

Cite this: *Dalton Trans.*, 2012, **41**, 5782

www.rsc.org/dalton

COMMUNICATION

A water soluble and air-stable tripalladium cluster†

Fu-Ming Yang, Po-Yuan Chen, Chun-Chin Lee, Yi-Hung Liu, Shie-Ming Peng, Pi-Tai Chou and Shiuh-Tzung Liu*

Received 12th January 2012, Accepted 28th March 2012

DOI: 10.1039/c2dt30079f

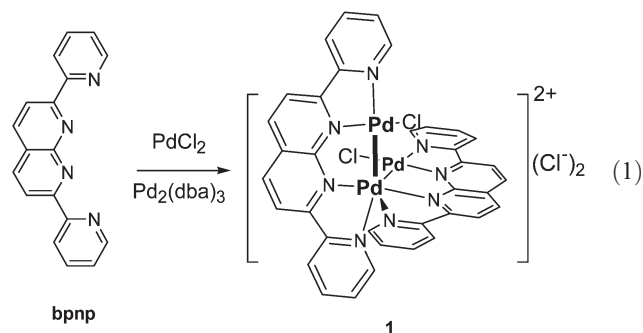
Complexation of 2,7-dipyridin-2-ynaphthyridine (bpnp) with a mixture of (PhCN)₂PdCl₂ and Pd₂(dba)₃ resulted in the formation of a water soluble and air-stable tripalladium cluster [Pd₃(bpnp)₂Cl₂]₂, which was characterized by NMR spectroscopic and X-ray crystallographic analyses.

Small-size clusters of palladium have been of interest as models of a Pd metal surface.^{1–3} Quite a few tripalladium clusters with metal–metal bonds are known and there are two types of core frameworks: triangular and linear-Pd₃ species.^{1–3} The triangular species are typically stabilized by bridging ligands on Pd–Pd bonds such as phosphido,^{4–6} halides,^{5,7,8} μ₃- or μ₂-CO,^{9–12} μ₂-SO₂,^{7,13–15} isocyanide,¹⁶ imido,¹⁷ chelating phosphines^{10–13,16,18} and π-systems.^{19–23} For linear Pd₃, Balch and coworkers reported the first crystal structure of [(CH₃NC)₆(Ph₃P)₂Pd₃]²⁺, in which each palladium exhibits slightly distorted square planar geometry with the Pd–Pd distance at 2.5921 (5) Å,²⁴ whereas Murahashi and Kurosawa revealed that the linear tri- and polynuclear palladium species could be synthesized through the stabilization of polyene ligands.^{19–21,25} A few other linear Pd₃ clusters stabilized *via* bridging ligands such as isocyanide¹⁹ and arylphosphine²³ have also been described. Here we would like to report the preparation of a tripalladium species with three metal ions arranged in a “L” shape.

When a mixture of Pd₂(dba)₃ and (PhCN)₂PdCl₂ was treated with **bpnp** (**bpnp** = 2,7-dipyridin-2-ynaphthyridine) in CH₂Cl₂ at ambient temperature, a dark brown solid precipitated out from the reaction solution (eqn (1)). Upon re-crystallization from an aqueous solution, blackish brown crystals were isolated, which is a water or methanol soluble material. The electronic absorption spectrum in water shows intense bands at 248 (log ε = 4.46), 265 (4.42), 290 (3.56), 302 (4.30), 335 (4.30) and 360 (4.34) attributed to the π–π* transition of **bpnp**. In addition, a broad band appears at 467 (3.37) nm due to ligand-to-metal charge transfer.

Department of Chemistry, National Taiwan University, 1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106. E-mail: stliu@ntu.edu.tw; Fax: + (8862)23636359

† Electronic supplementary information (ESI) available: experimental details including characterization of compounds and theoretical calculation. CCDC 850847 and 850848 for **1** and [(Pd₃(bpnp)₂Cl₂)(CoCl₄)] respectively. The contributed frontier orbitals and energy level for HOMO and LUMO are depicted in table S1. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30079f



Typical ESI-MS spectra of the complex showed the highest mass peak at *m/z* 991.02 amu corresponds to the mass of the complex ion [C₃₆H₂₄Cl₃N₈Pd₃]⁺, consisting of three palladium ions, two **bpnp** ligands and three chlorides. The molar conductivity of the complex in methanol (*Λ*_M ~ 169 cm² Ω^{–1} mol^{–1}) is consistent with formation of a 2 : 1 electrolyte, suggesting that the complex might be dissociated into [(Pd₃(bpnp)₂Cl₂)]²⁺ + 2Cl[–]. ¹H NMR spectroscopy showed twelve sets of signals for **bpnp** between 7.4 and 9.2 ppm, indicative of an un-symmetrical environment of the coordinating ligand.† These spectral data are not conclusive to disclose the details of the structure. In order to unambiguously characterize this compound, the molecular structure of **1** was determined (Fig. 1).§

The cationic part of **1** has non-crystallographic C₂ symmetry about the axis passing through Pd(1) and bisecting the mid-point

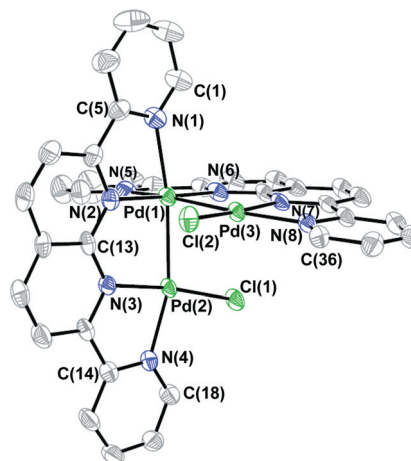
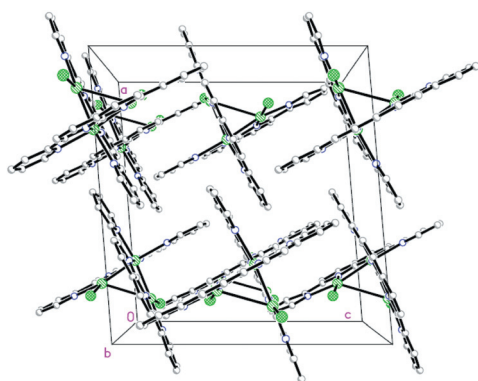


Fig. 1 ORTEP²⁷ plot of cationic part of **1** at the 50% probability level. Labels for the aromatic carbons have been omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) of **1**

Pd(1)–Pd(2)	2.5289(7)	Pd(1)–Pd(3)	2.5179(7)
Pd(2)–Cl(1)	2.2958(16)	Pd(3)–Cl(2)	2.2920(15)
Pd(1)–N(1)	2.229(6)	Pd(1)–N(2)	2.027(5)
Pd(1)–N(5)	2.184(6)	Pd(1)–N(6)	2.022(5)
Pd(2)–N(3)	2.015(5)	Pd(3)–N(7)	2.017(5)
Pd(2)–N(4)	2.086(5)	Pd(3)–N(8)	2.080(5)
Pd(2)–Pd(1)–Pd(3)	79.10(2)	N(5)–Pd(1)–N(6)	78.3(2)
N(1)–Pd(1)–N(2)	78.0(2)	N(3)–Pd(2)–N(4)	80.0(2)
N(1)–Pd(1)–N(6)	100.8(2)	N(7)–Pd(3)–N(8)	80.2(2)
N(3)–Pd(2)–Cl(1)	173.11(15)	N(7)–Pd(3)–Cl(2)	173.26(16)

**Fig. 2** Crystal packing of **1**.

defined by N(1)–N(5). Pd(1) is six-coordinate, being bonded to two **bpnp**, and two palladium centers, whereas the other two palladium ions are four-coordinate. The geometrical arrangement of the three palladium centers is unusual, in which three metal ions are arranged in a L shape as evidenced by the angle Pd(2)–Pd(1)–Pd(3) [79.10(2)°]. The bond distances of Pd(1)–Pd(2) and Pd(1)–Pd(3) are 2.5293(6) and 2.5186(6) Å, respectively. These Pd–Pd bond lengths are slightly shorter than those reported for linear or triangular tripalladium forms, presumably due to the confinement of metal ions within the pocket of **bpnp**. It is noticed that the two coordinated chloride ligands [Cl(1) and Cl(2)] are antiparallel to each other. Selected bond lengths and bond angles are listed in Table 1. All bond distances and angles are in normal ranges.

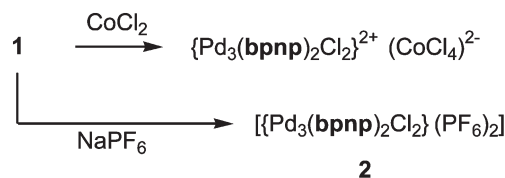
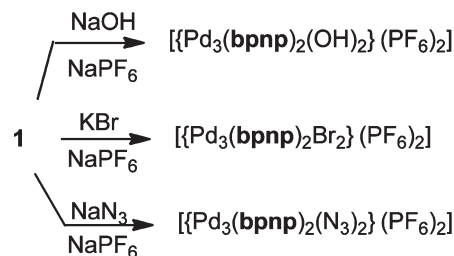
The X-ray structure analysis of **1** shows strong parallel π -stacking interactions between the aromatic rings of **bpnp** (Fig. 2). Since two **bpnp** ligands in **1** are perpendicular to each other, there is a two-dimensional π -stacking in the crystals. The centroid–centroid distance between the corresponding **bpnp** rings of the π - π interacting systems (3.82 Å) is in the normal range for this stacking mode.

For the oxidation states of palladium ions, it would be reasonable to assign that Pd(1) is zero and both Pd(2) and Pd(3) are +II based on the coordinating ligands. However, there are two more interpretations of the bonding in the compound.[¶] One assignment is +II for Pd(1) and +I for Pd(2) and Pd(3). The other is to view Pd(1) as PdL₄X₂(2+) [16 electrons] and Pd(2) as well as Pd(3) as PdL₂X₂ [18 electrons]. We have done the DFT calculation of this molecule at B3LYP/LANL2DZ (Pd) and 6-31G* (H, C, N, Cl) level. The calculated charge distribution for complex **1** is listed in Table 2. Evidently, the charge distribution of +0.307 for Pd(1), within the uncertainty of calculation, is

Table 2 The charge distribution for the selected atoms of complex **1**^a

Pd(1)	+0.307	N(3)	−0.616
Pd(2)	+0.283	N(4)	−0.495
Pd(3)	+0.283	N(5)	−0.428
Cl(1)	−0.406	N(6)	−0.578
Cl(2)	−0.406	N(7)	−0.616
N(1)	−0.428	N(8)	−0.495
N(2)	−0.578		

^a Estimated charges are based on Mulliken population analysis (see the ESI†).

**Scheme 1** Anion exchange of complex **1**.**Scheme 2** Ligand substitution of **1**.

more or less the same as that (+0.283) of Pd(2) and Pd(3). The result leads us to conclude that charges are equally distributed within three Pd atoms in compound **1** despite the difference in coordination environment between Pd(1) and Pd(2) (and Pd(3)).

Despite the lack of interaction between Pd(2) and Pd(3) in **1**, the core structure of this tripalladium species is nevertheless remarkably robust. This complex is air stable in the solid state and in solution, and is even stable in MeOH at reflux. To investigate the possibility of replacement of palladium ions with other metal ions, complex **1** was treated with an equal molar amount of CoCl₂. However, the main frame of the tripalladium cluster remained intact with the formation of dark brown crystals formulated as [{Pd₃(**bpnp**)₂Cl₂}(CoCl₄)] (Scheme 1), which was further identified by single crystal structural determination (see the ESI†). In addition, anion exchange of **1** could be achieved by treatment of the complex with NaPF₆ to form [Pd₃(**bpnp**)₂Cl₂](PF₆)₂ (**2**) (see the ESI†). Complex **2** is soluble in polar organic solvents such as acetone or THF.

Aqueous solutions of **1** (10^{−2} M) are acidic with pH~3.5. Presumably, the aquation of the chlorides in complex **1** takes place immediately, and the dissociation of protons from the coordinating aqua ligands makes the solution acidic.²⁶ In fact, the coordinating chlorides in **1** could be replaced by hydroxide ligands. By the treatment of NaOH in water, complex **1** was converted into the hydroxyl complex [Pd₃(**bpnp**)₂(OH)₂]²⁺ (Scheme 2) (see the ESI†). Such a ligand substitution is also applicable to the

bromide and azide, but not triphenylphosphine presumably due to steric reasons.

Due to the unique arrangement of palladium ions in this cluster, we are expecting many more interesting applications of this species, such as using them as building block for self-assembling, palladium-catalyzed reactions. The catalytic activity of this cluster is currently under investigation.

This work was funded by the National Science Council, Taiwan (NSC-100-2113-M002-001-MY3).

References

- † ¹H NMR data of **1**: (400 MHz, D₂O) δ 7.50(m, 2H), 7.82(d, J = 4.8 Hz, 1H), 8.08(t, J = 8 Hz, 1H), 8.2(t, J = 8 Hz, 1H), 8.39(d, J = 8 Hz, 1H), 8.64(m, 2H), 8.75(d, J = 8 Hz, 1H), 8.92(d, J = 8.8 Hz, 1H), 9.18(m, 2H).
- § Crystal data for **1**: C₃₆H₂₄Cl₄N₈OPd₃, Mw = 1045.63, Monoclinic; Space group $P2_1/c$; a = 15.4308(5), b = 16.6886(6), c = 14.3795(6) Å; α = 90°, β = 94.631(3)°, γ = 90°; V = 3690.9(2) Å³; Z = 4; $\rho_{\text{calcd.}}$ = 1.882 Mg m⁻³; $F(000)$ 2040; Crystal size 0.30 × 0.20 × 0.10 mm³, reflections collected: 28 632; independent reflections: 7989 [$R(\text{int})$ = 0.0397]; θ range 2.92 to 27.50°; goodness-of-fit on F^2 1.000; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0415, wR_2 = 0.1481; R indices (all data): R_1 = 0.0679, wR_2 = 0.1553.
- ¶ As suggested by the reviewer, it is quite unlikely for an octahedral coordination of a Pd(0) center.
- 1 P. D. Harvey, Y. Mugnier, D. Lucas, D. Evrard, F. Lemaître and A. Vallat, *J. Cluster Sci.*, 2004, **15**, 63.
- 2 A. D. Burrows and D. M. P. Mingos, *Coord. Chem. Rev.*, 1996, **154**, 19.
- 3 R. J. Puddephatt, L. Manojlovic-Muir and K. W. Muir, *Polyhedron*, 1990, **9**, 2767.
- 4 P. W. Dyer, J. Fawcett, M. J. Hanton, D. M. P. Mingos and A.-M. Williamson, *Dalton Trans.*, 2004, 2400.
- 5 K. R. Dixon and A. D. Rattray, *Inorg. Chem.*, 1978, **17**, 1099.
- 6 M. Sommovigo, M. Pasquali, F. Marchetti, P. Leoni and T. Beringbelli, *Inorg. Chem.*, 1994, **33**, 2651.
- 7 A. D. Burrows, A. A. Gosden and C. M. Hill, *J. Organomet. Chem.*, 1993, **452**, 251.
- 8 G.-G. Luo, R.-B. Huang, L.-R. Lin and L.-S. Zheng, *Inorg. Chem. Commun.*, 2008, **11**, 818.
- 9 N. M. Boag, D. Boucher, J. A. Davies, R. W. Miller, A. A. Pinkerton and R. Syed, *Organometallics*, 1988, **7**, 791.
- 10 G. Ferguson, B. R. Lloyd, L. Manojlovic-Muir, K. W. Muir and R. J. Puddephatt, *Inorg. Chem.*, 1986, **25**, 4190.
- 11 M. C. Jennings, R. J. Puddephatt, L. Manojlovic-Muir, K. W. Muir and B. N. Mwariri, *Organometallics*, 1992, **11**, 4164.
- 12 T. Zhang, M. Drouin and P. D. Harvey, *Chem. Commun.*, 1996, 877.
- 13 A. M. Williamson, G. R. Owen, D. M. P. Mingos, R. Vilar, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2003, 2526.
- 14 S. Arifhodzic-Radojevic, A. D. Burrows, N. Choi, M. McPartlin, D. M. P. Mingos, S. V. Tarlton and R. Vilar, *Dalton Trans.*, 1999, 3981.
- 15 S. Otsuka, Y. Tatsuno, M. Miki, T. Aoki, M. Matsumoto, H. Yoshioka and K. Nakatsu, *J. Chem. Soc., Chem. Commun.*, 1973, 445.
- 16 M. Rashidi, E. Kristof, J. J. Vittal and R. J. Puddephatt, *Inorg. Chem.*, 1994, **33**, 1497.
- 17 S. W. Lee and W. C. Trogler, *Inorg. Chem.*, 1990, **29**, 1099.
- 18 T. Tanase, H. Takahata, H. Ukaji, M. Hasegawa and Y. Yamamoto, *J. Organomet. Chem.*, 1997, **538**, 247.
- 19 T. Murahashi and H. Kurosawa, *Coord. Chem. Rev.*, 2002, **231**, 207.
- 20 T. Murahashi, H. Kurosawa, N. Kanehisa and Y. Kai, *J. Organomet. Chem.*, 1997, **530**, 187.
- 21 T. Murahashi, M. Fujimoto, M.-A. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki and H. Kurosawa, *Science*, 2006, **313**, 1104.
- 22 T. Murahashi, Y. Hashimoto, K. Chiyoda, M. Fujimoto, T. Uemura, R. Inoue, S. Ogoshi and H. Kurosawa, *J. Am. Chem. Soc.*, 2008, **130**, 8586.
- 23 S. Kannan, A. J. James and P. R. Sharp, *J. Am. Chem. Soc.*, 1998, **120**, 215.
- 24 A. L. Balch, J. R. Boehm, H. Hope and M. M. Olmstead, *J. Am. Chem. Soc.*, 1976, **98**, 7431.
- 25 T. Murahashi, E. Mochizuki, Y. Kai and H. Kurosawa, *J. Am. Chem. Soc.*, 1999, **121**, 10660.
- 26 S. Wimmer, P. Castan, F. L. Wimmer and N. P. Johnson, *J. Chem. Soc., Dalton Trans.*, 1989, 403.
- 27 G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, 1997; *ORTEP*.