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Amidinato- and triazenido-bridged binuclear complexes of palladium and platinum

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Abstract—The reaction of $[M_2Cl_2(\mu-Cl)_2(PR_3)_2]$ (M = Pd or Pt; PR₃ = PEt₃, PBu₃, PMe₂Ph, PMePh₂) with lithium amidinate or sodium triazenide gave binuclear complexes containing amidinato- or triazenido-bridges, $[M_2Cl_2(\mu-ArNENAr)_2(PR_3)_2]$ (E = CH, CMe or N). These complexes were characterized by elemental analysis and NMR (¹H, ³¹P or ¹⁹⁵Pt) data. The structures of two complexes, $[Pd_2Cl_2\{\mu-PhNC(Me)NPh\}_2(PMe_2Ph)_2]$ (10) and $[Pt_2Cl_2(\mu-PhNNNPh)_2(PEt_3)_2]$ (11) were established by single crystal X-ray structural analyses. The ¹⁹⁵Pt NMR data show coupling between two metal centers in the *cis* triazenido-bridged complex. The corresponding amidinate bridged complex does not show coupling. The role of the bridging ligand in mediating interaction between the metal centers is probed through Extended Huckel Theory (EHT) calculations. It is suggested that M–M interactions are primarily affected by the bridging ligands. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: palladium; platinum; amidine; triazene; X-ray structure; Extended Huckel Theory

INTRODUCTION

Recently we have synthesised and characterised a series of binuclear palladium and platinum complexes [1-5] of the type $[M_2X_2(\mu-Y)_2L_2)]$ (I and II). In particular, molecules with anionic bidentate three-atom bridging ligands showed unusual properties. For example, complexes containing bridging carboxylate [2] and triazenido [3] groups exhibited unusually strong M-M interactions with a formal bond order of zero, whereas such interactions were vanishingly small for the corresponding acetamidinato [4]- and 2- hydroxypyridinato [5]-bridged complexes. This has motivated us to initiate a systematic study on palladium and platinum complexes with anionic threeatom ligands. Amidines are one of the members of this class of ligands. They are known to stabilize metal-metal bonds [6]. Amidines coordinate either in the neutral form (via amine-N or imine-N atom) or as

the amidinate ion [7, 8]. Electronic and steric properties of an amidine ligand can be modified by varying the organic substituents on the nitrogen atoms and the central carbon atom. For example, formamidinate ligands are known to favour unusual structural features in metal complexes [9, 10].



(where M = Pd or Pt; X = halide, alkyl or aryl groups, Y = anionic one-atom bridging ligand such as halide, SR etc., two-atom bridging ligand such as pyrazolate ion or three-atom bridging ligands such as AcO, RNNNR⁻, RNCR'NR⁻, etc.)

Herein we report, as part of our ongoing investigation, synthesis and characterisation of palladium

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and platinum complexes with amidinate ligands. For comparison, X-ray structure and ¹⁹⁵Pt NMR data for a triazenido-bridged platinum complex, $[Pt_2Cl_2(\mu-PhNNNPh)_2(PEt_3)_2]$ (11) are also included.

RESULTS AND DISCUSSION

Amidinato-bridged binuclear palladium and platinum complexes, $[M_2Cl_2(\mu$ -ArN=CH-NAr)₂ (PR₃)₂] (M=Pd or Pt; Ar=tol, MeOC₆H₄) can readily be obtained by the reaction of $[M_2Cl_2(\mu$ -Cl)₂(PR₃)₂] (M=Pd or Pt; PR₃=PEt₃, PBu₃, PMe₂Ph or PMePh₂) with the lithium salt of formamidine in 1:2 molar ratio. The treatment of $[M_2Cl_2(\mu$ -Cl)₂(PR₃)₂] with formamidines affords mononuclear complexes containing neutral formamidine. These complexes are yellow to orange coloured crystalline solids, soluble in common organic solvents.

The ${}^{31}P{}^{1}H$ NMR spectra (Table 1) of these complexes exhibited a single resonance for tertiary phosphines indicating the formation of only one isomeric form exclusively. The magnitude of ${}^{1}J(Pt-P)$ for the $[Pt_2Cl_2{\mu-tolNCHNtol}_2(PMe_2Ph)_2]$ is comparable to the corresponding acetamidinato- and triazenidobridged [3, 4] platinum complexes. The ¹H NMR spectra of these complexes showed two singlets of equal integration each for methyl and methoxy protons of aryl groups attached to the nitrogen atoms. One can be assigned to the NAr group trans to the phosphine and other trans to the terminal chloride. The sym trans configuration is further substantiated by the presence of one NCHN resonance for the formamidinate group, however in the platinum complex two closely spaced singlets were observed. The complexes containing PMe₂Ph ligands displayed two doublets due to $J({}^{31}P-{}^{1}H)$ couplings for methyl protons indicating non-equivalence of the methyl groups. The ¹⁹⁵Pt NMR spectrum of $[Pt_2Cl_2\{\mu\text{-tolNC}(H)Ntol\})_2(PMe_2Ph)_2)]$ exhibited a doublet at δ -3245 ppm with ${}^{1}J({}^{195}\text{Pt}-{}^{31}\text{P})$ 3555 Hz. The ^{195}Pt NMR spectrum of $[\text{Pt}_2\text{Cl}_2(\mu\text{-}$ PhNNNPh)₂(PEt₃)₂] (11) showed a doublet at δ -3194 ppm with ${}^{1}J({}^{195}Pt-{}^{31}P)$ 3542 Hz (Fig. 1). Unlike the amidinato bridged complex 10, the spectrum of 11 also showed ⁿJ(Pt-Pt) coupling of 1535 Hz in the ¹⁹⁵Pt

Table 1. ¹H and ³¹P{¹H} NMR data for the palladium and platinum complexes with amidimes

Complex	$\delta^{31}\mathbf{P}$	¹ H NMR data		
[PtCl ₂ (dtfH)(PBu ₃)] (1)	- 7.0ª	0.96(t, 7.2 Hz, PCCCMe); 1.46–1.65 (m, PCH ₂ CH ₂ _);1.87 (m, PCH ₂); 2.32 (s, tol-Me, 6 H); 6.95(d, 8.4 Hz, 2 H); 7.14(d, 7.6 Hz, 4 H); 7.42(d, 8.3 Hz, 2 H)		
$[Pt_2Cl_2(\mu-dtf)_2(PMe_2Ph)_2] (2)$	-26.2 ^b	$[C_6H_4]$;8.18(d,d, 10.7 Hz, NCHN); 8.97 (d, 12 Hz, NH-) 1.73, 1.95 (each d, 11.6 Hz, PMe ₂); 2.13 (s), 2.26 (s) (each 6 H, tol-Me); 6.60(d) 6.74 (d), 6.97 (d), 7.15 (d) (each 6.2 Hz, C ₆ H ₄); 7.31-7.41 (m), 7.70-7.76 (m) Pbl: 7.57, 7.61 (each s, NCHN)		
$[Pd_2Cl_2(\mu-dtf)_2(PEt_3)_2] (3)$	21.8	1.03 (d,t, 7.7 Hz (t), 16 Hz(d), PCH ₂ Me); 1.62 (m), 1.86(m) (PCH ₂ $-$); 2.18(s), 2.34(s) (tol-Me); 6.71 (s)*; 7.07 (d), 7.37 (d) (each 8.2 Hz, C ₆ H ₄); 7.34 (s, NCHN)		
$[Pd_2Cl_2(\mu\text{-bpmpf})_2(PEt_3)_2]$ (4)	22.0	1.06 (d,t, 7.7 Hz(t), 16 Hz(d), PCH ₂ Me); 1.56–1.61 (m), 1.80–1.89 (m) (PCH ₂ -); 3.69(s); 3.80(s) (OMe); 6.48(d), 6.73(d), 6.83(d), 7.41 (d) (each 8.8 Hz, C, H, b); 7.28 (c), 7.24 (c) (N)CHN)		
$[Pd_2Cl_2(\mu-dtf)_2(PBu_3)_2] (5)$	15.7	$\begin{array}{l} \textbf{0.50 (t, 7.2 Hz, PCCCMe); 1.32 (m, PCCH_2CH_2); 1.46-1.86 (m, PCH_2-); 2.18 \\ (s), 2.34 (s) (tol-Me); 6.68 (d,)^{**}; 7.06(d), 7.40 (d) (each 8.2 Hz, C_6H_4); 7.35(s, NCLE) \\ \end{array}$		
$[Pd_2Cl_2(\mu\text{-bpmpf})_2(PBu_3)_2]$ (6)	15.8	NC <i>HN</i>) $0.91(t, 7.2 \text{ Hz}, \text{PCCC}Me)$; $1.24-1.46$ (m, $\text{PCCH}_2\text{CH}_2-$); 1.87 (m, PCH_2-); $3.68(s), 3.81$ (s) (OMe); 6.47 (d), 6.69 (d), 6.83 (d), 7.44 (d) (each 8.8 Hz, $C_6\text{H}_4$); 7.20 (c), 7.22 (c), 7.25 (c) (CLDN)		
$[Pd_{2}Cl_{2}(\mu-dtf)_{2}(PMe_{2}Ph)_{2}] (7)$	1.0	1.29 (s), 1.35 (s), (1.5 (s) (INCHIN) 1.72 (d), 1.95 (d) (each 12.2 Hz, PMe ₂); 2.11 (s), 2.26 (s) (tol-Me); 6.51 (d), 6.60(d), 6.98 (d) (each 8.2 Hz, C_6H_4 , 6 H); 7.21-7.40 (m), 7.60-7.65 (m, Pb + C H (2H) + NC(HN)		
$[Pd_2Cl_2(\mu-bpmpf)_2(PMe_2Ph)_2]$ (8)	1.1	$1.72 (d), 1.92 (d) (each 12.2 Hz, PMe_2); 3.62 (s), 3.75 (s) (OMe); 6.24 (d) 6.58 (d), 6.74 (d) (each 8.8 Hz, C, H, 6 H); 7.24.7 58 (m, Pb+C, H, (2 H)+NCHN)$		
$[Pd_2Cl_2(\mu-dtf)_2(PMePh_2)_2]$ (9)	13.8	(a), $0.1 \times (a)$ (due to bill, $c_{4,14}^{(1)}$, 0.12×1.56 (d), $1.11 \times c_{4,14}^{(1)}$ (2.11) + 1.011×1.56 2.25 (d, 12.0 Hz, PMe); 2.05 (s), 2.33 (s) (tol-Me); 6.35 (d), 6.42 (d) ($C_{6}H_{4}, 4$ H); 7.05 (m), 7.44 (m), 8.03 (m) (Ph + $C_{6}H_{4}$ + NCHN)		
$[Pd_2Cl_2(\mu-dpa)_2(PMe_2Ph)_2] (10)$	2.9	1.78 (s, CMe); 1.84 (d) 2.08 (d) (each 12.4 Hz PMe ₂); 6.17–7.18 (m), 8.06 (m) [Ph]		
$[Pt_2Cl_2(\mu-dpt)_2(PEt_3)_2] (11)$	-12.2°	1.06 (m, 18 H, PC <i>Me</i>); 1.69 (m, 6 H), 1.91(m, 6 H) (PCH ₂ -); 6.99 (m) 7.60 (t, 7.3 Hz), 7.32 (t, 7.8 Hz) 7.60 (d, 7.9 Hz) [20 H, Ph]		

 $dtfH = tolN = C(H)NHtol; \ dtf = [tolNC(H)Ntol]^{-}; \ bpmpf = [MeOC_6H_4NC(H)NC_6H_4OMe]^{-} \ dpa = [PhNC(Me)NPh]^{-} \ dpa = [PhNNNPh]^{-} \ (a)^1J(Pt-P) = 3351 \ Hz \ (b)^1J(Pt-P) = 3570 \ Hz \ (c)^1J(Pt-P) = 3496 \ Hz \ * \ integrated \ to \ 4 \ H \ protons \ **AB \ quartet, \ integrated \ to \ 4 \ H \ protons.$



Fig. 1. ¹⁹⁵Pt{¹H}NMR spectrum of $[Pt_2Cl_2(\mu-PhNNNPh)_2(PEt_3)_2]$ in CDC1₃.

NMR spectrum indicating significant platinum platinum interaction as reported earlier by us [3].

A few reactions of formamidinato-bridged palladium complexes were also investigated. The complex $[Pd_2Cl_2{\mu-tolNCHNtol}_2(PBu_3)_2]$ on treatment with an ethereal solution of HCl afforded a mononuclear complex, $[PdCl_2(tolN=CH-NHtol)(PBu_3)]$ ($\delta^{-31}P$ 26.1 ppm) formed by protonation of the bridging ligand eq. (1). A similar species ($\delta^{-31}P$ 26.1 ppm) was formed when $[Pd_2Cl_2(\mu-Cl)_2(PBu_3)_2]$ was treated with di-p-tolylformamidine. It is interesting to note that the triazenido-bridged complexes react reversibly with HCl [3]. Addition of triphenylphosphine to a CDCl₃ solution of $[Pd_2Cl_2{\mu-tolNCHNtol}_2(PBu_3)_2]$ has no effect on its ³¹P NMR spectra indicating non-lability of the formamidinato-bridges with neutral donor ligands.

$$[Pd_2Cl_2\{\mu - tolNC(H)Ntol\}_2(PBu_3)_2] + 2HCl \rightarrow 2[PdCl_2\{tolNHC(H)Ntol\}(PBu_3)].... (1)$$

The molecular structures of acetamidinato- and triazenido-bridged complexes, $[Pd_2Cl_2]$ μ -PhNC(Me)N- $Ph_{2}(PMe_{2}Ph_{2})$ (10)and $[Pt_2Cl_2(\mu PhNNPh_{2}(PEt_{3})_{2}$ (11) were established by X-ray diffraction. The structures of 10 and 11 comprise of four molecules per unit cell separated by normal van der Waals distances. Molecular structures together with the crystallographic numbering scheme are shown in ORTEP drawings (Figs 2 and 3). Each molecule consists of two distorted square planar metal (Pd or Pt) atoms bridged together by [PhNC(Me)N-Ph]⁻ or [PhNNNPh]⁻ groups. The bridging ligands in both molecules are *cis* with respect to each other, whereas the ancillary ligands Cl and PR₃ are trans related.

In **10** the C–N bond distances $[N(1A)-C(11A), N(1B)-C(11A), N(1C)-C(11B), N(1D)-C(11B) [av. 1.326 Å] are intermediate between the typical C–N (1.48 Å) and C=N (1.24 Å) covalent bond distances, indicating <math>\pi$ -electron delocalozation in the NCN skeleton. This is further substantiated by the sum of inter bond angles around carbon (359.9°) and nitrogen (av. 359.7(5)°) atoms of the NCN skeleton. The NCN bite angles [121.7(6), 122.6(6)°] and bite distances [(N(1A)–N(1B) 2.321 Å and N(1C)–N(1D) 2.324 Å] are of the same magnitude as reported for other bridging ami-

dinato-bridged complexes [11–13]. There are distinctly two types of Pd-N distances (Table 2). One with chloride trans to nitrogen is shorter than the other one where phosphine is *trans* to nitrogen, owing to the stronger trans influence of the phosphine. The two Pd-N distances lie in the range 1.86 and 2.15 Å reported in several palladium complexes [6, 11, 14–16]. The two Pd-P and Pd-Cl distances are essentially identical and compare well with the reported values [17, 18]. The Pd–Pd separation [2.914(2) Å] is shorter than the $[Pd_2(\mu-NHCPhNH)_2(\eta^3-C_3H_5)_2]$ [3.218(1)Å], however it is comparable to $[Pt_2(\mu-PhNCHNPh)_2(\eta^2-PhN (CHNPh)_2$ (2.918(9) Å) [13]. The two palladium atoms lie within the distances reported for binuclear complexes containing anionic three-atom bridging ligands (Table 3) [19-25].

The complex **11** has two platinum atoms at a separation of 2.9302(8) Å (Table 4). This distance is comparable with other binuclear complexes containing anionic three atom bridging ligands (Table 3). The two N–N bonds are nearly equivalent and the N–N– N angle is 116.6(6)° indicating pronounced π -electron deloclization [20]. The Pt–N bond distance *trans* to the phosphine ligand is longer than the Pt–N bond *trans* to the chloride. The bridging PhNNNPh ligands are *cis* with respect to each other. Unlike complex **10**, complex **11** has a crystallographically imposed C₂ symmetry.

The face to face juxtaposition of two square planar d⁸ metal centres is expected to result in antibonding interactions between the metal centres on the basis of qualitative molecular orbital theory. However, the frequent occurrence of short contacts in such units has caused much debate [26] regarding the possible ways by which these metal-metal interactions could become favorable. Recent work in this area has suggested several factors which make the metal-metal interaction in these systems less antibonding [27]. In the present work, it was possible to observe Pt-Pt coupling in the ¹⁹⁵Pt NMR spectra of the triazenidobridged complexes, whereas in the corresponding acetamidinato-bridged platinum derivatives no coupling between the metal centres could be observed. The metal-metal distance in the complex 10 should be comparable to that of complex 11 since M-M distances are primarily controlled by the ligand [28]. It is

3533



Fig. 2. Molecular structure with crystallographic numbering scheme for $[Pd_2Cl_2\{\mu-PhNC(Me)NPh\}_2(PMe_2Ph)_2]$ (10) (phenyl groups are omitted for clarity).



Fig. 3. ORTEP view with crystallographic numbering scheme for $[Pt_2Cl_2(\mu-PhNNNPh)_2(PEt_3)_2]$ (11) (phenyl groups are omitted for clarity).

3534

Amidinato- and triazenido-bridged binuclear complexes of palladium and platinum

	(10)	
2.097(5)	Pd(2)–N(1C)	2.112(5)
2.059(5)	Pd(2)–N(1B)	2.062(5)
2.262(2)	Pd(2)–P(2)	2.262(2)
2.311(2)	Pd(2)–Cl(2)	2.314(2)
1.817(7)	P(2)–C(21)	1.810(7)
1.799(7)	P(2)–C(22)	1.806(7)
1.831(8)	P(2)–C(211)	1.809(8)
1.440(8)	N(1C)-C(1C)	1.431(9)
1.321(8)	N(1C)-C(11B)	1.297(9)
1.438(8)	N(1D)-C(1D)	1.422(8)
1.332(8)	N(1D)-C(11B)	1.354(8)
2.914(2)		
88.5(2)	N(1B)-Pd(2)-N-(1C)	89.0(2)
176.5(2)	N(1C)-Pd(2)-P(2)	176.2(2)
91.1(2)	N(1C)-Pd(2)-Cl(2)	90.4(2)
93.2(2)	N(1B)-Pd(2)-P(2)	93.0(2)
175.2(2)	N(1B)-Pd(2)-Cl(2)	174.5(2)
86.92(8)	P(2)-Pd(2)-Cl(2)	87.31(8)
124.0(5)	C(11A)-N(1B)-Pd(2)	126.6(5)
124.7(5)	C(11B)-N(1C)-Pd(2)	124.5(5)
121.7(6)	N(1C)-C(11B)-N(1D)	122.6(6)
118.8(6)	N(1C)-C(11B)-C(12B)	118.7(7)
119.4(6)	N(1D)-C(11B)-C(12B)	118.6(6)
	$\begin{array}{c} 2.097(5)\\ 2.059(5)\\ 2.262(2)\\ 2.311(2)\\ 1.817(7)\\ 1.799(7)\\ 1.831(8)\\ 1.440(8)\\ 1.321(8)\\ 1.321(8)\\ 1.32(8)\\ 2.914(2)\\ 88.5(2)\\ 176.5(2)\\ 91.1(2)\\ 93.2(2)\\ 175.2(2)\\ 86.92(8)\\ 124.0(5)\\ 124.7(5)\\ 121.7(6)\\ 118.8(6)\\ 119.4(6)\\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 2.Selected bond lengths (Å) and angles (°) for $[Pd_2Cl_2\{\mu-PhNC(Me)NPh\}_2(PMe_2Ph)_2]$ (10)

Table 3. Pd-Pd distance in some binuclear palladium complexes

Complex	Pd–Pd distance (Å)	Reference
$[Pd_2{\mu-MeNNNMe}_2(\eta^3-C_4H_7)_2]$	2.97	19
$[Pd_2\{\mu\text{-tolNNNtol}\}_2(\eta^3\text{-}C_4\text{H}_7)_2]$	2.86	20
$[Pd_2(\mu - OAc)_2(\eta^3 - C_3H_5)_2]$	2.94	21
$[Pd_2(\mu-NHCPhNH)_2(\eta^3-C_3H_5)_2]$	3.128(1)	11
$[Pd_2(\mu-Cl)_2(\eta^3-C_3H_5)_2]$	3.460	22
$[Pd_2Cl_2(\mu-OAc)_2(PMe_2Ph)_2]$	2.946(2)	23
$[Pd_2Cl_2(\mu-Spy)_2(PMe_3)_2]$	2.942(2)	24
$[Pd_2Cl_2(\mu-Spy)_2(PMe_2Ph)_2]$	2.921(2)	25
$[Pd_2Cl_2(\mu-Spy)_2(PMePh_2)_2]$	2.982(3)	25

 $Spy = SC_5H_4N$ (2-mercaptopyridinate ion).

possible that the ligand controls, not only the distance but the interaction between the two metal centres in a significant fashion. In order to probe the role of the ligand in mediating metal-metal interactions, we have carried out Extended Huckel Theory (EHT) calculations on model systems. Our results suggest that in addition to the factors identified earlier, the nature of bridging ligands and their relative disposition (Scheme 1) in the metal complex could play a significant role in determining the metal-metal interactions.

Calculations were carried out using the program CACAO [29], on model complexes constructed using the crystallographic coordinates for the heavy atoms wherever available. In other cases, models were constructed based on observed metal-ligand geometries of related d⁸ complexes. The reduced overlap population (ROP) computed by EHT, gives a measure of the relative interaction between the metal centres in various complexes studied. Being fully aware of the limitations of EHT to reliably quantify interaction energies, we merely interpret trends in the computed ROP as done by Aullon and Alvarez [30]. The computed ROPs along with the M–M distances and the nature of the bridge are given in Table 5 together with the ROP computed in the absence of the bridging ligand. In general the bridging ligand has greater influence on metal–metal interactions in these systems compared to the ancillary ligands Cl and PH₃. While

Pt(1A)-Pt(1)	2.9302(8)	P(1)-C(3)	1.73(2)
Pt(1)-CI(1)	2.323(2)	P(1)-C(5)	1.809(9)
Pt(1)–P(1)	2.257(2)	N(1A)-N(1B)	1.319(9)
Pt(1)–N(1A)	2.014(6)	N(1B)–N(1C)	1.296(8)
Pt(1A)–N(1C)	2.110(6)	N(1C)-C(1B)	1.460(9)
P(1)–C(1)	1.79(2)	N(1A)-C(1A)	1.453(8)
P(1)-Pt(1)-N(1A)	93.9(2)	Pt(1)-N(1A)-C(1A)	122.5(5)
C1(1)-Pt(1)-P(1)	89.12(7)	N(1A)-N(1B)-N(1CA)	116.6(6)
C1(1)-Pt(1)-N(1A)	175.4(2)	N(1BA)-N(1C)-C(1B)	109.6(6)
Pt(1)-N(1A)-N(1B)	127.6(4)	N(1B)-N(1A)-C(1A)	109.4(6)
Pt(1A)-N(1CA)-N(1B)	115.8(4)	Pt(1)-P(1)-C(1)	124.1(6)
Pt(1A)–N(1CA)–C(1BA)	134.4(5)	Pt(1)-P(1)-C(3)	113.7(7)
		Pt(1)-P(1)-C(5)	113.6(3)

Table 4. Selected bond lengths (Å) and angles (°) for [Pt₂CI₂(µ-PhNNNPh)₂ (PEt₃)₂] (11)



X-Y-X = O=C(Me)-O or HN=N-NH or HN=C(H)-NH

Scheme 1. X-Y-X = O = C(Me) - O or HN = N - NH or HN = C(H) - NH

	Geometry		Pt–Pt				
		Cl and PH ₃	Distance (Å)	Coupling constant (Hz)	ROP ($\times 10^3$)		
Complex	Bridge				With bridge	Without bridge	Ref.
[Pt ₂ (NNN) ₂ Cl ₂ (PH ₃) ₂]	cis	trans	2.930	1587	59	54	3
	trans	trans			50		
	cis	cis			59	53	
	trans	cis			46		
[Pt ₂ (OAc) ₂ Cl ₂ (PH ₃) ₂]	cis	trans	2.943	1148	42	52	2
	trans	trans			26		
	cis	cis			41	50	
	trans	cis			26		
$[Pt_2(NCN)_2Cl_2(PH_3)_2]$	cis	trans	2.912		36	56	13
	trans	trans		Not observed	25		4
	cis	cis			34	57	
	trans	cis			25		

Table 5. Reduced Overlap Populations computed by EHT

Bridging ligands: NNN=HNNNH; OAc=OC(CH₃)O; NCN=HNC(H)NH.

the σ donor and π - acceptor capabilities of the ligand, PH₃ (with no d orbitals on the P) would be different from that of PPh₃, we expect the trends would be similar even if PPh₃ were to be used in the calculations. The bridging ligand reduces the observed ROP except in the case of triazenide ligand where the ROP is increased marginally. It is also important to note that the relative orientation of the supporting ligands Cl and PH₃, do not change the ROP to a significant degree. However, the *cis* or *trans* nature of the bridging ligand changes the ROP between the metal centres by approximately 0.01 units which is 20% of the computed ROP. This suggests that the metal-metal interaction is significantly affected by the nature and relative orientation of the bridging ligand.

The ROP in these three cases are not very different. However, it is important to note the relative changes the ligands bring about in the computed ROP. For the amidinato complex and the acetato complex, the ROP is decreased by 36% and 19% respectively on adding the bridging ligands. In the case of amidinato complex, the reduction in the ROP is even greater (55%) when the bridging ligands are trans. A significant change is observed in the case of the triazenido complex where a small increase (1%) in the computed ROP is observed. To understand how the amidinato complex enhances the antibonding interaction between the metal centres, and the triazenido ligand decreases the antibonding interaction, a fragment molecular orbital analysis was carried out. The results of this analysis suggest that the bridging ligand primarily interacts through its non bonding σ donor orbitals and the empty π^* orbitals. Apart from donation of electrons to the empty metal orbitals, the σ orbitals interact with the metal-metal σ (cis or trans geometry) and π (*trans* geometry only) orbitals. The empty π^* orbitals on the other hand have the appropriate symmetry to interact with the metal-metal δ type orbitals. The former interaction results in the interaction of the filled shells and reduces the ROP and the latter is responsible for a marginal increase in ROP. In the trans geometry, there is a greater reduction in the M-M ROP due to destabilisation of the π type M–M bonding orbitals. The metal–metal interaction is significantly decreased on adding the amidinato bridging ligands, because of the larger overlap of the the nonbonding electrons in the ligand with the filled metal–metal σ orbital. In addition, the amidinato ligand is a poor π acceptor because the π^* levels lie much higher in energy and have smaller contributions on the interacting atoms compared to the π acceptor orbitals of the triazenido ligand. On the other hand the triazenido ligand has suitable π^* orbitals of low energy which stabilize the M–M δ bond. As a result the triazenido ligand increases the M-M ROP, albeit, to a small extent.

Our results are in complete agreement with a recent study carried out on the interaction between d⁸ metal centres stacked in a face to face fashion by Aullon and Alvarez [28]. While the nature of bridging ligands has not been addressed, the effect of π acidic ligands in modulating the ROP of the interacting metal centres has been studied. They have noted an increase in the ROP with increase in the number of π acid-ligands surrounding the metal atom. Where structures are available, the corresponding M–M distances observed in such complexes are also smaller. The X-ray crystallographic database analysis done by them demonstrates the generality of the phenomenon. Similarly, π donor ligands were shown to increase the antibonding effect between the metal atoms.

On the basis of the results obtained above, it is clear how the nature and relative disposition of the bridge determines whether one observes Pt-Pt coupling in the ¹⁹⁵Pt NMR. There are two three-atom bridged complexes for which Pt-Pt coupling have been observed and one, the amidinato-bridged complex where there is no Pt-Pt coupling. In the case of the amidinato complex some of us had studied earlier [4], the geometry of the bridging ligands are *trans* and no Pt-Pt coupling was observed. This is readily explained by the large reduction in ROP (55%) with amidinato ligands in the trans geometry. In cases where the bridging ligands are cis to each other, the reduction in ROP is less, especially in the case of triazenido- and acetatobridged complexes. Hence it is possible to observe the Pt-Pt coupling in the ¹⁹⁵Pt NMR spectra of the latter systems.

EXPERIMENTAL

Formamidines (ArN=CH–NHAr); Ar = 4-MeC₆H₄ (tol), 4-MeOC₆H₄) [31] and [M₂Cl₂(μ -Cl)₂(PR₃)₂] (M = Pd or Pt) [32] and [Pt₂Cl₂(μ -PhNNNPh)₂(PEt₃)₂]³ were prepared according to the literature methods. All the reactions were carried out in dried and distilled analytical grade solvents under a nitrogen atmosphere. The ¹H, ³¹P{¹H} and ¹⁹⁵Pt {¹H} NMR spectra were recorded on a Bruker DPX-300 spectrometer in freshly prepared CDCl₃ solutions. Chemical shifts are referred to internal chloroform peak (δ CHCl₃ 7.26 ppm) for ¹H, external 85% H₃PO₄ for ³¹P and external Na₂PtCl₆ solution in D₂O for ¹⁹⁵Pt. Elemental analyses were carried out by the Analytical Chemistry Division of this research centre.

Preparation of [PtCl₂{tolNCH-NHtol}(PBu₃)]

To a dichloromethane (10 cm^3) solution of $[Pt_2Cl_2(\mu-Cl)_2(PBu_3)_2]$ (119 mg, 0.127 mmol) was added a dichloromethane (5 cm³) solution of N,N' - di-p-tolylformamidine (64 mg, 0.284 mmol) and the reaction mixture was stirred for 1 h at room temperature. The solvent was stripped off in vacuo and the residue was recrystallised from hexane as a pale yellow colored solid (70 mg, 40% yield).

A. Singha *et all*

Recry.solvent melting point % analyses found (calcd.) Complex (% yield) $(^{\circ}C)$ Η Ν C $[PtCl_2(dtfH)(PBu_3)](1)$ hexane (40) 124-126 47.2 (46.8) 6.2 (6.3) 3.9 (4.0) $[Pt_2Cl_2{\mu-dtf}_2(PMe_2Ph)_2]$ (2) benzene-hexane (60) 250-255 (d) 47.2 (46.7) 4.1 (4.4) 4.7 (4.7) $[Pd_2Cl_2{\mu-dtf}_2(PEt_3)_2]$ (3) benzene-hexane (48) 195-199 (d) 49.6 (52.2) 6.4 (6.3) 5.6 (5.8) 194-199 (d) $[Pd_2Cl_2{\mu-bpmpf}_2)(PEt_3)_2](4)$ benzene-hexane (62) 48.0 (48.9) 5.3 (5.8) 5.3 (5.4) $[Pd_2Cl_2\{\mu-dtf\}_2(PBu_3)_2](5)$ hexane (62) 170-172 55.6 (57.1) 7.1 (7.5) 4.6 (4.9) $[Pd_2Cl_2{\mu-bpmpf}_2(PBu_3)_2]$ (6) benzene-hexane (62) 180 - 18253.5 (54.1) 6.7 (7.0) 4.8 (4.7) 5.6 (5.2) $[Pd_2Cl_2{\mu-dtf}_2(PMe_2Ph)_2]$ (7) 198-203 (d) 54.6 (54.9) 5.5 (5.6) benzene-hexane (58) $[Pd_2Cl_2{\mu-bpmpf}_2(PMe_2Ph)_2]$ (8) benzene-hexane (59) 192-196 (d) 51.7(51.6) 4.0 (4.9) 5.5 (5.2) $[Pd_2Cl_2{\mu-dtf}_2(PMePh)_2)_2]$ (9) benzene-hexane (59) 206–210 (d) 58.7 (59.5) 4.9 (5.0) 49(49) $[Pd_2Cl_2\{\mu-dpa)_2(PMe_2Ph)_2]$ (10) benzene-hexane (59) 186-190 (d) 53.3 (54.0) 5.1 (4.9) 5.8 (5.7) 174-178 (d) 39.7 (39.5) CH₂Cl₂-benzene-4.5 (4.6) $[Pt_2Cl_2\{\mu-dpt\}_2(PEt_3)_2]$ (11) 7.5 (7.7) hexane (65)

Table 6.Physical and analytical data for palladium and platinum complexes with amidine ligands

 $dtfH = tolN = CH-NHtol; \ dtf = [tolNC(H)Ntol]^{-}; \ bpmpf = \ [MeOC_{6}H_{4}NC(H)NC_{6}H_{4}OMe]^{-} \quad dpa = [PhNC(Me)NPh]^{-}; \ dpt = [PhNNPh]^{-}.$

Preparation of $[Pd_2Cl_2\{\mu\text{-tolNC}(H)Ntol\}_2(PMe_2Ph)_2)]$

To a lithioformamidinate suspension, prepared by neutralizing a THF solution of N,N'-di-p-tolylformamidine (98 mg, 0.436 mmol) with a hexane solution of n-butyllithium (0.45 N, 1 cm³, 0.45 mmol), solid [Pd₂Cl₂(μ -Cl)₂(PMe₂Ph)₂)] (128 mg, 0.203 mmol) was added. The resulting solution was stirred for two days at room temperature under a nitrogen atmosphere. The solvents were removed in vacuo and the residue was extracted with benzene (3 × 3 cm³) and filtered. The filterate was concentrated *in vacuo* and the residue was recrystallised from benzene-hexane mixture in 58% (119 mg) yield as an orange crystalline solid. Similarly all other complexes were prepared. Pertinent data are given in Table 6.

Reaction between $[Pd_2Cl_2\{\mu-tolNC(H)Ntol\}_2(PBu_3)_2]$ and PPh_3

To a CDCl₃ solution of $[Pd_2Cl_2\{\mu\text{-tolNC}(H)Ntol\}_2$ (PBu₃)₂] (24.5 mg, 0.022 mmol) in a 5 mm NMR tube was added solid triphenylphosphine (11.5 mg, 0.044 mmol). The resulting solution was studied by ³¹P NMR spectroscopy.

Reaction between $[Pd_2Cl_2\{\mu-tolNC(H)Ntol\}_2(PBu_3)_2]$ and HCl

To a dichloromethane (5 cm^3) solution of $[Pd_2Cl_2\{\mu - tolNC(H)Ntol\}_2(PBu_3)_2]$ (26.7 mg, 0.024 mmol) was added an ethereal solution of HCl (0.02 cm³, 2.44 N, 0.048 mmol). After stirring for 30 min, the solvent was stripped off and the residue was dissolved in CDCl₃. The resulting solution was studied by ³¹P NMR spectroscopy.

Crystallography

All measurements for $[Pd_2Cl_2\{\mu-PhNC(Me)N Ph_{2}(PMe_{2}Ph)_{2}$ (10) were made at $20 \pm 2^{\circ}C$ on a Rigaku AFC 6S diffractometer using graphite monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). The crystallographic data together with data collection and structure refinement details are given in Table 7. The numbering scheme employed is shown in Fig. 2 drawn with the ORTEP program [33]. All the data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterson method and direct methods [34] and refined by full-matrix least-squares on F². Neutral atom scattering factors were taken from Cromer and Waber [35]. Anamolous dispersion effects were included in F_{calc} [36]. The values of $\Delta f'$ and $\Delta f''$ were those of Cromer [37]. All calculations were performed using the TEXSAN [38] crystallographic software package of the Molecular Structure Corporation.

The crystal data for the complex $[Pt_2Cl_2{\mu-PhNNNPh}_2(PEt_3)_2]$ (11) were collected on an Enraf Nonius CAD-4 with monochromated MoK α . Three check reflections were measured for every 100 reflections; these showed no decay in intensity during the period of data collection. The structure was solved by Patterson and full matrix least squares refinement on F_o using SHELX -76 [39]. The refinement was carried out first with isotropic thermal parameters and subsequently with anisotropic thermal parameters for all non-hydrogen atoms. The scattering factors for Pt were taken from International tables for X-ray crystallography [35] and the absorption corrections were made using Psi data [40].

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	10	11
Empirical Formula	$C_{44}H_{48}Cl_2N_4P_2Pd_2$	$C_{36}H_{50}Cl_2N_6P_2Pt_2$
Formula Weight	978.50	1089.87
Temperature	293(2) K	293 K
Wavelength	0.71073 Å	0.7107 Å
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c
Unit cell dimensions	a = 12.158(6) Å	a = 23.028(1) Å
	b = 19.490(7) Å	b = 9.834(3) Å
	c = 19.290(8) Å	c = 19.066(1) Å
	$\beta = 90.49(2)^{\circ}$	$\beta = 109.32(3)^{\circ}$
Volume	4571(3)Å ³	4074(1)Å ³
Z	4	4
Density	1.422 Mg/m^3	1.7767g/cm^3
Absorption coefficient	$1.007 \mathrm{mm}^{-1}$	$71.73 \mathrm{cm}^{-1}$
F(000)	1984	2112
Crystal Size	$0.47 \times 0.32 \times 0.17 \text{ mm}$	$0.4 \times 0.3 \times 0.25 \text{mm}$
θ range for data collection	2.09 to 27.50°	$2 \leq 2\theta \leq 50^{\circ}$
Index ranges	$0 \leq h \leq 15$,	$0 \leq h \leq 24, 0 \leq k \leq 10,$
-	$0 \le k \le 25, -25 \le 1 \le 25$	$-20 \le 1 \le 20$
Reflections collected	10912	4125
Independent reflections	10427	$3582 (R_{int} = 0.042)$
•	$(R_{int} = 0.0337)$	
Absorption correction	SHELXA	Empirical
Max. and min. transmission	0.927 and 0.383	1.277 and 0.899
Refinement method	Full-matrix least-squares on	Full-matrix least squa-
	\mathbf{F}^2	res on F ₀
Data/restraints/parameters	10419/0/494	2999/0/163
Goodness-of-fit on F ²	1.018	1.2102
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0652, wR2 = 0.0756	$R_1 = 0.0346,$
		wR2 = 0.0399
R indices (all data)	R1 = 0.1644, wR2 = 0.2996	—
Extinction coefficient	0.00019(5)	—
Largest diff. peak and hole	0.664 and −0.656 eÅ ⁻³	$1.2 \text{ and } -1.1 \text{ e}\text{\AA}^{-3}$

Table 7. Crystal data and structure refinement details for $[Pd_2Cl_2\{\mu-PhNC(Me)NPh\}_2 (PMe_2Ph)_2]$ (10) and $[Pt_2Cl_2\{\mu-PhNNNPh\}_2(PEt_3)_2]$ (11)

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A. Singha et all

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