Transition Metal–Carbon Bonds. Part 51.[1] Action of Amines on Buta-1,3-diene Complexes of Type *cis,cis*-$[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$: Crystal Structures of $[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$ ‡ (*meso* Isomer) and $[(Et_3P)ClPt(Me_2NCH_2CHCHCH_2NMe_2)PtCl(PEt_3)]$ § (Two *trans*-fused Five-membered Rings)

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Treatment of chloro-bridged complexes $[Pt_2Cl_4(PR_3)_2]$ ($PR_3 = PMe_2Ph$, PEt_3, or PPr^n_3) with buta-1,3-diene over several days gives the μ-butadiene complexes *cis,cis*-$[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$; such complexes have not previously been fully characterized. Buta-1,3-diene is prochiral and the product is shown to be the *meso* isomer for $PR_3 = PMe_2Ph$, by *X*-ray crystallography. A low-temperature study in $CDCl_3$ shows that at −30 °C buta-1,3-diene reacts rapidly and reversibly with $[Pt_2Cl_4(PPr^n_3)_2]$ to give *trans*-$[PtCl_2(PPr^n_3)(C_4H_6)]$; a very small amount of *cis*-$[PtCl_2(PPr^n_3)(C_4H_6)]$, in which the butadiene is monodentate, was also probably formed. Treatment of $[NBu^n_4]_2[Pt_2X_6]$ with buta-1,3-diene gave the μ-butadiene complexes $[NBu^n_4]_2[Pt_2X_6(\mu\text{-}C_4H_6)]$ (X = Cl or Br). Treatment of $[Pt_2Cl_4(PMe_2Ph)_2]$ with isoprene at −60 °C reversibly gives a new species, probably *trans*-$[PtCl_2(PMe_2Ph)(\text{isoprene})]$, and at room temperature probably *cis*-$[PtCl_2(PMe_2Ph)(\text{isoprene})]$, although we could not separate this *cis* species from the bridged complex. Treatment of *cis,cis*-$[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$ with an excess of dimethylamine (even at −78 °C) rapidly gave $[(PhMe_2P)ClPt(Me_2NCH_2CHCHCH_2NMe_2)PtCl(PMe_2Ph)]$ (5a); a similar reaction gave the PEt_3 complex (5d), the crystal structure of which shows the presence of two *trans*-fused five-membered rings. Treatment of *cis,cis*-$[Pt_2Cl_4(PPr^n_3)_2(\mu\text{-}C_4H_6)]$ with methylamine similarly gave $[(Pr^n_3P)ClPt(MeHNCH_2CHCHCH_2NHMe)PtCl(PPr^n_3)]$ as a mixture of three isomers due to the positioning of the N–Me groups; one isomer was isolated pure. Proton, ^{13}C, ^{31}P, and ^{195}Pt n.m.r. and i.r. data are given. Crystals of both the title compounds are monoclinic, space group $P2_1/n$, with $Z = 2$ and molecular symmetry C_i. Those of $[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$ have $a = 1.9658(4)$, $b = 0.9741(3)$, $c = 0.6557(1)$ nm, and $\beta = 94.24(2)°$. Those of (5d) have $a = 0.8015(3)$, $b = 1.3461(3)$, $c = 1.3070(3)$ nm, and $\beta = 97.56(3)°$. Final *R* factors were 0.042 for 1 391 and 0.040 for 1 584 observed reflections, respectively.

In previous papers in this series we showed how chloro-bridged binuclear complexes of type $[Pt_2Cl_4(PR_3)_2]$ react rapidly and reversibly with olefins to give labile complexes of type *trans*-$[PtCl_2(PR_3)(\text{olefin})]$, which were detected at low temperatures by n.m.r. spectroscopy.[2-4] At or near room temperature, there is a slow (reversible) formation of the corresponding *cis* complexes, *cis*-$[PtCl_2(PR_3)(\text{olefin})]$, which were first characterized twenty years ago.[5] We and others[6,7-10] have shown that complexes of type $[PtCl_2(PR_3)(\text{olefin})]$ of *cis* configuration are susceptible towards nucleophilic attack on the co-ordinated olefin by amines ($NR^1R^2R^3$), initially to give a zwitterionic species, $R^1R^2R^3N\text{-}C\text{-}C\text{-}PtCl_2(PR_3)$. If the amine is primary or secondary then, in the presence of base, deprotonation can occur and nitrogen co-ordinates to platinum to give a chelate. Thus we have shown that the allene complex $[PtCl_2(C_3H_4)(PPr^n_3)]$, with t-butylamine in the presence of a base {either $NaOPr^i$ or NH_2Bu^t}, gives $[PtCl(PPr^n_3)\{C(=CH_2)CH_2NHBu^t\}]$, a chelate complex containing a four-membered ring, whereas treatment of the allene complex with an excess of methylamine gives the binuclear complex $[Pt_2Cl_2(PPr^n_3)_2\{C(=CH_2)CH_2NHMe\}_2]$, containing an eight-membered ring.[6] In the early work on olefin complexes of the type *cis*-$[PtCl_2(PR_3)(\text{olefin})]$ some binuclear butadiene complexes were prepared but were too insoluble to characterize properly. They were formulated as $[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$ but were too insoluble to measure molecular weights or dipole moments and no n.m.r. or i.r. spectroscopic measurements were made. By analogy, with the mono-olefin complexes, $[PtCl_2(PR_3)(\text{olefin})]$, whose configuration was established as *cis* by dipole moment measurements, it seemed very likely that each double bond of the co-ordinated butadiene was *cis* with respect to the tertiary phosphine and co-ordinated with the C=C axis almost vertical to the $PtCl_2P$ plane. However, each double bond of the butadiene is prochiral and therefore the complexes of type $[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$ could exist as *meso* or DL isomers, *i.e.* with the butadiene in a *cisoid* fashion, as configurations (1) (*meso*) or (2) (DL) or, if in a *transoid* fashion, (3) (*meso*) or (4) (DL). We have now studied the action of buta-1,3-diene on the bridged complexes $[Pt_2Cl_4(PR_3)_2]$ in more detail and established the stereochemistry of a bridged butadiene adduct $[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$ by *X*-ray crystallography.

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* Author for crystallographic queries.

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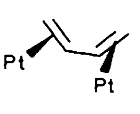
‡ *meso*-μ-1—2-η:3—4-η-Buta-1,3-diene-bis[dichloro(dimethylphenylphosphine)platinum].

§ μ-[1,4-Bis(dimethylamino)butane-2,3-diyl-$NC^3(Pt^1),N'C^2(Pt^2)$]-bis[chloro(triethylphosphine)platinum].

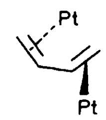
We have also studied the action of amines on these μ-butadiene complexes and established the structures of the product(s).

RESULTS AND DISCUSSION

The complexes $[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$ were prepared by treating an acetone solution of a chloro-bridged complex $[Pt_2Cl_4(PR_3)_2]$ ($PR_3 = PMe_2Ph$, PEt_3, or PPr^n_3) with butadiene over several days. Elemental analytical, molecular weight, and far-i.r. [ν(Pt–Cl)] data are in Table 1. The presence of two strong absorption bands at *ca.* 280 and 325 cm^{-1} in the i.r. spectrum indicated a *cis-cis* geometry for both $PtCl_2$ moieties; similar values are found for complexes of the type *cis*-$[PtCl_2(PR_3)$(mono-olefin)].[2,4] The values of ^1J(Pt–P) from the ^{31}P n.m.r. spectra were *ca.* 3 000 Hz (Table 2), also typical of a *cis* geometry for a complex of this type {values of ^1J(Pt–P) for the *trans* isomers, *trans*-$[PtCl_2(PR_3)$(mono-olefin)], are somewhat higher, at 3 300—3 400 Hz}.[2-4] From the ^{31}P n.m.r. spectra we could also measure values of ^3J(Pt–Pt), and for the PPr^n_3 complex ^4J(Pt–P). The ^{31}P n.m.r. data are in Table 2. The PMe_2Ph complex was too insoluble for n.m.r. studies but the platinum-195 chemical shifts for the PPr^n_3 and PEt_3 complexes were measured and are very similar (737 and 715 p.p.m. respectively), see Table 2.



(1)



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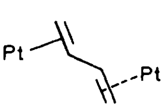

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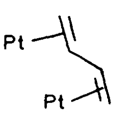
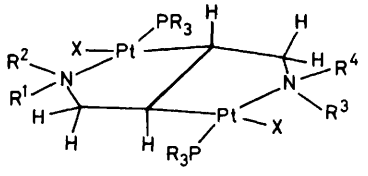


(4)

The portion of the ^1H n.m.r. spectrum of $[Pt_2Cl_4(PPr^n_3)_2(\mu\text{-}C_4H_6)]$ due to the butadiene showed three complex multiplets centred at δ 3.98, 4.70, and 5.77, as expected of an $[AMX]_2$ spin system. Some of the coupling constants were identified, see Table 3. These results established that the complexes were of type *cis,cis*-$[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$ but in order to establish whether a complex of this type is *meso* or DL, a structural investigation by *X*-ray diffraction was undertaken. Of the three complexes of type *cis-cis*-$[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$ the PMe_2Ph complex gave the best formed single crystals and its crystal structure has been determined. The structure with atom numbering is shown in Figure 1. The butadiene is in a *transoid* arrangement with the two $PtCl_2(PMe_2Ph)$ moieties on opposite sides of the butadiene, *i.e.* the complex is *meso*. Selected bond lengths and angles are given in Table 4. As might be expected the bond length Pt–Cl(1) *trans* to P is 237.3(4) pm, considerably longer than Pt–Cl(2) *trans* to C=C [229.3(4) pm]. The olefinic double bond C(9)–C(10), at 145.2(22) pm, is significantly longer than in free butadiene [133.7(5) pm].[11]



Complex	PR_3	X	R^1	R^2	R^3	R^4
(5a)	PMe_2Ph	Cl	Me	Me	Me	Me
(5b)	PMe_2Ph	Br	Me	Me	Me	Me
(5c)	PMe_2Ph	I	Me	Me	Me	Me
(5d)	PEt_3	Cl	Me	Me	Me	Me
(5e)	PEt_3	Br	Me	Me	Me	Me
(5f)	PEt_3	I	Me	Me	Me	Me
(5g)	PPr^n_3	Cl	Me	H	H	Me
(5h)	PPr^n_3	Cl	H Me	Me H	H Me	Me H
(5i)	PPr^n_3	Cl	H	Me	Me	H

Phosphorus-31 *N.M.R. Study of the Action of Buta*-1,3-*diene on* $[Pt_2Cl_4(PR_3)_2]$.—We have previously shown, by extensive ^{31}P-{^1H} n.m.r. studies, at variable temper-

TABLE 1

Analytical (calculated values in parentheses) and i.r. data

Complex	Analysis (%) C	H	N	Cl	M.p. (θ_c/°C)	ν(Pt-Cl)/ cm^{-1}
cis,cis-$[Pt_2Cl_4(PPr^n_3)_2(\mu\text{-}C_4H_6)]$ [a]	29.25(29.15)	5.25(5.35)		15.5(15.65)	160 [b]	280, 325
cis,cis-$[Pt_2Cl_4(PEt_3)_2(\mu\text{-}C_4H_6)]$	23.35(23.35)	4.4(4.4)		16.9(17.25)	150 [b]	283, 328
cis,cis-$[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$	27.95(27.85)	3.15(3.25)		16.65(16.55)	130 [b]	292, 333
$[NBu^n_4]_2[Pt_2Cl_6(\mu\text{-}C_4H_6)]$ [c]	38.0(37.85)	6.75(6.9)	2.45(2.45)		157—159	319, 340 [d]
$[NBu^n_4]_2[Pt_2Br_6(\mu\text{-}C_4H_6)]$	30.9(30.7)	5.4(5.6)	2.0(2.0)		140—150	
(5a) [e]	33.05(32.75)	4.45(4.6)	3.1(3.2)	7.75(8.05)	230 [b]	267
(5b)	29.75(29.35)	4.0(4.2)	2.85(2.9)		210 [b]	
(5c)	27.2(27.15)	3.7(3.8)	2.6(2.65)		200 [b]	
(5d) [f]	28.75(28.6)	5.85(5.75)	3.35(3.35)	8.5(8.45)	170 [b]	255
(5e)	26.1(25.9)	5.35(5.2)	3.0(3.0)		200 [b]	
(5f)	23.3(23.5)	4.9(4.75)	2.75(2.75)		150 [b]	
(5g), (5h), (5i) mixed isomers	32.3(32.2)	6.55(6.3)	3.15(3.15)		220 [b]	[g]
(5g) or (5h) or (5i) single isomer [h]	31.8(32.2)	6.25(6.3)	3.1(3.15)		200 [b]	[g]

[a] Molecular weight 893(907). [b] Decomposes without melting. [c] Conductivity in acetone at 20 °C, Λ = 148 S cm^2 mol^{-1}. [d] Only two bands visible. [e] Molecular weight 890(880). [f] Molecular weight 818(840). [g] Not identified in spectrum. [h] See Discussion section.

TABLE 2

Phosphorus-31 and ^{195}Pt n.m.r. data

Complex	δ(P) [a]	^1J(Pt–P)/Hz	^4J(Pt–P)/Hz	$\vert^3J$(Pt–Pt$\vert$/Hz	δ(Pt)
cis,cis-[$Pt_2Cl_4(PPr^n{}_3)_2(\mu\text{-}C_4H_6)$] [c]	7.4(6.8) [c]	3 026(3 054) [c]	−4	635	737
cis,cis-[$Pt_2Cl_4(PEt_3)_2(\mu\text{-}C_4H_6)$] [c]	16.2(14.0) [c]	3 044(3 075) [c]	*d*	632	715
(5a)	−14.9	4 220	−15	259	
(5b)	−15.8	4 192	−15	346	
(5c)	−16.9	4 147	−14	413	
(5d)	4.5	4 148	−11	347	
(5e)	3.6	4 132	−15	440	
(5f)	2.7	4 018	−15	501	
(5g), (5h), (5i)	−2.0	4 099	−6	296	
	−2.4	4 073	−6	—	
	−3.1	4 027	−10	—	

[a] In p.p.m. to high frequency of H_3PO_4; in $CDCl_3$, J(P–P) *ca.* 0 for all complexes. [b] In p.p.m. to high frequency of Ξ (^{195}Pt) = 21.4 MHz. [c] Minor component in parentheses. [d] Not resolved.

ature, of [$Pt_2Cl_4(PR_3)_2$]–olefin systems that labile complexes of type *trans*-[$PtCl_2(PR_3)$(olefin)] are formed rapidly, even at low temperatures,[2-4] but that such complexes are increasingly dissociated as the temperature rises. We have now carried out similar studies with buta-1,3-diene. Addition of 5 mol equivalents of the diene to a solution of [$Pt_2Cl_4(PPr^n{}_3)_2$] in $CDCl_3$ at −30 °C causes *ca.* 70% conversion of the chloride-bridged complex to a new species, the ^{31}P-{^{1}H} n.m.r. spectrum of which showed it to be mononuclear (absence of Pt–Pt coupling) with phosphorus *trans* to olefin, ^1J(Pt–P) 3 453 Hz, δ(P) 6.0 p.p.m. When the solution was warmed to −10 °C the proportion of this mononuclear species decreased slightly. At both these temperatures, a second product (present to the extent of *ca.* 1% of the *trans* mononuclear species) was also observed. This minor product had δ(P) 5.5 p.p.m. and ^1J(Pt–P) 3 100 Hz. We could not observe any long-range phosphorus–platinum coupling, *i.e.* ^4J(P–Pt), and the resonances were too weak to have observed platinum–platinum coupling, even if present. The absence of phosphorus–platinum coupling may indicate that the minor species is mononuclear and from the value of ^1J(Pt–P) we suggest that it is *cis*-[$PtCl_2(PPr^n{}_3)(C_4H_6)$] in which the butadiene is monodentate. A few *very* weak resonances were also present in the spectrum but we could not identify these, nor indeed satellites due to coupling to ^{195}Pt. It is interesting that a mononuclear complex *cis*-[$PtCl_2(PR_3)(C_4H_6)$] is only formed in a small amount, even in the presence of a large excess of buta-1,3-diene, whereas the μ-butadiene complex is produced in high yield. This suggests that the second double bond of butadiene is more readily co-ordinated than the first.

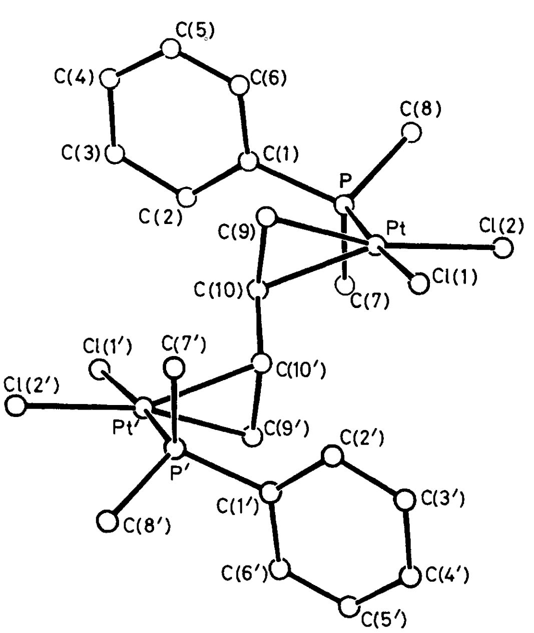
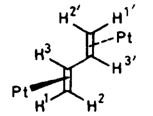


FIGURE 1 The molecular structure and atom numbering of *meso,cis,cis*-[$Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)$]

TABLE 3

Hydrogen-1 n.m.r. data (δ/p.p.m.) for the butadiene ligand in [$Pt_2Cl_4(PPr^n{}_3)_2(\mu\text{-}C_4H_6)$] in $CDCl_3$ at 100 MHz



δ(H^1) = 3.98   δ(H^2) = 4.70   δ(H^3) = 5.77
$^2J(H^1H^2)$ *ca.* 0 Hz $|^3J(H^1H^3) + {}^4J(H^1H^{3'})| = 6.6$ Hz
$|^3J(H^2H^3) + {}^4J(H^2H^{3'})| = 13.2$ Hz
$J(PtH^1) = 60$ Hz, $J(PtH^2) = 64$ Hz, $J(PtH^3)$, $J(PtH^{3'})$ not identified

Freshly prepared solutions of the butadiene bridged complexes *cis,cis*-[$Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)$] with PR_3 = PEt_3 or $PPr^n{}_3$ each showed the presence of two species. For the PEt_3 complex(es) the major species (*ca.* 99% of the whole) is clearly the *meso* isomer (1)/(3) from the result discussed below. The minor species, *ca.* 1% of the whole, which has very similar ^{31}P n.m.r. parameters to the major species (see Table 2) is probably very closely related to it and might be a different rotamer of the *meso* form. N.m.r. studies at variable temperature have shown that there is a considerable energy barrier to rotation of a co-ordinated olefin around the platinum–olefin bond in mono-olefin complexes of type *cis*-[$PtCl_2(PR_3)$(mono-olefin)] [12,13] and n.m.r. patterns corresponding to the two rotamers are ' frozen out ' at low temperatures. However, with the allene complex *cis*-[$PtCl_2(PPr^n{}_3)(C_3H_4)$] the allene is not rotating at room temperature but at 60 °C some broadening of resonances occurs corresponding to slow rotation, *i.e.* the energy barrier to rotation in allene complexes is higher than in olefin complexes.[4] It is possible therefore that in the μ-butadiene complex *cis,cis*-$[Pt_2Cl_4(PPr^n_3)_2(\mu\text{-}C_4H_6)]$ the energy barrier to rotation around the Pt C=C bonds is high. Alternatively, the minor species (present as *ca.* 1% of the whole) is the DL isomer. Solutions of the butadiene complex *cis,cis*-$[Pt_2Cl_4(PPr^n_3)_2(\mu\text{-}C_4H_6)]$ gradually dissociate, *e.g.* after 24 h at *ca.* 20 °C, dissociation to the bridged complex $[Pt_2Cl_4(PPr^n_3)_2]$ is *ca.* 90% complete.

TABLE 4

Bond distances (pm) and angles (°) for $[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$, estimated standard deviations in parentheses

(*a*) Distances		(*b*) Angles	
Pt–Cl(1)	237.3(4)	Cl(1)–Pt–Cl(2)	88.5(1)
Pt–Cl(2)	229.3(4)	Cl(2)–Pt–P	87.2(1)
Pt–P	226.0(4)	Cl(2)–Pt–C(9)	165.4(4)
Pt–C(9)	213.8(15)	Cl(2)–Pt–C(10)	155.3(4)
Pt–C(10)	217.9(14)	Cl(1)–Pt–C(9)	87.3(4)
C(9)–C(10)	145.2(22)	Cl(1)–Pt–C(10)	96.1(4)
C(10)–C(10′)	147.1(21)	C(9)–C(10)–C(10′)	119.3(12)
P–C(1)	181.0(16)	Pt–P–C(1)	114.3(5)
P–C(7)	181.9(17)	Pt–P–C(7)	111.3(6)
P–C(8)	184.4(15)	Pt–P–C(8)	114.0(5)

We also prepared the new μ-butadiene complexes $[NBu^n_4]_2[Pt_2X_6(\mu\text{-}C_4H_6)]$ (X = Cl or Br) from $[NBu^n_4]_2[Pt_2X_6]$ and butadiene in acetone (see Table 1 for characterization and the Experimental section for further details). We were unable to prepare the corresponding iodide $[NBu^n_4]_2[Pt_2I_6(\mu\text{-}C_4H_6)]$ by an analogous method. Olefin complexes of platinum(II) containing iodide ligands are rare, although we have recently reported the isolation of $[NBu^n_4][PtI_3(allene)]$.[4] We have also found that treatment of $[Pt_2Cl_4(PPr^n_3)_2(\mu\text{-}C_4H_6)]$ in acetone with either lithium bromide or sodium iodide caused displacement of the butadiene to give $[Pt_2X_4(PPr^n_3)_2]$ (X = Br or I), but we have not treated these halogen-bridged complexes with butadiene.

In an attempt to prepare complexes of isoprene we treated a solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ in $CDCl_3$ with a ten-fold excess of isoprene at −60 °C. This gave a new species (*ca.* 5% of the mixture), characterized by its ^{31}P n.m.r. pattern, $\delta(P)$ 5.9 p.p.m., $^1J(Pt\text{–}P)$ 3 455 Hz, which reverts back to $[Pt_2Cl_4(PMe_2Ph)_2]$ at room temperature. The value of $^1J(Pt\text{–}P)$ is typical for phosphorus *trans* to olefin and we formulate this labile species as *trans*-$[PtCl_2(PMe_2Ph)(isoprene)]$.

Treatment of a dichloromethane solution of $[Pt_2Cl_4(PMe_2Ph)_2]$ with an excess of isoprene at room temperature gives, after several days, a mixture of a new species, $\delta(P)$ 15.0 p.p.m., $^1J(Pt\text{–}P)$ 3 546 Hz, and unchanged bridged complex, $[Pt_2Cl_4(PMe_2Ph)_2]$, which we could not separate. The absence of platinum–platinum coupling in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum suggests that this new species is probably mononuclear. The i.r. spectrum of the mixture had two bands at 312 and 285 cm^{-1} which are attributable to $\nu(Pt\text{–}Cl)$ of the new species and are typical values for a complex of type *cis*-$[PtCl_2(PR_3)(olefin)]$. We tentatively suggest that the new complex is *cis*-$[PtCl_2(PMe_2Ph)(isoprene)]$ although the value of $^1J(Pt\text{–}P)$ is high, and that it is the $C{=}CH_2$ bond of the isoprene which is co-ordinated. When we treated a solution of $[Pt_2Cl_4(PPr^n_3)_2]$ with cyclopentadiene for 8 d, no new complex was formed, as evidenced by the ^{31}P n.m.r. spectrum.

Nucleophilic Addition of Amines to the Butadiene Complexes.—The addition of amines to olefins co-ordinated to platinum(II) has attracted some attention. Some of our work [6] to give four-membered and eight-membered ring compounds is outlined above. Green and other workers [7,9,12] have shown that amines attack platinum(II)–olefin complexes to give zwitterionic species or ring compounds with a four-membered ring and dimethylallene complexes of platinum(II) have been shown to give zwitterionic complexes.[10] More recently it has been shown that attack of poorly basic aromatic amines on olefins co-ordinated to platinum(II) gives enamine complexes.[14]

We reasoned that primary or secondary amines would attack the co-ordinated butadiene of complexes of the type *cis,cis*-$[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$ and then, with loss of a proton, could co-ordinate to a platinum to give either a four- or a five-membered ring. It seemed most likely that the initial attack would occur specifically *trans* to platinum and that two, *trans*-fused, five-membered rings would be formed. Addition of dimethylamine (⩾4 mol per mol of complex) to a suspension of *cis,cis*-$[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$ in dichloromethane caused rapid dissolution of the insoluble bridged complex to give a colourless solution. From this solution we isolated $Me_2NH_2^+Cl^-$ and the desired complex $[(PhMe_2P)ClPt(Me_2NCH_2CHCHCH_2NMe_2)PtCl(PMe_2Ph)]$ (5a) [a crystal structure determination of the corresponding PEt_3 complex (5d) confirms the presence of *trans*-fused five-membered rings (see below)]. Microanalytical and molecular-weight data are in Table 1. The far-i.r. spectrum showed one strong band, at 267 cm^{-1}, due to $\nu(Pt\text{–}Cl)$, the low value being characteristic of *trans* σ-bonded carbon. In the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum, the large value of $^1J(Pt\text{–}P)$ (4 220 Hz) is consistent with phosphorus *trans* to nitrogen and *cis* to an alkyl group. The presence of a *cis* alkyl ligand has been shown to increase $^1J(Pt\text{–}P)$ relative to most other ligands.[15] A

TABLE 5

Carbon-13 n.m.r. data for (5a) in $CDCl_3$

	$\delta(^{13}C)$/p.p.m.	J(PC)/Hz	J(PtC)/Hz
*C*H	35.4	4	743
		1	29
*C*H$_2$	72.3	6	76
		3	22
N(*C*H$_3$)$_2$	51.1	2	8
	46.2	2	15
P(*C*H$_3$)$_2$	16.9	43	36
	13.9	39	51
P(*C*$_6$H$_5$)	134.6	57	78
	130.6	13	35
	128.6	10	0
	130.5	0	0

value for ^3J(Pt–Pt) of 259 Hz was also measured from the ^{31}P-{^{1}H} n.m.r. spectrum. In the ^{13}C-{^{1}H} n.m.r. spectrum (Table 5) there are two resonances due to N-methyl and two due to P-methyl and the carbons of the butadiene residue are all coupled to platinum. The ^{1}H n.m.r. spectrum is complex and was not analysed fully, although the non-equivalence of the two N-methyls and of the two P-methyls is apparent. We find that the conversion of the μ-butadiene complex to (5a) is rapid even at −78 °C (as shown by a ^{31}P-{^{1}H} n.m.r. experiment) and did not detect a zwitterionic intermediate. This contrasts with a similar treatment of an allene complex $[PtCl_2(PR_3)(C_3H_4)]$ for which a zwitterionic intermediate was readily detected.[6] We converted the chloro-complex into the corresponding bromo- and iodo-complexes, (5b) and (5c), by metathesis. We also prepared the triethylphosphine analogue (5d) by treating $[Pt_2Cl_4(PEt_3)_2(\mu\text{-}C_4H_6)]$ with dimethylamine: the corresponding bromo- and iodo-complexes, (5e) and (5f), were made from the chloro-complexes by metathesis. Characterizing data are in Tables 1 and 2, and further details are in the Experimental section. Somewhat surprisingly, we were unable to prepare the tri-n-propylphosphine analogue by treating $[Pt_2Cl_4(PPr^n_3)_2(\mu\text{-}C_4H_6)]$ with dimethylamine, possibly because of increased steric requirement of PPr^n_3. However, this μ-butadiene complex was attacked by methylamine to give a mixture of three products. This mixture analysed correctly for $[(Pr^n_3P)ClPt(MeHNCH_2CHCHCH_2NHMe)PtCl(PPr^n_3)]$ (C, H, and N) [but the ^{31}P{^{1}H} n.m.r. spectrum (Table 2) showed that three very similar species were present which, we suggest, are the three geometrical isomers, (5g), (5h), and (5i). We were able to separate by fractional crystallization from this mixture a single isomer characterized by δ(P) −2.0 p.p.m. and ^1J(Pt–P) 4 099 Hz. This showed in its ^{1}H n.m.r. spectrum a single N–CH_3 resonance at δ(H) 4.30 p.p.m. with $^3J(H\text{–N–C}H_3)$ 6 Hz and $^3J(Pt\text{–N–C}H_3)$ 28 Hz. The presence of only one N–CH_3 resonance suggested that this isomer was either (5g) or (5i). We thought it possible that the N–H protons in the complexes would be acidic and that treatment with a base might change the proportions of the three isomers (5g), (5h), and (5i) in the mixture. However, treatment of a mixture of the isomers with sodium propan-2-oxide in CDCl$_3$–propan-2-ol solution failed to alter the proportions of the three isomers.

The two chloro-complexes (5a) and (5d) with fused five-membered rings show very low values for ν(Pt–Cl) (*ca.* 260 cm^{-1}). Such a low frequency would normally be associated with high lability and therefore one might expect metathesis with bromide or iodide ion to go rapidly. However, in refluxing acetone solution, it goes slowly and in poor yield. This inertness might be due to the rigid structure imposed by the two fused five-membered rings which make the formation of a five-co-ordinate intermediate difficult. Molecular models and the crystal structural determination of compound (5d) (see below) show that the platinums are not sterically hindered.

Determination of the Structure of $[(Et_3P)ClPt(Me_2NCH_2CHCHCH_2NMe_2)PtCl(PEt_3)]$ (5d) *by X-Ray Diffraction.*—It was important to determine the structure of one of these amine addition products, and the one which gave the best single crystals was that formed by attack of dimethylamine on $[Pt_2Cl_4(PEt_3)_2(\mu\text{-}C_4H_6)]$. The structure of the complex, which contains two *trans*-fused five-membered rings, is shown in Figure 2. Bond lengths and angles are given in Table 6 and are as expected. The *trans*-fused five-membered ring structure also indicates that the μ-butadiene complex from which it was made must have been *meso*.

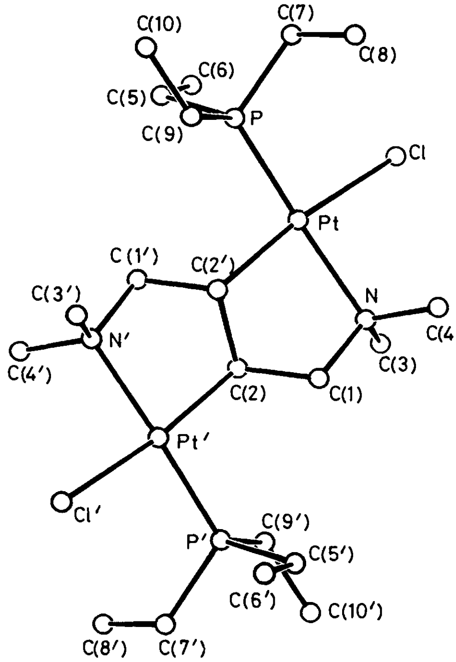


FIGURE 2 The molecular structure and atom numbering of $[(Et_3P)ClPt(Me_2NCH_2CHCHCH_2NMe_2)PtCl(PEt_3)]$ (5d)

TABLE 6

Bond distances (pm) and angles (°) for (5d) with estimated standard deviations in parentheses

(*a*) Distances		(*b*) Angles	
Pt–Cl	242.0(4)	Cl–Pt–P	94.0(1)
Pt–P	221.4(3)	Cl–Pt–N	89.0(3)
Pt–N	218.0(9)	P–Pt–C(2′)	94.6(3)
Pt–C(2′)	206.7(12)	N–Pt–C(2′)	83.6(4)
N–C(1)	151.8(16)	Pt–N–C(1)	105.8(7)
N–C(3)	153.0(16)	Pt–C(2′)–C(2)	105.4(7)
N–C(4)	148.1(18)	N–C(1)–C(2)	108.8(9)
C(1)–C(2)	150.9(18)	C(1)–C(2)–C(2′)	105.5(9)
C(2)–C(2′)	156.0(16)	Pt–N–C(3)	110.3(7)
P–C(5)	183.6(13)	Pt–N–C(4)	111.2(7)
P–C(7)	181.7(15)	C(1)–N–C(3)	108.8(9)
P–C(9)	186.0(12)	C(1)–N–C(4)	112.3(9)
C(5)–C(6)	152.6(21)	Pt–P–C(5)	116.3(4)
C(7)–C(8)	160.6(22)	Pt–P–C(7)	113.9(5)
C(9)–C(10)	153.4(20)	Pt–P–C(9)	113.8(4)

EXPERIMENTAL

The general techniques used were the same as in other recent papers from this laboratory.[6] The ^{1}H, ^{31}P-{^{1}H}, and ^{13}C-{^{1}H} n.m.r. spectra were recorded with a JEOL FX100Q spectrometer using an internal lock. Except where stated otherwise, measurements were made at ambient temperature (*ca.* 296 K). Platinum-195 shifts were recorded on a JEOL FX90Q spectrometer.

TABLE 7

Fractional atomic co-ordinates for the complexes, with estimated standard deviations in parentheses

(*a*) $[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$

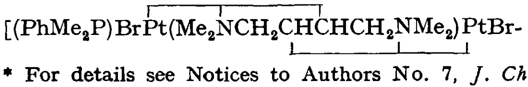
	X	*Y*	*Z*
Pt	0.119 79(3)	0.017 44(5)	0.397 16(8)
Cl(1)	0.070 6(2)	0.176 4(4)	0.154 9(6)
Cl(2)	0.216 9(2)	0.148 5(4)	0.417 8(6)
P	0.175 1(2)	−0.128 0(4)	0.620 7(6)
C(1)	0.137 4(7)	−0.297 4(15)	0.628 8(22)
C(2)	0.101 9(8)	−0.341 0(19)	0.788 5(28)
C(3)	0.075 1(10)	−0.480 1(28)	0.770 2(47)
C(4)	0.086 9(12)	−0.565 3(23)	0.603 8(44)
C(5)	0.121 5(8)	−0.517 2(18)	0.461 7(37)
C(6)	0.147 1(9)	−0.388 4(17)	0.466 1(27)
C(7)	0.177 7(10)	−0.061 0(18)	0.880 2(25)
C(8)	0.264 6(7)	−0.160 1(15)	0.569 2(24)
C(9)	0.038 2(7)	−0.118 8(15)	0.304 3(23)
C(10)	0.023 9(6)	−0.058 6(16)	0.498 9(24)

(*b*) Complex (5d)

	X	*Y*	*Z*
Pt	−0.152 63(6)	0.131 91(3)	0.068 59(3)
P(1)	−0.152 3(4)	0.269 6(2)	−0.024 1(2)
Cl	−0.267 0(6)	0.212 5(3)	0.209 5(3)
N	−0.189 9(13)	−0.011 2(7)	0.140 3(8)
C(1)	−0.123 6(16)	−0.088 6(9)	0.071 3(9)
C(2)	0.030 4(16)	−0.047 6(8)	0.031 0(9)
C(3)	−0.087 1(19)	−0.016 6(10)	0.247 4(10)
C(4)	−0.369 3(18)	−0.027 2(10)	0.151 6(12)
C(5)	0.044 5(17)	0.341 0(10)	−0.008 9(10)
C(6)	0.094 7(21)	0.374 6(11)	0.102 4(13)
C(7)	−0.304 7(19)	0.361 6(10)	0.005 5(12)
C(8)	−0.495 1(20)	0.322 5(15)	−0.018 3(14)
C(9)	−0.210 4(19)	0.249 6(10)	−0.165 1(9)
C(10)	−0.208 6(21)	0.342 6(11)	−0.232 8(12)

The complexes *cis-cis*-$[Pt_2Cl_4(PR_3)_2(\mu\text{-}C_4H_6)]$ [PR_3 = PMe_2Ph (new), PEt_3, or $PPr^n{}_3$ (both described previously but not fully characterized)] were prepared by treating $[Pt_2Cl_4(PR_3)_2]$ in acetone with butadiene, as described previously.[5] The complexes of type $[NBu^n{}_4]_2[Pt_2X_6(\mu\text{-}C_4H_6)]$ (X = Cl or Br) were prepared in a similar fashion, *i.e.* by treating the salts $[NBu^n{}_4]_2[Pt_2X_6]$ in acetone with an excess of butadiene over several days. They were recrystallized from acetone–diethyl ether. Yields were better than 80%.

$[(PhMe_2P)ClPt(Me_2NCH_2CHCHCH_2NMe_2)PtCl(PMe_2Ph)]$ (5a).—Dimethylamine (0.2 g, 4.4 mmol) was added to a suspension of *cis-cis*-$[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$ (0.443 g, 0.51 mmol) in dichloromethane (15 cm^3). The mixture was stirred until the solid dissolved. The solvent was removed under reduced pressure and the residue washed with water, dried, and recrystallized from acetone. This gave the required product (5a) as white needles (0.385 g, 87%). Complex (5d) was prepared similarly in 46% yield.



$[(PhMe_2P)BrPt(Me_2NCH_2CHCHCH_2NMe_2)PtBr(PMe_2Ph)]$ (5b).—The chloro-analogue (5a) (0.17 g, 0.19 mmol) and lithium bromide (0.5 g) were refluxed together in acetone (10 cm^3) for 4 h. The solvent was removed under reduced pressure and the residue recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C). This gave the required product as white microcrystals (0.18 g, 96%).

The other bromide and the iodides were prepared similarly from the appropriate chloride (yields in parentheses): (5c) (32%); (5e) (46%); (5f) (32%).

Action of Methylamine on cis,cis-$[Pt_2Cl_4(PPr^n{}_3)_2(\mu\text{-}C_4H_6)]$.—The bridged butadiene complex (0.168 g, 0.185 mmol) was treated with methylamine (*ca.* 1.5 g) in dichloromethane (10 cm^3). The resultant precipitate of $MeNH_3Cl$ was filtered off and the solvent evaporated under reduced pressure. This gave a mixture of three isomers, (5g), (5h), and (5i). Yield 0.147 g, 89%. When recrystallized from dichloromethane at −30 °C a single isomer was obtained, see Discussion section.

Crystal data. $[Pt_2Cl_4(PMe_2Ph)_2(\mu\text{-}C_4H_6)]$, $C_{20}H_{28}Cl_4P_2Pt_2$, M = 862.38, Monoclinic, a = 1.9658(4), b = 0.974 1(3), c = 0.655 7(1) nm, β = 94.24(2)°, U = 1.252 3(5) nm^3, Z = 2, D_c = 2.287 Mg m^{-3}, $F(000)$ = 804, space group $P2_1/n$, Mo-K_α radiation, graphite monochromatised, λ = 71.069 pm, μ(Mo-K_α) = 118.4 cm^{-1}. (5d), $C_{20}H_{48}Cl_2N_2P_2Pt_2$, M = 839.65, Monoclinic, a = 0.801 5(3), b = 1.346 1(3), c = 1.307 0(3) nm, β = 97.56(3)°, U = 1.397 9(7) nm^3, Z = 2, D_c = 1.995 Mg m^{-3}, $F(000)$ = 804, space group $P2_1/n$, Mo-K_α radiation, graphite monochromatised, λ = 71.069 pm, μ(Mo-K_α) = 104.2 cm^{-1}.

Structure determination. Cell dimensions for each compound were determined by least-squares treatment of the setting angles of 15 reflections having $35 < 2\theta < 40°$. Intensities of all independent reflections with $2\theta < 45°$ were measured in the ω—2θ scan mode using scan speeds, according to intensity, between 4.9 and 29.3° min^{-1}. The structure analyses used those reflections having $I > 3\sigma(I)$ (1 391 for the μ-butadiene complex and 1 584 for the dimethylamine derivative); the numbers of 'unobserved' reflections were 256 and 257 respectively. Solution of the structures by Patterson and difference syntheses followed by full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and no allowance for hydrogens gave final R values of 0.042 and 0.040 respectively (R' = 0.051 and 0.055). Atomic scattering factors were taken from ref. 16 and weights were derived from the modified variances $\sigma^2(I) = \sigma_c{}^2(I) + (0.03I)^2$, σ_c being the variance from counting statistics. The atomic co-ordinates and their standard deviations are in Table 7 and the observed and calculated structure factors and the anisotropic thermal parameters are in Supplementary Publication No. SUP 23223 (20 pp.).*

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REFERENCES

[1] Part 50, S. Al-Jibori, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 1572.

[2] J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Organomet. Chem.*, 1979, **181**, 213.

[3] J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 64.

[4] J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 121.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

[5] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662.

[6] J. R. Briggs, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 575.

[7] I. M. Al-Najar and M. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1651.

[8] I. M. Al-Najar, M. Green, S. J. S. Kerrison, and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 1979, 311.

[9] I. M. Al-Najar, M. Green, J. K. K. Sarhan, I. M. Ismail, and P. J. Sadler, *Inorg. Chim. Acta*, 1980, **44**, L187.

[10] A. De Renzi, B. D. Blasio, A. Panunzi, C. Pedone, and A. Vitagliano, *J. Chem. Soc., Dalton Trans.*, 1978, 1392.

[11] Interatomic Distances Supplement, Spec. Publ. No. 13, The Chemical Society, London, 1965, p. 109.

[12] C. E. Holloway, G. Halley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1969, 53.

[13] J. Ashley-Smith, I. Donek, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1974, 128.

[14] A. De Renzi, P. Ganis, A. Panunzi, A. Vitagliano, and G. Valle, *J. Am. Chem. Soc.*, 1980, **102**, 1722.

[15] F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 1968, 2700.

[16] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.