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Pyrazolato-bridged arylpalladium(II) complexes, $[Pd_2Ar_2(\mu\text{-}pz/dmpz)_2(PR_3)_2]$: Synthesis and characterization

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ABSTRACT

The reactions of $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ with pyrazole or 3,5-dimethylpyrazole in the presence of methanolic sodium hydroxide yield pyrazolato-bridged binuclear arylpalladium complexes, $[Pd_2Ar_2(\mu\text{-}pz')_2(PR_3)_2]$ (Ar = Ph or C_6H_4Me-4 (tol); pz′ = pz or dmpz; $PR_3 = PEt_3$, PMe_2Ph). These complexes exist exclusively in sym-*trans* form both in solution (by NMR) and in the solid state (by X-ray). The molecular structures of $[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$, $[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]$ and $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$ have been established by X-ray diffraction analyses. The former is a centrosymmetric dimer while the latter two adopt a boat like conformation. The Pd···Pd separation in pyrazolato-bridged complexes is influenced by steric demands of particular pyrazolato-ligand.

1. Introduction

Organometallic chemistry of binuclear palladium(II) complexes has been dominated by cyclometallated and η^3-allyl derivatives [1–5] with scant attention on alkyl and arylpalladium complexes. The latter are believed to be the active intermediates in several organic transformations involving arylhalides (e.g. Suzuki reaction) and palladium compounds as catalysts [6,7]. Under exploration of the chemistry of arylpalladium complexes may possibly be due to non-availability of a convenient preparative route for a suitable synthon such as $[Pd_2Ar_2(\mu\text{-}Cl)_2(L_2)]$. For the synthesis of the latter, Anderson employed a reaction between $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ and R_2Hg [8], but the toxicity of mercury compounds and tedious process to remove the side product (RHgCl) render this method of limited utility. We have recently described a convenient synthesis of $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ by employing triorganobismuth compounds [7].

Pyrazolate/substituted pyrazolate ion is a versatile ligand in stabilizing bi- and tri-nuclear metal complexes in which particular moieties around metal ions or atoms are bridged by an exo-bidentate pyrazolate ligand [9–11]. These complexes show interesting photophysical properties [11,12] and have been employed in catalytic reactions [13].

In this paper we describe the synthesis and characterization of binuclear pyrazolato-bridged arylpalladium(II) complexes.

2. Results and discussion

Treatment of chloro-bridged arylpalladium complexes $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ with pyrazoles in 1:2 stoichiometry in the presence of 2 mol equivalents of sodium hydroxide yielded bis pyrazolato-bridged complexes, $[Pd_2Ar_2(\mu\text{-}pz')_2(PR_3)_2]$ (eq. (1)). The latter could be recrystallized from benzene-hexane mixture as colorless crystalline solids in 74–88% yield.

$$[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2] + 2\ pz'H + 2\ NaOH \rightarrow [Pd_2Ar_2(\mu\text{-}pz')_2(PR_3)_2] + 2\ NaCl + 2\ H_2O \tag{1}$$

(Ar = Ph or C_6H_4Me-4 (tol); pz′ = pz or dmpz; $PR_3 = PEt_3$ or PMe_2Ph)

The ^1H and ^{13}C NMR spectra of these complexes exhibited a single set of resonances attributable to bridging pyrazolate group indicating the existence of a sym-*trans* isomer in solution. For the sym-*cis* isomer two sets of such resonances are expected. Interestingly, the analogous platinum complexes $[Pt_2Ar_2(\mu\text{-}pz')_2(PR_3)_2]$ exist as a mixture of *cis* and *trans* isomer in solution and their

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Table 1
Physical, analytical and NMR (^{1}H, ^{13}C, ^{31}P) spectral data (in $CDCl_3$) for $[Pd_2Ar_2(\mu\text{-pz}')_2(PR_3)_2]$.[a]

Complex	% Yield of recrystallized product	m.p. (°C)	% Analysis found (calc.)			NMR data		
			C	H	N	^{1}H	^{13}C	^{31}P
$[Pd_2Ph_2(\mu\text{-pz})_2(PEt_3)_2]$	(79)	180	49.65 (48.90)	5.90 (6.28)	7.49 (7.59)	1.13–1.26 (m, 18H, CH_3CH_2P), 1.40–1.45 (m, 12H, CH_2P), 5.92 (s, 2H, CH–4 of pz), 6.92–7.54 (m, PdPh + NCH – pz)	8.1 (s, CH_3CH_2P), 15.4 (d, CH_2P, $J(P–C) = 28$ Hz), 102.7 (s, C-4 of pz), 122.5, 126.8 138.4, 154.9 (C-1)(PdPh); 136.3, 137.2 (CHN-pz)	21.1
$[Pd_2Ph_2(\mu\text{-dmpz})_2(PEt_3)_2]$	(81)	150	51.26 (51.47)	6.69 (6.85)	6.94 (7.05)	1.10–1.15 (m, 18H, CH_3CH_2P), 1.58–1.73 (m, 12H, CH_2P), 2.12, 2.24 (each s, Me of dmpz), 5.41 (s, 2H, CH-4 of dmpz), 6.86–6.97 (m), 7.75 (d, 7 Hz, 4H, C_6H_4)	8.3 (s, CH_3CH_2P), 14.2, 14.8 (each s, Me of dmpz), 16.3 (d, $^1J(P–C) = 28$ Hz, CH_2P), 102.0 (s, C-4 of dmpz), 122.2 (s, C_6H_5), 125.9 (s, C_6H_5), 138.1 (s, C_6H_5), 144.7 (s, 5-C of dmpz), 147.4 (s, 3-C of dmpz), 152.0 (s, C-1 of C_6H_5)	16.1
$[Pd_2tol_2(\mu\text{-pz})_2(PEt_3)_2]$	(82)	190	50.05 (50.20)	5.81 (6.58)	7.87 (7.32)	1.11–1.21 (m, CH_3CH_2P); 1.39–1.44 (m, CH_2P); 2.23 (s, tol, Me); 5.92 (s, CH-4, pz); 7.00, 7.22 (each s, pz); 6.82, 7.41 (each d, 7.5 Hz)	8.1 (s, CH_3CH_2P), 15.3 (d, $^1J(P–C) = 29$ Hz CH_2P), 20.9 (s, Me of tol), 102.7 (s, C-4 of pz), 135.8, 137.0 (CHN, pz); 127.7, 138.1 (CH-tol); 131.4 (C-4, tol); 149.7 (C-1, tol)	21.3
$[Pd_2tol_2(\mu\text{-dmpz})_2(PEt_3)_2]$	(88)	190	53.2 (52.62)	6.89 (7.11)	2.04 (6.82)	1.07–1.17 (m, CH_3CH_2P); 1.62–1.74 (m, CH_2P); 2.09 (s, tol, Me); 2.21, 2.23 (each s, Me, dmpz); 5.39 (s, CH-4, dmpz); 6.78, 7.58 (each, d, 7.8 Hz, tol)	8.4 (s, CH_3CH_2P), 14.2, 14.8 (each s, Me of dmpz), 16.3 (d, $J(P–C) = 28$ Hz, CH_2P), 20.8 (s, Me of tol), 102.0 (s, , C-4 of dmpz), 126.9 (s, tol CH), 129.4 (s, dmpz), 131.1 (s, C-4 tol), 137.7 (s, tol CH), 144.7 (s, dmpz), 147.0 (C-1, tol)	16.4
$[Pd_2Ph_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	(78)	140	52.33 (52.52)	4.76 (4.92)	–	1.20, 1.29 (each d, $^2J(P–H) = 10$ Hz, PMe_2), 5.83 (s, 2H, H-4, pz), 6.91 (br, CHN); 6.99 (t, Ph); 7.15 (s, CHN, pz); 7.39–7.79 (m, Ph)	14.1, 15.4 (each d, $^1J(P–C) = 33$ Hz, PMe_2), 103.0 (s, C-4, pz), 136.5, 137.5 (each s, CHN, pz); 122.6, 126.9, 138.3, 154.2 (C-1) (Pd–Ph) 128.6 (d, 10 Hz); 130.1 (s); 131.4 (d, 11 Hz) (PPh)	1.8
$[Pd_2Ph_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$	(88)	165	54.94 (54.75)	5.50 (5.56)	–	1.36, 1.42 (each d, 10.5 Hz, Me_2P), 2.04, 2.19 (each s, Me of dmpz), 5.44 (s, 2H, CH-4 of dmpz), 6.89 (m, 6H, 3, 4, 5, C_6H_5Pd), 7.37–7.85 (m, Ph)	14.3, 14.6 (each d, $J(P–C) = 32$, 39 Hz, Me_2P), 15.2 (s, Me) 102.2 (s, C-4 of dmpz); 144.9, 147.1 (each s, CHN, dmpz); 122.3 (s), 126.2 (s), 138.0 (s), 151.9 (C-1)[Pd–Ph] 128.3, 130.2, 132.2 (d, 10 Hz); 134.5 (d, C-1) [PPh]	0.4
$[Pd_2tol_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	(74)	130	53.80 (53.67)	5.1 (5.25)	6.74 (6.95)	1.21, 1.30 (each d, $J(P–H) = 9.5$ Hz, PMe_2), 2.25 (s, 6H, $CH_3C_6H_4$), 5.84 (s, 2H, CH-4 of pz), 6.83–7.82 (m, tol + pz)	14.2, 15.5 (each d, $J(P–C) = 33$ Hz, PMe_2), 20.9 (s, Me, tol), 102.9 (s, C-4 of pz), 136.2, 137.5 (each s, CHN, pz); 127.9, 135.1 (C-4), 138.2, 149.2 (C-1) [Pd-tol] ; 128.6 (d, 10 Hz); 130.1 (s); 131.5 (d, 11 Hz), 134.5 (d, C-1) [PPh]	1.9

$[Pd_2tol_2(\mu\text{-}dmpz)_2(PMe_2Ph)_2]$	(85)	175	56.33 (55.75)	5.77 (5.84)	6.52 (6.50)	1.34, 1.41 (each d, 10.5 Hz, Me_2P), 2.03 (s, Me, tol), 2.22 (br, Me of dmpz), 5.44 (s, 2H, H-4 of dmpz), 6.75 (br, 6H, C_6H_5Pd), 7.45–7.90 (m, Ph)	14.3, 14.9 (each d, 12.9 Hz, PMe_2), 15.3 (s, Me, dmpz), 20.8 (s, tol Me), 102.2 (s, C-4 of dmpz), 144.8, 147.0 (CHN, dmpz); 127.2, 131.2 (C-4), 137.7 (Pd-tol) C-1 not detected; 128.3 (d, 10 Hz), 130.2 (s); 132.3 (d, 11 Hz); 134.5 (d, C-1) [PPh]	0.6

[a] All complexes were recrystallized from benzene-hexane as colorless crystalline solids.

relative concentration varies from one preparation to another [14]. The ^{31}P NMR spectra (Table 1) displayed single resonances indicating the presence of only one isomeric species in solution. These resonances are considerably shielded with respect to the signals for the corresponding chloro-bridged $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ derivatives ($PR_3 = PEt_3$ (~27.0 ppm) and PMe_2Ph (~3.8 ppm)) [7].

The molecular structures of $[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$, $[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]$ and $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$ with atomic numbering scheme are shown in Figs. 1–3 and the selected interatomic parameters are listed in Tables 2–4.

The complex $[Pd_2tol_2(\mu\text{-}Cl)_2(Me_2Ph)_2]$ is a centrosymmetric sym-*trans* dimer with the inversion center lying in the planar Pd_2Cl_2 ring. The two distorted square-planar metal centers are held together by bridging chloride ligands. The coordination environment around each palladium atom is defined by two *cis* bridging Cl atoms, phosphorus of PMe_2Ph and a C-α carbon atom of the aryl group. Various interatomic parameters are similar to those reported for $[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$ and $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ [7].

The complexes, $[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]$ and $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$ are comprised of two square-planar metal fragments which are held together by two pyrazolato bridges. Both complexes have similar sym-*trans* geometry around palladium atom which can be defined by two *cis* pyrazolato nitrogen atoms, aryl carbon atom and the phosphorus atom. The molecules adopt a boat like conformation as is observed for pyrazolate bridged binuclear palladium and platinum complexes [1,12,15,16]. The Pd–N bond distances vary between 2.091(13) and 2.130(6) Å with the distances *trans* to Pd–C being slightly longer reflecting stronger *trans* influence of the aryl group than the phosphine ligand. These values are in accord with those reported for pyrazolato-bridged palladium complexes [1,15]. The Pd–C and Pd–P bond distances are well in agreement with the reported values, e.g. $[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (Pd–C = 1.992(8) Å and Pd–P = 2.216(2) Å) [7].

The nature of bridging pyrazolate ligand governs the Pd···Pd separation. The Pd···Pd separation in pz-bridged complex (3.645 Å) is longer than the dmpz-bridged (3.395 Å) derivative. The effect of substituent in pyrazolate group on metal–metal separation has been reported in $[Pt_2(C{\cap}N)_2(pz')_2]$ ($C{\cap}N$ = 2-(2,4-difluorophenyl) pyridine; pz′ = pyrazolate, 3,5-dimethylpyrazolate, 3-methyl-5-*tert*-butylpyrazolate and 3,5-bis(*tert*-butyl)pyrazolate) [12]. The Pd···Pd separation in $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$ is much longer than the analogous chloro derivative $[Pd_2Cl_2(\mu\text{-}dmpz)_2(PMe_2Ph)_2]$ (Pd···Pd = 3.115 Å) [15].

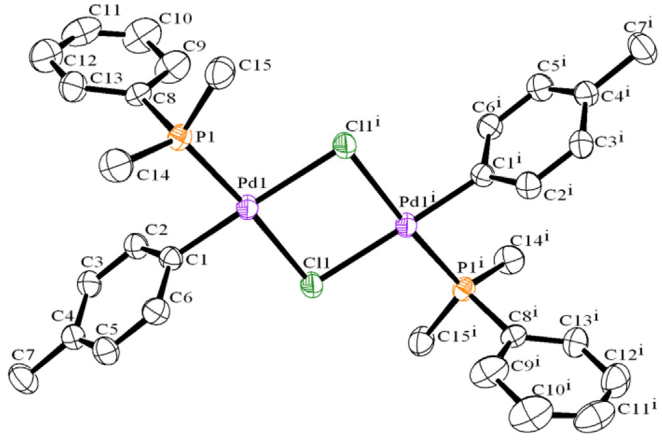

Fig. 1. ORTEP diagram of $[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (ellipsoids with 25% probability) (hydrogen atoms are omitted for clarity).

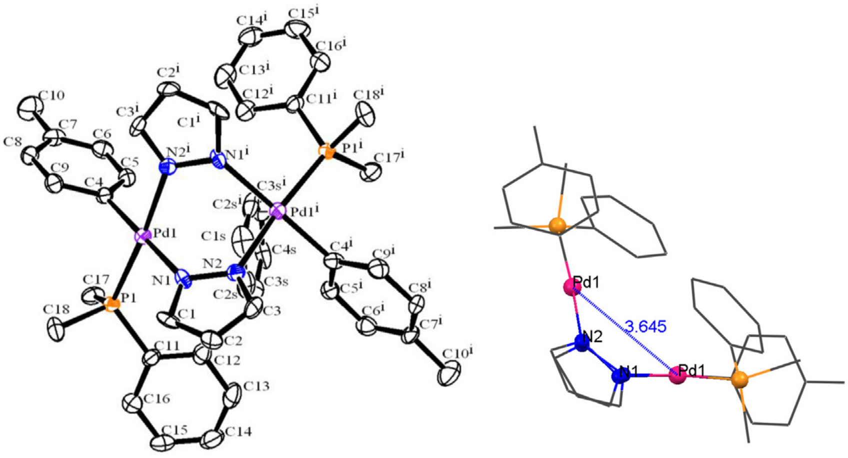

Fig. 2. ORTEP diagram of $[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]\cdot C_6H_6$ (ellipsoids with 25% probability) (solvent molecule and hydrogen atoms are omitted for clarity).

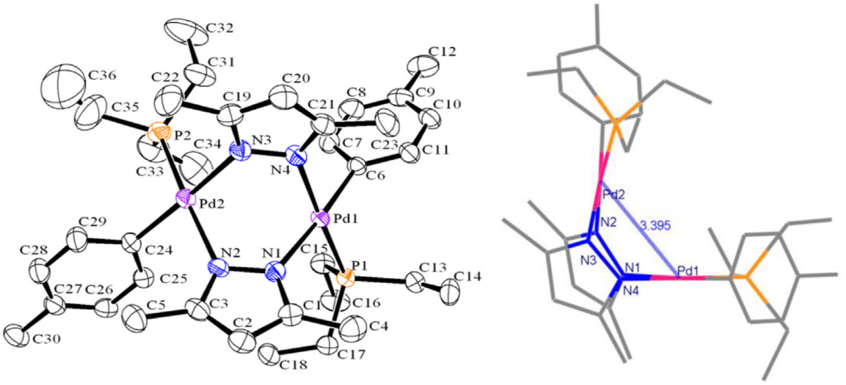

Fig. 3. ORTEP diagram of $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$ (ellipsoids with 25% probability) (hydrogen atoms are omitted for clarity).

3. Experimental

3.1. Materials and methods

The complexes $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ (Ar = Ph, 4-MeC_6H_4 (tol); PR_3 = PEt_3, PMe_2Ph) were prepared according to literature method [7]. Pyrazole and 3,5-dimethylpyrazole were obtained from commercial sources. All reactions were carried out under an argon atmosphere in dry and distilled solvents. Microanalyses were carried out on a Thermo Fischer EA 1110-CHNS instrument. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker Avance-II 300 MHz NMR spectrometer operating at 300.13, 75.47 and 121.49 MHz, respectively. Chemical shifts are relative to internal $CHCl_3$ for ^1H and ^{13}C NMR spectra and external 85% H_3PO_4 for ^{31}P NMR spectra.

Table 2
Selected bond lengths (Å) and angles (°) for $[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$.

Pd1–Cl1	2.420(2)	Pd1–C1	1.992(8)
Pd1^i–Cl1	2.449(2)	Pd1···Pd1^i	3.574
Pd1–P1	2.216(2)		
Pd1^i–Cl1–Pd1	94.46(8)	C1–Pd1–Cl1^i	175.5(2)
Cl1^i–Pd1–Cl1	85.54(8)	P1–Pd1–Cl1^i	98.21(8)
C1–Pd1–Cl1	91.4(2)	C1–Pd1–P1	84.9(2)
P1–Pd1–Cl1	176.00(8)		

Table 3
Selected bond lengths (Å) and angles (°) for $[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]\cdot C_6H_6$.

Pd1–C4	1.998(17)	Pd1–N2^i	2.107(13)
P1–Pd1	2.251(4)	N1–N2	1.359(17)
Pd1–N1	2.091(13)	Pd1···Pd1^i	3.645
C4–Pd1–P1	86.7(5)	C4–Pd1–N2^i	89.1(1)
N1–Pd1–P1	95.3(4)	N1–Pd1–N2^i	88.7(5)
N2^i–Pd1–P1	175.1(4)	N2–N1–Pd1	123.2(10)
C4–Pd1–N1	176.2(7)	N1–N2–Pd1^i	122.3(10)

3.2. Syntheses

3.2.1. Synthesis of $[Pd_2tol_2(\mu\text{-}pz)_2(PEt_3)_2]$

To a suspension of $[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (55 mg, 0.078 mmol) in methanol was added a solution of pyrazole (11 mg, 0.161 mmol)

Table 4
Selected bond lengths (Å) and angles (°) for $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$.

C6–Pd1	2.040(6)	C24–Pd2	2.020(7)
P1–Pd1	2.2608(19)	P2–Pd2	2.251(2)
N1–Pd1	2.130(6)	N2–Pd2	2.098(6)
N4–Pd1	2.091(6)	N3–Pd2	2.117(6)
N2–N1	1.366(8)	N4–N3	1.350(8)
		Pd1···Pd2	3.395
C6–Pd1–P1	85.8(2)	C24–Pd2–P2	86.8(2)
N1–Pd1–P1	97.93(15)	N3–Pd2–P2	96.00(18)
N4–Pd1–P1	177.51(16)	N2–Pd2–P2	172.08(19)
C6–Pd1–N1	175.7(2)	C24–Pd2–N3	172.8(3)
C6–Pd1–N4	91.7(2)	C24–Pd2–N2	91.7(3)
N4–Pd1–N1	84.5(2)	N2–Pd2–N3	86.4(2)
N2–N1–Pd1	119.1(4)	N4–N3–Pd2	122.0(4)
N1–N2–Pd2	117.4(4)	N3–N4–Pd1	116.0(4)

Table 5

Crystallographic data and structural refinement details for $[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$, $[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]\cdot C_6H_6$ and $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$.

Complex	$[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$	$[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]\cdot C_6H_6$	$[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$
Chemical formula	$C_{30}H_{36}Cl_2P_2Pd_2$	$C_{36}H_{42}N_4P_2Pd_{2.}$ C_6H_6	$C_{36}H_{58}N_4P_2Pd_2$
Formula weight	742.23	883.58	821.60
Crystal size (mm^3)	0.10 × 0.10 × 0.02	0.30 × 0.20 × 0.10	0.18 × 0.14 × 0.04
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	P*bca*	F*dd*2	$P2_1/c$
Unit cell dimensions			
a (Å)	13.4798(9)	11.5157(12)	12.7222(4)
b (Å)	14.1654(11)	15.800(4)	17.3525(3)
c (Å)	16.1889(9)	44.185(8)	18.6587(5)
α (°)	90.00	90	90.00
β (°)	90.00	90	107.149(3)
γ (°)	90.00	90	90.00
Volume ($Å^3$)	3091.2(4)	8039.0(3)	3936.0(2)
ρ calcd. ($g\,cm^{-3}$)	1.595	1.460	1.356
Z	4	8	4
μ (mm^{-1})/F(000)	12.081/1488	1.008/3600	8.346/1696
Limiting indices	$-16 \leq h \leq 9$	$-14 \leq h \leq 8$	$-11 \leq h \leq 15$
	$17 \leq k \leq 16$	$-11 \leq k \leq 20$	$-20 \leq k \leq 20$
	$-19 \leq l \leq 8$	$0 \leq l \leq 57$	$-22 \leq l \leq 22$
θ Range of data collection (°)	5.29–70.09	2.59–27.47	3.55–70.12
Reflections collected/unique	2862/2028	3501/2778	7329/5758
Data/restraints/parameters	2862/0/167	2778/1/227	7329/5/409
Final R_1, ωR_2 indices	0.0636/0.1741	0.0601/0.1216	0.0630/0.1806
R_1, ωR_2 (all data)	0.0906/0.1994	0.1125/0.1674	0.0857/0.1953
Goodness of fit on F^2	1.088	1.227	1.108

in methanolic ($10\ cm^3$) sodium hydroxide (6 mg, 0.15 mmol). The mixture was stirred at room temperature for 5 h, the solvent was evaporated *in vacuo* and the residue was extracted with dichloromethane ($3 \times 5\ cm^3$). This solution was concentrated to 5 ml and after adding hexane, gave colorless crystals of the title complex (49 mg, 82% yield). Similarly all other complexes were prepared and pertinent data are summarized in Table 1.

3.3. *Crystallography*

Intensity data of $[Pd_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]\cdot C_6H_6$ were collected on a Rigaku AFC 7S diffractometer fitted with Mo-Kα (λ-0.71069 Å) radiation while the data for $[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)]$ and $[Pd_2tol_2(\mu\text{-}dmpz)_2(PEt_3)_2]$ were collected on Agilent SuperNova, Titan fitted with Cu-Kα (λ-1.54184 Å) at room temperature (298 ± 2 K). The intensity data were corrected for Lorenz, polarization and absorption effects with an empirical procedure [17,18]. The structures were solved by direct methods [19] and refinement was on F^2 [20]. The non-hydrogen atoms were modeled with anisotropic displacement parameters while the hydrogen atoms were fixed in their calculated positions. Molecular structures were drawn using ORTEP [21]. Crystal data and refinement details are given in Table 5.

4. Conclusion

A convenient preparation for binuclear arylpalladium complexes $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ has been described and its utility for the synthesis of pyrozolato-bridged complexes has been demonstrated. The Pd⋯Pd separation in the pyrazolato complexes is influenced by the nature of the substituent in the pyrazolato ring.

Acknowledgments

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Appendix A. Supplementary material

CCDC 962919, 962920 and 962921 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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