Synthesis and molecular structure of $[\{Pd_2(CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P)_2(\mu_3\text{-3,5-dmpz-}N,N',C^4)_2Ag(\mu\text{-}ClO_4)\}_2]$ (3,5-dmpz = 3,5-dimethylpyrazolato), a silver derivative showing unprecedented η^1-azolato coordination

Larry R. Falvello, Juan Forniés,* Antonio Martín, Rafael Navarro, Violeta Sicilia and Pablo Villarroya

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C. S. I. C., 50009 Zaragoza, Spain. E-mail:forniesj@posta.unizar.es

Received (in Cambridge, UK), 29th July 1998, Accepted 29th September 1998

The reaction of $[Pd_2(CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P)_2(\mu\text{-3,5-dmpz})_2]$ (1) with $AgClO_4$ renders $[\{Pd_2(CH_2C_6H_4P(o\text{-tolyl})_2\text{-}\kappa C,P)_2(\mu_3\text{-3,5-dmpz-}N,N',C^4)_2Ag(\eta^2\text{-}\mu\text{-}ClO_4)\}_2]$ (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 μ-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 reactions[2i] 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 '$M_2(\mu\text{-azolato})_2$' moiety uses its π-electron system to accommodate a transition metal cation.

In view of the paucity of dipalladium and diplatinum complexes with μ-azolato bridging groups[3] we decided to explore the synthesis and reactivity of compounds of the type $[M_2(C\text{^}P)_2(\mu\text{-}L)_2]$ [M = Pd, Pt; C^P = $CH_2C_6H_4P(o\text{-tolyl})_2$; HL = pyrazole (Hpz), 3,5-dimethylpyrazole (H3,5-dmpz)]. The reaction of $[Pd_2(C\text{^}P)_2(\mu\text{-3,5-dmpz})_2]$ (**1**)† with $AgClO_4$ renders **2**‡ [eqn. (1)].

$$\underset{\mathbf{1}}{2[Pd_2(C\text{^}P)_2(\mu\text{-3,5-dmpz})_2]} + 2\,AgClO_4 \longrightarrow \underset{\mathbf{2}}{[\{Pd_2(C\text{^}P)_2(\mu_3\text{-3,5-dmpz-}N,N',C^4)_2Ag(\eta^2\text{-}\mu\text{-}ClO_4)\}_2]} \quad (1)$$

Compound **2**, as has been established by an X-ray study§ (Fig. 2), is formed by two $\{Pd_2(C\text{^}P)_2(\mu_3\text{-3,5-dmpz-}N,N',C^4)_2Ag(\eta^2\text{-}\mu\text{-}ClO_4)\}$ units bridged by two perchlorate groups and related to each other by a crystallographic center of symmetry. Each unit contains a dinuclear palladium fragment '$Pd_2(C\text{^}P)_2(\mu\text{-3,5-dmpz})_2$' 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.

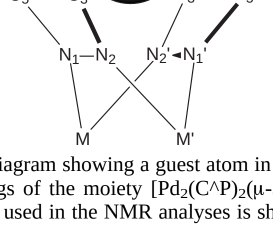

Fig. 1 Schematic diagram showing a guest atom in the cleft formed by the two pyrazolate rings of the moiety $[Pd_2(C\text{^}P)_2(\mu\text{-3,5-dmpz})_2]$ .The atom numbering scheme used in the NMR analyses is shown.

The palladium fragment '$Pd_2(C\text{^}P)_2(\mu\text{-3,5-dmpz})_2$' 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 Pd···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

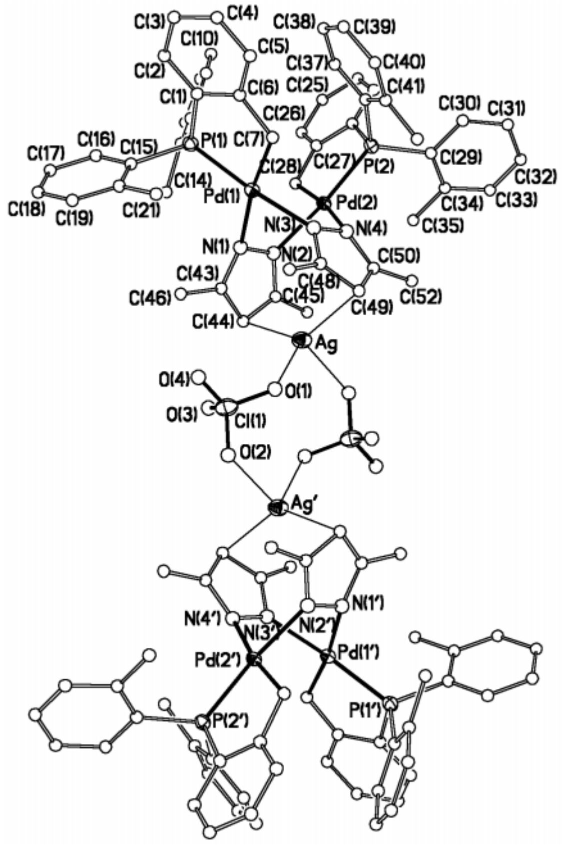

Fig. 2 Molecular structure for compound **2.** Selected bond distances: Pd(1)–C(7) = 2.034(5), Pd(1)–P(1) = 2.2251(13), Pd(2)–C(28) = 2.042(5), Pd(2)–P(2) = 2.2268(13), Pd(1)–N(1) = 2.138(4), Pd(1)–N(3) = 2.097(4), Pd(2)–N(2) = 2.092(4), Pd(2)–N(4) = 2.136(4), Ag–C(44) = 2.410(5), Ag–C(49) = 2.420(5),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

containing the same C^P group.[4] The dmpz groups are planar, and the angle between them in each '$Pd_2(C\text{^}P)_2(\mu\text{-}3,5\text{-dmpz})_2$' 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 C^4 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–C^4 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 η^1-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–η^1-arene complexes such as $[AgB_{11}CH_{12}\cdot 2C_6H_6]$ [2.400(7) Å],[5a] [Ag(deltaphane)-(O_3SCF_3)] (2.41–2.48 Å),[5b] [Ag{(*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene}(O_3SCF_3)] [2.579(4) Å],[5c] and [indene·$AgClO_4$]$_2$ [2.47(2) Å],[5d] and are clearly shorter than the Ag–C distances observed in Ag–η^2-arene complexes, such as [Ag(25,26,27,28-tetramethoxycalix(4)arene)(NO_3-*O*,*O*′)] [2.504(5), 2.643(5), 2.527(5), 2.549(5) Å],[5e] $[\{AuAg(C_6F_5)_2(C_6H_6)_n\}]$ [2.48, 2.50 Å][5f] and [catena(μ-η^4-*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 ClO_4 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-ClO_4 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 '$M_2L_2(\mu\text{-pz})_2$' compounds, indicating that in spite of the η^1 interaction to the silver centre, the pyrazolato rings maintain their aromaticity. The mass spectrum (FAB$^+$) of **2** shows the molecular peak for the cation $[Pd_2(C\text{^}P)_2(\mu_3\text{-}3,5\text{-dmpz-}N,N',C^4)_2Ag]^+$ (1119). The sharp ^{31}P, ^1H and ^{13}C NMR signals of **2** at room temperature and their observed shifts with respect to those in the starting material, **1**, indicate that the silver–η^1-dmpz bonds are present in solution. Especially significant are the changes observed in the ^{13}C NMR spectrum of **2** with respect to that of **1**, mainly in the signal due to the C atoms η^1-bonded to silver, the C^4 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 C^4 atoms to the P, ^{107}Ag, and ^{109}Ag 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.

The authors thank the Dirección General de Enseñanza Superior (Spain) for financial support (Projects PB95-0003-C02-01 and PB95-0792).

Notes and references

† $[Pd_2(C\text{^}P)_2(\mu\text{-}3,5\text{-dmpz})_2]$ (**1**): NMR spectra (RT, CD_2Cl_2) 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, H^4 3,5-dmpz) 1.68 (s, 6H, 3,5-dmpz), 2.32 (s, 6H, 3,5-dmpz), 2.28 [s, 2H, CH_2 (C^P)], 2.83 [s, 2H, CH_2 (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, C^3,C^5 (3,5-dmpz)], 103.1 [d, C^4, ^4J(C–P) 3.2 Hz], 14.3 (s, Me, 3,5-dmpz), 12.6 (s, Me, 3,5-dmpz), 28.6 (s, CH_2, 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)].

‡ $[\{Pd_2(C\text{^}P)_2(\mu_3\text{-}3,5\text{-dmpz-}N,N',C^4)_2Ag(\eta^2\text{-}\mu\text{-}ClO_4)\}_2]$ (**2**). To a solution of $[Pd_2(C\text{^}P)_2(\mu\text{-}3,5\text{-dmpz})_2]$ (**1**; 0.1136 g, 0.112 mmol) in CH_2Cl_2–OEt_2 (50 : 4 mL) was added $AgClO_4$ (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 Et_2O and 2 mL of CH_2Cl_2 a white solid formed immediately, **2** (0.08 g, 58.50%). (Found: C, 51.10; H, 3.96; N, 4.58. $Ag_2C_{104}Cl_2H_{108}N_8O_8P_4Pd_4$ requires C, 51.31; H, 4.47; N, 4.60%). NMR spectra (RT, $CDCl_3$): δ_P 39.1 (s); δ_H 5.52 (s, H^4, 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, CH_2 (C^P)], 3.11 [d, CH_2 (C^P)], 2.74 [s, Me (C^P)], 1.88 [s, Me (C^P)]; δ_C 152.1 (s), 151.7 (s) [C^3, C^5 (3,5-dmpz)], 86.8 [m, C^4 (3,5-dmpz)], 14.6 [s, Me (3,5-dmpz)], 13.2 [s, Me (3,5-dmpz)], 29.0 [s, CH_2 (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**·$CH_2Cl_2\cdot C_5H_{12}$: $C_{52}H_{54}AgClN_4O_4P_2Pd_2\cdot CH_2Cl_2\cdot C_5H_{12}$, $M = 1374.12$; triclinic, space group $P1$ (no. 2), $a = 12.686(2)$, $b = 15.050(2)$, $c = 17.349(3)$ Å, $\alpha = 112.190(15)$, $\beta = 108.53(2)$, $\gamma = 90.996(15)°$, $U = 2872.2(7)$ Å^3, $Z = 1$, $T = 150$ K, $\mu = 1.201$ mm^{-1}, graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, yellowish prism with dimensions 0.45 × 0.22 × 0.20 mm, Nonius CAD4 diffractometer, ω scans, data collection range $4 < 2\theta < 50°$, 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-93[7]) converged to final residual indices $R1 = 0.043$, $wR2 = 0.111$. (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.

1 (*a*) S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115; (*b*) A. P. Sadimenko and S. S. Basson, *Coord. Chem. Rev.*, 1996, **147**, 247; (*c*) G. La Monica and G. A. Ardizzoia, *Prog. Inorg. Chem.*, 1997, **46**, 151; (*d*) J. E. Cosgriff and G. B. Deacon, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 286.

2 (*a*) R. Usón, L. A. Oro, M. A. Ciriano, D. Carmona, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem.*, 1982, **224**, 69; (*b*) C. Tejel, J. M. Villoro, M. A. Ciriano, J. A. López, E. Eguizabal, F. J. Lahoz, V. I. Bakhmutov and L. A. Oro, *Organometallics*, 1996, **15**, 2967; (*c*) D. O. K. Fjeldsted, S. R. Stobart and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1985, **107**, 8258; (*d*) A. Tiripicchio, F. J. Lahoz, L. A. Oro and M. T. Pinillos, *J. Chem. Soc., Chem. Commun.*, 1984, 936; (*e*) R. D. Brost and S. R. Stobart, *Inorg. Chem.*, 1989, **24**, 4308; (*f*) R. D. Brost, D. O. K. Fjeldsted and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1989, 488; (*g*) D. C. Boyd, G. S. Rodman and K. R. Mann, *J. Am. Chem. Soc.*, 1986, **108**, 1779; (*h*) J. L. Marshall, S. R. Stobart and H. B. Gray, *J. Am. Chem. Soc.*, 1984, **106**, 3027; (*i*) C. Claver, P. Kalck, M. Ridmy, A. Thorez, L. A. Oro, M. T. Pinillos, M. C. Apreda, F. H. Cano and C. Foces-Foces, *J. Chem. Soc., Dalton Trans.*, 1988, 1523; (*j*) D. L. Lichtenberger, A. S. Copenhaver, H. B. Gray, J. L. Marshall and M. D. Hopkins, *Inorg. Chem.*, 1988, **27**, 4488.

3 (*a*) V. K. Jain, S. Kannan and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1992, 2231; (*b*) V. K. Jain, S. Kannan and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1993, 3625; (*c*) V. Y. Kukushkin, E. A. Aleksandrova, V. M. Leovac, E. Z. Iveges, V. K. Belsky and V. E. Konovalov, *Polyhedron*, 1992, **11**, 2691; (*d*) V. K. Jain and S. Kannan, *Polyhedron*, 1992, **11**, 27; (*e*) A. Singhal, V. K. Jain and S. Kannan, *J. Organomet. Chem.*, 1993, **447**, 317; (*f*) G. López, J. Ruiz, G. García, J. M. Martí, G. Sánchez and J. García, *J. Organomet. Chem.*, 1991, **412**, 435; (*g*) G. López, J. Ruiz, G. García, C. Vicente, J. Casabó, E. Molins and C. Miravitlles, *Inorg. Chem.*, 1991, **30**, 2605.

4 (*a*) W. A. Herrmann, Ch. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller and H. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1844; (*b*) L. R. Falvello, J. Forniés, A. Martín, R. Navarro, V. Sicilia and P. Villarroya, *Inorg. Chem.*, 1997, **36**, 6166.

5 (*a*) K. Shelly, D. C. Finster, Y. J. Lee, W. R. Scheidt and C. A. Reed, *J. Am. Chem. Soc.*, 1985, **107**, 5955; (*b*) H. C. Kang, A. W. Hanson, B. Eaton and V. Boekelheide, *J. Am. Chem. Soc.*, 1985, **107**, 1979; (*c*) J. E. Gano, G. Subramaniam and R. Birnbaum, *J. Org. Chem.*, 1990, **55**, 4760; (*d*) P. F. Rodesiler, E. A. Hall Griffith and B. L. Amma, *J. Am. Chem. Soc.*, 1972, 761; (*e*) W. Xu, R. J. Puddephatt, K. W. Muir and A. A. Torabi, *Organometallics*, 1994, **13**, 3054; (*f*) R. Usón, A. Laguna, M. Laguna and B. R. Manzano, *J. Chem. Soc., Dalton Trans.*, 1984, 285; (*g*) H. Schmidbaur, W. Bublack, M. W. Haenel, B. Huber and G. Muller, *Z. Naturforsch. Teil B*, 1988, **43**, 702.

6 (*a*) S. Kitagawa, M. Kondo, S Kawata, S. Wada, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1995, **34**, 1455.

7 G. M. Sheldrick, SHELXL-93, a Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

Communication 8/05938A