View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1992. Downloaded by Temple University on 31/10/2014 16:29:44.

Pyrazolato-bridged Binuclear Palladium(II) Compounds: Synthesis and Crystal Structure*

Vimal K. Jain,[a] **S. Kannan**[b] and **Edward R. T. Tiekink**[c]
[a] *Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India*
[b] *Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India*
[c] *Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001, Australia*

Pyrazolato-bridged binuclear palladium(II) complexes of the type $[Pd_2X_2(\mu\text{-L–L})_2(PR_3)_2]$ [L–L = pz (pyrazolate) or dmpz (3,5-dimethylpyrazolate); X = Cl, Br or I; PR_3 = PBu_3, PMe_2Ph or $PMePh_2$] have been prepared. They were characterized by elemental analysis, ^1H and ^{31}P NMR data and in the case of $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$ by single-crystal X-ray diffraction methods. The structure determination shows two Pd atoms bridged by two dmpz ligands which form asymmetric Pd–N bond distances, an observation that may be correlated with the different *trans* influences associated with the Cl and P atoms which complete the square-planar geometries about the Pd atoms: monoclinic, space group $P2_1/c$, a = 20.164(1), b = 10.140(1), c = 16.129(3) Å, β = 111.71(1)°, and Z = 4. The structure was refined to final R = 0.027 for 2906 reflections with $I \geqslant 2.5\sigma(I)$.

Binuclear platinum-group complexes stabilized through a variety of bridging ligands have attracted much attention in recent years owing to their rich reaction chemistry and relevance in homogeneous catalysis. Pertinent to this paper are the pyrazolato-bridged complexes which have been studied;[1–17] the catalytic activity of some of these complexes has been assessed.[7,9] The bridging pyrazolate ligand (pz) acts in an *exo*-bidentate fashion in these complexes and both the five- and six-membered metallacyclic rings 'M(μ-pz)(μ-X)M' and 'M(μ-pz)$_2$M' (X = single-atom donor ligand) are usually puckered.

Reaction of $[Pt_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ with pyrazole/3,5-dimethylpyrazole (dmpz) in the presence of methanolic sodium hydroxide has been reported to give mixed chloro/pyrazolato-bridged complexes,[2,18] however reaction in 1:2 stoichiometry with the sterically demanding 3,5-dimethylpyrazole in methanolic solution gives, in addition to the methoxo/pyrazolato-bridged complex, a chloro-bridged dinuclear platinum complex containing terminal azolato groups.[2] When this latter reaction is extended to the analogous $[Pd_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ system a bis(pyrazolato)-bridged complex is formed exclusively; these studies are reported in this contribution.

Experimental

The complexes $[Pd_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ (PR_3 = PBu_3, PMe_2Ph or $PMePh_2$) were prepared according to literature methods.[19] Pyrazole, 3,5-dimethylpyrazole, and tertiary phosphines were obtained from commercial sources. Analytical grade solvents were used throughout. Elemental analysis were performed by the Analytical Chemistry Division (Bhabha Atomic Research Centre). Proton and ^{31}P NMR spectra were recorded in $CDCl_3$ solution on a Varian FT-80A spectrometer operating at 79.542 and 32.203 MHz, respectively. Chemical shifts are relative to the internal chloroform peak (δ 7.26) for ^1H and external 85% H_3PO_4 for ^{31}P spectra.

Preparation of $[Pd_2Cl_2(\mu\text{-pz})_2(PBu_3)_2]$.—To a suspension of $[Pd_2Cl_2(\mu\text{-Cl})_2(PBu_3)_2]$ (120 mg, 0.16 mmol) in methanol was added a solution of pyrazole (23 mg, 0.34 mmol) in methanolic (5 cm^3) sodium hydroxide (320 μl, 0.98 mol dm^{-3}). The mixture was stirred at room temperature for 5 h, the solvent was evaporated *in vacuo* and the residue extracted with dichloromethane (3 × 5 cm^3) and hexane (5 cm^3). A pale yellow product was obtained after 3–4 h (105 mg, 81% yield).

Preparation of $[Pd_2Br_2(\mu\text{-pz})_2(PBu_3)_2]$.—To an acetone solution (20 cm^3) of $[Pd_2Cl_2(\mu\text{-pz})_2(PBu_3)_2]$ (75 mg, 0.09 mmol) was added an excess of powdered KBr and the mixture stirred at room temperature for 24 h. The solvent was evaporated *in vacuo* and the residue extracted with dichloromethane. To this was added hexane (5 cm^3) and on cooling greenish crystals were obtained (75 mg, 90%). Similarly $[Pd_2Br_2(\mu\text{-dmpz})_2(PBu_3)_2]$ and the iodo complexes, employing KI, were prepared. Analytical data for these complexes are given in Table 1.

Crystallography.—Intensity data for a yellow, spherical crystal of $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$ of *ca.* 0.3 mm diameter were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with Mo-Kα radiation (graphite monochromator), λ = 0.7107 Å. The ω–2θ scan technique was employed to measure the intensities of 4457 reflections up to a maximum Bragg angle of 22.5°. The data set was corrected for Lorentz and polarization effects but not for absorption.

Crystal data. $C_{26}H_{36}Cl_2N_4P_2Pd_2$, M = 750.2, monoclinic, space group $P2_1/c$, a = 20.164(1), b = 10.140(1), c = 16.129(3) Å, β = 111.71(1)°, U = 3063.9(7) Å^3, D_c = 1.626 g cm^{-3}, Z = 4, $F(000)$ = 1504. 4457 Reflections measured, 4005 unique, and 2906 with $I \geqslant 2.5\sigma(I)$, R = 0.027, R' = 0.029.

The structure was solved by direct methods[20] and refined by a full-matrix least-squares procedure based on F.[21] The P-bound phenyl atoms were refined as hexagonal rigid groups with individual isotropic thermal parameters and the remaining non-H atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in the model at their calculated positions and assigned a common isotropic thermal parameter which was refined. A weighting scheme of the form $w = 1.67/[\sigma(F) + 0.0003F^2]$ was introduced and the refinement

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

View Article Online

Published on 01 January 1992. Downloaded by Temple University on 31/10/2014 16:29:44.

Table 1 Analytical and physical data for $[Pd_2X_2(\mu\text{-L–L})_2(PR_3)_2]$

Complex	Recrystallization solvent	Yield (%)	M.p./°C	Analysis (%)* C	H	N
$[Pd_2Cl_2(\mu\text{-pz})_2(PBu_3)_2]$	CH_2Cl_2–hexane	81	145	43.7 (43.8)	7.5 (7.4)	6.8 (6.8)
$[Pd_2Br_2(\mu\text{-pz})_2(PBu_3)_2]$	CH_2Cl_2–hexane	90	157	40.0 (39.5)	7.1 (6.6)	6.0 (6.1)
$[Pd_2I_2(\mu\text{-pz})_2(PBu_3)_2]$	CH_2Cl_2–hexane	85	187	35.4 (35.8)	6.4 (6.0)	5.2 (5.6)
$[Pd_2Cl_2(\mu\text{-dmpz})_2(PBu_3)_2]$	CH_2Cl_2–hexane	79	110	46.8 (46.5)	7.6 (7.8)	6.4 (6.4)
$[Pd_2Br_2(\mu\text{-dmpz})_2(PBu_3)_2]$	CH_2Cl_2–hexane	92	137	42.9 (42.2)	7.1 (7.1)	5.8 (5.8)
$[Pd_2I_2(\mu\text{-dmpz})_2(PBu_3)_2]$	CH_2Cl_2–hexane	85	147	38.8 (38.5)	7.0 (6.5)	5.2 (5.3)
$[Pd_2Cl_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	CH_2Cl_2–EtOH	77	142–143	38.0 (38.1)	4.1 (4.1)	7.9 (8.1)
$[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$	CH_2Cl_2–EtOH	77	226–227	42.0 (41.6)	5.2 (4.8)	7.5 (7.5)
$[Pd_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$	CH_2Cl_2–EtOH	75	230 (decomp.)	49.4 (49.5)	4.7 (4.6)	6.4 (6.4)

* Calculated values in parentheses.

Table 2 Fractional atomic coordinates ($\times 10^5$ for Pd, $\times 10^4$ for remaining atoms) for $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$

Atom	x	y	z
Pd(1)	16 851(2)	11 578(4)	34 758(3)
Pd(2)	31 162(2)	−1 142(4)	35 652(3)
Cl(1)	1 052(1)	2 179(1)	2 146(1)
Cl(2)	3 073(1)	−2 319(1)	3 206(1)
P(1)	822(1)	−362(1)	3 132(1)
P(2)	3 254(1)	407(2)	2 283(1)
N(11)	2 247(2)	242(4)	4 642(3)
N(12)	2 828(2)	−467(4)	4 652(3)
N(21)	2 547(2)	2 444(4)	3 753(3)
N(22)	3 181(2)	1 813(4)	3 917(3)
C(11)	1 558(3)	718(6)	5 608(4)
C(12)	2 159(3)	61(5)	5 413(3)
C(13)	2 691(3)	−782(6)	5 940(4)
C(14)	3 098(3)	−1 092(6)	5 431(4)
C(15)	3 742(3)	−1 968(7)	5 645(4)
C(21)	2 104(3)	4 709(6)	3 782(5)
C(22)	2 683(3)	3 728(5)	3 902(4)
C(23)	3 414(3)	3 936(6)	4 173(4)
C(24)	3 708(3)	2 692(6)	4 169(4)
C(25)	4 468(3)	2 287(7)	4 394(5)
C(111)	26(3)	223(6)	3 277(4)
C(121)	1 071(3)	−1 871(5)	3 768(4)
C(131)	547(1)	−957(4)	1 999(2)
C(132)	1 054(1)	−1 620(4)	1 757(2)
C(133)	870(1)	−2 118(4)	895(2)
C(134)	177(1)	−1 953(4)	274(2)
C(135)	−330(1)	−1 290(4)	515(2)
C(136)	−146(1)	−792(4)	1 377(2)
C(211)	3 032(3)	2 104(6)	1 949(4)
C(221)	2 653(4)	−466(7)	1 320(4)
C(231)	4 142(2)	145(4)	2 277(2)
C(232)	4 642(2)	−575(4)	2 963(2)
C(233)	5 337(2)	−718(4)	2 988(2)
C(234)	5 532(2)	−142(4)	2 326(2)
C(235)	5 032(2)	577(4)	1 640(2)
C(236)	4 337(2)	720(4)	1 616(2)

on 243 parameters continued until convergence. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied and the maximum residual electron-density peak in the final difference map was 0.57 e Å^{-3}. Fractional atomic coordinates are listed in Table 2 and the numbering scheme employed is shown in Fig. 1 which was drawn with ORTEP[22] with 15% probability ellipsoids. Scattering factors for neutral Pd (corrected for f' and f'') were from ref. 23 while those for the remaining atoms were those incorporated in SHELX 76.[21] Refinement was performed on a SUN4/280 workstation.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond distances and angles.

Results and Discussion

Treatment of the chloro-bridged binuclear palladium complexes $[Pd_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ with pyrazole (Hpz) or 3,5-dimethylpyrazole (Hdmpz) in 1:2 stoichiometry in the presence of 2 mol equivalents of sodium hydroxide afforded the bis(pyrazolato)-bridged dinuclear palladium(II) complexes, $[Pd_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ (L–L = pz or dmpz; PR_3 = PBu_3, PMe_2Ph or $PMePh_2$), Table 1. Interestingly, when 1 mol equivalent of Hpz and of sodium hydroxide were employed bis(pyrazolato)-bridged complexes formed exclusively leaving half of the chloro-bridged compound unreacted, rather than yielding a complex of the type $[Pd_2Cl_2(\mu\text{-Cl})(\mu\text{-L–L})(PR_3)_2]$. It is noteworthy that the platinum analogue of the latter species can be readily obtained from a similar reaction.[2,18] Metathesis of $[Pd_2Cl_2(\mu\text{-L–L})_2(PR_3)_2]$ with KBr or KI in acetone solution gave the corresponding bromo or iodo complexes.

The ^{31}P NMR spectra (Table 3) of these complexes exhibited a single sharp singlet in all cases suggesting the presence of only one isomeric species, *i.e. sym-trans* or *sym-cis*. The resonances are considerably shielded with respect to those observed for the corresponding $[Pd_2Cl_2(\mu\text{-Cl})_2(PR_3)_2]$ species.

The ^1H NMR spectra of these complexes (Table 3) exhibited the expected integration and peak multiplicites. The signal due to the methyl protons of the dmpz ligand appeared as two equally intense resonances indicating non-equivalence. Similarly, two sets of signals were observed for the protons at the 3 and 5 positions of the pz ligand. Non-equivalence of the groups attached at the 3 and 5 positions of the pz and dmpz ligands may be ascribed to the different *trans* influences of the ligands (Cl or PR_3) *trans* to the bridging L–L ligand. Further, when the *trans* ligands are the same as in the cases of $[Ru_2(\mu\text{-dmpz})_2(CO)_6]$[14] and $[NBu_4][Pd_2(\mu\text{-L–L})_2(C_6F_5)_4]$[24] only one signal for these groups is observed. The complexes containing PMe_2Ph displayed two doublets attributable to the PMe protons. The

View Article Online

Published on 01 January 1992. Downloaded by Temple University on 31/10/2014 16:29:44.

Table 3 Proton and ^{31}P-{^1H} NMR data (δ) for $[Pd_2X_2(\mu\text{-L-L})_2(PR_3)_2]$ in $CDCl_3$ solution

Complex	^{31}P NMR	^1H NMR*
$[Pd_2Cl_2(\mu\text{-pz})_2(PBu_3)_2]$	20.9	7.40 (br d, 2 H, pz NCH), 7.05 (br, 2 H, pz NCH), 6.02 (m, 2 H, H^4 of pz), 1.60–1.20, 0.95, 0.90 (br, 54 H, Bu)
$[Pd_2Br_2(\mu\text{-pz})_2(PBu_3)_2]$	20.2	7.42 (br d, 2 H, pz NCH), 7.02 (br, 2 H, pz NCH), 6.00 (m, 2 H, H^4 of pz), 1.80–1.15, 0.95, 0.90 (br, 54 H, Bu)
$[Pd_2I_2(\mu\text{-pz})_2(PBu_3)_2]$	19.0	7.48 (br d, 2 H, pz NCH), 7.00 (br, 2 H, pz NCH), 5.98 (m, 2 H, H^4 of pz), 1.90–1.15, 0.90, 0.85 (br, 54 H Bu)
$[Pd_2Cl_2(\mu\text{-dmpz})_2(PBu_3)_2]$	19.6	5.50 (br, 2 H, H^4 of pz), 2.30 (s, 6 H, Me of dmpz), 2.15 (s, 6 H, Me of dmpz), 1.90–1.15, 0.93, 0.88 (br, 54 H, Bu)
$[Pd_2Br_2(\mu\text{-dmpz})_2(PBu_3)_2]$	19.2	5.48 (br, 2 H, H^4 of pz), 2.30 (s, 6 H, Me of dmpz), 2.15 (s, 6 H, Me of dmpz), 1.95–1.15, 0.90, 0.85 (br, 54 H, Bu)
$[Pd_2I_2(\mu\text{-dmpz})_2(PBu_3)_2]$	18.1	5.48 (br, 2 H, H^4 of pz), 2.25 (s, 6 H, Me of dmpz), 2.15 (s, 6 H, Me of dmpz), 2.00–1.10, 0.95, 0.88, (br, 54 H, Bu)
$[Pd_2Cl_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	3.9	7.92–7.30 (m, 12 H, pz NCH and Ph), 6.66 (t, 2 H, pz NCH, *J* 2), 5.92 (m, 2 H, H^4 of pz, *J* 2), 1.79 (d, 6 H, PMe, *J* 12.0), 1.52 (d, 6 H, PMe, *J* 11.7)
$[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$	2.4	7.85–7.32 (m, 10 H, Ph), 5.43 (br, 2 H, H^4 of pz), 2.31 (s, 6 H, Me of dmpz), 1.89 (d, 6 H, PMe, *J* 11.7), 1.84 (s, 6 H, Me of dmpz), 1.55 (d, 6 H, PMe, *J* 11.7)
$[Pd_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$	14.0	7.82–7.19 (m, 20 H, Ph), 5.25 (br, 2 H, H^4 of pz), 2.40 (s, 6 H, Me of dmpz), 1.92 (d, 6 H, PMe, *J* 11.3), 1.72 (s, 6 H, Me of dmpz)

* s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants in Hz.

Table 4 Selected bond distances (Å) and angles (°) for $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$

Pd(1)–Cl(1)	2.297(1)	Pd(2)–Cl(2)	2.303(1)
Pd(1)–P(1)	2.236(1)	Pd(2)–P(2)	2.249(1)
Pd(1)–N(11)	2.026(4)	Pd(2)–N(12)	2.072(4)
Pd(1)–N(21)	2.084(4)	Pd(2)–N(22)	2.026(4)
P(1)–C(111)	1.806(5)	P(2)–C(211)	1.809(6)
P(1)–C(121)	1.806(6)	P(2)–C(221)	1.809(6)
P(1)–C(131)	1.807(4)	P(2)–C(231)	1.814(4)
N(11)–N(12)	1.370(6)	N(21)–N(22)	1.366(6)
N(11)–C(12)	1.333(6)	N(21)–C(22)	1.334(6)
N(12)–C(14)	1.331(6)	N(22)–C(24)	1.330(7)
C(11)–C(12)	1.513(7)	C(21)–C(22)	1.491(8)
C(12)–C(13)	1.389(7)	C(22)–C(23)	1.389(8)
C(13)–C(14)	1.395(8)	C(23)–C(24)	1.396(8)
C(14)–C(15)	1.503(8)	C(24)–C(25)	1.495(8)
Cl(1)–Pd(1)–P(1)	88.1(1)	Cl(2)–Pd(2)–P(2)	90.2(1)
Cl(1)–Pd(1)–N(11)	179.4(1)	Cl(2)–Pd(2)–N(22)	178.2(1)
Cl(1)–Pd(1)–N(21)	92.9(1)	Cl(2)–Pd(2)–N(12)	92.8(1)
P(1)–Pd(1)–N(11)	91.8(1)	P(2)–Pd(2)–N(22)	90.8(1)
P(1)–Pd(1)–N(21)	174.4(1)	P(2)–Pd(2)–N(12)	170.8(1)
N(11)–Pd(1)–N(21)	87.3(2)	N(22)–Pd(2)–N(12)	86.5(2)
Pd(1)–P(1)–C(111)	112.9(2)	Pd(2)–P(2)–C(211)	113.4(2)
Pd(1)–P(1)–C(121)	114.5(2)	Pd(2)–P(2)–C(221)	113.8(2)
Pd(1)–P(1)–C(131)	113.6(1)	Pd(2)–P(2)–C(231)	115.4(1)
C(111)–P(1)–C(121)	106.2(3)	C(211)–P(2)–C(221)	101.3(3)
C(111)–P(1)–C(131)	106.6(2)	C(211)–P(2)–C(231)	105.8(2)
C(121)–P(1)–C(131)	102.1(2)	C(221)–P(2)–C(231)	105.8(3)
Pd(1)–N(11)–N(12)	115.7(3)	Pd(2)–N(12)–N(11)	114.0(3)
Pd(1)–N(11)–C(12)	135.1(4)	Pd(2)–N(12)–C(14)	137.4(4)
Pd(1)–N(21)–N(22)	113.3(3)	Pd(2)–N(22)–N(21)	116.0(3)
Pd(1)–N(21)–C(22)	138.6(4)	Pd(2)–N(22)–C(24)	133.9(4)
N(12)–N(11)–C(12)	109.0(4)	N(11)–N(12)–C(14)	108.1(4)
N(22)–N(21)–C(22)	107.8(4)	N(21)–N(22)–C(24)	109.3(4)
N(11)–Pd(1)–P(1)–C(111)	104.9(3)	N(22)–Pd(2)–P(2)–C(231)	101.2(2)
N(11)–Pd(1)–P(1)–C(121)	−16.8(3)	N(22)–Pd(2)–P(2)–C(211)	−21.1(3)
N(11)–Pd(1)–P(1)–C(131)	−133.5(2)	N(22)–Pd(2)–P(2)–C(221)	−136.2(3)

methyl groups may be anisochronous on both phosphine ligands or the two phosphines are non-equivalent as observed in the case of $[M_2Cl_2(\mu\text{-Cl})(\mu\text{-SEt})(PMe_2Ph)_2]$ (M = Pd or Pt).[25,26] Confirmation of the dinuclear structures proposed for the complexes reported above was afforded by a single-crystal X-ray structure analysis of $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$.

The molecular structure of $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$ is shown in Fig. 1 and selected interatomic bond distances and angles are listed in Table 4. The molecule is comprised of two Pd atoms bridged by two dmpz ligands such that the Pd ··· Pd separation is 3.115(1) Å; the molecule has approximate two-fold symmetry with respect to the heavy atoms (*i.e.* excluding C and H atoms). The two remaining sites in the square-planar geometry about each Pd atom are occupied by terminal Cl atoms and the PMe_2Ph ligands. Deviations from the least-squares plane through the atoms defining the square plane about the Pd(1) atom are 0.009(2), −0.008(1), 0.079(4) and −0.082(5) Å for the Cl(1), P(1), N(11) and N(21) atoms, respectively (χ^2 = 722.8); Pd(1) lies 0.0569(4) Å out of this

View Article Online

Published on 01 January 1992. Downloaded by Temple University on 31/10/2014 16:29:44.

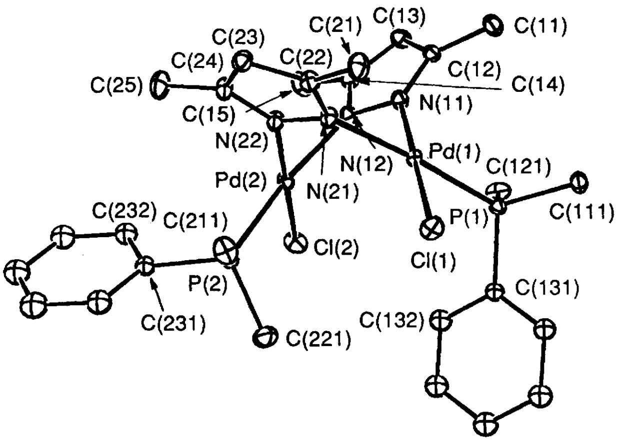

Fig. 1 Molecular structure and crystallographic numbering scheme for [$Pd_2Cl_2(\mu$-dmpz$)_2(PMe_2Ph)_2$]

plane in the direction of C(11). A greater distortion from ideal square-planar geometry is noted for the Pd(2) atom with the Cl(2), P(2), N(12) and N(22) atoms lying 0.020(2), −0.018(2), −0.158(5) and 0.171(5) Å out of the least-squares plane, respectively (χ^2 = 2759.7) with Pd(2) lying 0.0701(4) Å out of this plane in the direction of C(25). The dihedral angle formed between the two square-planar geometries is 111.9(7)°. The two dmpz ligands are each planar within experimental error and the dihedral angle between the two planes is 81.7°.

Each dmpz ligand bridges two Pd atoms forming disparate Pd–N bond distances reflecting the different *trans* influences of the Cl and P donor atoms. The shorter Pd–N(11) and Pd(2)–N(22) distances [each 2.026(4) Å] have the N atoms *trans* to the Cl atom whereas the longer Pd(1)–N(21) and Pd(2)–N(12) bond distances of 2.084(4) and 2.072(4) Å respectively have the N atoms approximately *trans* to the P donor atoms, Table 4. The structure determination of [$Pd_2Cl_2(\mu$-dmpz$)_2(PMe_2Ph)_2$] is consistent with the spectroscopic results (see above), in particular the interpretation of the chemical shifts found for the protons (or methyl-group protons) in the 3 and 5 positions of the pz (dmpz) ligands, suggesting similar *sym-trans* structures are adopted by the other complexes of general formula [$Pd_2X_2(\mu$-L–L$)_2(PR_3)_2$] reported in this paper.

Acknowledgements

The Australian Research Council is thanked for support of the crystallographic facility. Thanks are also due to Drs. J. P. Mittal and D. D. Sood for their encouragement and interest in this work, and the Head, Analytical Chemistry Division for providing the microanalytical results.

References

1 S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115.
2 F. Bonati, H. C. Clark and C. S. Wong, *Can. J. Chem.*, 1980, **58**, 1435.
3 D. A. Johnson, W. C. Deese and M. L. Howe, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 53; W. C. Deese, D. A. Johnson and A. W. Cordes, *Inorg. Chem.*, 1981, **20**, 1519; W. C. Deese and D. A. Johnson, *J. Organomet. Chem.*, 1982, **232**, 325.
4 A. W. Coleman, D. T. Eadie, S. R. Stobart, M. J. Zaworotko and J. L. Atwood, *J. Am. Chem. Soc.*, 1982, **104**, 922.
5 A. B. Goel, S. Goel and D. Vanderveer, *Inorg. Chim. Acta*, 1984, **82**, L9.
6 B. M. Lonie, S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1985, **63**, 688.
7 P. Kalck, A. Thorez, M. T. Pinillos and L. A. Oro, *J. Mol. Catal.*, 1985, **31**, 311.
8 D. G. Harrison and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1986, 285.
9 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.
10 F. Barceló, P. Lahuerta, M. A. Ubeda, C. Foces-Foces, F. H. Cano and M. Martínez-Ripoll, *Organometallics*, 1988, **7**, 584.
11 M. T. Pinillos, C. Tejel, L. A. Oro, M. C. Apreda, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1989, 1133.
12 R. D. Brost and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1989, 498.
13 R. D. Brost, D. O. K. Fjeldsted and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1989, 488.
14 J. A. Cabeza, C. Landázuri, L. A. Oro, D. Belletti, A. Tiripicchio and M. T. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1989, 1093.
15 M. T. Pinillos, A. Elduque, L. A. Oro, F. J. Lahoz, F. Bonati, A. Tiripicchio and M. T. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1990, 989.
16 M. A. Garcia, A. M. Lopez, M. A. Esteruelas, F. J. Lahoz and L. A. Oro, *J. Organomet. Chem.*, 1990, **388**, 365.
17 A. Elduque, L. A. Oro, M. T. Pinillos, C. Tejel, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc., Dalton Trans.*, 1991, 2807.
18 V. J. Jain and S. Kannan, *Polyhedron*, 1992, **11**, 27.
19 F. R. Hartley, *The Chemistry of Platinum and Palladium*, Wiley, New York, 1973.
20 G. M. Sheldrick, SHELXS 86, Program for the Automatic Solution of Crystal Structure, University of Göttingen, 1986.
21 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
22 C. K. Johnson, ORTEP II, ORNL Report 5136, Oak Ridge National Laboratory, TN, 1976.
23 J. A. Ibers and W. C. Hamilton, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 149.
24 G. Lopez, J. Ruiz, G. Garcia, C. Vicente, J. Casabo, E. Molins and C. Miravitlles, *Inorg. Chem.*, 1991, **30**, 2605.
25 V. K. Jain, R. P. Patel, K. V. Muralidharan and R. Bohra, *Polyhedron*, 1989, **8**, 2151.
26 V. K. Jain, R. P. Patel and K. Venkatasubramanian, *Polyhedron*, 1991, **10**, 851.

Received 11*th February* 1992; *Paper* 2/00706A