# Synthesis and characterization of mono- and bi-nuclear palladium(II) and platinum(II) complexes containing acetamidine ligands

**Anshu Singhal and Vimal K. Jain**

**Abstract**: The reactions of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with acetamidines in 1:2 stoichiometry afforded mononuclear complexes, $[MCl_2\{ArNHC(Me)NAr\}(PR_3)]$ (**I**) (M = Pd or Pt; $R_3 = Et_3$, $Bu_3$, $Me_2Ph$, $MePh_2$; Ar = Ph or 4-$MeC_6H_4$ (tol)). Treatment of $[M_2Cl_4(PR_3)_2]$ with Li[ArNC(Me)NAr] under anerobic conditions gave acetamidino-bridged binuclear complexes, $[M_2Cl_2(\mu\text{-}ArNC(Me)NAr)_2(PR_3)_2]$ (**II**). The reaction of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}allyl)_2]$ with Ag[ArNC(Me)NAr] gave acetamidino-bridged allyl complexes $[Pd_2(\mu\text{-}ArNC(Me)NAr)_2(\eta^3\text{-}allyl)_2]$ (**III**). All the complexes were characterized by elemental analyses and NMR ($^1H$, $^{31}P$, $^{195}Pt$) spectroscopy. The mononuclear complexes (**I**) exist in two isomeric forms differing in the coordination of monodentate acetamidine ligand. The $^{31}P$ and $^{195}Pt$ NMR data on binuclear complexes (**II**) indicate that there is no significant Pt–Pt interaction. The allyl complexes (**III**) (allyl = $C_3H_5$) exhibit formation of all three possible isomers, whereas methallyl (allyl = $C_4H_7$) derivatives exist only in one configuration.

*Key words*: palladium, platinum, acetamidine, NMR ($^1H$, $^{31}P$, $^{195}Pt$), mononuclear complexes, binuclear complexes.

**Résumé** : Les réactions du composé $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ avec les acétamidines dans un rapport de 1 : 2 conduisent aux complexes mononucléaires $[MCl_2\{ArNHC(Me)NAr\}(PR_3)]$ (**I**) (M = Pd ou Pt; $R_3 = Et_3$, $Bu_3$, $Me_2Ph$, $MePh_2$; Ar = Ph ou 4-$MeC_6H_4$(tol). En traitant le composé $[M_2Cl_4(PR_3)_2]$ avec le Li[ArNC(Me)NAr], dans des conditions anaérobiques, on obtient les complexes binucléaires avec le groupe acétamidino ponté, $[M_2Cl_2(\mu\text{-}ArNC(Me)NAr)_2(PR_3)_2]$ (**II**). La réaction du $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}allyl)_2]$ avec Ag[ArNC(Me)NAr] donne les complexes allyliques avec le groupe acétamidino ponté : $[Pd_2(\mu\text{-}ArNC(Me)NAr)_2(\eta^3\text{-}allyl)_2]$ (**III**). On a caractérisé tous les complexes par analyse élémentaire et par la spectroscopie de RMN du $^1H$, $^{31}P$, et $^{195}Pt$. Le complexe mononucléaire (**I**) existe sous deux formes isomères qui diffèrent par la coordination du ligand acétamide monodentate. Les données de la RMN du $^{31}P$ et du $^{195}Pt$ indiquent qu'il n'y a pas d'interaction Pt–Pt significative dans les complexes binucléaires (**II**). Les complexes allyliques (**III**) (allyle = $C_3H_5$) montrent la formation de tous les trois isomères possibles, tandis que les dérivés méthallyliques (allyl = $C_4H_7$) existent seulement dans une seule configuration.

*Mots clés* : palladium, platine, acétamidine, RMN du $^1H$, $^{31}P$, $^{195}Pt$, complexes mononucléaires, complexes binucléaires.

[Traduit par la rédaction]

## Introduction

Recently we isolated a series of binuclear palladium(II) and platinum(II) complexes containing one-, two-, and three-atom donor bridging ligands (1–3). The complexes with three-atom donor bridging ligands, e.g., carboxylate (2) and triazenido (3), show unusually strong metal–metal interactions in the $d^8$ configuration of the metal ion. To assess whether a metal–metal interaction in a $d^8$ configuration is a general feature of a three-atom bridging ligand, we have chosen amidines that are isoelectronic to carboxylate and triazenes as ligands.

A wide variety of platinum group metal complexes of amidines as well as their anions are now known. The anion acts in a monodentate (4, 5), bidentate chelating (6, 7), or bridging (8–10) fashion and also assists in stabilizing metal–metal bonds (11) in a manner similar to isoelectronic 1,3-di-substituted triazenido, carboxylato groups, etc. The amidino complexes are usually obtained either by the reaction of $[RNCR'NR]^-$ with metal salts or by deprotonation of coordinated neutral amidine in a precursor "M(NRCR'NHR)." Neutral amidines have two possible bonding sites, namely, via the amine-N or the imine-N atom; coordination through the latter is usually observed (4, 5, 12) rather than through more the basic amine-N atom.

In view of the above and in pursuance of our interest in platinum group metal complexes we have synthesized a series of mono- and bi-nuclear palladium(II) and platinum(II) complexes with acetamidines.

## Results and discussion

The reaction of the chloro-bridged dimers $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with acetamidines in 1:2 stoichiometry readily afforded mononuclear complexes of the type

Received December 15, 1995.

*This paper is dedicated to Professor Howard C. Clark in recognition of his contributions to Canadian chemistry.*

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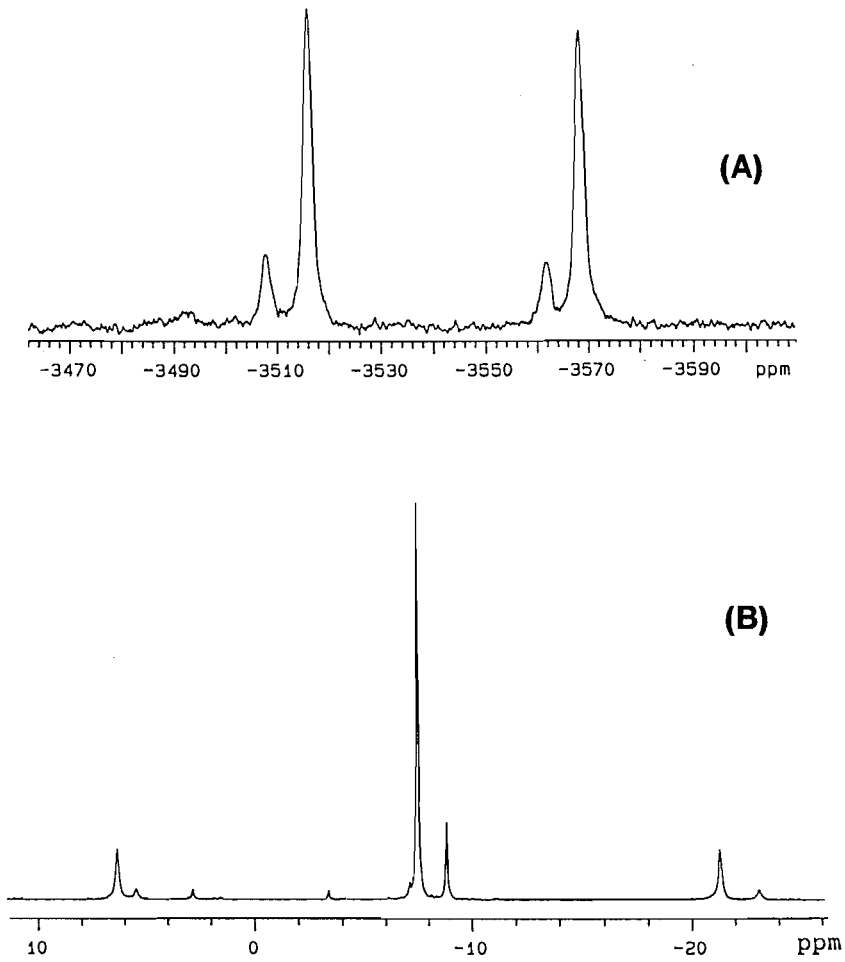
**Fig. 1.** $^{195}Pt\{^1H\}$ (*A*) and $^{31}P\{^1H\}$ NMR spectra (*B*) of the complex $[PtCl_2(PBu_3)\{PhNC(Me)NHPh\}]$ in $CDCl_3$.

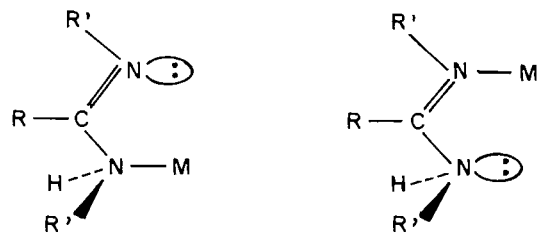



$[MCl_2(PR_3)\{ArNC(Me)NHAr\}]$ (**I**) (M = Pd or Pt; $R_3 = Et_3$, $Bu_3$, $Me_2Ph$, $MePh_2$; Ar = Ph or 4-$CH_3C_6H_4$ (tol)). The palladium complexes are yellow while the analogous platinum complexes are pale yellow.

The $^{31}P$ spectra of most of these complexes showed two resonances, except for a few platinum complexes where one resonance with platinum satellites was observed. Similarly, the $^{195}Pt$ NMR spectrum of $[PtCl_2(PBu_3)\{PhNC(Me)NHPh\}]$ displayed two doublets (δ −3542.2 ppm (d), $^1J$(Pt–P) 3361 Hz (major isomer); δ −3534.8 ppm (d), $^1J$(Pt–P) 3474 Hz (minor isomer)) (Fig. 1). The $^1J$(Pt–P) coupling constants (Table 1) indicate that in every case nitrogen is *trans* to the phosphine ligand (13). One would expect a magnitude of $^1J$(Pt–P) ~3600 Hz for *cis* configuration (phosphine *trans* to chloride). The palladium complexes appear to have a *trans* configuration since the IR spectra in the region 500–200 $cm^{-1}$ for both series of complexes are comparable.

There are two different N donor atoms in amidines. Accordingly, two signals in the $^{31}P$ NMR spectra can be attributed to the molecules containing amino-N and imino-N coordinated ligand (Fig. 2). No isomerization was noticed on keeping the solution for few hours. We recently reported ligation via different nitrogen atoms in a triazene complex

**Fig. 2.** Amine–N and imine–N coordination for amidine ligand.




$[PtCl_2(PBu_3)(PhNNNHPh)]$ (3). Interestingly, the X-ray analysis of $[Pt\{C_6H_3)(CH_2NMe_2)_2$-2,6$\}\{tolNC(H)NHtol\}]$-$[CF_3SO_3]$ revealed coordination through imino nitrogen, and this configuration is retained in solution (5). Coordination through imino nitrogen has been suggested for the allyl complexes (5), $[PdCl(\eta^3\text{-}C_3H_5)\{ArNC(H)NHAr\}]$; however, for these complexes Toniolo and co-workers (14) reported ligation via the more basic amine N atom.

In the $^1H$ NMR spectra the CMe and NH signals for the imine-coordinated isomer appeared at δ ~1.8 and 8.50–9.06 ppm, respectively. The assignment was made by comparison

**Table 1.** $^1H$ and $^{31}P\{^1H\}$ NMR data for palladium and platinum complexes containing acetamidine ligands.

| Complex | $^{31}P$ NMR data $\delta$ ($^1J$ (Pt–P)) | $^1H$ NMR data[b] |
|---|---|---|
| $[PdCl_2(PBu_3)\{PhN{=}C(Me)NHPh\}]$ | 25.1<br>25.2 | 0.86 (apparent q, due to overlapping triplets, P–$CH_3$), 1.39–1.58 (m, $PCCH_2CH_2$-); 1.85 (br, $PCH_2$), 2.69 (s, CMe-); 6.45 (s, NH); 7.01–7.43 (m, Ph), 8.64 (s, NH). |
| $[PdCl_2(PMe_2Ph)\{PhN{=}C(Me)NHPh\}]$ | 4.68[a]<br>4.81 | 1.76 (d, 12.6 Hz, $PMe_2$); 1.78 (d, 12.3 Hz, $PMe_2$),[a]1.82 (s, CMe),[a] 2.68 (s, =CMe); 6,42 (s, NH); 7.01 (d, 7.5 Hz), 7.16–7.43 (m), 7.75–7.86 (m) [Ph]; 8.57 (s, NH).[a] |
| $[PdCl_2(PMePh_2)\{PhN{=}C(Me)NHPh\}]$ | 14.9<br>15.0[a] | 2.00 (d, 12.3 Hz, PMe), 2.01 (d, 12.0 Hz, PMe),[a] (d, 12.0 Hz, PMe); 1.85 (s, CMe),[a] 2.74 (s, CMe); 6.46 (s, NH); 7.02 (d, 7.3 Hz), 7.22–7.46 (m); 7.67–7.77 (m) [Ph]; 8.64 (s, NH).[a] |
| $[PdCl_2(PEt_3)\{tolN{=}C(Me)NHtol\}]$ | 31.8[c] | 1.17 (m, $PCCH_3$); 1.80 (s, =CMe-); 1.86 (m, $PCH_2$-); 2.32, 2.33, 2.35 (each s, tol Me for both isomers), 2.65 (s, =CMe-); 6.40 (s, NH), 6.89 (d, 8 Hz), 7.09–7.30 (m) [$C_6H_4$]; 8.50 (s, NH). |
| $[PtCl_2(PEt_3)\{PhN{=}C(Me)NHPh\}]$ | 0.62[d]<br>(3320 Hz) | 1.14 (dt, 17 Hz (d), 7.7 Hz (t), PC-$CH_3$); 1.84 (m, $PCH_2$-); 1.87 (s, =CMe); 7.16–7.44 (m, Ph), 9.06 (s, NH). |
| $[PtCl_2(PBu_3)\{PhN{=}C(Me)NHPh\}]$ | –7.5[a]<br>(3357 Hz)<br>–8.8<br>(3470 Hz) | 0.79 (t, 7.3 Hz, P–$CH_3$),[a] 0.84 (t, 7.3 Hz, P–$CH_3$), 1.32 (m, P-C-C-$CH_2$-); 1.45 (s, CMe);[a] 1.49–1.88 (m, $PCH_2CH_2$); 2.75 (s, CMe), 6.18 (s, NH), 6.74–7.83 (m, Ph); 9.56 (s, NH). |
| $[PtCl_2(PMe_2Ph)\{PhN{=}C(Me)NHPh\}]$ | –23.7[a]<br>(3373 Hz)<br>–25.0<br>(3482 Hz) | 1.74 (d, 11.5 Hz, $PMe_2$), 1.76 (d, 11.5 Hz, $PMe_2$);[a] 1.87 (s, =CMe-),[a] 2.73 (s, =CMe-); 6.49 (s, NH), 7.02–7.48 (m), 7.78–7.88 (m) [Ph]; 8.87 (s, NH).[a] |
| $[PtCl_2(PBu_3)\{tolN{=}C(Me)NHtol\}]$ | –7.9[d]<br>(3290 Hz) | 0.88 (t, 7.1 Hz, P–$CH_3$); 1.37–1.60 (m, PC-$CH_2$-$CH_2$-), 1.80 (m, $PCH_2$); 1.86 (s, =CMe-), 2.33 (s), 2.37 (s) (tol Me); 7.11–7.19 (m, $C_6H_4$); 8.95 (s, NH). |
| $[PtCl_2(PMe_2Ph)\{tolN{=}C(Me)\text{-}NHtol\}]$ | –23.8[a]<br>(3357 Hz)<br>–25.1<br>(3465 Hz) | 1.72 (d, 11.2 Hz, $PMe_2$), 1.75 (d, 11 Hz, $PMe_2$),[a] 1.84 (s, =CMe-),[a] 2.88 (s, =CMe-), 2.32, 2.34 (each s, tol-Me); 2.33, 2.35 (each s, tol-Me),[a] 6.43 (s, NH), 6.81 (d), 7.10--7.41, 7.78–7.88 (m) [Ph + $C_6H_4$]; 8.85 (s, NH).[a] |
| $[Pd_2Cl_2(\mu\text{-}PhNC(Me)NPh)_2(PEt_3)_2]$ | 17.3 | 1.06 (d, t, 15.6 Hz (d), 7.8 Hz (t, P-C-$CH_3$); 1.62 (m), 1.87 (m) ($PCH_2$-); 1.72 (s, CMe); 6.78–7.41 (m) [Ph]. |
| $[Pd_2Cl_2(\mu\text{-}PhNC(Me)NPh)_2(PMe_2Ph)_2]$ | 2.9 | 1.78 (s, CMe); 1.84 (d), 2.08 (d) (each 12.4 Hz $PMe_2$); 6.71–7.18 (m), 8.06(m) [Ph]. |
| $[Pd_2Cl_2\{\mu\text{-}PhNC(Me)NPh\}_2(PMePh_2)_2]$ | 13.7 | 1.16 (s, CMe); 2.42 (d, 12.0 Hz, PMe); 6.95–7.95 (m) [Ph]. |
| $[Pd_2Cl_2\{\mu\text{-}tolNC(Me)Ntol\}_2(PBu_3)_2]$ | 10.4 | 0.94 (t, 7.2 Hz, PCCCCH$_3$); 1.39 (m, PCCCH$_2$-); 1.66 (m, PC-$CH_2$); 1.94 (s, CMe); 2.06–2.38 (m, $PCH_2$-); 2.15 (s), 2.16 (s) (tol-Me); 6.76–7.09 (m, $C_6H_4$). |
| $[Pd_2Cl_2\{\mu\text{-}tolNC(Me)Ntol\}_2(PMe_2Ph)_2]$ | 3.7 | 1.71 (s, CMe); 1.96 (d), 2.00 (d) (each 12.4 Hz $PMe_2$); 2.24 (s), 2.27 (s) (tol-Me); 6.30 (br, tol, $C_6H_4$); 6.57 (d), 6.82 (d), 6.83 (d) (each 8.2 Hz, tol, $C_6H_4$); 7.49 (m), 8.11 (m) [Ph]. |

**Table 1** (*concluded*).

| Complex | $^{31}$P NMR data δ ($^{1}J$ (Pt–P)) | $^{1}$H NMR data[b] |
|---|---|---|
| $[Pt_2Cl_2\{\mu\text{-PhNC(Me)NPh}\}_2(PBu_3)_2]$[e] | −8.4 (3630 Hz) | 0.80 (t, 7.2 Hz, $PCCCCH_3$); 1.17 (m), 1.46 (m) ($PCH_2CH_2CH_2$]; 1.42 (s, CMe); 6.88–7.40 (m, Ph). |
| $[Pt_2Cl_2\{\mu\text{-PhNC(Me)NPh}\}_2(PMe_2Ph)_2]$[f] | −23.8 (3690 Hz) | 1.48 (d, 11.3 Hz, $PMe_2$); 1.81 (s, CMe); 6.74–7.72 (m, Ph). |
| $[Pd_2\{\mu\text{-PhNC(Me)NPh}\}_2(\eta^3\text{-}C_3H_5)_2]$ | — | 1.70 (s), 1.71 (s) [=CMe]; 2.71 (d, 12.2 Hz, *anti* proton), 3.09 (d, 6.9 Hz, *syn* proton); 5.24 (m, central CH) (for major isomer containing equivalent allyl groups); 2.37 (d), 2.62(d) (each 12 Hz, *anti* proton); 2.99(d), 3.42 (d) (each 7 Hz, *syn* proton); 4.98 (m) (central CH) (second isomer with nonequivalent allyl groups), 2.28 (d, 12.4 Hz, *anti* proton), 3.35 (d, 7 Hz, *syn* proton) (this isomer is present in small concentration); 6.22–7.22 (m, Ph). |
| $[Pd_2\{\mu\text{-PhNC(Me)NPh}\}_2(\eta^3\text{-}C_4H_7)_2]$ | — | 1.74 (s, =CMe); 1.81 (s, Me of allyl); 2.54 (s, $CH_2$ *anti*), 2.82 (s, $CH_2$ *syn*), 6.75–7.18 (m, Ph). |
| $[Pd_2\{\mu\text{-tolNC(Me)Ntol}\}_2(\eta^3\text{-}C_3H_5)_2]$ | — | 1.68, 1.69 (each s, =CMe-), 2.25 (s), 2.27 (s), 2.29 (s), 2.31 (s) (tol-Me + *anti* protons of allyl); 2.68 (d, 12.2 Hz, *anti* proton); 3.06 (d, 6.8 Hz, *syn* proton); 5.22 (m, central CH) (for major isomer containing equivalent allyl groups). 2.59 (d, 12 Hz, *anti* proton),[g] 2.95 (d, 6.8 Hz), 3.38 (d, 6.8 Hz) (*syn* proton); 4.97 (m) (for the isomer with nonequivalent allyl groups); 3.3 (d, 6.8 Hz) (for the isomer with smaller concentration); 6.49–7.02 (m, $C_6H_4$). |
| $[Pd_2\{\mu\text{-tolNC(Me)Ntol}\}_2(\eta^3\text{-}C_4H_7)_2]$ | | 1.70 (s, =CMe-); 1.80 (s, Me allyl); 2.27 (s, tol-Me); 2.50 (s, $CH_2$ *anti*); 2.87 (s, $CH_2$ *syn*), 6.64 (d, 8 Hz), 6.92 (d, 8 Hz) ($C_6H_4$). |

[a]Due to major isomer.

[b]s = singlet, d = doublet, t = triplet, m = multiplet, dt = doublet of triplet; br = broad.

[c]Chemical shift degeneracy; two isomers are present in a 1:1 ratio as evident from the $^{1}$H NMR spectrum.

[d]Only one isomer is formed.

[e]NMR data for the complex prepared from the acetato-bridged platinum complex $^{31}P\{^{1}H\}$ in $CDCl_3$: −8.4 ($^{1}J$ = 3629 Hz, major); −10.3 (minor) ppm. $^{1}$H NMR spectrum is similar to the spectrum for the complex prepared from the chloro-bridged platinum derivative.

[f]NMR data for the complex prepared from the acetato-bridged platinum complex $^{31}P\{^{1}H\}$ in $C_6D_6$: δ −24.3 ($^{1}J$ = 3747 Hz, minor isomer); −25.4 ($^{1}J$ = 3690 Hz, major isomer); $^{1}$H in $C_6D_6$: 1.14 (d, 11.3 Hz, $PMe_2$, major); 1.19 (d, 11.1 Hz, minor); 1.37 (s, CMe, minor); 1.40 (s, CMe, major); 6.55–7.63 (m, Ph).

[g]Another doublet due to the *anti* protons is merged to tol-Me signal.

with the spectra (5) of $[PdCl(\eta^3\text{-}C_3H_5)(ArNC(H)NHAr)]$ and $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}\{tolNC(H)NHtol\}][CF_3SO_3]$. The resonances for the amine-coordinated isomer were assigned at δ 6.2–6.5 ppm (NH) and ~2.7 ppm (CMe). In general, the imine-coordinated isomer predominated and for a few platinum complexes was formed exclusively. The magnitude of $^1J$(Pt–P) for the imine-coordinated isomer is smaller (~110 Hz) than that of the corresponding amine-coordinated complex. This is in agreement with the fact that $^1J$(Pt–P) for the complexes containing $sp^3$ hybridized nitrogen is greater than for those complexes with $sp^2$ hybridized N donor atom (3).

### Acetamidinato-bridged binuclear complexes

The binuclear acetamidinato-bridged palladium(II) and platinum(II) complexes can readily be obtained by the following reaction routes (eqs. [1] and [2])

[1] $[M_2Cl_2(\mu\text{-}X)_2(PR_3)_2] + 2LiAm \longrightarrow [M_2Cl_2(\mu\text{-}Am)_2(PR_3)_2] + 2LiX$

[2] $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2] + AgAm \longrightarrow [Pd_2(\mu\text{-}Am)_2(\eta^3\text{-allyl})_2] + 2AgCl$

(M = Pd or Pt; X = Cl or OAc; $Am^-$ = PhNC(Me)NPh or tolNC(Me)Ntol; $R_3 = Et_3$, $Bu_3$, $Me_2Ph$, $MePh_2$; allyl = $C_3H_5$ or $C_4H_7$).

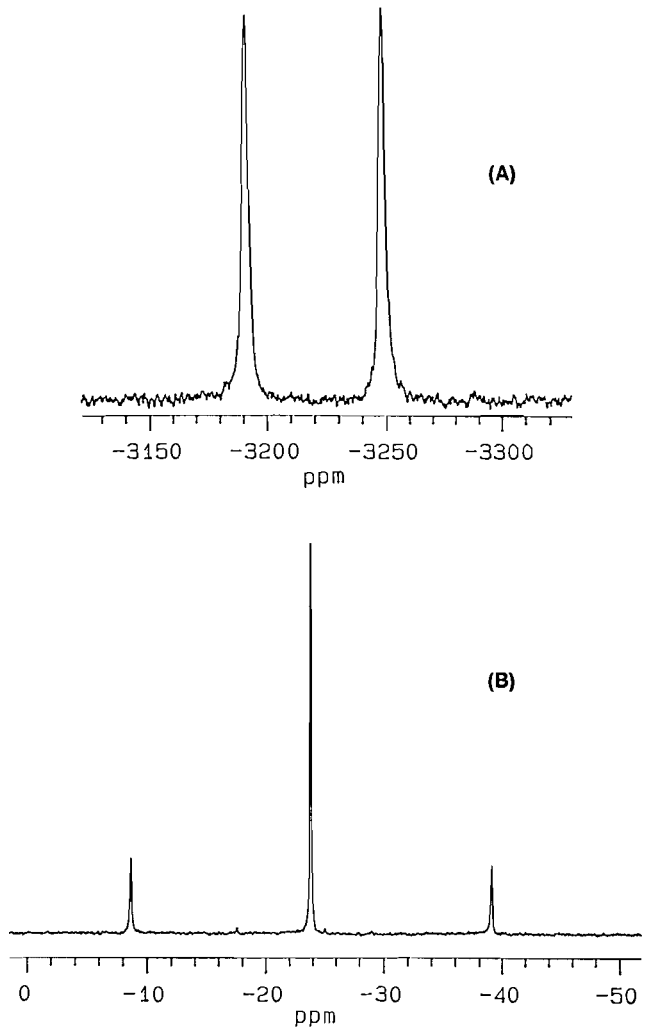
The palladium complexes are orange while the analogous platinum complexes are lemon-yellow crystalline solids, soluble in common organic solvents. The mass spectrum of $[Pd_2Cl_2(\mu\text{-tolNC(Me)Ntol})_2(PBu_3)_2]$ showed a molecular ion peak at 1163, suggesting binuclear composition of these complexes. Besides a number of other peaks, peaks at *m/e* 581 and 546 can be assigned to mononuclear ions $[PdCl(PBu_3)(tolNC(Me)Ntol)]^+$ and $[Pd(PBu_3)(tolNC(Me)Ntol)]^+$, respectively.

### NMR Spectra of II

The $^1H$ NMR spectra showed the expected integration and peak multiplicities (Table 1). The $^{31}P$ NMR spectra displayed a single resonance for tertiary phosphines. The $^1J$(Pt–P) couplings for these complexes are comparable to those of the corresponding triazenido-bridged complexes (3). The platinum NMR spectra of $[Pt_2Cl_2(\mu\text{-PhNC(Me)NPh})_2(PR_3)_2]$ showed a single doublet ($R_3 = Bu_3$: $\delta^{195}Pt\{^1H\}$ −3244 (d) ppm, $^1J$(Pt–P) = 3635 Hz; $R_3 = Me_2Ph$: δ −3220 (d) ppm, $^1J$(Pt–P) = 3692 Hz) (Fig. 3). Interestingly, when the complexes were prepared from the acetato-bridged platinum complexes (X = OAc, eq. [1]), two isomeric forms, sym *cis* and sym *trans*, were revealed by the $^{31}P$ NMR data. One of the peaks had chemical shifts and coupling constant consistent with the spectra of the complexes prepared by the chloro-bridged route (X = Cl, eq. [1]). The second peak showed a slightly higher coupling constant (~57 Hz) than the other, and has been assigned to the sym *cis* isomer based on our earlier data on binuclear complexes. The palladium complexes existed exclusively in one isomeric form irrespective of the method of preparation (X = Cl or OAc; eq. [1]).

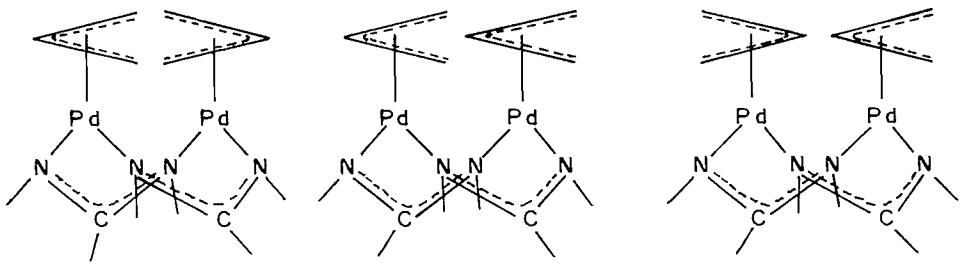
The complexes with isoelectronic bridging carboxylate (2) and triazene (3) ligands, $[Pt_2Cl_2(\mu\text{-}Y)_2(PR_3)_2]$ (Y = $RCOO^-$ or

**Fig. 3.** $^{195}Pt\{^1H\}$ (*A*) and $^{31}P\{^1H\}$ NMR (*B*) spectra of the complex $[Pt_2Cl_2(\mu\text{-PhNC(Me)NPh}\}_2(PMe_2Ph)_2]$ in $CDCl_3$.




ArNNNAr⁻), show platinum–platinum interaction with formal bond order zero as revealed by presence of $^nJ$(Pt–P) and $^nJ$(Pt–Pt) couplings in the $^{31}P$ and $^{195}Pt$ NMR spectra (2, 3). Accordingly, one would expect similar behaviour for acetamidino-bridged complexes. However, such couplings were not present in the $^{31}P$ and $^{195}Pt$ NMR spectra (Fig. 3). This suggests that metal–metal interactions in these complexes are vanishingly small. The observed trend of M—M separation is evident from the X-ray structures of $[Pd_2(\mu\text{-tolNNNtol})_2(\eta^3\text{-allyl})_2]$ (Pd—Pd = 2.856(1) Å) (15), $[Pd_2(\mu\text{-OAc})_2(\eta^3\text{-allyl})_2]$ (Pd—Pd = 2.94 Å) (16), and $[Pd_2(\mu\text{-NHC(Ph)NH})_2(\eta^3\text{-allyl})_2]$ (Pd—Pd = 3.128(1) Å (17). The Pd—Pd separation in the latter can be compared with the pyrazolato-bridged complexes, $[M_2Cl_2(\mu\text{-}Me_2pz)_2(PR_3)_2]$ (M = Pd, 3.115(1) Å; M = Pt, 3.170(1) Å) (18, 19). For bis-pyrazolato-bridged binuclear platinum complexes $^nJ$(Pt–P) and $^nJ$(Pt–Pt) are not observed. The bite distances of bridging triazenido, carboxylato, and amidino groups in Ni(II), Pd(II), and Pt(II) lantern-type complexes are of the order of ~2.23, ~2.25, and ~2.34 Å, respectively (20). This trend of ligand bite is reflected in the

**Fig. 4.** Different isomers for the $[Pd_2(\mu\text{-amidino})_2(\eta^3\text{-allyl})_2$ complex.



$^nJ$(Pt–Pt) and $^nJ$(Pt–P) couplings for $[Pt_2Cl_2(\mu\text{-}Y)_2(PR_3)_2]$ complexes where Y = $ArNNNAr^-$, $RCOO^-$, $ArNC(Me)NAr^-$. Seemingly, the ligand-induced metal–metal interactions in binuclear $d^8$ metal complexes stabilized with isoelectronic bridging ligand (e.g., three-atom bridging ligands) are influenced by the ligand bite angle.

### NMR spectra of allyl complexes, III

The methallyl palladium complexes showed only one set of resonances in the $^1H$ NMR spectra, indicating the existence of only one isomer. However, the allyl complexes exhibited three sets of resonances. This indicates that there are all three possible isomers (Fig. 4) in solution. It may be noted that earlier workers have reported one (17), two (21), and three (22) isomers for $[Pd_2(\mu\text{-amidino})_2(\eta^3\text{-allyl})_2]$ complexes.

## Experimental

The complexes $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (M = Pd or Pt; $R_3 = Et_3$, $Bu_3$, $Me_2Ph$, $MePh_2$) (23), $[M_2Cl_2(\mu\text{-}OAc)_2(PR_3)_2]$ (2), $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ (24, 25), acetamidines (22, 26), ArN=C(Me)-NHAr (Ar = Ph, 4-$MeC_6H_4$ (tol), and silver amidinate (22) were prepared by literature methods. All reactions were carried out in dried and distilled analytical grade solvents under a nitrogen atmosphere. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XLR-300 or Bruker AMX-500 spectrometer in freshly prepared $CDCl_3$ or $C_6D_6$ solutions. Chemical shifts are referred to internal solvent peak ($CHCl_3$ δ 7.26 ppm) for $^1H$ and 85% $H_3PO_4$ for $^{31}P$. $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Varian XLR-300 instrument operating at 64.49 MHz and the spectra were referenced with external $Na_2PtCl_6$ in $D_2O$. Elemental analyses were carried out by the Analytical Chemistry Division of this research centre. Melting points were determined in capillary tubes in the open and were uncorrected. Representative examples of the synthetic routes to the various compounds are reported below. Analytical data for the complexes are given in Table 2.

### Preparation of $[PtCl_2\{PhN{=}C(Me)\text{-}NHPh\}(PMe_2Ph)]$

To a dichloromethane solution (15 $cm^3$) of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (111 mg, 0.137 mmol), a solution of *N,N*-diphenylacetamidine (58.6 mg, 0.279 mmol) in dichloromethane (5 $cm^3$) was added with stirring at room temperature. After an hour of stirring, the solvent was stripped off and the residue was recrystallized from dichloromethane–hexane mixture (1:2, v/v) in 78% (131 mg) yield as a pale yellow crystalline solid.

### Preparation of $[Pd_2Cl_2(\mu\text{-}PhNC(Me)NPh\}_2(PMe_2Ph)_2]$

To a THF solution (20 $cm^3$) of Li[PhNC(Me)NPh], prepared in situ by neutralizing *N,N'*-diphenylacetamidine (70.5 mg, 0.336 mmol) with a hexane solution (0.69 M, 0.5 $cm^3$) of *n*-BuLi, was added solid $[Pd_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (105 mg, 0.166 mmol) with vigorous stirring. The reactants were stirred at room temperature for 2 days. The solvents were stripped off in vacuo. The residue was extracted with benzene and filtered. The filtrate was concentrated in vacuo and the residue was recrystallized from benzene–hexane solution in 59% (95.9 mg) yield.

### Preparation of $[Pd_2Cl_2(\mu\text{-}tolNC(Me)Ntol\}_2(PBu_3)_2]$

To a THF solution (20 $cm^3$) of Li[tolNC(Me)Ntol], prepared as in earlier preparation from *N,N'*-di-*p*-tolylacetamidine (94 mg, 0.395 mmol) and *n*-BuLi solution in hexane (0.8 $cm^3$, 0.53 M), solid $[Pd_2Cl_2(\mu\text{-}OAc)_2(PBu_3)_2]$ (146 mg, 0.181 mmol) was added. The reaction mixture was stirred at room temperature for 30 h. The solvents were removed in vacuo and the residue was extracted with benzene and filtered. The filtrate was evaporated in vacuo and the residue was recrystallized from hexane (yield, 128 mg, 61%).

### Preparation of $[Pt_2Cl_2(\mu\text{-}PhNC(Me)NPh\}_2(PMe_2Ph)_2]$

To a THF solution (10 $cm^3$) of Li[PhNC(Me)NPh], prepared from *N,N'*-diphenylacetamidine (83 mg, 0.393 mmol) and *n*-BuLi solution (0.8 $cm^3$, 0.5 M), a benzene solution (10 $cm^3$) of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (154 mg, 0.191 mmol) was added with vigorous stirring. The reaction mixture was stirred at room temperature for 60 h. The solvents were stripped off in vacuo and the residue was extracted with benzene and filtered. The filtrate as concentrated to 2 $cm^3$ and layered with hexane (5 $cm^3$), whereupon crystals of the title complex were obtained (yield 133 mg, 60%).

### Preparation of $[Pd_2(\mu\text{-}PhNC(Me)NPh\}_2(\eta^3\text{-}C_4H_7)_2]$

To a dichloromethane solution (15 $cm^3$) of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2]$ (80 mg, 0.203 mmol) was added silver diphenylacetamidinate (147 mg, 0.42 mmol). The reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane and filtered. The filtrate was concentrated in vacuo to 2 $cm^3$ and layered with hexane (5 $cm^3$), which on cooling in a freezer gave the crystals of the title complex (yield 49 mg, 33%).

**Table 2.** Physical and analytical data for the palladium and platinum complexes containing acetamidine ligands.

| Complex | Recrystallization solvent (% yield) | Melting point (°C) | % Analysis found (calcd.) C | H | N |
|---|---|---|---|---|---|
| $[PdCl_2(PBu_3)\{PhN{=}C(Me)NHPh\}]$ | Hexane (52) | Liquid | 52.3 (52.9) | 6.7 (7.0) | 4.8 (4.7) |
| $[PdCl_2(PMe_2Ph)\{PhN{=}C(Me)NHPh\}]$ | Benzene–hexane (74) | 160–162 | 50.4 (50.3) | 4.7 (4.8) | 5.1 (5.3) |
| $[PdCl_2(PMePh_2)\{PhN{=}C(Me)NHPh\}]$ | Benzene–hexane (65) | 155–157 | 55.8 (55.2) | 4.9 (4.6) | 5.3 (4.8) |
| $[PdCl_2(PEt_3)\{tolN{=}C(Me)Ntol\}]$ | Ether–hexane (68) | 128–130 | 49.3 (49.5) | 6.3 (6.2) | 5.8 (5.3) |
| $[PtCl_2(PEt_3)\{PhN{=}C(Me)NHPh\}]$ | Benzene–hexane (63) | 135–137 | 39.8 (40.4) | 5.0 (4.9) | 4.6 (4.7) |
| $[PtCl_2(PBu_3)\{PhN{=}C(Me)NHPh\}]$ | Hexane (54) | Liquid | 45.9 (46.0) | 6.2 (6.1) | 4.0 (4.1) |
| $[PtCl_2(PMe_2Ph)\{PhN{=}C(Me)NHPh\}]$ | $CH_2Cl_2$–hexane (78) | 165–167 | 43.0 (43.0) | 3.7 (4.1) | 5.5 (4.6) |
| $[PtCl_2(PBu_3)\{tolN{=}C(Me)NHtol\}]$ | Hexane (60) | 78–80 | 47.5 (47.6) | 7.1 (6.4) | 4.2 (4.0) |
| $[PtCl_2(PMe_2Ph)\{tolN{=}C(Me)NHtol\}]$ | $CH_2Cl_2$–hexane (92) | 190–192 | 44.4 (44.8) | 4.2 (4.5) | 4.8 (4.4) |
| $[Pd_2Cl_2\{\mu PhNC(Me)NPh\}_2(PEt_3)_2]$ | Ether–hexane (55) | 128–130[a] | 50.8 (51.1) | 5.9 (6.0) | 5.9 (6.0) |
| $[Pd_2Cl_2\{\mu\text{-}PhNC(Me)NPh\}_2(PMe_2Ph)_2]$ | Benzene–hexane (59) | 186–190[a] | 53.3 (54.0) | 5.1 (4.9) | 5.8 (5.7) |
| $[Pd_2Cl_2\{\mu\text{-}PhNC(Me)NPh\}_2(PMePh_2)_2]$ | Ether–hexane (58) | 169–172[a] | 58.9 (58.8) | 4.8 (4.9) | 5.1 (5.2) |
| $[Pd_2Cl_2\{\mu\text{-}tolNC(Me)Ntol\}_2(PBu_3)_2]$ | Hexane (61) | 134–136 | 57.5 (57.8) | 8.2 (7.6) | 5.1 (4.8) |
| $[Pd_2Cl_2\{\mu\text{-}tolNC(Me)Ntol\}_2(PMe_2Ph)_2]$ | Ether–hexane (65) | 188–190[a] | 56.1 (55.7) | 5.4 (5.4) | 4.9 (5.4) |
| $[Pt_2Cl_2\{\mu\text{-}PhNC(Me)NPh\}_2(PBu_3)_2]$ | Paste (49) | — | 48.8 (48.6) | 6.4 (6.2) | 4.1 (4.4) |
| $[Pt_2Cl_2\{\mu\text{-}PhNC(Me)NPh\}_2(PMe_2Ph)_2]$ | Benzene–hexane (56) | 126–129 | 45.6 (45.7) | 4.1 (4.2) | 5.4 (4.8) |
| $[Pd_2\{\mu\text{-}PhNC(Me)NPh\}_2(\eta^3\text{-}C_3H_5)_2]$ | $CH_2Cl_2$–hexane (35) | 135–137[a] | 57.5 (57.2) | 5.1 (5.1) | 8.4 (7.9) |
| $[Pd_2\{\mu\text{-}PhNC(Me)NPh\}_2(\eta^3\text{-}C_4H_7)_2]$ | $CH_2Cl_2$–hexane (33) | 138–140[a] | 58.7 (58.3) | 5.2 (5.4) | 8.0 (7.6) |
| $[Pd_2\{\mu\text{-}tolNC(Me)Ntol\}_2(\eta^3\text{-}C_3H_5)_2]$ | $CH_2Cl_2$–hexane (43) | 127–130[a] | 60.1 (59.3) | 5.8 (5.8) | 7.6 (7.3) |
| $[Pd_2\{\mu\text{-}tolNC(Me)Ntol\}_2(\eta^3\text{-}C_4H_7)_2]$ | $CH_2Cl_2$–hexane (71) | 100–105[a] | 60.8 (60.2) | 5.8 (6.1) | 8.3 (7.0) |

[a]Melts with decomposition or decomposes.



## Acknowledgements

We thank Drs. J.P. Mittal and C. Gopinathan for encouragement of this work. We are grateful to authorities of the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology (RSIC, IIT), Powai for providing $^1H$, $^{31}P$, and $^{195}Pt$ NMR spectra on a Varian XLR-300 spectrometer, and Head and Mr. V.R. Joshi of the Analytical Chemistry Division, Bhabha Atomic Research Centre, for providing microanalyses for some of the complexes.

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