

Stepwise, ring-closure synthesis and characterization of a homoleptic palladium(II)-pyrazolato cyclic trimer

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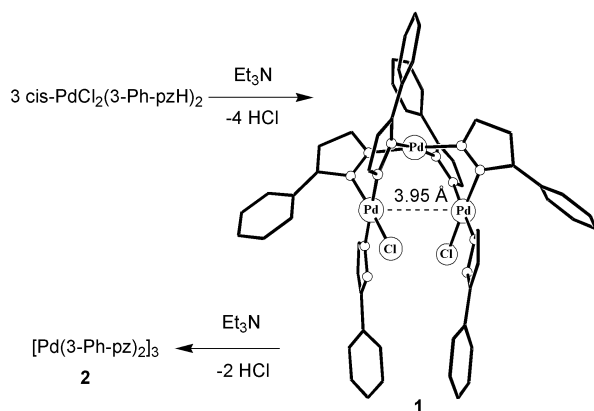
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A triangular homoleptic complex, $[\text{Pd}(\mu\text{-}3\text{-Ph-pz})_2]_3$, is prepared by the stepwise formation of an open-chain trimer and subsequent ring-closure; D_3 molecular symmetry results from the one-directional arrangement of the unsymmetrically substituted pyrazolato ligands; the palladium atoms are held in close proximity, with Pd–Pd distances of 2.997(1)–3.087(1) Å.

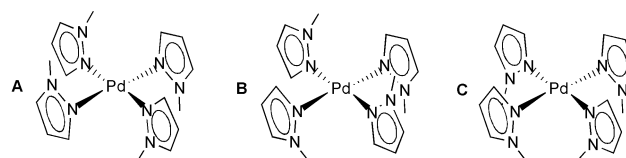
The use of rigid ligands and metal-centres of appropriate coordination algorithms for the construction of molecular assemblies of predetermined geometry is one of the main themes of supramolecular chemistry. In this context, bridging bidentate ligands with an approximately 60° angle formed between their electron donating orbitals, have been employed for the synthesis of triangular species. Metalcyclic trimers of Pd^{II} or Pt^{II} with 1,2-phenylene diisocyanide,¹ 2,2'-bipyrazine,² bis(benzimidazol)benzene,³ 4,7-phenanthroline,⁴ and triazole,⁵ are among some of the recent examples. Pyrazoles also are known to favour the formation trimeric metallacycles, and some homoleptic trimers of monovalent two-coordinate metals, $[\text{M}(\mu\text{-pz}^*)]_3$ (pz^* = pyrazolate, or substituted pyrazolate anion), have been reported for $\text{M} = \text{Cu}$, Ag and Au .^{6–8} In contrast, the homoleptic pyrazolato complexes of divalent metals, $[\text{M}(\mu\text{-pz})_2]_n$ ($\text{M} = \text{Cu}$, Zn , Cd , Hg , Pt) are typically intractable open-chain polymers,^{9,10} with the notable exception of one sealed-tube preparation of trimeric, but still intractable, $[\text{Pt}(\mu\text{-pz})_2]_3$.¹⁰ Substitution around the pyrazole ring offers the possibility of modifying the steric bulk and solubility of the resulting metal pyrazolates and may allow the solution study of complexes of the type $[\text{M}(\mu\text{-pz}^*)_2]_n$.

The reaction of $\text{cis-PdCl}_2(3\text{-Ph-pzH})_2$ † with stoichiometric amount of a base gives the open-chain trimer $\text{Pd}_3(\mu\text{-}3\text{-Ph-pz})_4(3\text{-Ph-pzH})_2\text{Cl}_2$ **1**.‡ Further reaction of **1** with base, or reaction of $\text{cis-PdCl}_2(3\text{-Ph-pzH})_2$ with excess base, give the homoleptic metalcyclic complex $[\text{Pd}(\mu\text{-}3\text{-Ph-pz})_2]_3$ **2** (Scheme 1), which has been characterised in solution§ and in the solid state.¶

Scheme 2 shows the three possible symmetric orientations of four pyrazolato ligands around a homoleptic square-planar



Scheme 1 Ball-and-stick drawing of **1** from preliminary crystallographic coordinates.



Scheme 2

metal centre. Rotation of the ligands around the metal–nitrogen bond allows the interconversion of the three coordination modes, unless the rotation is restricted, *i.e.* by bulky substituents on the pyrazole ring. Oligomerization of type A or B centres can lead to one- and two-dimensional structures, respectively, while type C centres can yield metallacycles. Complex **1** consists of type C palladium centres appropriately organized to form a metallacycle upon formal elimination of two equivalents of HCl (Scheme 1). The distances between the central and outer Pd-atoms are 3.22 and 3.31 Å, while the two outer Pd-atoms are 3.95 Å apart.

Complex **2** consists of three homoleptic, four-coordinate Pd centres, bridged by six pyrazolato ligands (Fig. 1). Even though **2** has no crystallographic symmetry, its molecular symmetry approaches D_3 , with one short and two longer Pd–Pd distances. In solution, however, the magnetic equivalence of all six 3-Ph-pz ligands indicates an average D_3 structure. The unsymmetrical substitution of the pyrazole rings results in an one-directional arrangement of phenyl groups on each side of the Pd_3 -plane (*e.g.*, three phenyls on the right side above the plane, and three on the left below it, in the enantiomer shown in Fig. 1)

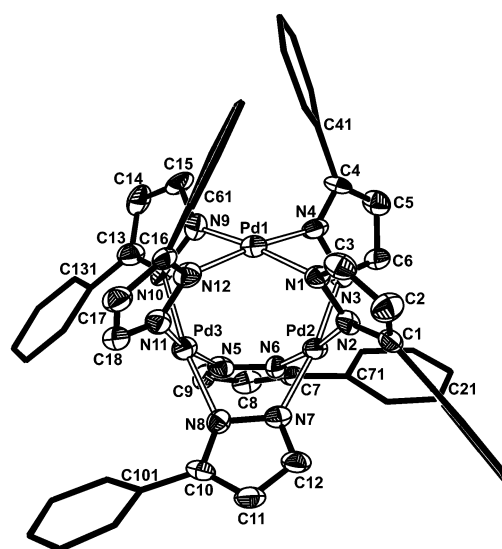


Fig. 1 An ORTEP drawing of **2** with ellipsoids at the 30% probability level. Phenyl groups as wire-frame, only *ipso* atoms labeled, hydrogen atoms omitted for clarity. Selected distances (Å) and angles ($^\circ$): Pd(1)–Pd(2) 2.997(1), Pd(1)–Pd(3) 3.079(1), Pd(2)–Pd(3) 3.087(1), Pd–N 1.963(9)–2.027(8), N–N 1.348(9)–1.364(9), N–Pd–N(*trans*) 170.2(4)–170.6(4), N–Pd–N(*cis*) 86.0(3)–92.9(3), Pd–N–N 111.1(8)–119.0(8) $^\circ$.

so as to avoid steric repulsions between them. In the centrosymmetric *Pbcn* space group, the enantiomeric forms of **2** are co-crystallized as a racemic mixture. The coordination of Pd-atoms approaches square planar, but with Pd(1), Pd(2) and Pd(3) deviating from the best-fit plane of their four N-atoms and away of the trimer centre by 0.040, 0.047, and 0.053 Å respectively. In addition, the short Pd–Pd distances, of 2.997(1)–3.087(1) Å, impose a strain on the Pd–N–N angles, which average 114.9(8)° for **2**. Those angles are more acute than the ideal 120° angle (for sp² N-atoms) found in the unrestrained structure of [Au(μ-3,5-Ph₂-pz)]₃.^{7b} The Pd–Pd distances of **2** are significantly shorter than the distances of L₂Pd(μ-pz*)₂PdL₂ complexes (3.115(1)–3.2297(7) Å),¹¹ and the corresponding M^{II}–M^{II} distances of L₂M(μ-pz*)₂ML₂ complexes of metals with smaller ionic radii than palladium, such as Cu (3.85–3.89 Å), Zn (3.69 Å) and Cd (3.96 Å),^{9d} but only marginally shorter than the Pt–Pt distances of [Pt(μ-pz)₂]₃, 3.034(1)–3.067(1) Å.¹⁰

The structure of **2** is reminiscent of that of the homoleptic carboxylate trimers [Pd(μ-OCOR)₂]₃.¹² The question of whether Pd–Pd bonding interactions exist in those trimeric palladium carboxylates with Pd–Pd distances of 3.131(1) to 3.191(1) Å, was originally raised, and answered negatively, by Cotton *et al.* several years ago.^{12b} Recently, however, palladium acetate with Pd–Pd distances of 3.081(2)–3.203(1) Å, has been shown to be luminescent.¹³ States arising from the formally non-bonding interaction of filled palladium d-orbitals and modified by d–p mixing have been proposed to be responsible for the luminescence of [Pd(OCOME)₂]₃. This, along with the discovery of even shorter Pd–Pd distances in **2**, bring up again the question regarding the nature of d⁸–d⁸ interactions in palladium trimers.

The structural parallel between carboxylate and pyrazolato complexes, exemplified here by the comparison of [Pd(μ-OCOR)₂]₃ and [Pd(μ-3-Ph-pz)₂]₃, is pointing to wide unexplored areas of pyrazole chemistry. Studies are under way to explore the implications of the palladium–pyrazolato metal-lacycle opening/closing reactions in homogeneous catalysis.

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Notes and references

† *cis*-PdCl₂(3-Ph-pzH)₂ is prepared quantitatively from the reaction of (NH₄)₂PdCl₄ and 10% excess of 3-Ph-pzH in MeOH.

‡ The poor quality of the crystals of **1** have only allowed a preliminary X-ray structural study. However, the stoichiometry and the heavy atom coordinates of **1**, as depicted in Scheme 1, are established with certainty. Preliminary crystal data for **1**: triclinic, *P* $\bar{1}$, *a* = 10.441(5), *b* = 11.228(5), *c* = 25.672(11) Å, α = 96.225(9), β = 92.231(8), γ = 106.875(9)°, *V* = 2855(2) Å³, *Z* = 2, *R*1 = 0.1526 for 667 parameters and 1610 reflections with *I* > 2σ(*I*).

§ *Preparation of 2*: to 40.5 mg (0.087 mmol) of *cis*-PdCl₂(3-Ph-pzH)₂ in 3 ml CH₂Cl₂ was added 2.4 ml of a 0.072 M NEt₃/CH₂Cl₂ solution (0.174 mmol). The orange solution changed rapidly to yellow and after 3 h the

solvent was removed under vacuum and the solid product **2** washed three times with 2 ml portions of MeOH; yield, 17.1 mg (50%), mp = 174 °C (with decomposition). ¹H NMR (300 MHz, CDCl₃, ppm): δ 5.95 (d, 1H, pz-5-H), 5.98 (d, 1H, pz-4-H), 7.49 (pseudo-t, 1H, Ph *p*-H), 7.76 (pseudo-t, 2H, Ph *m*-H), 8.43 (d, 2H, Ph *o*-H). ¹³C NMR (125.77 MHz, CDCl₃, ppm): δ 104.4 (pz-4-C), 127.1, 128.2, 128.7, 133.5 (Ph), 139.8 (pz-5-C), 150.9 (pz-3-C).

¶ *Crystal data for 2*: Bruker-AXS SMART-1000 diffractometer, *M* = 1178.20, orthorhombic, *Pbcn* (no. 60), *a* = 39.095(9), *b* = 12.364(4), *c* = 21.697(6) Å, *V* = 10487(5) Å³, *Z* = 8, *D*_c = 1.492 Mg m⁻³, *T* = 298(2) K, μ = 1.065 mm⁻¹, 25417 reflections measured (1.88 < θ < 23.27), 7535 independent (*R*_{int} = 0.158), *R*1 = 0.0526 (for 2874 reflections with *I* > 2σ(*I*)), 0.185 (all data), *wR*2 = 0.071, for 622 parameters with no restraints. CCDC reference number 179003. See <http://www.rsc.org/suppdata/cc/b2/b201301k/> for crystallographic data in CIF or other electronic format.

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