Pergamon

Polyhedron Vol. 14, No. 2, pp. 285–291, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 \$9.50+0.00

0277–5387(94)E0171–9

TRIAZENIDO-BRIDGED BINUCLEAR PALLADIUM(II) AND PLATINUM(II) COMPLEXES

ANSHU SINGHAL AND VIMAL K. JAIN*

Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India

(*Received* 3 *March* 1994; *accepted* 11 *April* 1994)

Abstract—Triazenido-bridged binuclear palladium(II) and platinum(II) complexes of the type $[M_2X_2(\mu\text{-ArNNNAr})_2(PR_3)_2]$ (where M = Pd or Pt; X = Cl, Me, *p*-tol; Ar = Ph, *p*-tol or *p*-C_6H_4F; PR_3 = PEt_3, PBu_3, PMe_2Ph or $PMePh_2$) have been prepared by the reaction of $[M_2X_2(\mu\text{-Cl})_2(PR_3)_2]$ with free triazene in the presence of NaOH. These complexes were characterised by elemental analyses, IR and NMR (^1H, ^{31}P, ^{195}Pt) spectroscopy. Variable temperature NMR data reveal that the eight-membered metallocyclic ring has a rigid conformation. ^{195}Pt NMR data showed the existence of significant metal–metal interaction. A few reactions of these complexes have also been investigated by NMR spectroscopy.

Recently we have reported a number of four-, five-, six- and eight-membered binuclear palladium(II) and platinum(II) complexes.[1,2] Organochalcogenides, pyrazoles and carboxylates have been employed as bridging ligands in the formation of these metallocycles. The eight-membered carboxylato-bridged diplatinum complexes are non-rigid[3] and show unusually strong metal–metal interactions in a d^8 configuration of the metal ion as revealed by ^{195}Pt NMR spectroscopy.[2] This has led us to examine binuclear palladium(II) and platinum(II) complexes with three-atom donors as bridging ligands.

The triazenide anion, $RN{=}N{-}NR^-$, is a "small bite" three-atom donor ligand and acts in a monodentate, chelating or bridging fashion towards transition metal ions suggesting a formal analogy to the carboxylate group. The triazenide anion has been proved a versatile ligand in constructing binuclear molecules.[4] A number of mononuclear palladium and platinum complexes[5] and a few binuclear palladium complexes[3,6] with triazene have been reported.

In view of the above, we have synthesised and characterised a series of binuclear palladium and platinum complexes containing bridging triazene moiety. The results of these studies are reported in this paper.

EXPERIMENTAL

The complexes $[M_2X_2(\mu\text{-Cl})_2(PR_3)_2]$ (M = Pd or Pt; $PR_3 = PEt_3$, PBu_3, PMe_2Ph or $PMePh_2$),[7] $[M_2Cl_2(\mu\text{-OAc})_2(PR_3)_2]$,[3] $[M_2R_2(\mu\text{-Cl})_2(PR_3)]$[9] and triazenes,[8] $ArN{=}N{-}NHAr$ [Ar = Ph, *p*-C_6H_4Me (tol), *p*-C_6H_4F] were prepared by literature methods. All the reactions were carried out in dried and distilled analytical grade solvents under nitrogen. The ^1H NMR spectra were recorded on a Bruker AC-200 or AMX-500 spectrometer. Chemical shifts are referred to internal solvent peak ($CHCl_3$ δ 7.26 ppm). $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT-80A or Bruker AMX-500 spectrometer and chemical shifts are reported in ppm relative to external H_3PO_4. $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Varian XLR-300 instrument operating at 64.49 MHz and spectra were referenced with external Na_2PtCl_6 in D_2O. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer as Nujol mulls. Microanalyses of these complexes were carried out in the Analytical Chemistry Division of this research centre. Molecular weights were determined osmometrically in benzene.

---

*Author to whom correspondence should be addressed.

Preparation of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PEt_3)_2]$

To a benzene–methanol solution (1 : 1, 10 cm^3) of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (115 mg, 0.15 mmol), a solution of 1,3-diphenyltriazene (62 mg, 0.31 mmol) in methanolic sodium hydroxide (0.63 cm^3, 0.502 N, 0.31 mmol) was added with vigorous stirring under nitrogen. The reactants were stirred at room temperature for 5 h. The solvents were stripped off *in vacuo* and the residue was extracted with benzene (3 × 5 cm^3) and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallised from dichloromethane–benzene–hexane (1 : 1 : 2, v/v) mixture as golden yellow prismatic crystals (yield 106 mg, 65%). Similarly, other bis(triazenido)-bridged complexes of palladium and platinum were prepared. Pretinent data are summarised in Table 1.

Reaction of $[Pd_2Cl_2(\mu\text{-}OAc)_2(PBu_3)_2]$ *with 1,3-diphenyltriazene*

A dichloromethane solution (5 cm^3) of 1,3-diphenyltriazene (103 mg, 0.522 mmol) was added to a stirred dichloromethane solution (10 cm^3) of $[Pd_2Cl_2(\mu\text{-}OAc)_2(PBu_3)_2]$ (188 mg, 0.233 mmol). Reactants were stirred at room temperature for 3 h. The solvent was evaporated *in vacuo*, and the residue was dried for 20 h at 0.1 mm Hg. The orange solid was recrystallised from benzene–hexane (99 mg, 39%). $[Pd_2Cl_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ was prepared by a similar method. These complexes show data similar to those prepared from chloro-bridged metal complexes.

Reaction of $[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ *with* PPh_3

To a $CDCl_3$ solution of $[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ (41 mg, 0.033 mmol) in a 10 mm NMR tube was added solid triphenylphosphine (17 mg, 0.066 mmol). The resulting solution was studied by ^{31}P NMR spectroscopy. The reactions of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ and $[Pd_2Me_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ with triphenylphosphine were investigated by ^{31}P NMR spectroscopy in a similar manner.

Reaction of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$ *with* HCl

To a $CDCl_3$ solution of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$ (72 mg, 0.057 mmol) in a 10 mm NMR tube was added an ethereal solution of HCl (0.2 ml, 1.0 N) which immediately turned green. This solution was studied by NMR spectroscopy. When this solution was passed through a Florisil column a yellow coloured solution was obtained, the ^{31}P NMR spectrum of which was identical to that of the parent complex.

Table 1. Physical and analytical data for $[M_2X_2(\mu\text{-}ArNNNAr)_2(PR_3)_2]$

Complex	Recrystallising solvent (% yield)	M.p. (°C)	Analysis found (calc.) (%)		
			C	H	N
$[Pd_2Cl_2(\mu\text{-}PhNNNPh)_2(PEt_3)_2]$	CH_2Cl_2–hexane (45)	178^{a}	46.9(47.4)	5.3(5.5)	8.9(9.2)
$[Pd_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$	Hexane (59)	173–175	53.7(53.3)	6.8(6.9)	7.6(7.8)
$[Pd_2Cl_2(\mu\text{-}tolNNNtol)_2(PBu_3)_2]$	Hexane (51)	142–144	54.5(54.9)	7.2(7.3)	7.0(7.4)
$[Pd_2Cl_2(\mu\text{-}FC_6H_4NNNC_6H_4F)_2(PBu_3)_2]$	C_6H_6–hexane (54)	155–157	50.3(50.0)	6.5(6.1)	7.7(7.3)
$[Pd_2Cl_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$	CH_2Cl_2–hexane (67)	212–215	49.9(50.4)	4.3(4.4)	8.4(8.8)
$[Pd_2Cl_2(\mu\text{-}PhNNNPh)_2(PMePh_2)_2]$	$CHCl_3$–hexane (63)	192–195^{a}	55.6(55.8)	4.5(4.3)	8.0(7.8)
$[Pd_2Me_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$	C_6H_6–hexane (71)	125–126	57.5(57.4)	7.2(7.7)	7.9(8.1)
$[Pd_2Me_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$	C_6H_6–hexane (73)	180–182^{a}	56.3(55.3)	5.2(5.3)	9.5(9.2)
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PEt_3)_2]$	CH_2Cl_2–C_6H_6–hexane	174–178^{a}	39.7(39.5)	4.5(4.6)	7.5(7.7)
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$	Hexane (48)	148–150	46.4(45.8)	6.1(5.9)	6.7(6.7)
$[Pt_2Cl_2(\mu\text{-}FC_6H_4NNNC_6H_4F)_2(PBu_3)_2]$	C_6H_6–hexane (45)	137–139^{a}	42.7(43.3)	5.1(5.3)	6.2(6.3)
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$	CH_2Cl_2–hexane (65)	185–188^{a}	42.1(42.5)	3.7(3.7)	7.1(7.4)
$[Pt_2Cl_2(\mu\text{-}tolNNNtol)_2(PMe_2Ph)_2]$	$CHCl_3$–hexane (49)	198–200^{a}	44.2(44.6)	4.1(4.2)	7.9(7.1)
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PMePh_2)_2]$	$CHCl_3$–hexane (51)	215–220^{a}	47.5(47.9)	3.7(3.7)	6.3(6.7)
$[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$	CH_2Cl_2–hexane (78)	165–170^{a}	51.9(52.2)	4.2(4.5)	6.1(6.8)
$[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PMePh_2)_2]$	CH_2Cl_2–hexane (71)	136–138	55.9(56.3)	4.2(4.4)	5.8(6.1)

[a] Decomposition temperature.

Reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ *with* 1,3-*diphenyltriazene*

To a $CDCl_3$ solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (56 mg, 0.06 mmol), solid 1,3-diphenyltriazene (26 mg, 0.13 mmol), was added and the reaction was monitored by ^{31}P NMR spectroscopy. The reactions of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ with aniline, *N*,*N*-dimethylaniline and PhN=CHPh were carried out in a similar manner and studied by ^{31}P NMR spectroscopy.

RESULTS AND DISCUSSION

The reaction of $[M_2X_2(\mu\text{-}Cl)_2(PR_3)_2]$ with two moles of 1,3-diphenyltriazene in the presence of methanolic sodium hydroxide gave bis(1,3-diaryltriazenido)-bridged complexes of the type $[M_2X_2(\mu\text{-}ArNNNAr)_2(PR_3)_2]$ [M = Pd or Pt; X = Cl, Me or *p*-C_6H_4Me(tol); Ar = Ph, *p*-C_6H_4Me(tol), *p*-C_6H_4F; $PR_3 = PEt_3$, PBu_3, PMe_2Ph, $PMePh_2$]. The dipalladium complexes $[Pd_2Cl_2(\mu\text{-}ArNNNAr)_2(PR_3)_2]$ can also be prepared by the reaction of $[Pd_2Cl_2(\mu\text{-}OAc)_2(PR_3)_2]$ with free triazene.

All these complexes are air stable yellow to orange–red crystalline solids, soluble in common organic solvents. Molecular weight determination of some representative complexes $[M_2X_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$: M, X = Pd, Cl, 1068 (calc. 1080.8); M, X = Pd, Me, 1100 (calc. 1040); M, X = Pt, Cl, 1266 (calc. 1258.2) indicates their binuclear formulation. The IR spectra of these complexes displayed bands in the region 1100–1600 cm^{-1} characteristic of the triazene skeleton. Although attempts have been made to distinguish between the various structural possibilities based on IR data, in the present case an unambiguous differentiation between monodentate, chelating and bridging modes could not be made. A band in the region 320–330 cm^{-1}, absent in the organometallic derivatives and free ligands, has been assigned to the terminal M—Cl stretching vibrations[10] for $[M_2Cl_2(\mu\text{-}ArNNNAr)_2(PR_3)_2]$ complexes.

The $^{31}P\{^1H\}$ NMR spectra (Table 2) of these complexes exhibited a single resonance indicating the presence of only one isomeric form. The spectra of the platinum complexes were flanked by ^{195}Pt satellites. The $^1J(Pt—P)$ has been reduced significantly from the parent chloro-bridged platinum precursors and is comparable to that of the bis (pyrazolato)-bridged binuclear platinum complexes.[9,11] Interestingly the spectra, in spite of four-bond separation between the two platinum ms, showed $^nJ(Pt\cdots P)$ couplings of the order Hz (Fig. 1). Such couplings have not rted in six-membered bis(pyrazolato)-bridged platinum complexes.[9,11] The $^{195}Pt\{^1H\}$ NMR spectra of $[Pt_2Cl_2(\mu\text{-}ArNNNAr)_2(PBu_3)_2]$, where Ar = Ph and *p*-$C_6H_4F$, displayed doublets at δ −3195 ppm [$^1J(Pt—P) = 3524$ Hz, $^nJ(Pt\cdots Pt) = 1587$ Hz] and δ −3204 ppm [$^1J(Pt—P) = 3502$ Hz, $^nJ(Pt\cdots Pt) = 1551$ Hz], respectively (Fig. 2). The ^{31}P and ^{195}Pt NMR spectra of these complexes are similar to those of $[Pt_2Cl_2(\mu\text{-}OAc)_2(PR_3)_2]$ complexes for which a short Pt—Pt distance with formal bond order zero has been suggested. The magnitudes of $J(Pt\cdots P)$ and $J(Pt\cdots Pt)$ for triazenido-bridged complexes are much higher than the corresponding values for analogous carboxylate complexes indicating shorter Pt···Pt separation (consequently stronger metal–metal bonding interactions) in the former. The observed trend is evident from the X-ray structures of $[Pd_2(tolNNNtol)_2(methallyl)_2]$,[12] $[Pd_2(\mu\text{-}OAc)_2(allyl)_2]$[13] and $[Pd_2(\mu\text{-}Cl)_2(methallyl)_2]$[14] in which Pd···Pd separations are 2.86, 2.94 and 3.438 Å, respectively. In the organoplatinum complexes, $[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PR_3)_2]$, $^2J(Pt\cdots P)$ was vanishingly small. This may be attributed to an increased Pt···Pt separation due to the strong *trans* influence of tolyl groups attached to platinum.

The ^1H NMR spectra exhibited expected integration and peak mulplicities. Palladium–methyl complexes showed a doublet for the Pd—Me protons with $^3J(P—H) \sim 4$ Hz. The aryl groups attached to nitrogen are magnetically non-equivalent as C_6H_4 group exhibited two separate sets of resonances for the protons at 2,6- and 3,5-positions. Similarly the methyl protons of the tolyl group exhibited two singlets.

The carboxylate bridged complexes, $[M_2X_2(\mu\text{-}OAc)_2(PR_3)_2]$ show a dynamic stereochemistry.[3] Structurally analogous triazenido-bridged complexes may be expected to show a similar behaviour. Thus, ^1H NMR spectrum of $[Pd_2Me_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ was recorded in the temperature range −50 to +50°C. However no noticeable change was observed in the spectrum indicating rigidity of the triazenido-bridged complexes. The complexes containing dimethylphenylphosphine exhibited two doublets for P—Me protons. However, in the case of $[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ only one doublet was observed in the temperature range −50 to +50°C.

A few reactions of triazenido-bridged palladium and platinum complexes have been investigated. The complex $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$ reacts reversibly with HCl. Thus, when a $CDCl_3$ solution of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$ was treated with HCl, a green solution [δ ^{31}P −0.1 ppm, $^1J(Pt—P) = 3440$ Hz] was formed which gave the parent complex (as revealed by ^{31}P NMR) after

Table 2. ^{1}H and ^{31}P{^{1}H} NMR data for $[M_2X_2(\mu\text{-ArNNNAr})_2(PR_3)_2]$ in $CDCl_3$

Complex	^{31}P{^{1}H} NMR data			^{1}H NMR data^b δ (in ppm)
	δ (ppm)	$^1J(^{195}Pt—^{31}P)$ (Hz)	$^nJ(Pt—P)^a$ (Hz)	
$[Pd_2Cl_2(\mu\text{-PhNNNPh})_2(PEt_3)_2]$	19.6			1.09 (m, 18H, $PCCH_3$) ; 1.71 (m, 6H), 1.94 (m, 6H) [PCH_2—] ; 6.91 (t, 7.2 Hz, 2H) ; 7.01 (t, 7.7 Hz, 4H) ; 7.17 (t, 7.3 Hz, 2H) ; 7.33 (m, 4H) ; 7.59 (d, 8.2 Hz, 4H) ; 8.02 (d, 8.2 Hz, 4H) [Ph]
$[Pd_2Cl_2(\mu\text{-PhNNNPh})_2(PBu_3)_2]$	16.1			0.86 (t, 7.2 Hz, 18H P—$CCCCH_3$) ; 1.27 (m, 12H, $PCCCH_2$—) ; 1.51 (m, 12H, PC—CH_2) ; 1.63 (m, 6H), 1.88 (m, 6H)[PCH_2—] ; 6.89 (t, 7.2 Hz, 2H) ; 6.96 (t, 7.7 Hz, 4H) ; 7.15 (t, 2H) ; 7.30 (m, 4H) ; 7.58 (d, 8 Hz, 4H) ; 8.03 (d, 7.8 Hz, 4H)[Ph]
$[Pd_2Cl_2(\mu\text{-tolNNNtol})_2(PBu_3)_2]$	15.5			0.86 (t, 7.3 Hz, 18H, $PCCCCH_3$) ; 1.26 (m, 12H, $PCCCH_2$—) ; 1.49 (m, 12H, $PCCH_2$—) ; 1.63 (m, 6H), 1.86 (m, 6H) [PCH_2—] ; 2.21 (s, 6H tol—Me) ; 2.37 (s, 6H, tol—Me) ; 6.78 (d, 8.3 Hz, 4H) ; 7.10 (d, 8.3 Hz, 4H) ; 7.45 (d, 8.3 Hz, 4H) ; 7.90 (d, 8.3 Hz, 4H)[C_6H_4]
$[Pd_2Cl_2(\mu\text{-}FC_6H_4NNNC_6H_4F)_2(PBu_3)_2]$	15.0			0.86 (t, 7.3 Hz, 18H, $PCCCCH_3$) ; 1.28 (m, 12H, $PCCCH_2$—) ; 1.48 (m, 12H, PC—CH_2—) ; 1.65 (m, 6H), 1.87 (m, 6H) [PCH_2—] ; 6.73 (t, 8.5 Hz, 4H) ; 7.01 (t, 8.5 Hz, 4H) ; 7.51 (m, 4H) ; 7.93 (m, 4H) [C_6H_4]
$[Pd_2Cl_2(\mu\text{-PhNNNPh})_2(PMe_2Ph)_2]$	1.27			1.65 (d, 12 Hz, 6H), 2.03 (d, 12 Hz, 6H) [PMe_2] ; 6.71–7.95 (m, 30H, Ph)
$[Pd_2Cl_2(\mu\text{-PhNNNPh})_2(PMePh_2)_2]$	9.1			2.38 (d, 12 Hz, 6H, PMe) ; 6.71 (br) ; 6.89 (t, 7.5 Hz), 7.11–7.52 (m), 7.91 (d, 7.8 Hz), 8.11 (m) [40H, Ph]
$[Pd_2Me_2(\mu\text{-PhNNNPh})_2(PBu_3)_2]$	5.8			0.45 (d, 3.8 Hz, 6H, Pd—Me) ; 0.87 (t, 7.2 Hz, 18H, $PCCCCH_3$) ; 1.26–1.52 (m, 36H, $PCH_2CH_2CH_2$—) ; 6.86 (t, 7.2 Hz) ; 7.07 (m) ; 7.32 (t, 7.5 Hz), 7.70 (d, 7.7 Hz), 8.00 (d, 7.7 Hz) [20H, Ph]

$[Pd_2Me_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$	−4.1			0.51 (d, 4.6 Hz, 6H, Pd—Me); 1.37 (d, 10 Hz, 6H), 1.52 (d, 10 Hz, 6H) [PMe]; 6.85 (m), 7.05 (m), 7.27–7.47 (m), 7.61 (d) 7.81 (d) [30H, Ph]
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PEt_3)_2]$	−12.2	3496		1.06 (m, 18H, $PCCH_3$); 1.69 (m, 6H), 1.91 (m, 6H) [PCH_2—]; 6.99 (m), 7.6 (t, 7.3 Hz), 7.32 (t, 7.8 Hz), 7.60 (d, 7.9 Hz), 7.97 (d, 7.9 Hz) [20H, Ph]
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$	−15.7	3500	52	0.87 (t, 7.1 Hz, 18H, $PCCCCH_3$); 1.26–1.87 (m, 36H, $PCH_2CH_2CH_2$—); 6.95–7.18 (m), 7.30 (t, 7.5 Hz), 7.58 (d, 7 Hz), 7.97 (d, 7.7 Hz) [20H, Ph]
$[Pt_2Cl_2(\mu\text{-}FC_6H_4NNNC_6H_4F)_2(PBu_3)_2]$	−15.2	3484	51	0.87 (t, 7.2 Hz, 18H, $PCCCCH_3$), 1.28 (m, 12H, $PCCCH_2$—), 1.38 (m, 12H, $PCCH_2$—), 1.61 (m, 6H), 1.83 (m, 6H) [PCH_2—]; 6.72 (t, 8.4 Hz, 4H); 6.99 (t, 8.7 Hz, 4H), 7.52 (d, d, 4H), 7.87 (d, d, 4H) [C_6H_4]
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$	−28.3	3527	52	1.65 (d, 12 Hz, 6H, PMe); 1.99 (d, 12 Hz, 6H, PMe); 6.77 (m), 7.08 (t), 7.21–7.64 (m), 7.88 (d, 8.0 Hz) [30H, Ph]
$[Pt_2Cl_2(\mu\text{-}tolNNNtol)_2(PMe_2Ph)_2]$	−28.2	3514	52	1.62 (d, 11.9 Hz, 6H, PMe); 1.97 (d, 11.9 Hz, 6H, PMe); 2.14 (s, 6H, tol—Me); 2.30 (s, 6H, tol—Me) 6.6 (d, 7.7 Hz, 4H); 7.05 (m), 7.26–7.36 (m), 7.6 (m), 7.8 (d, 7.7 Hz, 4H) [Ph + C_6H_4]
$[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PMePh_2)_2]$	−13.8	3596	59	2.32 (d, 12 Hz, 6H, PMe); 6.72–8.10 (m, 40H, Ph)
$[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$	−22.2	3932	-	1.52 (d, 10 Hz, 12H, PMe); 2.27 (s, 6H, tol—Me); 6.76 (d, 8.3 Hz, 4H, tol), 7.31 (d, 7.3 Hz, 4H, tol); 6.80–7.05 (m), 7.44 (br), 7.92 (m) [30H, Ph]
$[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PMePh_2)_2]$	−5.7	4027	-	1.43 (d, 10.7 Hz, 6H, PMe); 2.24 (s, 6H, tol—Me); 6.54–7.82 (m, 48H, Ph + C_6H_4)

---

[a] $J(Pt\cdots P)$ could not be resolved at 500 MHz due to CSA, thus spectra were recorded at 80 MHz.

[a] s = singlet, d = doublet; t = triplet, q = quartet, m = multiplet, br = broad.

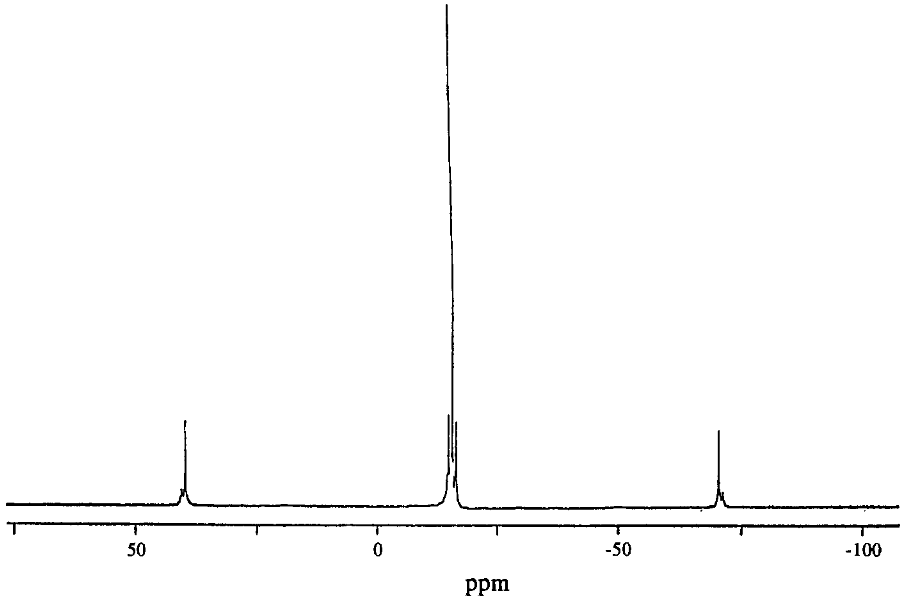

Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3^n)_2]$ in $CDCl_3$ on a varian FT-80A.

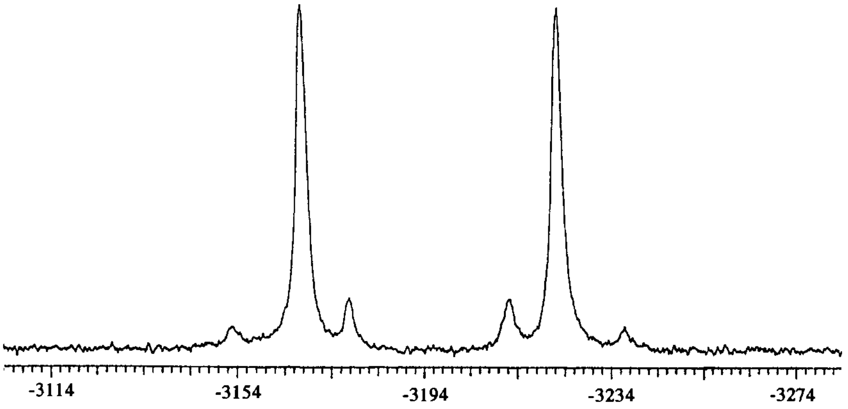

Fig. 2. $^{195}Pt\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PBu_3)_2]$ in $CDCl_3$ on a varian XLR-300.

passing through a Florisil column. The product formed on treatment of HCl may be a protonated species $[PtCl(PhNNNHPh)(PBu_3)]$. To ascertain this, the reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ with PhNNNHPh was carried out in $CDCl_3$. The ^{31}P NMR spectrum displayed a signal at δ -6.3 ppm, $^1J(Pt—P) = 3372$ Hz. The observed variation in the chemical shifts and coupling constants may be due to ligation through different nitrogen atoms of the triazene ligand. Therefore, we have investigated the bridge cleavage reactions of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ with different types of nitrogen donors namely $PhNH_2$, $PhNMe_2$, PhN=CHPh. The ^{31}P NMR spectra of their reactions showed single resonances at δ -5.2 ppm ($^1J = 3534$ Hz), -3.8 ppm ($^1J = 3488$ Hz), -7.8 ppm ($^1J = 3455$ Hz), respectively. This indicates that the signal is more shielded with smaller $^1J(Pt—P)$ for sp^2 hybridized nitrogen than that of sp^3. In every case nitrogen is *trans* to the phosphine.[15] The factors controlling the coordination of a particular nitrogen exclusively in the triazene complexes are not quite clear. Interestingly, no isomerisation takes place on leaving the solutions for a few days at room temperature.

Insertion of CO across the Pd—Me[16] and metal triazenido[17] bonds has been reported. However, the ^{31}P NMR spectrum of $[Pd_2Me_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ did not show any change when CO was bubbled (at 1 atm. and room temperature), through its $CDCl_3$ solution for 20 min.

Addition of triphenylphosphine (2–4 equivalents) to the $CDCl_3$ solutions of $[Pd_2Me_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ or $[Pt_2Cl_2(\mu\text{-}PhNNNPh)_2(PMe_2Ph)_2]$ has no effect on their ^{31}P NMR spectra indicating non-lability of the triazenido-bridges. However, when the organoplatinum complex, $[Pt_2tol_2(\mu\text{-}PhNNNPh)_2(PR_3)_2]$, was treated with triphenylphosphine a complex mixture of products formed. [$PR_3 = PMePh_2$, δ ^{31}P, 18.4 ppm (~18%, $^1J = 3215$ Hz), 15.2 ppm (~25%, $^1J = 3116$ Hz) for PPh_3; 9.2 ppm (~27%, $^1J = 3190$ Hz), 5.9 ppm (~29%, $^1J = 3088$ Hz) for $PMePh_2$.] [$PR_3 = PMe_2Ph$, δ ^{31}P, 18.5 ppm (~11%, $^1J = 3227$ Hz), 14.5 ppm (~21%, $^1J = 3016$ Hz) for PPh_3; −3.2 ppm (~33%, $^1J = 3131$ Hz), −7.8 ppm (~19%, $^1J = 2953$ Hz), −16.7 ppm (~15%, $^1J = 3130$ Hz) for PMe_2Ph.] None of the resonances were attributed to the mixed ligand species, $[Pt(tol)(PhNNNPh)(PPh_3)(PR_3)]$, mainly due to the absence of $^2J(P\cdots P)$. The reactivity of organoplatinum complexes may be attributed to the absence of platinum–platinum interaction, as indicated by ^{31}P NMR data, similar to the pyrazolato-bridged complexes. However, non-reactivity of other complexes towards neutral donors may be ascribed to short metal–metal distances.

Acknowledgements—We thank Dr. J. P. Mittal for encouragement of this work. We are grateful to TIFR for providing ^1H and ^{31}P NMR spectra on 500 MHz National NMR facility and Head, Analytical Chemistry Division, BARC for providing microanalyses for some of the samples.

REFERENCES

1. V. K. Jain, R. P. Patel, K. V. Muralidharan and R. Bohra, *Polyhedron* 1989, **8**, 2151; V. K. Jain, R. P. Patel and K. Venkatasubramanian, *Polyhedron* 1991, **10**, 851; V. K. Jain and S. Kannan, *J. Organomet. Chem.* 1991, **405**, 265; V. K. Jain and S. Kannan, *J. Organomet. Chem.* 1991, **418**, 349; V. K. Jain and S. Kannan, *Polyhedron* 1992, **11**, 27; V. K. Jain, S. Kannan and R. Bohra, *Polyhedron* 1992, **11**, 1551; V. K. Jain, S. Kannan and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.* 1992, 2231; V. K. Jain and S. Kannan, *J. Organomet. Chem.* 1992, **439**, 231; V. K. Jain, S. Kannan, R. J. Butcher and J. P. Jasinski, *J. Chem. Soc., Dalton Trans.* 1993, 1509; A. Singhal and V. K. Jain, *J. Chem. Soc., Dalton Trans.* 1993, 1515.
2. S. Kannan and V. K. Jain, *Mag. Res. Chem.* 1990, **28**, 1007.
3. J. Powell and T. Jack, *Inorg. Chem.* 1972, **11**, 1039.
4. D. S. Moore and S. D. Robinson, *Adv. Inorg. Chem. Radiochem.* 1986, **30**, 1; M. B. Husthouse, M. A. Mazid, T. Clark and S. D. Robinson, *Polyhedron* 1993, **12**, 563.
5. S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Chem. Commun.* 1971, 1315; K. R. Ling, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.* 1974, 1205; M. Corbelt, B. F. Hoskins, N. J. McLeod and B. S. O'Day, *Aust. J. Chem.* 1975, **28**, 2377; G. Bombieri, A. Immirzi and L. Toniolo, *Inorg. Chem.* 1976, **15**, 2428; L. Toniolo, A. Immirzi, U. Croatto and G. Bombieri, *Inorg. Chim. Acta* 1976, **19**, 209; A. Immirzi, G. Bombieri and L. Toniolo, *J. Organomet. Chem.* 1976, **118**, 355; T. Boschi, U. Belluco, L. Toniolo, R. Favez and R. Roulet, *Inorg. Chim. Acta* 1979, **34**, 37; C. J. Creswell, M. A. Queiros and S. D. Robinson, *Inorg. Chim. Acta* 1982, **60**, 157; M. Gomez, G. Muller and J. Sales, *Polyhedron* 1993, **12**, 1171.
6. T. Jack and J. Powell, *J. Organomet. Chem.* 1971, **27**, 133; P. Hendriks, J. Kuyper and K. Vrieze, *J. Organomet. Chem.* 1976, **120**, 285.
7. F. R. Hartley, *The Chemistry of Platinum and Palladium*. Applied Science Publishers Ltd, London (1973).
8. W. W. Hartman and J. B. Dickey, *Organic Synthesis* (Edited by A. H. Blatt), Vol 2, p. 163. Wiley, New York (1943).
9. A. Singhal, V. K. Jain and S. Kannan, *J. Organomet. Chem.* 1993, **447**, 317.
10. R. J. Goodfellow, P. L. Goggin and L. M. Venanzi, *J. Chem. Soc. A* 1967, 1897; M. J. Taylor, A. L. Odell and H. A. Raethel, *Spectrochim. Acta* 1968, **24A**, 1855; D. M. Adams and P. J. Chandler, *J. Chem. Soc. A* 1969, 588.
11. V. K. Jain, S. Kannan and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.* 1993, 3625.
12. S. S. Candeloro, N. V. Pavel and L. Toniolo, *J. Organomet. Chem.*, 1976, **108**, 409.
13. M. R. Churchill, *Nature* (*London*) 1964, **204**, 777.
14. R. Mason and A. G. Wheeler, *J. Chem. Soc. A* 1968, 2549.
15. A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. A* 1966, 1707.
16. Y. Hayashi, K. Isobe, Y. Nakamura and S. Okeya, *J. Organomet. Chem.* 1986, **310**, 127.
17. L. Toniolo, *Inorg. Chim. Acta* 1979, **35**, L367; R. Rossi, A. Duatti, L. Margon and L. Toniolo, *Inorg. Chim. Acta* 1981, **48**, 243.