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Synthesis and X-ray crystal structure of an anionic heteronuclear metallamacrocyclic triangle†

José Vicente,*[a] María-Teresa Chicote,[a] Miguel M. Alvarez-Falcón[a] and Peter G. Jones*[b]

[a] *Grupo de Química Organometálica, Departamento de Química Inorgánica, Universidad de Murcia, Aptdo. 4021, Murcia, 30071 Spain. E-mail: jvs1@um.es; Fax: +34 968 364143; Tel: +34 968 364143; http://www.um.es/gqo/*

[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, 38023 Braunschweig, Germany. E-mail: p.jones@tu-bs.de*

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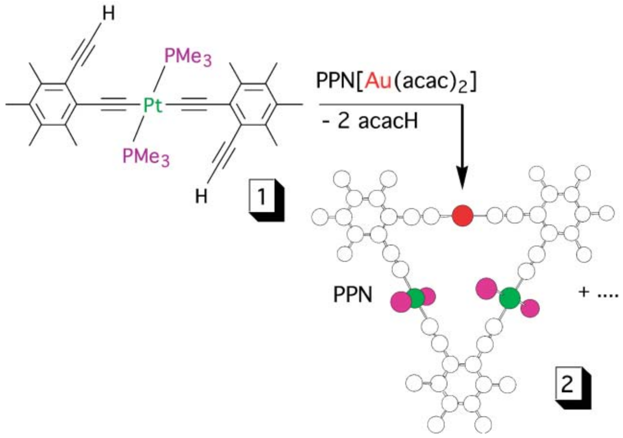
***trans*-[Pt{C≡C(Ar)C≡CH}$_2$(PMe$_3$)$_2$] (Ar = C$_6$Me$_4$-3,4,5,6) (1) reacts with PPN[Au(acac)$_2$] (Hacac = acetylacetone; 1 : 1.16 molar ratio; PPN = (Ph$_3$P)$_2$N) to give PPN[{Au{Pt(PMe$_3$)$_2$}$_2$}{μ-Ar(C≡C)$_2$}$_3$] (2) the crystal structure of which showed the anions as quasi equilateral triangles stacked parallel to each other through C–H···Au interactions, resulting in channels of rhombic cross-section.**

The growing interest in the search for novel metallamacrocycles is associated with their ability to mimic biological systems, and their relationship with supramolecular chemistry, intramolecular self-assembly, molecular recognition, crystal engineering, nanotechnology and catalysis. The concepts, principles and strategies on which the development of this chemistry is based have recently been widely reviewed.[1,2] In spite of their connection with such varied fields, they form a homogeneous group of compounds because: (i) most use N donor ligands to coordinate the metal centers, (ii) most have the metals at the corners, (iii) the non-metal atoms in the cycle are different (usually, C, N, O) and they are (iv) quadrilateral,[2] (v) neutral or cationic, and (vi) homonuclear. In this communication, we report a novel type of metallamacrocycle which is the first not to follow any of the above-mentioned characteristics.

Trying to extend the limits of the "acac method"[3] we prepared *trans*-[Pt{C≡C(Ar)C≡CH}$_2$(PMe$_3$)$_2$] (Ar = C$_6$Me$_4$-3,4,5,6) (**1**)† and reacted it with PPN[Au(acac)$_2$][4] (1 : 1.16, in degassed CH$_2$Cl$_2$ under N$_2$). The addition of Et$_2$O to the concentrated reaction mixture produced an orange suspension from which the complex PPN[{Au{Pt(PMe$_3$)$_2$}$_2$}{μ–Ar(C≡C)$_2$}$_3$] (**2**)† was isolated in 55% yield (Scheme 1).



Scheme 1

When a 2 : 1 molar ratio (Pt : Au) was used, the NMR spectra of the mixture revealed the presence of unreacted **1** along with minor amounts of **2** and other products, which is consistent with the necessary presence of two equivalents of the acac anion per mol of complex **1** (*i.e.* equimolar amounts of complexes **1** and [Au(acac)$_2$]$^-$) to form the dianionic bridging ligand C≡C(Ar)C≡C^{2-}. The role of the acac ligand is not simply that of a base because the reaction between **1** and [Au(acac)$_2$]$^-$ (2 : 1) with excess of Et$_2$NH gives a mixture not containing complex **2**.

Single-crystal X-ray analysis of **2**·H$_2$O shows the anions (Fig. 1), PPN cations and a lattice H$_2$O molecule.‡ The anion is a 21-membered metallacycle of a quasi equilateral triangular form, made up only of carbon and metal atoms with Cent-C–C≡C–M–C≡C–C-Cent sides of 11.96 (M = Au) and 12.00, 12.01 (M = Pt) Å length, with the vertices at the centroids (Cent) of the aryl rings (see ESI for details†). The triangles are nearly planar (mean deviation 0.22 Å) and stack parallel to the *a* axis, each rotated by 60° with respect to its closest neighbours (Fig. 2); note that the cell is approximately hexagonal in form. The following intermolecular C–H···Au interactions (normalised to C–H 1.08 Å) are observed from the methyl hydrogens of both PMe$_3$ ligands above and below one platinum atom: H···Au, 2.80, 2.85, 2.88 Å; C–H···Au, 161, 163, 158°. This stacking results in the formation of metallatubes of rhombic cross-section (Fig. 3) with the PPN cations at the periphery. Columnar packing of [Au(pyrazolate)]$_3$ triangles has been observed previously.[5]

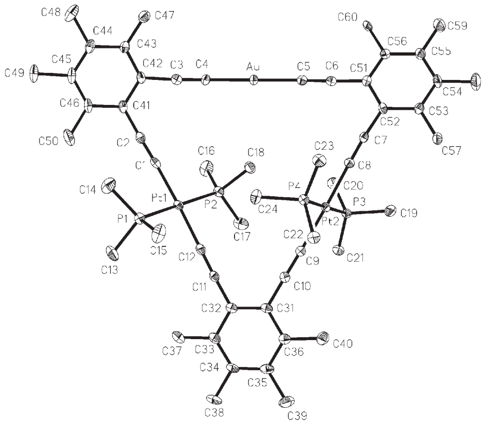


Fig. 1 Ellipsoid representation of the anion of **2** (50% probability level; hydrogens omitted for clarity).

A search of the Cambridge Crystallographic Database[6] reveals that **2**·H$_2$O is the first metallamacrocyclic triangle that is (i) anionic, (ii) heteronuclear or (iii) a carbametallacycle containing gold or platinum. The nonbonding Pt–Pt (5.935Å) and Au–Pt (6.038, 6.228 Å) distances are longer than those found in other gold (3.3–4.31 Å)[7,8] or platinum (5.65 Å)[9] triangles.

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† Electronic supplementary information (ESI) available: experimental details for the preparation of **1** and **2**; listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2**; cif file for **2**. See http://www.rsc.org/suppdata/cc/b4/b409921d/

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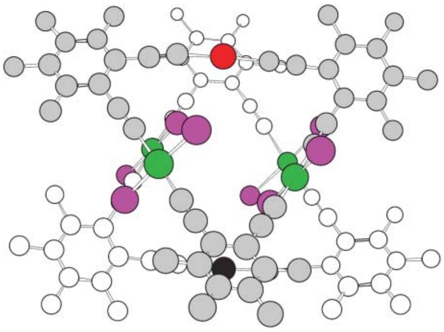

Fig. 2 Rhombic channels in **2**. The carbon atoms are in white (back) and grey (front).

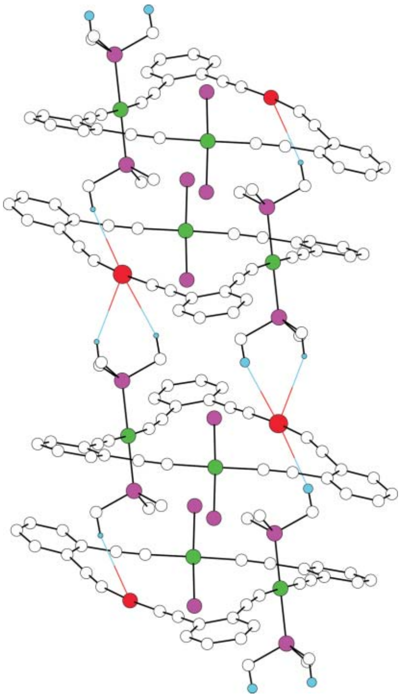

Fig. 3 Columnar stacking in **2**. The Me groups of the PMe_3 ligands not involved in CH···Au contacts and those in C_6Me_4 are omitted. In the other PMe_3 ligands, the three Me carbons and the hydrogen atoms involved in CH···Au contacts are shown.

Compared to the number of molecular ring systems described to date, triangles are surprisingly scarce.[1,2,10] Although an equilateral triangle is the expected geometry for a complex with the dianion $C{\equiv}C(Ar)C{\equiv}C^{2-}$, such as **2**, the tendency to give squares is so marked that the isolated product of the reaction of equimolar amounts of $HC{\equiv}CC_6H_4C{\equiv}CH$–2 and $[PdCl_2(PEt_3)_2]$, in the presence of CuCl as catalyst, is the square $[Pd\{C{\equiv}CC_6H_4C{\equiv}C\text{–}2\}(PEt_3)_2]_4$.[11] On occasions, the triangles form in equilibria with dimers,[8] squares,[12] or rhomboids[13] depending on subtle changes in the molecular components to be assembled.

The synthesis of other related homo- and heterometallamacrocycles is currently under investigation.

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Notes and references

‡ Crystal data for **2**·H_2O: $C_{90}H_{104}AuNOP_6Pt_2$, $M = 1988.71$, triclinic, $a = 13.444(2)$, $b = 18.759(3)$, $c = 18.827(3)$ Å, $\alpha = 118.064(6)$, $\beta = 92.078(6)$, $\gamma = 91.734(6)^\circ$, $U = 4181.2(11)$ Å^3, $T = 133(2)$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo–Kα) = 5.248 mm^{-1}, reflections: 68098 collected, 20677 independent ($R_{int} = 0.1069$). Final $wR2 = 0.1094$ (all data), $R1 = 0.0452$ [$I > 2\sigma(I)$]. Phosphine methyl hydrogens were refined as ideally staggered using a riding model; other methyls, some hydrogens of which were indistinct, as rigid groups. CCDC 243077. See http://www.rsc.org/suppdata/cc/b4/b409921d/ for crystallographic data in .cif or other electronic format.

1 M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; B. Olenyuk, A. Fechtenkötter and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1998, 1707; P. J. Stang, *Chem.–Eur. J.*, 1998, **4**, 19; J. A. R. Navarro and B. Lippert, *Coord. Chem. Rev.*, 1999, **185–186**, 653; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; G. F. Swiegers and T. J. Malefeste, *Chem. Rev.*, 2000, **100**, 3483; B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; K. Severin, *Coord. Chem. Rev.*, 2003, **245**, 3; J. J. Bodwin, A. D. Cutland, R. G. Malkani and V. L. Pecoraro, *Coord. Chem. Rev.*, 2001, **216–217**, 489–512.

2 F. Würthner, C.-C. You and C. R. Saha-Möller, *Chem. Soc. Rev.*, 2004, **33**, 133.

3 J. Vicente and M. T. Chicote, *Coord. Chem. Rev.*, 1999, **193–195**, 1143.

4 J. Vicente and M. T. Chicote, *Inorg. Synth.*, 1998, **32**, 172.

5 J. Barberá, A. Elduque, R. Giménez, F. J. Lahoz, J. A. López, L. A. Oro and J. L. Serrano, *Inorg. Chem.*, 1998, **37**, 2960.

6 CCDC, *CSD version 5.25*, January 2004.

7 H. H. Murray, R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem.*, 1988, **27**, 26; R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem.*, 1990, **297**, 5003; A. Tiripicchio, M. Tiripichio-Camellini and G. Minghetti, *J. Organomet. Chem.*, 1979, **171**, 399; L. G. Vaughan, *J. Am. Chem. Soc.*, 1970, **92**, 730; A. Hayashi, M. M. Olmstead, S. Attar and A. L. Balch, *J. Am. Chem. Soc.*, 2002, **124**, 5791; M. A. Rawashdeh-Omary, M. A. Omary, J. P. Fackler, R. Galassi, B. R. Pietroni and A. Burini, *J. Am. Chem. Soc.*, 2001, **123**, 9689.

8 F. Mohr, M. C. Jennings and R. J. Puddephatt, *Angew. Chem., Int. Ed.*, 2004, **43**, 969.

9 P. Espinet, K. Soulantica, J. P. H. Charmant and A. G. Orpen, *Chem Commun.*, 2000, 915.

10 J. Forniés, J. Gómez, E. Lalinde and M. T. Moreno, *Chem.–Eur. J.*, 2004, **10**, 888.

11 K. Onitsuka, S. Yamamoto and S. Takahashi, *Angew. Chem., Int. Ed.*, 1999, **38**, 174.

12 M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi and K. Ogura, *Chem. Commun.*, 1996, 1535; F. S. McQuillan, T. E. Berridge, C. Hongli, T. A. Hamor and C. J. Jones, *Inorg. Chem.*, 1998, **37**, 4959; M. Ferrer, L. Rodriguez and O. Rossell, *J. Organomet. Chem.*, 2003, **681**, 158; M. Ferrer, M. Mounir, O. Rossell, E. Ruiz and M. A. Maestro, *Inorg. Chem.*, 2003, **42**, 5890; K. Fujita, M. Owaki and R. Yamaguchi, *Chem Commun.*, 2002, 2964.

13 P. N. W. Baxter, J.-M. Lehn and K. Rissanen, *Chem. Commun.*, 1997, 1323; T. Yamamoto, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2003, **125**, 12309.