

Synthesis and molecular structure of $\{[\text{Pd}_2(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P})_2(\mu_3\text{-}3,5\text{-dmpz-}N,N',\text{C}^4)_2\text{Ag}(\mu\text{-ClO}_4)]_2\}$ ($3,5\text{-dmpz} = 3,5\text{-dimethylpyrazolato}$), a silver derivative showing unprecedented $\eta^1\text{-azolato}$ coordination

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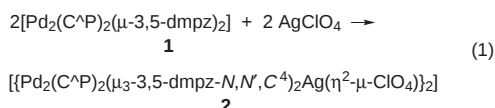
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The reaction of $[\text{Pd}_2(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P})_2(\mu_3\text{-}3,5\text{-dmpz})_2]$ (1) with AgClO_4 renders $\{[\text{Pd}_2(\text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2-\kappa\text{C},\text{P})_2(\mu_3\text{-}3,5\text{-dmpz-}N,N',\text{C}^4)_2\text{Ag}(\eta^2\text{-}\mu\text{-ClO}_4)]_2\}$ (2), a palladium–silver derivative displaying an unprecedented dmpz bridging ligand η^1 bonded to the Ag centers, involving only the C^4 atom of each dmpz ligand.

The chemistry of dimetallic compounds containing two $\mu\text{-azolato}$ bridging groups has been intensively developed in the last three decades,¹ especially in the case of dirhodium and diiridium derivatives.² Studies of these systems have included substitution reactions,^{2a,b} oxidative additions,^{2c,d} kinetics,^{2e,f} electrochemistry,^{2g} photochemistry,^{2h} hydroformylation reactions²ⁱ and theoretical studies.^{2j} Pyrazolate ligands have a proven ability to hold two metal atoms in close proximity, while permitting a wide range of intermetallic separations. Compounds with two bridging azolato groups show a boat conformation of the central ' M_2N_4 ' six membered ring. The π -electron rich cleft between the two azolato rings in these molecules offers a potentially interesting site for further complexation (Fig. 1). To our knowledge there has been no previous report of a complex in which a dimetallic ' $\text{M}_2(\mu\text{-azolato})_2$ ' moiety uses its π -electron system to accommodate a transition metal cation.

In view of the paucity of dipalladium and diplatinum complexes with $\mu\text{-azolato}$ bridging groups³ we decided to explore the synthesis and reactivity of compounds of the type $[\text{M}_2(\text{C}^\wedge\text{P})_2(\mu\text{-L})_2]$ [$\text{M} = \text{Pd}, \text{Pt}$; $\text{C}^\wedge\text{P} = \text{CH}_2\text{C}_6\text{H}_4\text{P}(\text{o-tolyl})_2$; $\text{HL} = \text{pyrazole (Hpz)}, 3,5\text{-dimethylpyrazole (H}3,5\text{-dmpz)}$]. The reaction of $[\text{Pd}_2(\text{C}^\wedge\text{P})_2(\mu_3\text{-}3,5\text{-dmpz})_2]$ (1)[†] with AgClO_4 renders 2 $\ddagger$ [eqn. (1)].



Compound 2, as has been established by an X-ray study $\S$ (Fig. 2), is formed by two $\{[\text{Pd}_2(\text{C}^\wedge\text{P})_2(\mu_3\text{-}3,5\text{-dmpz-}N,N',\text{C}^4)_2\text{Ag}(\eta^2\text{-}\mu\text{-ClO}_4)]\}$ units bridged by two perchlorate groups and related to each other by a crystallographic center of symmetry. Each unit contains a dinuclear palladium fragment

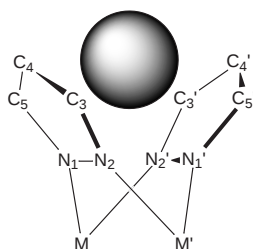


Fig. 1 Schematic diagram showing a guest atom in the cleft formed by the two pyrazolate rings of the moiety $[\text{Pd}_2(\text{C}^\wedge\text{P})_2(\mu_3\text{-}3,5\text{-dmpz})_2]$. The atom numbering scheme used in the NMR analyses is shown.

' $\text{Pd}_2(\text{C}^\wedge\text{P})_2(\mu_3\text{-}3,5\text{-dmpz})_2$ ' and a silver atom located in the cleft between the two dmpz groups and η^1 -bonded to the C^4 atoms of the dmpz ligands.

The palladium fragment ' $\text{Pd}_2(\text{C}^\wedge\text{P})_2(\mu_3\text{-}3,5\text{-dmpz})_2$ ' consists of a typical head to tail dimer with bridged 3,5-dmpz anions, with the usual boatlike conformation of the Pd_2N_4 six-membered metallocycle. The $\text{Pd}\cdots\text{Pd}$ distance (3.2297(7) Å) is slightly longer than those observed in other Pd (or Pt) complexes with two pyrazolate bridging ligands.^{3a–c} The bond distances and angles in the metallocycles in compound 2 are similar to those observed in palladium and platinum compounds

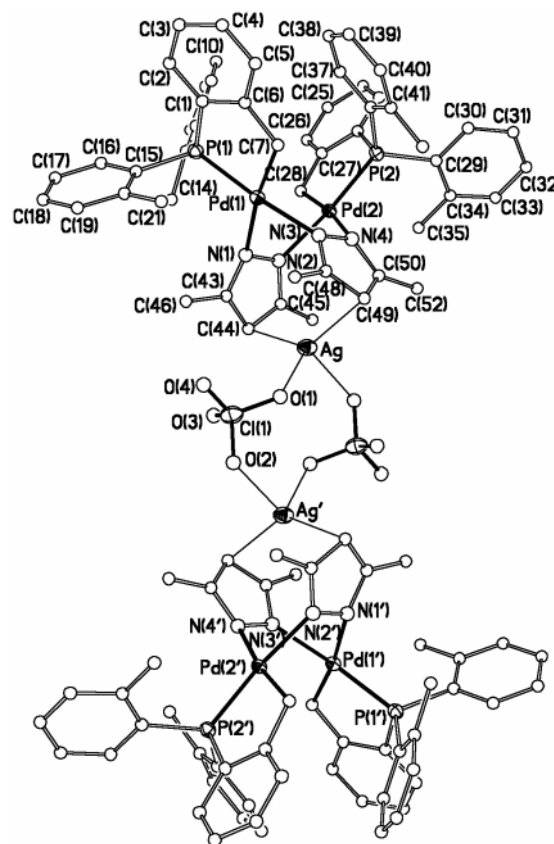


Fig. 2 Molecular structure for compound 2. Selected bond distances: $\text{Pd}(1)\text{--C}(7) = 2.034(5)$, $\text{Pd}(1)\text{--P}(1) = 2.2251(13)$, $\text{Pd}(1)\text{--C}(28) = 2.042(5)$, $\text{Pd}(2)\text{--P}(2) = 2.2268(13)$, $\text{Pd}(1)\text{--N}(1) = 2.138(4)$, $\text{Pd}(1)\text{--N}(3) = 2.097(4)$, $\text{Pd}(2)\text{--N}(2) = 2.092(4)$, $\text{Pd}(2)\text{--N}(4) = 2.136(4)$, $\text{Ag--C}(44) = 2.410(5)$, $\text{Ag--C}(49) = 2.420(5)$, $\text{Ag--O}(1) = 2.431(4)$, $\text{Ag--O}(2') = 2.464(4)$, $\text{N}(1)\text{--N}(2) = 1.371(6)$, $\text{N}(1)\text{--C}(43) = 1.331(6)$, $\text{C}(43)\text{--C}(44) = 1.405(7)$, $\text{C}(44)\text{--C}(45) = 1.410(7)$, $\text{N}(2)\text{--C}(45) = 1.332(6)$, $\text{N}(3)\text{--N}(4) = 1.375(6)$, $\text{N}(3)\text{--C}(48) = 1.342(6)$, $\text{C}(48)\text{--C}(49) = 1.405(7)$, $\text{C}(49)\text{--C}(50) = 1.405(7)$, $\text{N}(4)\text{--C}(50) = 1.330(7)$ Å. Selected bond angles: $\text{Ag--C}(44)\text{--C}(43) = 94.5(3)$, $\text{Ag--C}(44)\text{--C}(45) = 89.1(3)$, $\text{Ag--C}(49)\text{--C}(48) = 86.7(3)$, $\text{Ag--C}(49)\text{--C}(50) = 95.7(3)^\circ$.

containing the same C[∧]P group.⁴ The dmpz groups are planar, and the angle between them in each 'Pd₂(C[∧]P)₂(μ-3,5-dmpz)₂' fragment is 44.8°. Bond lengths and angles around the N and C atoms of the 3,5-dmpz are identical to those observed in other complexes.^{3a}

The extraordinary structural feature of this compound is the unprecedented coordination mode of the 3,5-dmpz groups to Ag⁺. The silver cation is located in the cleft between, and approximately equidistant from, the two 3,5-dmpz rings at a distance of 2.410(5) Å and 2.420(5) Å from C(44) and C(49) respectively, the C⁴ atom of each dmpz ring (Fig. 1). The Ag–C(49) and Ag–C(44) vectors are nearly perpendicular to the corresponding dmpz rings, the angles between the perpendicular to the corresponding rings and the Ag–C⁴ bonds being 5.9° [Ag–C(49)] and 4.0° [Ag–C(44)] respectively. The long Ag–C(48) (2.728 Å), Ag–C(50) (2.917 Å), Ag–C(43) (2.883 Å) and Ag–C(45) (2.773 Å) distances seem to exclude any bond interaction between Ag and these atoms. So, both 3,5-dmpz rings seem to be η¹-coordinated [C(44) and C(49)] to the silver atom. The Ag–C bond lengths (ca. 2.415 Å) are similar to the shortest values found in Ag–η¹-arene complexes such as [AgB₁₁CH₁₂·2C₆H₆] [2.400(7) Å],^{5a} [Ag(deltaphane)-(O₃SCF₃)] (2.41–2.48 Å),^{5b} [Ag{(Z)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene}(O₃SCF₃)] [2.579(4) Å],^{5c} and [indene-AgClO₄]₂ [2.47(2) Å],^{5d} and are clearly shorter than the Ag–C distances observed in Ag–η²-arene complexes, such as [Ag(25,26,27,28-tetramethoxycalix(4)arene)(NO₃-O,O')] [2.504(5), 2.643(5), 2.527(5), 2.549(5) Å],^{5e} [{AuAg(C₆F₅)₂(C₆H₆)_n}] [2.48, 2.50 Å]^{5f} and [catena(μ-η⁴-rac(2)(1,5-naphthalino(2)paracyclophane)(μ-perchlorato-O,O',O'')silver(i)] [2.365, 2.607 Å].^{5g}

Finally, the Ag coordination is completed by two Ag–O bonds [Ag–O(1) = 2.431(4), Ag–O(2A) = 2.464(4) Å], one from each of the two bridging ClO₄ groups, in such a way that Ag shows a distorted tetrahedral coordination environment. The Ag–O bond distances are in the range found in complexes with triflate,^{5b} nitrate^{5e} or for μ-ClO₄ bonded to silver.⁶

As has been mentioned, the bond distances and angles in the dmpz groups in **2** are very similar to those observed in uncomplexed 'M₂L₂(μ-pz)₂' compounds, indicating that in spite of the η¹ interaction to the silver centre, the pyrazolato rings maintain their aromaticity. The mass spectrum (FAB⁺) of **2** shows the molecular peak for the cation [Pd₂(C[∧]P)₂(μ-3,5-dmpz-N,N',C⁴)₂Ag]⁺ (1119). The sharp ³¹P, ¹H and ¹³C NMR signals of **2** at room temperature and their observed shifts with respect to those in the starting material, **1**, indicate that the silver–η¹-dmpz bonds are present in solution. Especially significant are the changes observed in the ¹³C NMR spectrum of **2** with respect to that of **1**, mainly in the signal due to the C atoms η¹-bonded to silver, the C⁴ atom of each dmpz group. For compound **2** it appears at 86.8 ppm, i.e., shifted upfield by 16.34 ppm, and which becomes a multiplet, probably as a consequence of the coupling of the C⁴ atoms to the P, ¹⁰⁷Ag, and ¹⁰⁹Ag nuclei. Due to the poor resolution of this spectrum, no individual values for the coupling constants could be extracted.

Studies of the reactivity of other palladium and platinum pyrazolate complexes towards other Lewis acid metal complexes are in progress.

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Notes and references

† [Pd₂(C[∧]P)₂(μ-3,5-dmpz)₂] (**1**): NMR spectra (RT, CD₂Cl₂) were recorded on either a Varian Unity-300 or a Bruker ARX-300 spectrometer using the standard references: δ_p 35.6 (s); δ_H 5.57 (s, 2H, H⁴ 3,5-dmpz) 1.68 (s, 6H, 3,5-dmpz), 2.32 (s, 6H, 3,5-dmpz), 2.28 [s, 2H, CH₂ (C[∧]P)], 2.83 [s, 2H, CH₂ (C[∧]P)], 2.87 [s, 6H, Me (C[∧]P)], 1.61 [s, 6H, Me (C[∧]P)]; δ_C 145.7 [d, ³J(C–P) 3.0 Hz], 147.2 [d, ³J(C–P) 2.3 Hz, C³, C⁵ (3,5-dmpz)], 103.1 [d, C⁴, ⁴J(C–P) 3.2 Hz], 14.3 (s, Me, 3,5-dmpz), 12.6 (s, Me, 3,5-dmpz), 28.6 (s, CH₂, C[∧]P), 22.3 [d, ³J(C–P) 13.8 Hz, Me (C[∧]P)], 21.6 [d, ³J(C–P) 8.6 Hz, Me (C[∧]P)].

‡ [{Pd₂(C[∧]P)₂(μ-3,5-dmpz-N,N',C⁴)₂Ag(η²-μ-ClO₄)₂] (**2**). To a solution of [Pd₂(C[∧]P)₂(μ-3,5-dmpz)₂] (**1**; 0.1136 g, 0.112 mmol) in CH₂Cl₂–OEt₂ (50 : 4 mL) was added AgClO₄ (0.0233 g, 0.112 mmol), and the mixture was stirred for 5 h at room temperature. After filtration through Celites, the resulting solution was evaporated to dryness. Upon addition of 15 mL of Et₂O and 2 mL of CH₂Cl₂ a white solid formed immediately, **2** (0.08 g, 58.50%). (Found: C, 51.10; H, 3.96; N, 4.58. Ag₂C₁₀₄Cl₂H₁₀₈N₈O₈P₄Pd₄ requires C, 51.31; H, 4.47; N, 4.60%). NMR spectra (RT, CDCl₃): δ_p 39.1 (s); δ_H 5.52 (s, H⁴, 3,5-dmpz), 2.43 (s, Me, 3,5-dmpz), 1.91 (s, Me, 3,5-dmpz), 2.53 [d, ²J(H–H) 15.0 Hz, CH₂ (C[∧]P)], 3.11 [d, CH₂ (C[∧]P)], 2.74 [s, Me (C[∧]P)], 1.88 [s, Me (C[∧]P)]; δ_C 152.1 (s), 151.7 (s) [C³, C⁵ (3,5-dmpz)], 86.8 [m, C⁴ (3,5-dmpz)], 14.6 [s, Me (3,5-dmpz)], 13.2 [s, Me (3,5-dmpz)], 29.0 [s, CH₂ (C[∧]P)], 22.7 [d, ³J(C–P) 7.2 Hz, Me (C[∧]P)], 22.2 [d, ³J(C–P) 12.6 Hz, Me (C[∧]P)].

§ Crystal data for 2·CH₂Cl₂·C₅H₁₂: C₅₂H₅₄AgCl₂N₈O₄P₂Pd₂·CH₂Cl₂·C₅H₁₂, *M* = 1374.12; triclinic, space group P1 (no. 2), *a* = 12.686(2), *b* = 15.050(2), *c* = 17.349(3) Å, α = 112.190(15), β = 108.53(2), γ = 90.996(15)°, *U* = 2872.2(7) Å³, *Z* = 1, *T* = 150 K, μ = 1.201 mm^{−1}, graphite monochromated Mo-Kα radiation, λ = 0.71073 Å, yellowish prism with dimensions 0.45 × 0.22 × 0.20 mm, Nonius CAD4 diffractometer, ω scans, data collection range 4 < 2θ < 50°, semiempirical absorption correction based on ψ scans, transmission factors 0.891–0.861, 653 refined parameters with 10049 unique (*R*_{int} = 0.015) reflections (10547 measured). Full-matrix least-squares refinement of this model against *F*² (program SHELXL-93⁷) converged to final residual indices *R*₁ = 0.043, *wR*₂ = 0.111. (*R* factors defined in ref. 7), g.o.f. 1.03. Final difference electron density maps showed six peaks above 1 e Å^{−3} (from 2.68 to 1.35; largest diff. hole −1.45) lying close to the solvent molecules. CCDC 182/1038.

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