)
C(164)	7118(7)	2881(12)	2684(4)	62(8)
C(165)	7341(7)	2660(12)	2351(4)	65(7)
C(166)	7024(7)	1932(12)	2099(4)	51(7)
O*	5735(18)	6873(37)	914(12)	334(21)
C(1*)	5024(22)	6109(44)	357(13)	234(23)
C(2*)	5185(23)	7004(47)	679(15)	247(25)
C(3*)	6274(26)	7180(50)	1167(16)	296(29)
C(4*)	6733(22)	5858(47)	1287(14)	253(25)

[a] Starred items: equivalent isotropic U defined as one-third of the orthogonalized U_{ij} tensor.

TABLE 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for *cis*-$(PPh_3)_2BrPt(\mu\text{-}3,5\text{-}Ph_2\text{-}4\text{-}Br\text{-}pz)AuBr$ (**4b**)

Atom	x	y	z	U_{iso}[a]
Au	4634(1)	7201(1)	2449(1)	50(1)*
Pt	5851(1)	9176(1)	2830(1)	29(1)*
Br(1)	3854(4)	9602(4)	3398(2)	95(2)*
Br(2)	5315(5)	5229(3)	3017(2)	106(2)*
Br(3)	1818(4)	11865(3)	757(2)	101(2)*
P(1)	7231(6)	8622(5)	3679(2)	37(2)*
P(2)	7654(6)	8919(5)	2266(2)	34(2)*
N(1)	4442(17)	9702(15)	2120(7)	33(7)*
N(2)	4095(18)	8864(15)	1937(7)	35(7)*
C(1)	3833(23)	10745(20)	1776(10)	44(10)*
C(2)	2934(22)	10603(19)	1337(8)	39(9)*
C(3)	3114(24)	9447(20)	1474(9)	44(10)*
C(11)	6709(19)	9678(14)	4633(6)	76(8)
C(12)	6343(19)	10655(14)	4893(6)	84(9)
C(13)	5796(19)	11834(14)	4562(6)	97(11)
C(14)	5615(19)	12034(14)	3970(6)	115(13)
C(15)	5981(19)	11056(14)	3709(6)	77(8)
C(16)	6528(19)	9878(14)	4041(6)	38(5)
C(21)	6086(15)	6788(14)	4016(5)	50(6)
C(22)	6043(15)	5760(14)	4382(5)	59(7)
C(23)	6924(15)	5226(14)	4881(5)	73(8)
C(24)	7846(15)	5722(14)	5012(5)	74(8)
C(25)	7889(15)	6751(14)	4646(5)	61(7)
C(26)	7008(15)	7284(14)	4148(5)	41(5)
C(31)	9874(16)	7059(12)	3609(7)	58(7)
C(32)	11310(16)	6722(12)	3622(7)	75(8)
C(33)	11893(16)	7511(12)	3729(7)	87(9)
C(34)	11039(16)	8638(12)	3823(7)	86(9)
C(35)	9603(16)	8975(12)	3809(7)	56(7)
C(36)	9020(16)	8186(12)	3702(7)	35(5)
C(41)	8375(16)	6465(16)	2615(7)	58(7)
C(42)	9175(16)	5258(16)	2619(7)	89(10)
C(43)	10370(16)	4958(16)	2321(7)	102(11)
C(44)	10766(16)	5866(16)	2019(7)	92(10)
C(45)	9967(16)	7073(16)	2015(7)	63(7)
C(46)	8771(16)	7373(16)	2313(7)	55(6)
C(51)	7245(19)	10451(14)	1162(8)	68(8)
C(52)	6912(19)	10763(14)	574(8)	105(11)
C(53)	6479(19)	10034(14)	317(8)	80(9)
C(54)	6380(19)	8994(14)	648(8)	75(8)
C(55)	6713(19)	8682(14)	1235(8)	65(7)
C(56)	7146(19)	9410(14)	1492(8)	45(6)
C(61)	10053(14)	9397(11)	2421(7)	51(6)
C(62)	10686(14)	10186(11)	2474(7)	70(8)
C(63)	9874(14)	11384(11)	2484(7)	76(8)
C(64)	8429(14)	11792(11)	2442(7)	81(9)
C(65)	7796(14)	11003(11)	2389(7)	60(7)
C(66)	8608(14)	9805(11)	2379(7)	43(6)
C(71)	3884(18)	12267(14)	2328(5)	57(7)
C(72)	4083(18)	13310(14)	2361(5)	68(8)
C(73)	4410(18)	13986(14)	1879(5)	64(7)
C(74)	4537(18)	13618(14)	1364(5)	90(10)
C(75)	4338(18)	12575(14)	1331(5)	68(8)
C(76)	4011(18)	11899(14)	1813(5)	40(5)
C(81)	3411(12)	7666(13)	1110(7)	58(7)
C(82)	2851(12)	7065(13)	819(7)	67(7)
C(83)	1460(12)	7607(13)	609(7)	84(9)
C(84)	630(12)	8751(13)	690(7)	77(9)
C(85)	1190(12)	9352(13)	982(7)	58(7)
C(86)	2580(12)	8810(13)	1191(7)	40(5)

[a] Starred items: equivalent isotropic U defined as one-third of the orthogonalized U_{ij} tensor.

TABLE 6. Selected distances (Å) and angles (°) for *cis*-$Pt(PPh_3)_2Cl(3,5\text{-}Ph_2pz)$ (**1**)

Distances	
Pt–Cl	2.357(4)
Pt–P(1)	2.271(5)
Pt–P(2)	2.252(4)
Pt–N(1)	2.05(1)
P(1)–C(46)	1.82(1)
P(1)–C(56)	1.83(1)
P(1)–C(66)	1.83(1)
P(2)–C(16)	1.84(1)
P(2)–C(26)	1.83(1)
P(2)–C(36)	1.82(1)
N(1)–N(2)	1.32(3)
N(1)–C(1)	1.30(3)
N(2)–C(3)	1.37(3)
C(1)–C(2)	1.40(3)
C(2)–C(3)	1.44(3)
C(1)–C(76)	1.50(3)
C(3)–C(86)	1.46(3)
Angles	
Cl–Pt–P(2)	176.2(2)
N(1)–Pt–P(1)	171.5(4)
Cl–Pt–P(1)	86.3(2)
Cl–Pt–N(1)	85.4(3)
P(2)–Pt–P(1)	97.3(2)
P(2)–Pt–N(1)	91.0(3)
Pt–N(1)–N(2)	118.0(1)
C(1)–N(1)–N(2)	112.0(2)
N(1)–N(2)–C(3)	106.0(2)
N(1)–C(1)–C(2)	110.0(2)
C(1)–C(2)–C(3)	102.0(2)
N(2)–C(3)–C(2)	109.0(2)

structures (Figs. 2, 3 and 4) consist of a dimetallic unit bridged by a 3,5-diphenylpyrazolato ligand, which, in the case of complex **4b**, is partially halogenated at the 4-position. The geometries around the platinum atoms are, by and large, the same in all three structures and retain the features of the parent metalloligand **1**. The Group 11 metal atoms of **2b, 3** and **4b** are two-coordinate linear within 6.4°. The best-fit of the plane defined by the Pt, P, P and X atoms form dihedral angles with the bridging pyrazolato ring of 82.7, 82.6 and 86.8° for **2b, 3** and **4b**, respectively. The $Pt–N–N–M^I$ units are planar in all three structures. The $Pt\cdots M^I$ distances range from 3.317(2) to 3.425(3) Å, while the Pt–N–N and M^I–N–N angles range between 114(2) and 124(2)°. The M^I–N bond lengths follow the trend of the covalent radii [20] for M^I, namely $Cu < Au < Ag$. The Pt–N bond lengths for complexes **2b** and **3**, 2.06(2)–2.07(2) Å, are equal to the Pt–N bond length of **1**, 2.05(2) Å. For the Pt/Au complex **4b**, the Pt–N bond is 2.12(1) Å, possibly reflecting the competition of the two third-row metals for backdonation to the bridging pyrazolato. As in complex **1**, the $Pt–P_{cis}$ and $Pt–P_{trans}$ bonds have statistically equal lengths with the $Pt–P_{trans}$ bonds consistently longer by 0.018(7) to 0.053(12) Å.

TABLE 7. Selected distances (Å) and angles (°) for *cis*-$Pt(PPh_3)_2Br(\mu\text{-}3,5\text{-}Ph_2pz)CuCl$ (**2b**)

Distances	
Pt···Cu	3.351(4)
Pt–N(2)	2.07(2)
Pt–P(1)	2.309(9)
Pt–P(2)	2.256(8)
Pt–Br	2.434(4)
Cu–N(1)	1.86(3)
Cu–Cl	2.116(9)
N(1)–N(2)	1.43(3)
N(1)–C(1)	1.38(4)
N(2)–C(3)	1.29(4)
C(1)–C(2)	1.47(5)
C(2)–C(3)	1.44(4)
Angles	
P(1)–Pt–N(2)	172.4(7)
P(2)–Pt–Br	176.4(2)
P(1)–Pt–Br	85.6(2)
P(1)–Pt–P(2)	96.9(3)
P(2)–Pt–N(2)	90.5(7)
N(2)–Pt–Br	87.7(7)
N(1)–Cu–Cl	177.0(8)
Pt–N(2)–N(1)	114.0(2)
Cu–N(1)–N(2)	124.0(2)
N(2)–N(1)–C(1)	102.0(2)
N(1)–N(2)–C(3)	112.0(2)
N(1)–C(1)–C(2)	114.0(3)
C(1)–C(2)–C(3)	99.0(3)
C(2)–C(3)–N(2)	113.0(3)

Results and discussion

We have recently reported [18, 21] the synthesis and structural characterization of the homologous series $[M^I(\mu\text{-}3,5\text{-}Ph_2pz)]_3$, $M^I = Cu, Ag, Au$. The unusual property of the 3,5-diphenylpyrazolato ligand to form stable bonds with all three metals of the copper triad has been further exploited here in the characterization of three novel d^8–d^{10} heterobimetallic complexes, **2, 3** and **4**. This is an extension of our studies [22–24] involving homometallic d^8–d^{10} complexes. The syntheses of three different heterobimetallic complexes with almost constant metal–metal separation, 3.317(2)–3.425(3) Å, provide the basis for the study of small molecule activation at the *endo*-site of these complexes as a function of the electronic properties of the Pt/Cu, Pt/Ag or Pt/Au metal core. Besides the interest in their chemistry, the heterobimetallic complexes described here constitute the first step towards the systematic synthesis of heterotrimetallic metallocyclic pyrazolato complexes. Synthetic efforts along the directions outlined in Scheme 2 are part of ongoing research in our laboratories.

An important feature of the chemistry of the pyrazolato complexes **2–4** is the stabilization of the 1+ oxidation states of the Group 11 metals. Although the Cu^{II} complex $CuBr_2(3,5\text{-}Ph_2pzH)_2$ is stable both in the solid state and in solution, upon the addition of a

TABLE 8. Selected distances (Å) and angles (°) for *cis*-$Pt(PPh_3)_2Cl(\mu\text{-}3,5\text{-}Ph_2pz)AgCl$ (**3**)

Pt(1)· · ·Ag(1)	3.317(2)
Pt(1)–N(1)	2.073(16)
Pt(1)–P(1)	2.288(6)
Pt(1)–P(2)	2.258(5)
Pt(1)–Cl(1)	2.353(5)
Ag(1)–N(2)	2.076(18)
Ag(1)–Cl(3)	2.308(7)
N(1)–N(2)	1.39(3)
N(1)–C(1)	1.33(3)
N(2)–C(3)	1.38(3)
C(1)–C(2)	1.40(3)
C(2)–C(3)	1.37(4)
Pt(2)· · ·Ag(2)	3.368(2)
Pt(2)–N(3)	2.064(17)
Pt(2)–P(3)	2.257(6)
Pt(2)–P(4)	2.293(6)
Pt(2)–Cl(2)	2.336(7)
Ag(2)–N(4)	2.157(17)
Ag(2)–Cl(4)	2.312(8)
N(3)–N(4)	1.36(3)
N(3)–C(4)	1.39(3)
N(4)–C(6)	1.36(3)
C(4)–C(5)	1.46(3)
C(5)–C(6)	1.38(4)
Angles	
P(1)–Pt(1)–N(1)	168.3(4)
P(2)–Pt(1)–Cl(1)	174.1(2)
P(1)–Pt(1)–P(2)	100.2(2)
P(2)–Pt(1)–N(1)	90.9(4)
P(1)–Pt(1)–Cl(1)	85.3(2)
N(1)–Pt(1)–CL(1)	83.7(4)
N(2)–Ag(1)–Cl(3)	176.9(5)
P(4)–Pt(2)–N(3)	171.2(4)
P(3)–Pt(2)–Cl(2)	174.1(2)
P(4)–Pt(2)–P(3)	97.7(2)
P(3)–Pt(2)–N(3)	90.7(5)
P(4)–Pt(2)–Cl(2)	86.3(2)
N(3)–Pt(2)–Cl(2)	85.5(5)
N(4)–Ag(2)–Cl(4)	173.6(5)
Pt(1)–N(1)–N(2)	117.0(1)
Ag(1)–N(2)–N(1)	118.0(1)
N(2)–N(1)–C(1)	110.0(2)
N(1)–N(2)–C(3)	104.0(2)
N(1)–C(1)–C(2)	111.0(2)
C(1)–C(2)–C(3)	103.0(2)
N(2)–C(3)–C(2)	113.0(2)
Pt(2)–N(3)–N(4)	121.0(1)
Ag(2)–N(4)–N(3)	115.0(1)
N(4)–N(3)–C(4)	107.0(2)
N(3)–N(4)–C(6)	109.0(2)
N(3)–C(4)–C(5)	109.0(2)
C(4)–C(5)–C(6)	103.0(2)
N(4)–C(6)–C(5)	112.0(2)

TABLE 9. Selected distances (Å) and angles (°) for *cis*-$Pt(PPh_3)_2Br(\mu\text{-}3,5\text{-}Ph_2\text{-}4\text{-}Br\text{-}pz)AuBr$ (**4**)

Distances	
Pt· · ·Au	3.425(3)
Pt–N(1)	2.12(1)
Pt–P(1)	2.288(5)
Pt–P(2)	2.270(5)
Pt–Br(1)	2.423(3)
Au–N(2)	2.02(1)
Au–Br(2)	2.351(3)
N(1)–N(2)	1.37(3)
N(1)–C(1)	1.33(2)
N(2)–C(3)	1.37(2)
C(1)–C(2)	1.42(3)
C(2)–C(3)	1.36(3)
C(2)–Br(3)	1.86(1)
Angles	
P(1)–Pt–N(1)	171.9(4)
P(2)–Pt–Br(1)	176.0(1)
P(1)–Pt–P(2)	96.5(2)
P(2)–Pt–N(1)	91.5(4)
P(1)–Pt–Br(1)	85.5(1)
N(1)–Pt–Br(1)	86.5(4)
N(2)–Au–Br(2)	178.2(4)
Pt–N(1)–N(2)	119.1(9)
Au–N(2)–N(1)	119.8(9)
N(2)–N(1)–C(1)	110.1(15)
N(1)–N(2)–C(3)	107.2(14)
N(1)–C(1)–C(2)	107.0(18)
C(1)–C(2)–C(3)	106.8(14)
N(2)–C(3)–C(2)	108.7(19)

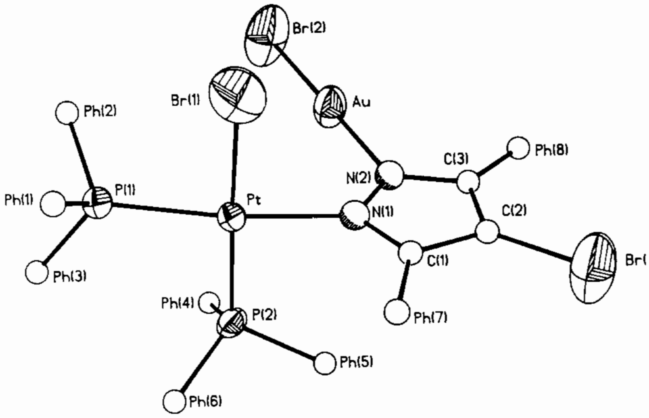
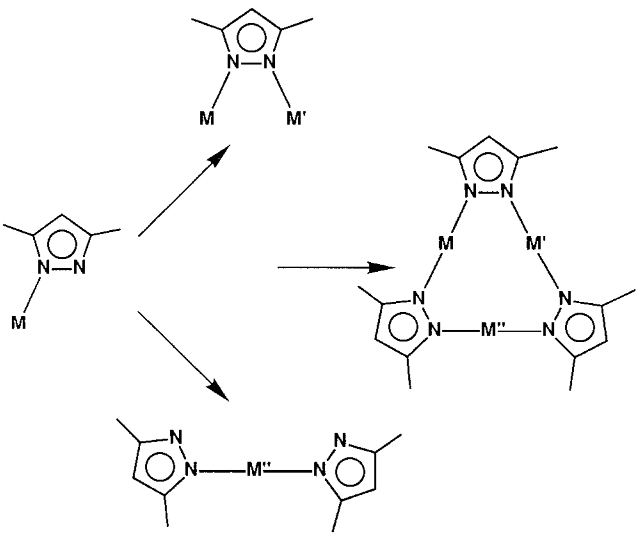


Fig. 4. A drawing of the structure of **4b**. Thermal ellipsoids are drawn at the 50% probability level. Carbon and nitrogen atoms of arbitrary radii. Phenyl groups are represented by their *ipso* carbon atoms. Cocrystallized solvent molecule not shown.

hindered amine the deeply colored solution turns very light yellow indicating the generation of a Cu^I species [25]. When the synthesis is followed by the addition of *cis*-$PtCl_2(PPh_3)_2$, the Cu^{II} species reacts giving the Pt/Cu^I complex **2b**. Similarly, an attempt to coordinate the pyrazolato metalloligand **1** to an Au^{III} center resulted in reduction to Au^I and formation of the Pt/Au^I complex **4b**. Stabilization of the +1 oxidation state of Au has been observed in the trimeric complexes $[Au(\mu\text{-}3,5\text{-}R_2pz)]_3$. The latter can be oxidized by I_2 only to a mixed-valence $Au_2{}^I/Au^{III}I_2$ product [26], while further oxidation can be carried out by aqua regia [27]. An $Au_2{}^I/Au^{III}$ species, $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3Cl_2$, was obtained



Scheme 2.

[23] through the reduction of $AuCl_3py$ in a reaction with Na[3,5-Ph_2pz]. Stabilization of the electron-rich d^{10} metals can take place via backdonation into the π^*-system of the pyrazolato ring. This seems particularly true in the case of complex **2b** which has a Cu–N bond of 1.86(3) Å, much shorter than the bond lengths measured in the trimeric complex [21] [Cu(μ-3,5-Ph_2pz)$]_3$.

The reactions of complex **1** with metals of the copper triad results in addition or ligand substitution reactions (syntheses of **2a, 3** and **4a**). The metalloligand **1** is a good coordinating ligand for all three Group 11 metal halides.

Supplementary material

Tables SI–SXIV listing crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for complexes **1, 2b, 3** and **4b** (23 pages); Tables SXV–SXVIII listing observed and calculated structure factors for **1, 2b, 3** and **4b** (169 pages) are available from the authors on request.

Acknowledgements

We acknowledge the financial support of this work by the National Science Foundation, CHE 8708625, and the Welch Foundation.

References

1 (a) S. Trofimenko, *Chem. Rev., 72* (1972) 497; (b) *Prog. Inorg. Chem., 34* (1986) 115.

2 (a) R. Usón, L. A. Oro, M. A. Ciriano, D. Carmona, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem., 224* (1982) 69; (b) A. Tiripicchio, F. J. Lahoz, L. A. Oro and M. T. Pinillos, *J. Chem. Soc., Chem. Commun.,* (1984) 936; (c) L. A. Oro, D. Carmona, M. P. Lamata, C. Foces-Foces and F. H. Cano, *Inorg. Chim. Acta, 97* (1985) 19; (d) A. W. Coleman, D. T. Eadie and S. R. Stobart, *J. Am. Chem. Soc., 104* (1982) 922; (e) G. W. Bushnell, D. O. K. Fjeldsted, S. R. Stobart and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.,* (1983) 580; (f) K. A. Beveridge, G. W. Bushnell, S. R. Stobart, J. L. Atwood and M. J. Zaworotko, *Organometallics, 2* (1983) 1447; (g) G. W. Bushnell, D. O. K. Fjeldsted, S. R. Stobart, M. J. Zaworotko, S. A. R. Knox and K. A. Macpherson, *Organometallics, 4* (1985) 1107; (h) J. L. Marshall, S. R. Stobart and H. B. Gray, *J. Am. Chem. Soc., 106* (1984) 3027; (i) G. Banditelli, A. L. Bandini, F. Bonati and G. Minghetti, *J. Organomet. Chem., 218* (1981) 229.

3 (a) K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie and S. R. Stobart, *J. Am. Chem. Soc., 104* (1982) 920; (b) J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart and M. J. Zaworotko, *Inorg. Chem., 23* (1984) 4050; (c) G. W. Bushnell, M. J. Decker, D. T. Eadie, S. R. Stobart, R. Vefghi, J. L. Atwood and M. J. Zaworotko, *Organometallics, 4* (1985) 2106.

4 (a) J. V. Caspar and H. B. Gray, *J. Am. Chem. Soc., 106* (1984) 3029; (b) D. O. K. Fjeldsted, S. R. Stobart and M. J. Zaworotko, *J. Am. Chem. Soc., 107* (1985) 8258; (c) R. D. Brost and S. R. Stobart, *J. Chem. Soc., Chem. Commun.,* (1989) 498.

5 (a) F. Barceló, P. Lahuerta, M. A. Ubeda, C. Foces-Foces, F. H. Cano and M. Martinez-Ripoll, *J. Chem. Soc., Chem. Commun.,* (1985) 43; (b) F. Barceló, P. Lahuerta, M. A. Ubeda, C. Foces-Foces, F. H. Cano and M. Martinez-Ripoll, *Organometallics, 7* (1988) 584.

6 (a) S. Nussbaum, S. Retting, A. Storr and J. Trotter, *Can. J. Chem., 63* (1985) 692; (b) G. Minghetti, G. Banditelli and F. Bonati, *Chem. Ind. (London),* (1977) 123; (c) A. L. Bandini, G. Banditelli, G. Minghetti and F. Bonati, *Can. J. Chem., 57* (1979) 3237; (d) F. Cariati, G. Micera, A. Scozzafava, G. Minghetti and G. Banditelli, *Inorg. Chem., 21* (1982) 3843; (e) A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti, F. Demartin and M. Manassero, *Inorg. Chem., 26* (1987) 1351.

7 (a) K. D. Karlin and J. Zubieta (eds.), *Copper Coordination Chemistry: Biological and Inorganic Perspectives,* Adenine, New York, 1983; (b) E. I. Solomon, *Copper Proteins,* Wiley–Interscience, New York, 1981.

8 (a) M. L. Co, R. A. Scott and K. O. Hodgson, *J. Am. Chem. Soc., 103* (1981) 986; (b) G. L. Woolery, L. Powers, J. Peisach and T. J. Spiro, *Biochemistry, 23* (1984) 3428; (c) G. L. Woolery, L. Powers, M. Winkler, E. I. Solomon and T. G. Spiro, *J. Am. Chem. Soc., 106* (1984) 86; (d) J. M. Brown, L. Powers, B. Kincaid, J. A. Larrabee and T. G. Spiro, *J. Am. Chem. Soc., 102* (1980) 4210.

9 A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti and M. T. Pinillos, *Inorg. Chim. Acta, 99* (1985) 165.

10 H. P. Berends and D. W. Stephan, *Inorg. Chem., 26* (1987) 749.

11 T. G. Schenck, C. R. C. Milne, J. F. Sawyer and B. Bosnich, *Inorg. Chem., 24* (1985) 2338.

12 (a) L. A. Oro, D. Carmona, P. L. Pérez, M. Esteban, A. Tiripicchio and M. Tiripicchio-Camelini, *J. Chem. Soc., Dalton Trans.,* (1985) 973; (b) C. J. Janke, L. J. Tortorelli, J. L. E. Burn, C. A. Tucker and C. Woods, *Inorg. Chem., 25* (1986) 4597.

13 A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti, F. Demartin and M. Manassero, *J. Organomet. Chem., 269* (1984) 91.

14 G. W. Busnell, K. R. Dixon, D. T. Eadie and S. R. Stobart, *Inorg. Chem., 20* (1981) 1545.

15 M. T. Pinillos, C. Tejel, L. A. Oro, M. C. Apreda, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.,* (1989) 1133.

16 D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds,* Wiley–Interscience, New York, 2nd edn., 1986.

17 J. C. Bailar and H. Itatani, *Inorg. Chem., 4* (1965) 1618.

18 H. H. Murray, R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem., 27* (1988) 26.

19 C. S. Gibson and W. M. Colles, *J. Chem. Soc.,* (1931) 2407.

20 W. W. Porterfield, *Inorganic Chemistry: A Unified Approach,* Addison-Wesley, Reading, MA, 1984, pp. 166–168.

21 R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem., 27* (1988) 4179.

22 A. M. Mazany and J. P. Fackler, Jr., *J. Am. Chem. Soc., 106* (1984) 801.

23 R. G. Raptis, H. H. Murray and J. P. Fackler, Jr., *Acta Crystallogr., Sect. C, 44* (1988) 970.

24 R. G. Raptis, L. C. Porter, R. J. Emrich, H. H. Murray and J. P. Fackler, Jr., *Inorg. Chem., 29* (1990) 4408.

25 (a) J. F. Weiss, G. Tollin and J. T. Yoke III, *Inorg. Chem., 3* (1964) 1344; (b) J. T. Yoke III, J. F. Weiss and G. Tollin, *Inorg. Chem., 2* (1963) 1201.

26 G. Minghetti, G. Banditelli and F. Bonati, *Inorg. Chem., 18* (1979) 658.

27 A. L. Bandini, G. Banditelli, F. Bonati, G. Minghetti and M. T. Pinillos, *Inorg. Chim. Acta, 99* (1985) 165.