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Binuclear pyrazolato-bridged organoplatinum(II) complexes: synthesis and characterization

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Abstract

Binuclear organoplatinum(II) complexes of the type $[Pt_2Ar_2(\mu\text{-}NN)_2(PR_3)_2]$ [Ar = Ph, C_6H_4Me-4 (tol), C_4H_3S-2 (th); NNH = pyrazole (pzH), 3,5-dimethylpyrazole (3,5-dmpzH), 3,4,5-trimethylpyrazole (3,4,5-tmpzH); $PR_3 = PBu_3$, PMe_2Ph, $PMePh)_2$] were prepared by reaction of $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ with NNH and sodium hydroxide in methanol. The reaction of $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$ with isopropylmercaptan gave a thiolato-bridged complex $[Pt_2tol_2(\mu\text{-}S^iPr)_2(PMe_2Ph)_2]$. All these complexes were characterized by elemental analyses and NMR (^1H and ^{31}P) spectroscopy. Some of the complexes could be isolated in the *trans* or *cis* form, others as a mixture of *cis* and *trans* isomers. Isomerization reactions have been studied by ^{31}P NMR spectroscopy.

1. Introduction

Binuclear complexes of platinum group metals have received much attention in recent years because of their structural features and reactivity, particularly with reference to homogeneous catalysis. Pyrazolato-bridged complexes of the types "$M(\mu\text{-}pz)_2M$" and "$M(\mu\text{-}X)(\mu\text{-}pz)M$" have been reported recently [1–9], and some of these have shown high catalytic activity [8]. In these complexes two metal centres are bridged by the *exo*-bidentate pyrazolate ligands and the flexibility of the pyrazolate-bridges usually leads to a puckered central metallocyclic ring.

To our knowledge bis(pyrazolate) bridged complexes of platinum of the type "$Pt(\mu\text{-}pz)_2Pt$", other than $[Pt_2(\mu\text{-}NN)_2(PC)_2]$ (NN = pz or 3,5-dmpz; PC = $^tBu_2PC(Me_2)CH_2$–) [3], have not been studied. Attempts to isolate such complexes by the reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with pyrazole lead to the formation of the products containing chloro-pyrazolate or methoxo-pyrazolate bridges or to a chloro-bridged dinuclear complex with terminal azolate groups [2,9]. When this reaction is extended to the $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ system "$Pt(\mu\text{-}pz)_2M$" complex is formed exclusively, and the results of this work are reported in this paper.

2. Experimental details

The complexes *cis*-$[PtCl_2(CH_2{=}CH_2)(PR_3)]$, $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ and Me_3SnAr were prepared according to literature methods [10,11]. Pyrazoles and tertiary phosphines were obtained from commercial sources. All the preparations were carried out under nitrogen. Elemental analyses were by the Analytical Chemistry Division of this Research Centre. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200 or Bruker AM-500 NMR spectrometers and chemical shifts are referenced to internal chloroform peak (δ 7.26 ppm). ^{31}P NMR spectra were recorded on a Varian FT-80A NMR spectrometer operating at 32.203 MHz and chemical shifts are relative to external 85% H_3PO_4.

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2.1. Preparation of $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$

To a methanol suspension of $[Pt_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (100 mg, 0.109 mmol) was added a solution of 3,5-dimethylpyrazole (23 mg, 0.239 mmol) in methanolic sodium hydroxide (0.29 ml (0.989 N), 0.287 mmol) with vigorous stirring under nitrogen. The whole solution was stirred at room temperature for 5 h. The solvent was stripped *in vacuo* and the residue was extracted with dichloromethane (3 × 5 ml). The volume was reduced to 5 ml and ethanol (5 ml) was added. On slow evaporation this gave colourless crystals of the title compound (78 mg, 0.075 mmol, 69%).

Other products were prepared similarly. Pertinent data for these complexes are summarized in Table 1.

2.2. Reaction of $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$ with PPh_3

To a $CDCl_3$ solution of $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$ (83 mg, 0.08 mmol) in an NMR tube, solid PPh_3 (46 mg, 0.175 mmol) was added and the reaction was studied by ^{31}P NMR spectroscopy. The reaction with free pyrazole was studied in similar manner.

2.3. Reaction between $[Pt_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ and pyrazole

To a $CDCl_3$ solution of $[Pt_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (118 mg, 0.128 mmol) solid pyrazole (17.5 mg, 0.257 mmol) was added and the ^{31}P NMR spectrum was recorded. After 24 h the spectroscopy was repeated.

TABLE 1. Physical and analytical data for $[Pt_2Ar_2(\mu\text{-}NN)_2(PR_3)_2]$ complexes

Complex [a]	Yield of recrystallized product (%) [b]	M.p. (°C)	Analyses (%): found (calc.)		
			C	H	N
$[Pt_2Ph_2(\mu\text{-}pz)_2(PBu_3)_2]$	45	144	46.7 (46.6)	6.5 (6.5)	4.9 (5.2)
$[Pt_2Ph_2(\mu\text{-}3,5\text{-}dmpz)_2(PBu_3)_2]$	42	166	48.2 (48.5)	6.5 (6.9)	4.3 (4.9)
$[Pt_2tol_2(\mu\text{-}pz)_2(PBu_3)_2]$	46	128	47.0 (47.5)	6.2 (6.7)	4.8 (5.0)
$[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PBu_3)_2]$	41	146	49.0 (49.4)	6.9 (7.1)	5.3 (4.8)
$[Pt_2th_2(\mu\text{-}pz)_2(PBu_3)_2]$	44	162	41.0 (41.6)	6.0 (6.1)	4.8 (5.1)
$[Pt_2th_2(\mu\text{-}3,5\text{-}dmpz)_2(PBu_3)_2]$	42	122	44.3 (43.8)	6.0 (6.5)	4.7 (4.9)
$[Pt_2Ph_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$	66	227–231(d)	44.3 (44.3)	4.7 (4.6)	5.3 (5.5)
$[Pt_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]$	68	220–222(d)	44.4 (44.0)	4.6 (4.3)	5.1 (5.7)
$[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$	69	230–233(d)	46.0 (46.2)	5.0 (4.8)	5.3 (5.4)
$[Pt_2tol_2(\mu\text{-}3,4,5\text{-}tmpz)_2(PMe_2Ph)_2]$	78	203–205(d)	47.0 (47.3)	5.1 (5.1)	5.4 (5.3)
$[Pt_2th_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$	62	170–180(d)	39.5 (39.9)	4.1 (4.1)	5.4 (5.5)
$[Pt_2th_2(\mu\text{-}3,4,5\text{-}tmpz)_2(PMe_2Ph)_2]$	66	219–220(d)	41.0 (41.1)	4.8 (4.4)	4.7 (5.3)
$[Pt_2Ph_2(\mu\text{-}pz)_2(PMePh_2)_2]$	48	142–144(d)	49.1 (49.0)	4.0 (3.9)	4.8 (5.2)
$[Pt_2Ph_2(\mu\text{-}3,5\text{-}dmpz)_2(PMePh_2)_2]$	52	206–210(d)	51.1 (50.8)	4.6 (4.4)	4.8 (4.9)
$[Pt_2Ph_2(\mu\text{-}3,4,5\text{-}tmpz)_2(PMePh_2)_2]$	47	162–164	50.9 (51.6)	4.5 (4.7)	–
$[Pt_2tol_2(\mu\text{-}pz)_2(PMePh_2)_2]$	51	202	49.8 (49.9)	4.0 (4.2)	4.4 (5.0)
$[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMePh_2)_2]$	55	218–220	51.8 (51.6)	4.9 (4.7)	4.5 (4.8)
$[Pt_2tol_2(\mu\text{-}3,4,5\text{-}tmpz)_2(PMePh_2)_2]$	62	130–132(d)	52.2 (52.4)	4.8 (4.9)	4.7 (4.7)

[a] pzH = pyrazole; 3,5-dmpzH = 3,5-dimethylpyrazole; 3,4,5-tmpzH = 3,4,5-trimethylpyrazole; tol = 4-MeC_6H_4; th = 2-C_4H_3S. [b] Recrystallized from dichloromethane-ethanol or benzene-hexane mixture on cooling for 10–15 h in a freezer.

To this a further 2 mg (0.02 mmol) of pyrazole was added to see whether isomerization had taken place. After storage for 24 h, methanolic sodium hydroxide solution was added and the resulting solution was studied by ^{31}P NMR.

2.4. Reaction of $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$ with ^iPrSH

To a $CDCl_3$ solution of $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$ (86 mg, 0.083 mmol) was added an excess of isopropyl mercaptan (0.1 ml). The reaction was monitored by ^{31}P NMR spectroscopy. The resonances for $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$ slowly vanished over a period of one week with simultaneous formation of $[Pt_2tol_2(\mu\text{-}S^iPr)_2(PMe_2Ph)_2]$. After a week solvent was evaporated and the residue was washed thoroughly with hexane and recrystallized from dichloromethane-ethanol as a pale yellow crystalline solid (60 mg, 0.06 mmol, 72%), m.p. 194–200 (dec.) (Found: C, 42.9; H, 4.8. $C_{36}H_{50}S_2P_2Pt_2$ required C, 43.3; H, 5.0%).

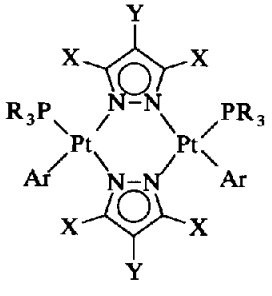
3. Results and discussion

The reaction of $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ with two moles of pyrazole in the presence of sodium hydroxide afforded bis-pyrazolate bridged complex, $[Pt_2Ar_2(\mu\text{-}NN)_2(PR_3)_2]$ exclusively (eqn. (1)).

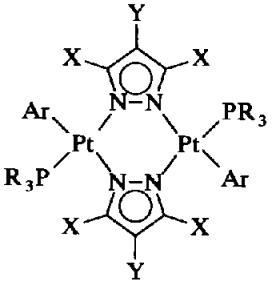
$$[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2] + 2NNH + 2NaOH \longrightarrow [Pt_2Ar_2(\mu\text{-}NN)_2(PR_3)_2] + 2NaCl + 2H_2O \quad (1)$$

where Ar = Ph, C_6H_4Me-4 (tol), C_4H_3S-2 (th); NNH = pyrazole (pzH), 3,5-dimethylpyrazole(3,5-dmpzH), 3,4,5-trimethylpyrazole (3,4,5-tmpzH); PR_3 = PBu_3, PMe_2Ph, $PMePh_2$.

All these complexes are white crystalline solids and can be recrystallized from dichloromethane-ethanol. Some of the bis(pyrazolate) complexes could be isolated as *cis* (I) or *trans* (II) isomer while others gave a mixture of the two forms. In general, separation of the two isomers was difficult since their solubilities were very similar.



cis (I)



trans (II)

The ^{31}P NMR spectra exhibited one or two resonances with platinum satellites. The former may be attributed to *cis* or *trans* isomer while the latter resonances are due to a mixture of two forms—the *trans* isomer usually predominated. The resonance with slightly larger coupling constant is on the basis of earlier reports [12] assigned to the *cis* isomer. It may be noted that the chloro-bridged complexes $[Pt_2R_2(\mu\text{-}Cl)_2(PR_3)_2]$ also exist as a mixture of *cis* and *trans* forms [11]. However, a relative ratio of the two isomers of bis(pyrazolate)-bridged complex differed than that of the chloro-bridged precursor and also varied from one preparation to another of the same complex. Isomerization may take place either after the formation of the complex or during the course of reaction. We have investigated these processes by ^{31}P NMR spectroscopy.

Catalytic amount of free ligand, protic solvents and temperature are some of the factors known to influence isomerization in platinum complexes. Thus the effects of these factors on isolated complexes were studied by ^{31}P NMR. No isomerization of *trans*-$[Pt_2Ph_2(\mu\text{-}3,4,5\text{-}tmpz)_2(PMePh_2)_2]$ (δ − 5.8, ^1J(Pt–P) = 3920 Hz) has been noticed when a chloroform solution was heated for 2 h or in the presence of catalytic amount of 3,4,5-trimethylpyrazole. When two equivalents of triphenylphosphine was added to a solution of $[Pt_2tol_2(\mu\text{-}3,5\text{-}dmpz)_2(PMe_2Ph)_2]$ (*trans* δ −18.0, ^1J(Pt–P) = 3923 Hz; *cis* δ −18.8, ^1J(Pt–P) = 3943 Hz) relative ratio of the two isomers did not change nor was any bridge cleavage of the dinuclear complex noticed even on keeping the solution for 24 h at room temperature. Clearly no isomerization takes place during the reaction.

When a $CDCl_3$ solution of $[Pt_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (*trans* δ −13.8, ^1J(Pt–P) 4904 Hz; *cis* (> 30%) δ −13.9 ppm) was treated with two equivalents of pyrazole, [Pt(tol)(Cl)(pzH)(PMe_2Ph)] (phosphine *trans* to chloride) (δ −17.6, ^1J(Pt–P) 4316 Hz) formed exclusively. The spectrum remained unaffected even on keeping the solution for 48 h at room temperature. This solution on treatment with stoichiometric quantity of methanolic sodium hydroxide gave *trans*-$[Pt_2tol_2(\mu\text{-}pz)_2(PMe_2Ph)_2]$ (δ −16.2, ^1J(Pt–P) 3903 Hz) as the only detectable species in the solution.

A similar reaction was carried out with a more sterically demanding pyrazole. Thus, when a $CDCl_3$ solution of $[Pt_2tol_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (*trans* δ 1.3, ^1J(Pt–P) 4764 Hz; *cis* (> 25%) δ 0.9 ppm) was treated with two equivalents of 3,5-dimethylpyrazole two isomers of [Pt(tol)(Cl)(3,5-dmpzH)(PBu_3)], phosphine *trans* to chloride (δ −4.6, ^1J(Pt–P) 4189 Hz) and phosphine *trans* to nitrogen (δ −3.8, ^1J(Pt–P) 4049 Hz) formed in approximate ratio 3:2. Their relative ratio did not change on keeping the solution for 24 h. To see whether

TABLE 2. ^1H and $^{31}P\{^1H\}$ NMR data for $[Pt_2Ar_2(\mu\text{-}NN)_2(PR_3)_2]$ complexes

Complex	$^{31}P\{^1H\}$ NMR data			^1H NMR data [a]
	δ (ppm)		^1J(Pt–P) (Hz)	
$[Pt_2Ph_2(\mu\text{-pz})_2(PBu_3)_2]$	*trans*	−5.0	3777	0.95 (t, 7 Hz), 1.32–1.55 (br)[Bu]; 5.78 (br, s, CH-4, pz), 6.81 (br, s, CH-pz); 6.95 (m, Ph); 7.50 (m, Ph + CH-pz)
$[Pt_2Ph_2(\mu\text{-3,5-dmpz})_2(PBu_3)_2]$	*trans*	−8.7	3767	0.75 (br), 1.40 (br)[Bu]; 2.05 (br, s, pz-Me); 2.17 (br, s,
	cis	−9.1	3793	pz-Me); 5.45 (s, br, CH-4, pz); 6.80 (br), 7.20 (br)[Ph] (*trans* isomer)
$[Pt_2tol_2(\mu\text{-pz})_2(PBu_3)_2]$	*trans*	−5.1	3789	0.80 (br), 1.40 (br)[Bu]; 2.15 (s, tol-Me); 5.90 (br, CH-4, pz); 6.65–7.40 (m, C_6H_4 + pz-3,5)
$[Pt_2tol_2(\mu\text{-3,5-dmpz})_2(PBu_3)_2]$	*trans*	−8.7	3779	0.77 (t, 7 Hz, MeCCCP); 1.23–1.42 (m, CH_2CH_2); 1.62
	cis	−9.1	3804	(m, PCH_2); 2.11 (s, pz-Me, 2Me); 2.19 (s, tol-Me, 2Me); 2.22 (s, pz-Me, 2Me); 5.50 (s, CH-4, pz); 6.70 (d, 7.5 Hz, C_6H_4); 7.57 (d, 7.5Hz, C_6H_4) (*trans* isomer)
$[Pt_2th_2(\mu\text{-pz})_2(PBu_3)_2]$	*trans*	−5.4	3560	0.85 (br), 1.50 (br)[Bu]; 6.15 (br, s, CH-4, pz); 6.50–7.45 (m, th + 3,5-pz)
$[Pt_2th_2(\mu\text{-3,5-dmpz})_2(PBu_3)_2]$	*trans*	−9.4	3549	0.80 (br), 1.5 (br)[Bu]; 2.05 (s, Me-pz); 2.22 (s, Me-pz); 5.50 (s, CH-4, pz); 6.65–7.30 (m, th)
$[Pt_2Ph_2(\mu\text{-3,5-dmpz})_2(PMe_2Ph)_2]$	*trans*	−18.1	3906	1.42(d), 1.56 (d), (10 Hz each, PMe_2 *trans* isomer);
	cis	−18.8	3929	1.46 (d), 1.52 (d) (10 Hz each, PMe_2; *cis* isomer); 2.03 (s); 2.17 (s) [Me-3 and 5, pz, *trans* isomer]; 1.88 (s), 2.25 (s) (Me-3,5, pz, *cis* isomer), 5.57 (s, CH-4, pz, *trans*); 5.46 (s), 5.73 (s) (CH-4, pz, *cis* isomer); 6.73–6.84 (m), 7.41–7.98 (m) [Ph].
$[Pt_2tol_2(\mu\text{-pz})_2(PMe_2Ph)_2]$	*trans*	−16.2	3903	1.37(d), 1.42 (d) [10 Hz each, PMe_2]; 2.18 (s, Me-tol); 5.85 (br), 6.00 (br), [CH-4, pz, *cis*]; 6.73 (d), 7.32 (d) [7.5 Hz each, C_6H_4]; 7.04 (br), 7.19 (br), 7.46 (br), 8.17 (br) [C_6H_5 + CH-3,5 pz].
$[Pt_2tol_2(\mu\text{-3,5-dmpz})_2(PMe_2Ph)_2]$	*trans*	−18.0	3923	1.41 (d), 1.52 (d) (10 Hz each, PMe_2 *trans* isomer),
	cis	−18.8	3943	1.46 (d), 1.53 (d) [10 Hz each, Pme_2, *cis* isomer], 2.19 (s, tol-Me *trans*); 2.01 (s), 2.16 (s) [Me-3,5 pz, *trans* isomer]; 2.15 (s, tol-Me *cis*); 1.88 (s), 2.24 (s) (Me-3 and 5 pz, *cis*); 5.57 (s, *trans* CH-4 pz); 5.47, 5.72 (s, CH-4 pz, *cis*); 6.64 (d, 8 Hz C_6H_4, *cis*); 6.66 (d, 8 Hz, C_6H_4, *trans*); 7.36–8.03 (m, Ph + C_6H_4).
$[Pt_2tol_2(\mu\text{-3,4,5-tmpz})_2(PMe_2Ph)_2]$	*trans*	−18.1	3901	1.36 (d), 1.48 (d) [10 Hz, PMe_2, *trans* isomer); 1.42 (d),
	cis	−18.9	3926	1.52 (d) (10 Hz each, PMe_2, *cis* isomer); 1.56 (s), 1.76 (s) (Me-4, pz *cis* isomer); 1.63 (s, Me-4, pz, *trans* isomer); 1.79 (s), 2.14 (s) [Me-3,5 pz, *cis* isomer]; 1.91 (s), 2.09 (s) [Me-3 and 5 pz, *trans* isomer]; 2.15 (s, tol-Me, *cis* isomer); 2.16 [s, tol-Me *trans* isomer]; 6.63 (d), 7.36 (d) [7 Hz each, C_6H_4 *cis* isomer); 6.66 (d), 7.51 (d) (7 Hz each C_6H_4, *trans* isomer); 7.41 (br), 7.98 (m) [Ph].
$[Pt_2th_2(\mu\text{-3,5-dmpz})_2(PMe_2Ph)_2]$	*trans*	−16.4	–	1.69 (d), 1.54 (d) (10 Hz each, PMe_2, *trans* isomer);
	cis	−18.7	3703	1.40 (d), 1.61 (d) (10 Hz each, PMe_2, *cis* isomer); 2.09 (s), 2.16 (s) (Me-3 and 5, pz, *trans* isomer); 1.89 (s), 2.23 (s) (Me-3,5 pz, *cis* isomer); 5.68 (s, CH-4, pz, *trans* isomer) 5.60 (s) 5.75 (s) (CH-4, pz, *cis* isomer); 6.53–8.17 (m, Ph + th)
$[Pt_2th_2(\mu\text{-3,4,5-tmpz})_2(PMe_2Ph)_2]$	*trans*	−16.7	3660	1.38 (d), 1.60 (d) [10 Hz, PMe_2]; 1.64 (s), 1.77 (s)
	cis	−18.9	3688	[Me-4, pz], 1.82 (s) 2.14 (s) [Me-3 and 5, pz], 6.84–8.16 (m, Ph + th) (*cis* isomer)
$[Pt_2Ph_2(\mu\text{-pz})_2(PMePh_2)_2]$	*trans*	−2.6	3962	1.50 (d, 10 Hz, PMe); 5.78 (br, CH-4, pz); 6.78–6.85 (m), 7.22–7.61 (m) [Ph + pz]
$[Pt_2Ph_2(\mu\text{-3,5-dmpz})_2(PMePh_2)_2]$	*trans*	−5.9	3949	1.46 (d, 10 Hz, PMe, *cis* isomer); 1.70 (d, 10 Hz, PMe
	cis	−3.2	–	*trans* isomer); 1.85 (s), 2.29 (s) (Me-3 and 5 pz, *trans*); 1.89 (s), 2.33 (s), (Me-3 and 5 pz, *cis* isomer); 5.46 (s, CH-4, pz *trans* isomer); 5.66 (s), 5.44 (s) (CH-4, pz *cis* isomer); 6.67–7.86 (m, Ph)
$[Pt_2Ph_2(\mu\text{-3,4,5-tmpz})_2(PMePh_2)_2]$	*trans*	−5.8	3920	1.67 (d, 10 Hz, PMe); 1.53 (s, Me-4, pz); 1.71 (s), 2.17 (s) (Me-3,5, pz); 6.66 (br), 7.11–7.55 (m) (Ph)

TABLE 2 (continued)

Complex	$^{31}P\{^1H\}$ NMR data		^1H NMR data [a]
	δ (ppm)	^1J(Pt–P) (Hz)	
$[Pt_2tol_2(\mu\text{-pz})_2(PMePh_2)_2]$	*trans* – 2.6 *cis* – 2.4	3974	1.48 (d, 10 Hz, PMe, *trans* isomer); 1.63 (d, 10 Hz, PMe, *cis* isomer); 2.16 (s, tol-Me, *trans* isomer); 2.20 (s, tol-Me *cis* isomer); 5.62 (s, CH-4, pz *cis* isomer); 5.77 (s, CH-4 pz, *trans* isomer); 6.58–7.58 (m, Ph + C_6H_4 + CH-3,5 pz)
$[Pt_2tol_2(\mu\text{-3,5-dmpz})_2(PMePh_2)_2]$	*trans* – 5.8 *cis* – 5.4	3962 4001	1.41 (d, 10 Hz, PMe, *cis* isomer); 1.69 (d, 10 Hz, PMe, *trans* isomer); 1.88 (s), 2.23 (s) (Me-3,5 pz, *cis* isomer); 1.85 (s), 2.29 (s) (Me-3,5, pz *trans* isomer), 2.21 (br, s, tol-Me *cis* + *trans* isomer); 5.46 (br CH-4 pz, *trans* isomer); 5.61 (br, CH-4 pz, *cis* isomer); 6.51 (d, 7 Hz, C_6H_4); 7.13–7.79 (m, Ph + C_6H_4)
$[Pt_2tol_2(\mu\text{-3,4,5-tmpz})_2(PMePh_2)_2]$	*trans* – 5.8 *cis* – 5.5	3936 3980	1.43 (d, 10 Hz, PMe, *cis* isomer); 1.66 (d, PMe, *trans* isomer); 1.71 (s), 2.13 (s), (Me-3,5 pz, *trans* isomer); 1.55 (s) (Me-4, pz *trans* isomer); 1.79, 2.11 (s) (Me-3,5 pz, *cis* isomer); 1.70 (s, Me-4 pz, *cis* isomer); 2.10 (s, tol-Me, *cis* isomer); 2.17 (s, tol-Me, *trans* isomer); 6.51 (d, C_6H_4); 7.12–7.76 (m, Ph + C_6H_4)

[a] Since spectra were recorded at high field ^nJ(Pt–H) is not determined because ^{195}Pt relaxes primarily *via* CSA. d = doublet, t = triplet, m = multiplet, br = broad.

protic solvents contribute to isomerization, methanol was added. ^{31}P spectrum of the resulting solution showed three peaks (δ –4.9, ^1J(Pt–P) 4099 Hz; δ –3.9, ^1J(Pt–P) 4024 Hz and δ –0.6 ppm, relative ratio 3:2:0.4) and did not change with time. The changes in the coupling constants and chemical shifts of the former two may be attributed to the solvent effects while the latter resonance may tentatively be assigned to the ionic species. This solution on treatment with two equivalents of aqueous sodium hydroxide readily gave two isomers of $[Pt_2tol_2(\mu\text{-3,5-dmpz})_2(PBu_3)_2]$ (*trans* δ –8.7, ^1J(Pt–P) 3779 Hz; *cis* δ –9.1, ^1J(Pt–P) 3804 Hz, 3:1 ratio). It can be inferred that isomerization is rapid and takes place during the process of proton abstraction from the mononuclear species, a process whose control is not yet clearly understood.

The reaction of $[Pt_2tol_2(\mu\text{-3,5-dmpz})_2(PMe_2Ph)_2]$ with isopropyl mercaptan was examined by ^{31}P NMR spectroscopy. Isopropyl mercaptan reacts slowly (about a week for completion) with the formation of *trans*-$[Pt_2tol_2(\mu\text{-S}^i\text{Pr})_2(PMe_2Ph)_2]$ (δ –16.3, ^1J(Pt–P) = 3792 Hz) [10].

The ^1H NMR spectra of these complexes were recorded at 200 and 500 MHz in $CDCl_3$. In the *cis* isomer two pyrazolate rings are magnetically non-equivalent hence two sets of resonances are expected for the substituents at 3, 4 and 5 positions of the ring. In the *trans* isomer both the pyrazolate rings are equivalent, and only one signal for the C-4 substituent is expected. However, substituents at 3 and 5-positions are non-equivalent due to different groups (PR_3 or Ar) *trans* to bridging nitrogens. In general spectra showed this trend and expected peak multiplicities. The complexes containing dimethyl(phenyl)phosphine exhibited two doublets for each isomer attributable to PMe_2 protons indicating non-equivalence of phosphine methyl groups. A similar behaviour for PMe_2Ph complexes has been reported earlier [13,14].

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