J. Chem. Research (S), 1999, 440–441†

# Trinuclear Comlexes of Palladium(II) Containing Bridging Thiolate and Pyrazolate Ligands†

**Anshu Singhal and Vimal K. Jain***

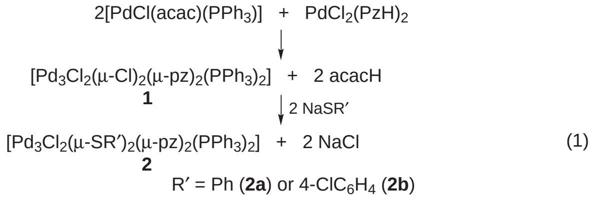
*Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai–400 085, India*

Trinuclear palladium(II) complexes of the type $[Pd_3X_2(\mu\text{-}Y)_2(\mu\text{-}pz)_2(PR_3)_2]$ [X = Cl or Ph; Y = Cl, SPh, $SC_6F_5$ or $SC_6H_4C1\text{-}4$; $PR_3 = PPh_3$ or $P(tol)_3$] are prepared and characterised by elemental analyses, NMR ($^1H$ and $^{31}P\text{-}\{^1H\}$) and FAB mass spectral data.

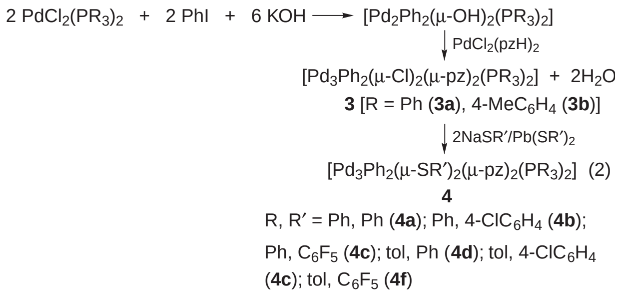
A wide variety of binuclear complexes of platinum group metal complexes stabilized by bridging ligands have been isolated and characterized.[1,2] However, there are only a few examples, $[M_3E_2(dppe)_2]^{2+}$ (M = Pd or Pt; E = S or Se),[3] $[Pd_3Cl_2(\mu\text{-}ScHx)_4(PMe_3)_2]$,[4] *etc.*, of tri- and high-nuclearity complexes stabilized by bridging ligands.[3–7] Rational strategies to prepare these molecules are emerging and these include (i) reaction of coordinatively unsaturated species with a molecular species containing additional donor site,[8] (ii) substitution reaction on a preformed trinuclear complex[9] and (iii) unprecedented formation of trinuclear complex.[4,10] In order to develop easy preparative routes to multimetal complexes and in pursuance of our interest in platinum group metal chemistry, we have synthesized a series of trinuclear palladium(II) complexes of the type $[Pd_3X_2(\mu\text{-}Y)_2(\mu\text{-}pz)_2(PR_3)_2]$.

## Results and discussion

Trinuclear palladium complexes of the type $[Pd_3X_2(\mu\text{-}Y)_2(\mu\text{-}pz)_2(PR_3)_2]$ have been prepared by the routes (1) and (2).



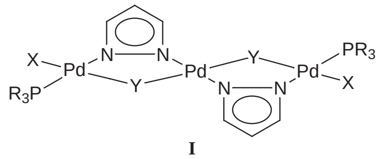
$$\begin{array}{l}
2[PdCl(acac)(PPh_3)] + PdCl_2(PzH)_2 \\
\downarrow \\
[Pd_3Cl_2(\mu\text{-}Cl)_2(\mu\text{-}pz)_2(PPh_3)_2] + 2\ acacH \\
\mathbf{1} \\
\downarrow \text{2 NaSR}' \\
[Pd_3Cl_2(\mu\text{-}SR')_2(\mu\text{-}pz)_2(PPh_3)_2] + 2\ NaCl \qquad (1) \\
\mathbf{2} \\
R' = Ph\ (\mathbf{2a})\ \text{or}\ 4\text{-}ClC_6H_4\ (\mathbf{2b})
\end{array}$$



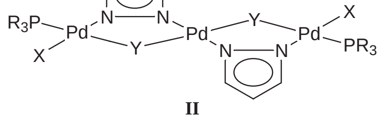
$$\begin{array}{l}
2\ PdCl_2(PR_3)_2 + 2\ PhI + 6\ KOH \longrightarrow [Pd_2Ph_2(\mu\text{-}OH)_2(PR_3)_2] \\
\downarrow PdCl_2(pzH)_2 \\
[Pd_3Ph_2(\mu\text{-}Cl)_2(\mu\text{-}pz)_2(PR_3)_2] + 2H_2O \\
\mathbf{3}\ [R = Ph\ (\mathbf{3a}),\ 4\text{-}MeC_6H_4\ (\mathbf{3b})] \\
\downarrow 2NaSR'/Pb(SR')_2 \\
[Pd_3Ph_2(\mu\text{-}SR')_2(\mu\text{-}pz)_2(PR_3)_2] \quad (2) \\
\mathbf{4} \\
R, R' = Ph, Ph\ (\mathbf{4a});\ Ph, 4\text{-}ClC_6H_4\ (\mathbf{4b}); \\
Ph, C_6F_5\ (\mathbf{4c});\ tol, Ph\ (\mathbf{4d});\ tol, 4\text{-}ClC_6H_4 \\
(\mathbf{4c});\ tol, C_6F_5\ (\mathbf{4f})
\end{array}$$

Trinuclear pyrazolato-bridged palladium complexes are yellow to yellow-orange and decompose before melting. The chloro pyrazolato-bridged complexes (**1** and **3**) are relatively less soluble in dichloromethane than the corresponding thiolato-pyrazolato-bridged derivatives (**2** and **4**). The analytical and FAB mass spectral data (**3a**, **4a** and **4f**) (*m/z* **4a** 1350 [M], 1273 [M – Ph], 1164 [M – (Ph + SPh)], 979 [M – ($PPh_3$ + SPh)], 912, 910; **4f**, 1614 [M], 1537 [M – Ph], 1338 [M – (Ph + $SC_6F_5$)], 1324, 1192, 1061) establish their trinuclear formulation. Although **3a** showed a molecular ion peak at *m/z* 1203, the spectrum was more complex and other peaks were not interpreted. In an attempt to grow single crystals of **1** from a dichloromethane–hexane solution, disproportionation took place. The solution when left overnight gave reddish brown crystals of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]\cdot CH_2Cl_2$. Preliminary structural analysis[11] revealed an analogous structure to those of related palladium complexes, $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (R = $Bu^n$ or OPh).[12]

The $^{31}P\text{-}\{^1H\}$ NMR spectra (Table 1) showed single resonances except in a few cases wherein an additional peak integrating to ≈10% was obtained. The substitution of bridging chloride by a thiolate group in complexes **1** and **3** results in deshielding of the $^{31}P\text{-}\{^1H\}$ NMR signal. The $^1H$ NMR spectra of these complexes exhibited a multiplet for H-4 pz protons. The H-3,5 proton resonances were usually merged with the phenyl protons signals. Although several isomeric forms are possible for these complexes, based on an analogy of *trans* disposition of the bridging ligands as reported for $[\{M(\mu\text{-}SR)(\mu\text{-}pz)(L)\}_2Pd]$ (M = Rh or Ir),[13,14] a similar configuration may be suggested (**I**). The binuclear palladium complexes $[Pd_2Cl_2(\mu\text{-}SR')(\mu\text{-}pz)(PR)_3)_2]$ adopt a *cis* configuration in which the phosphine ligands are *trans* to the bridging pyrazolate group.[15] However, for the analogous platinum complexes $[Pt_2Cl_2(\mu\text{-}SR')(\mu\text{-}pz)(PR_3)_2]$ the phosphine ligands are *trans* to the bridging SR′ group.[16] The presence of another $^{31}P$ resonance for some of the complexes reported here may be assigned tentatively to a configuration in which phosphine ligands are *trans* to the bridging Y ligand (Y = Cl or SR) (**II**). Similar structures have been reported for $[Pd\{Rh(\mu\text{-}SBu^t)(\mu\text{-}pz)I_2(CO)P(OMe)_3\}_2]$.[13]



**I**



**II**

## Experimental

The complexes $[Pd_2Ph_2(\mu\text{-}OH)_2(PR_3)_2]$ [R = Ph or tol (tol = 4-*MeC₆H₄*)],[17] $[PdCl_2(pzH)_2]$[18] and $[PdCl(acac)(PR_3)]$[19] were prepared according to literature methods. All the reactions were carried out in dried and distilled analytical grade solvents under a nitrogen atmosphere. The $^1H$ and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on a Varian XLR-300 spectrometer for freshly prepared $CDCl_3$ solutions. Chemical shifts are referred to the internal chloroform peak (δ 7.26) for $^1H$ and external 85% $H_3PO_4$ for $^{31}P$. FAB mass spectra

---

* To receive any correspondence.

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

**Table 1** Melting point, analytical and NMR ($^1$H and $^{31}$P-{$^1$H}) data for $[Pd_3X_2(\mu\text{-}Y)_2(\mu\text{-}pz)_2(PR_3)_2]$ complexes

| Complex | Recrystallisation solvent (% yield) | Mp/°C | Analysis (%) found (calc.) | | | $\delta_P$ | $\delta_H$ (*J*/Hz) |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | | |
| **1** | $CH_2Cl_2$–hexane<br>(60) | 205–209 | 44.7<br>(45.0) | 3.2<br>(3.2) | 4.8<br>(5.0) | 25.5 | 5.92(d, *J* 2.1, H-4 pz); 6.63 (s, H-3 pz); 7.33–7.86 (m, Ph) |
| **2a** | $CH_2Cl_2$–hexane<br>(60) | 200–202 | 51.2<br>(51.2) | 3.2<br>(3.2) | 4.3<br>(4.4) | 28.9 | 5.78 (d), 5.80 (d) (each *J* 1, H-4 pz); 6.24 (t, *J* 2.2, H-3 pz), 6.64 (t, *J* 7.5), 6.90–7.66 (m) [Ph]; 8.19 t, *J* 2.3 Hz H-5 pz) |
| **2b** | Acetone–MeOH<br>(62) | 182–185 | 49.0<br>(48.5) | 3.5<br>(3.3) | 4.6<br>(4.2) | 28.9<br>29.5 (≈10%) | 5.63, 5.65 (each s, H-4 pz); 6.03 (br, H-3 pz); 6.24 (t, *J* 7), 8.11 (br, minor), 8.17 (t, *J* 2.2) (H-5 pz) |
| **3a** | $CHCl_3$–hexane<br>(85) | 173–175 | 54.5<br>(53.9) | 4.0<br>(3.9) | 4.3<br>(3.7) | 31.0<br>31.7 (≈10%) | 5.75 (br, H-4 pz); 6.68 (br, s, H-3 pz); 6.71–6.97 (m), 7.10–7.35 m, 7.45–7.58 m [Ph + PPh + H-5 pz] |
| **3b** | $CHCl_3$–hexane<br>(70) | 162–164 | 55.7<br>(56.0) | 4.3<br>(4.5) | 4.2<br>(4.4) | 29.1 (major)<br>29.5 (minor) | 2.29 (s, tol-Me, major); 2.30 (s, tol-Me, minor); 5.72 br, H-4 pz); 6.56–7.46 [m Ph, $P(tol)_3$, H-3,5 pz] |
| **4a** | $CH_2Cl_2$–hexane<br>(65) | 150–152 | 59.0<br>(58.7) | 4.3<br>(4.2) | 4.1<br>(4.1) | 33.3 | 5.81 [d, t, *J* 2.2 (t), *J* 1.3 (d), H-4 pz]; 6.74–7.50 (m, Ph, PPh, H-3,5 pz) |
| **4b** | Acetone–hexane<br>(57) | 158–160 | 56.1<br>(55.8) | 3.8<br>(3.8) | 4.2<br>(3.9) | 33.1 | 5.82 [d, t, *J* 2.2 (t), 1.3 (d), H-4 pz]; 6.75–7.46 (m, Ph, PPh, H-3,5 pz) |
| **4c** | Acetone–hexane<br>(62) | 145–146 | 52.1<br>(51.8) | 3.1<br>(3.0) | 3.3<br>(3.7) | 31.0 | 5.72 [d, t, *J* 2.1 (t), 1.3 (d), H-4 pz, major]; 5.74 (t, *J* 2.3, H-4 pz, minor); 6.30–7.72 (m, Ph, PPh, H-3,5 pz) |
| **4d** | Acetone–hexane<br>(62) | 148–150 | 59.8<br>(60.3) | 4.4<br>(4.8) | 4.2<br>(3.9) | 31.4 | 2.21 (s, tol-Me); 5.75 (br, H-4 pz); 6.72–7.44 [m, Ph, $P(tol)_3$ H-3, 5 pz] |
| **4e** | Acetone–hexane<br>(65) | 160–165 | 56.9<br>(57.5) | 4.2<br>(4.4) | 4.2<br>(3.7) | 31.2 | 2.22 (s, tol-Me); 5.75 [d, t, *J* 2.2 (t), 1.2 (d) H-4 pz] 6.72–7.34 [m, Ph, $C_6H_4$, $P(tol)_3$, H-3,5 pz] |
| **4f** | Ether–hexane<br>(70) | 165–168 | 53.3<br>(53.6) | 3.4<br>(3.6) | 3.7<br>(3.6) | 29.4<br>29.9 (1:1) | 2.24 (s), 2.26 (s) [tol-Me]; 5.20 (t, *J* 1.3 H-4 pz], 5.72 (t, 2.2, H-4 pz); 6.11–7.59 [m, Ph $P(tol)_3$, H-3,5 pz] |

[a] Melts or melts with decomposition.

were recorded on a JEOL SX 102/DA-6000 mass spectrometer using xenon (6 kV, 10 mA) as the FAB gas. Elemental analysis were carried out by the Analytical Chemistry Division of this research centre.

*Preparations.*— (i) $[Pd_3Cl_2(\mu\text{-}Cl)_2(\mu\text{-}pz)_2(PPh_3)_2]$ **1**. To an acetone solution of [PdCl(acac)(PPh$_3$)] (157 mg, 0.312 mmol) was added an acetone solution (10 cm$^3$) of $[PdCl_2(pzH)_2]$ (50 mg, 0.160 mmol). The reactants were stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure and the residue dissolved in dichloromethane and precipitated by addition of hexane to give an orange-yellow solid which was filtered off and washed with hexane (150 mg, 60% yield).

(ii) $[Pd_3Cl_2(\mu\text{-}SC_6H_4Cl\text{-}4)_2(\mu\text{-}pz)_2(PPh_3)_2]$ **2b**. To an acetone solution (20 cm$^3$) of [PdCl(acac)(PPh$_3$)] (128 mg, 0.25 mmol), a solution of $[PdCl_2(pzH)_2]$ (41 mg, 0.13 mmol) in dichloromethane (5 cm$^3$) was added under a nitrogen atmosphere. The reactants were stirred for 2 h at room temperature during which a yellow solid precipitated. A methanolic solution (5 cm$^3$) of Na(SC$_6$H$_4$C1-4) (45 mg, 0.27 mmol) was added to the reaction mixture after 2 h. The reactants were stirred for 2 h and the solvents evaporated under vacuum. The residue was extracted with diethyl ether (2 × 5 cm$^3$) and filtered. The filtrate was concentrated to 2 cm$^3$ under reduced pressure and hexane (5 cm$^3$) layered at the top. After cooling in a freezer for 8 h the required was obtained in 62% yield (105 mg).

(iii) $[Pd_3Ph_2(\mu\text{-}Cl)_2(\mu\text{-}pz)_2(PPh_3)_2]$ **3a**. To an acetone suspension of $[Pd_2Ph_2(\mu\text{-}OH)_2(PPh_3)_2]$ (332 mg, 0.358 mmol) a solution of $[PdCl_2(pzH)_2]$ (112 mg, 0.36 mmol) in acetone was added dropwise over a period of 10 min. The reactants were stirred for 3 h during which a cream solid precipitated which was filtered off washed with acetone and dried *in vacuo* (369 mg; 85%). Similarly, $[Pd_3Ph_2(\mu\text{-}Cl)_2(\mu - pz)_2\{P(tol)_3\}_2]$ **3b** was prepared.

(iv) $[Pd_3Ph_2(\mu\text{-}SC_6F_5)_2(\mu\text{-}pz)_2(PPh_3)_2]$ **4c**. To an acetone (20 cm$^3$) suspension of $[Pd_3Ph_2(\mu\text{-}Cl)_2(\mu\text{-}pz)_2(PPh_3)_2]$ (98 mg, 0.81 mmol) a solution of NaSC$_6$F$_5$ (38 mg, 0.17 mmol) in methanol (5 cm$^3$) was added dropwise over a period of 10 min. The reactants were stirred for 2 h under a nitrogen atmosphere. The solvents were removed *in vacuo* and the residue was concentrated under reduced pressure to 2 cm$^3$ and layered with hexane (4 cm$^3$) which on cooling in a freezer overnight gave the required complex in 62% yield (77 mg). Other complexes (**4a**–**4f**) in the series were prepared in a similar manner.

The chloro-bridged trinuclear complexes $[Pd_3Ph_2(\mu\text{-}Cl)_2(\mu\text{-}(PR_3)_2]$ **3** can be prepared *in situ* and then treated with lead thiolate to get the corresponding thiolato-bridged complexes.

*Received, 26th January 1999; Accepted, 25th March 1999*
*Paper E/9/00715F*

## References

1 V. K. Jain, *Curr. Sci.*, 1990, **59**, 143.

2 H. Werner, *Adv. Organomet. Chem.*, 1981, **19,** 155; B. Chaudret, B. Belavaux and R. Poilblanc, *Coord. Chem. Rev.*, 1988, **86**, 191; D. G. Smith and H. B. Gray, *Coord. Chem. Rev.*, 1990, **100**, 169; G. K. Anderson, *Adv. Organomet. Chem.*, 1993, **35**, 1; K. Umakoshi and Y. Sasaki, *Adv. Inorg. Chem.*, 1993, **40**, 187.

3 K. Matsumato, N. Saiga, S. Tanaka and S. Ooi, *J. Chem. Soc., Dalton Trans.*, 1991, 1265.

4 E. M. Padilla and C. M. Jensen, *Polyhedron*, 1991, **10**, 89.

5 M. A. A. F. De C. T. Corrondo and A. C. Skapski, *J. Chem. Soc., Chem. Commun.*, 1976, 410; A. C. Skapski and M. L. Smarl, *J. Chem. Soc., Chem. Commun.*, 1970, 658.

6 A. L. Balch, J. R. Boehm, H. Hope and M. M. Olmstead, *J. Am. Chem. Soc.*, 1976, **98**, 1431; P. M. Bailey, E. A. Kelly and P. M. Maitlis, *J. Organomet. Chem.*, 1978, **144**, C52.

7 R. Uson, J. Fornies, M. Tomas, B. Menjon, J. Carnicer and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1990, 151; R. D. Adams, J. E. Babin and M. Tasi, *Organometallics*, 1987, **6**, 1717.

8 R. Uson, J. Fornies, M. A. Uson, M. Tomas and M. A. Ibanez, *J. Chem. Soc., Dalton Trans.*, 1994, 401.

9 M. Basato, A. Grassi and G. Valle, *Organometallics*, 1995, **14**, 4439.

10 S. Narayan, V. K. Jain and R. J. Butcher, *Polyhedron*, 1998, **17**, 2037.

11 A. Singhal, V. K. Jain and T. Manisekran, unpublished results [Pd-P 2.23; Pd-Cl = 2.67, 2.32, 2.43 Å].

12 W. J. Grigsby and B. K. Nicholson, *Acta Crystallogr., Sect. C*, 1992, **48**, 362; P. A. Chaloner, S. Z. Dewa and P. B. Hitchcock, *Acta Crystallogr., Sect. C.*, 1995, **51**, 232.

13 A. Elduque, L. A. Oro, M. T. Pinillos, C. Tejel, A. Tiripicchio and F. Ugozzoli, *J. Chem Soc., Dalton Trans.*, 1991, 2807.

14 M. T. Pinillos, A. Elduque, E. Martin, N. Navarro, F. J. Lahoj, J. A. Lopez and L. A. Oro, *Inorg. Chem.*, 1995, **34**, 111.

15 V. K. Jain, S. Kannan, R. J. Butcher and J. P. Jasinski, *J. Chem. Res. (S)*, 1996, 284.

16 V. K. Jain and S. Kannan, *Polyhedron*, 1992, **11**, 27.

17 V. V. Grushin and H. Alper, *Organometallics*, 1993, **12**, 1890.

18 M. T. Pinillos, C. Tejel, L. A. Oro, M. C. Apreda, F. C. Cano and C. Foces-Foces, *J. Chem., Soc., Dalton Trans.*, 1989, 1133.

19 R. Uson, J. Gimeno, L. A. Oro, J. M. Martinez-De Ilarduya and J. A. Cabeza, *J. Chem. Soc., Dalton Trans.*, 1983, 1729.