Transition Metal–Carbon Bonds. Part XXXII.[1] Hexamethyl Dewar Benzene; Dehydrohexamethyl Dewar Benzene and Related Complexes of Platinum(II) †

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Na_2PtCl_4 or $[Pt_2Cl_4(C_2H_4)_2]$ reacts with hexamethyl Dewar benzene (hmdb) to give $[PtCl_2(C_{12}H_{18})]$ in which $C_{12}H_{18}$(hmdb) is acting as a chelating diolefin. Metathesis gives the corresponding dibromide $[PtBr_2(C_{12}H_{18})]$ which with hydrobromic acid gives $[PtBr_2$(pentamethylcyclopentadiene)$]$. With sodium carbonate $[PtCl_2(C_{12}H_{18})]$ loses the elements of HCl to give $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ in which $C_{12}H_{17}$ is pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl which bridges two platinum atoms. With lithium bromide or sodium iodide $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ gives $[Pt_2X_2(\pi\text{-}C_{12}H_{17})_2]$ (X = Br or I) with bridging halogens and a π-allylic ligand pentamethylbicyclo[2,2,0]-hexa-2,5-dien-2-ylmethyl. $[Pt_2X_2(\pi\text{-}C_{12}H_{17})_2]$ show typical bridge-splitting reactions with ligands L = pyridine, isoquinoline, PPh_3, or $AsPh_3$ to give $[PtX(\pi\text{-}C_{12}H_{17})L]$ or with bipyridyl to give $[Pt(bipy)(\pi\text{-}C_{12}H_{17}]^+I^-$. With sodium cyclopentadienide or thallium acetylacetonate mononuclear species $[PtQ(\pi\text{-}C_{12}H_{17})]$ (Q = C_5H_5 or acac) are formed. $[Pt(acac)(\pi\text{-}C_{12}H_{17})]$ with hydrogen chloride gives $[Pt_2Cl_2(\pi\text{-}C_{12}H_{17})_2]$. ^1H n.m.r. and i.r. data are given and discussed.

THERE is much interest in complexes containing the ligand hexamethylbicyclo[2,2,0]hexa-2,5-diene (hexamethyl Dewar benzene, hmdb) and in related complexes.[2-12] We have reported briefly on some platinum(II) complexes derived from hmdb, namely dichloro-(hexamethylbicyclo[2,2,0]hexa-2,5-diene)platinum(II) and dichloro-di-π-(pentamethylbicyclo[2,2,0]hexa-2,5-dienylmethyl)diplatinum(II).[13] We now report more fully on these, and related, complexes. The various reactions we describe have been summarised in the Scheme.

Treatment of sodium chloroplatinite with hmdb in ethanol gives $[PtCl_2(hmdb)]$ (I) in 23% yield. The same complex (I) is formed in better (68%) yield from $[Pt_2Cl_4(C_2H_4)_2]$, but we were unable to prepare it starting with $[PtCl_2(PhCN)_2]$ (contrast with the palladium analogue). Analytical and other data on these and related complexes are given in Table 1.

The i.r. absorption spectrum of $[PtCl_2(C_{12}H_{18})]$ (I) shows a strong band at 1520 cm^{-1}, attributed to the carbon–carbon double bond stretching frequency, lowered as a result of co-ordination to the platinum atom.

TABLE 1

Analytical, molecular weight, and other data for some hexamethylbicyclo[2,2,0]hexa-2,5-diene (hmdb) complexes of platinum(II) and related complexes

	Configuration	Analytical data (%) [a] C	H	Halogen	M [a,b]	Melting or decomposition range °C
$[PtCl_2(C_{12}H_{18})]$	(I)	33·7 (33·65)	4·5 (4·25)	16·6 (16·55)	434 (428) [c]	104—112 [d]
$[PtBr_2(C_{12}H_{18})]$	(II)	27·3 (27·85)	3·45 (3·5)	30·3 (30·9)	535 (517) [e]	120—127 [d]
$[PtI_2(C_{12}H_{18})]$	(II)	23·65 (23·6)	2·95 (2·95)			105—112 [d]
$[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$	(VI)	36·6 (36·8)	4·3 (4·35)	9·3 (9·05)	776 (784)	175—202 [d]
$[Pt_2Br_2(\mu\text{-}C_{12}H_{17})_2]$	(VI)	33·25 (33·05)	4·15(3·95)		851 (872)	172—193 [d]
$[Pt_2Cl_2(\pi\text{-}C_{12}H_{17})_2]$	(VII)	36·9 (36·8)	4·4 (4·35)		640 650 (784)	157—163 [d]
$[Pt_2Br_2(\pi\text{-}C_{12}H_{17})_2]$	(VII)	33·3 (33·05)	4·05 (3·95)		862 (872)	145—149 [d]
$[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$	(VII)	29·95 (29·8)	3·4 (3·55)		835 (966)	159—169 [d]
$[Pt(acac)(\pi\text{-}C_{12}H_{17})]$	(IX)	45·0 (44·85)	5·55 (5·3)			111—115
$[Pt(C_5H_5)(\pi\text{-}C_{12}H_{17})]$	(IX)	48·8 (48·45)	5·4 (5·25)			101—105
$[PtCl(\pi\text{-}C_{12}H_{17})(PPh_3)]$	(VIII)	55·5 (55·1)	4·8 (4·95)		{ 605 625 (654)	159—163
$[PtI(\pi\text{-}C_{12}H_{17})(PPh_3)]$	(VIII)	48·65 (48·35)	4·6 (4·35)		737 (746)	149—153
$[PtI(\pi\text{-}C_{12}H_{17})(AsPh_3)]$	(VIII)	45·8 (45·65)	4·15 (4·1)		746 (790)	150—156
$[PtI(\pi\text{-}C_{12}H_{17})(C_9H_7N)]$	(VIII)	41·5 (41·2)	3·9 (3·95)		557 (612)	135—139 [d]
$[PtI(\pi\text{-}C_{12}H_{17})(C_5H_5N)]$ [e]	(VIII)	36·3 (36·3)	3·75 (3·95)		601 (562)	169—172 (decomp.)
$[PtI(\pi\text{-}C_{12}H_{17})(C_{10}H_8N_2)]I$	(X)	41·8 (41·35)	4·2 (3·95)			120—122
$[PtBr_2(C_{10}H_{16})]$	(IV)	24·4 (24·45)	3·3 (3·3)		495 (491) [c]	200—215

[a] Calculated values in parentheses. [b] Determined in benzene unless stated otherwise. [c] Determined in chloroform. [d] Compounds which decomposed without melting; the other compounds melted with or without decomposition. [e] Nitrogen analysis: 2·5 (2·5). Molar conductivity in nitrobenzene (*ca.* 1 × 10^{-3}M) = 25·1 Ω^{-1} mol^{-1} cm^2.

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† No reprints available.

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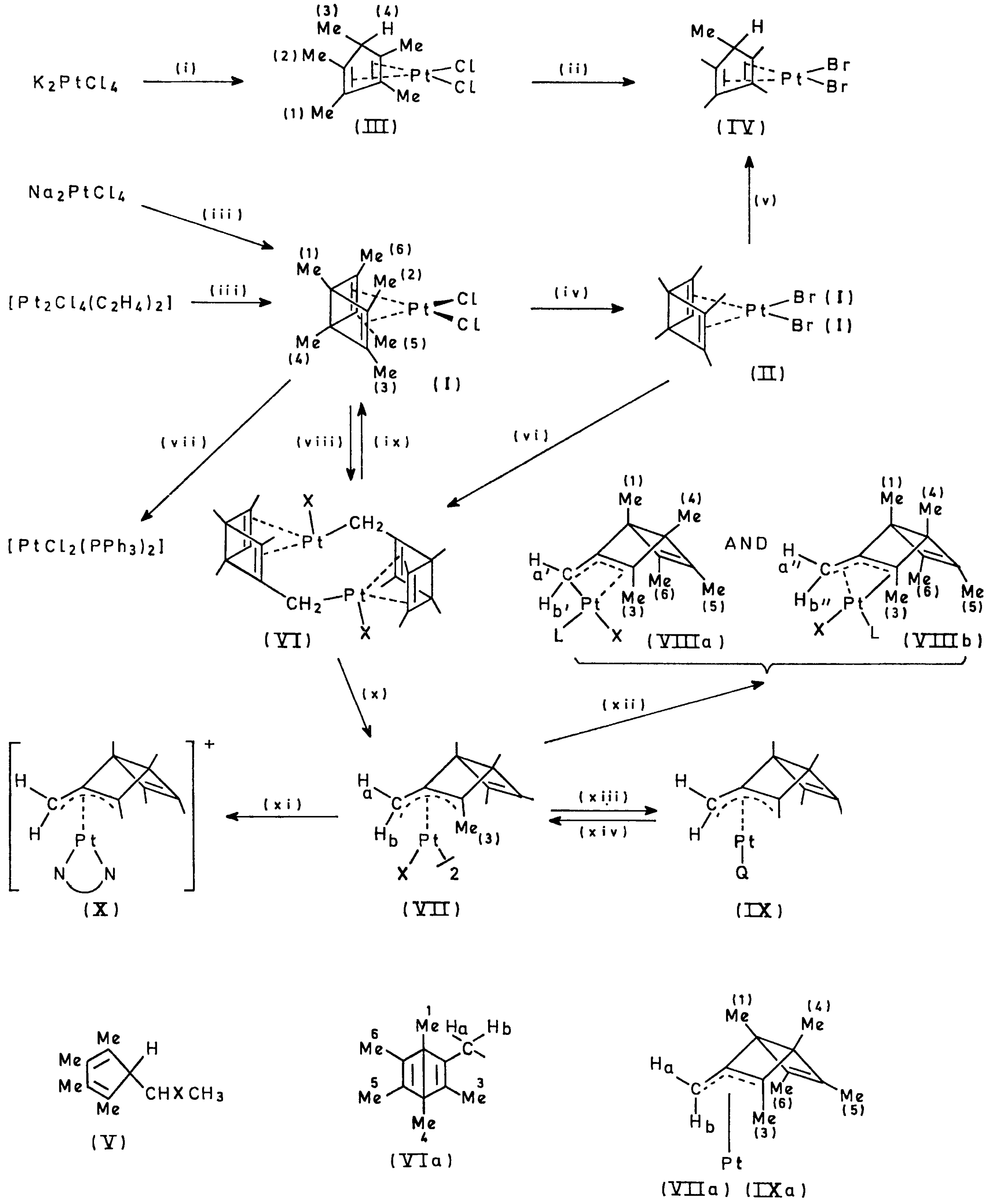

SCHEME

Reagents: (i) hmdb–$SnCl_2$; (ii) Br^-; (iii) hmdb; (iv) Br^- or I^-; (v) HBr; (vi) NaOMe; (vii) PPh_3; (viii) Na_2CO_3; (ix) HCl; (x) $X = Br^-$ or I^-; (xi) bipyridyl; (xii) L; (xiii) sodium cyclopentadienide or thallium acetylacetonate, $Q = \pi\text{-}C_5H_5$ or acac; (xiv) HCl, Q = acac.

There are no characteristic bands due to uncomplexed double bonds; *e.g.*, free hmdb shows a weak band at 1681 cm^{-1}. The far-i.r. region has two strong bands at 334 and 315 cm^{-1} (Table 2), absent from the spectrum of the corresponding bromide and therefore assigned to terminal platinum–chlorine stretching frequencies. The ^{1}H n.m.r. data for [$PtCl_2(C_{12}H_{18})$] (Table 3) indicate structure (II), similar data were reported by Maitlis *et al.*[12] The complexes [$PtX_2(C_{12}H_{18})$] (II; X = Br or I) were prepared from the dichloride by metathesis using the appropriate alkali-metal salt. The n.m.r. and near i.r. spectra of these complexes are very similar to those of [$PtCl_2(C_{12}H_{18})$] (see Tables). The chloro- and bromo-complexes are monomeric in chloroform (Table 1). These results are in agreement with the symmetrical mononuclear structures (I) or (II) in which hmdb is acting as a chelating ligand.

TABLE 2

I.r. data (cm^{-1}) for some hexamethylbicyclo[2,2,0]hexa-2,5-diene complexes of platinum(II) and related complexes (errors ±2 cm^{-1}, recorded as Nujol mulls unless otherwise stated)

Compound	ν(C=C)	ν(Pt–Cl)
[$PtCl_2(C_{12}H_{18})$]	1520s	334s, 315s
[$PtBr_2(C_{12}H_{18})$]	1508s	
[$PtI_2(C_{12}H_{18})$]	1506s	
[$Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2$] [a]	1497m, 1570m	316vs
[$Pt_2Br_2(\mu\text{-}C_{12}H_{17})_2$] [b]	1475m, 1567m	
[$Pt_2Cl_2(\pi\text{-}C_{12}H_{17})_2$]	1681w	272s, 238m
[$Pt_2Br_2(\pi\text{-}C_{12}H_{17})_2$]	1681w	
[$Pt_2I_2(\pi\text{-}C_{12}H_{17})_2$]	1681w	
[$PtCl(C_{12}H_{17})(PPh_3)$]		302s
hmdb [c]	1681w	

[a] Recorded as KCl disc. Recorded as KBr disc. [c] Recorded as thin film.

TABLE 3

N.m.r. data [a] for compounds of the type [$PtX_2(C_{12}H_{18})$] and [$Pt_2X_2(\mu\text{-}C_{12}H_{17})_2$] in $CDCl_3$ at 34°

	τ_1	J_{Pt}	τ_2	J_{Pt}	Comments
[$PtCl_2(C_{12}H_{18})$]	8·85	4·5	8·14	35·0	HMB (hexamethylbenzene) in $CDCl_3$ τ 7·77. After 5 days at 34° the ratio of HMB : [$PtCl_2(C_{12}H_{18})$] was *ca.* 10
[$PtBr_2(C_{12}H_{18})$]	8·85	4·5	8·17	37·5	After 1 day at 34°, HMB : [$PtBr_2(C_{12}H_{18})$] *ca.* 10
[$PtI_2(C_{12}H_{18})$]	8·87	4·0	8·18	41·0	
hmdb	8·97		8·46		

	τ_1	τ_4 [b]	τ_5	τ_6 [b]	τ_3	τ_a	τ_b [b]
[$Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2$]	8·83 J_{Pt} 2·0	9·06 J_{Pt} 4·0	8·16 J_{Pt} 7·5	8·31 J_{Pt} 8·0	7·61 J_{Pt} 5·5	6·32, 6·94	7·03, 7·41
[$Pt_2Br_2(\mu\text{-}C_{12}H_{17})_2$]	8·80 J_{Pt} 3·0	9·06 J_{Pt} 3·0	8·15 J_{Pt} 8·0	8·35 J_{Pt} 8·0	7·63 J_{Pt} 6·0	6·22, 6·84	6·98, 7·34

[a] J_{Pt} (±0·5 Hz) is the coupling with ^{195}Pt; the protons are identified as shown in structures (I) and (VIa). [b] We could not differentiate between the resonances due to the following pairs of proton types: 1 and 4; 5 and 6; *a* and *b*.

The complexes [$PtX_2(C_{12}H_{18})$] (X = Cl, Br, or I) are significantly more stable in chloroform solution than the corresponding palladium(II) analogues. Treatment of [$PtCl_2(C_{12}H_{18})$] with triphenylphosphine gave *cis*-[$PtCl_2(PPh_3)_2$] and hexamethylbenzene in nearly quantitative yields. Maitlis *et al.*[12] have reported on the preparation of [$PtCl_2(C_{12}H_{18})$] from ethylene–platinum chloride dimer and their results agree with our own. They also reported the preparation of [$PtCl_2(C_{10}H_{16})$] formed by treatment of hmdb with potassium chloroplatinite, and hydrochloric acid in methanol at 65° in the presence of a catalytic amount of stannous chloride. Structure (III) was assigned to the complex on the basis of the n.m.r. spectrum and the absence of a low frequency ν(C–H) in the i.r. spectrum (which is characteristic of complexes with an *exo*-hydrogen on the ring).[14] We have prepared [$PtCl_2(C_{10}H_{16})$] by this method and converted it into the corresponding dibromo-complex (IV) by metathesis with lithium bromide in acetone and our results (see Table 4 for ^{1}H n.m.r. and i.r. data) confirm the proposed structure for (IV).

When a suspension of [$PtBr_2(C_{12}H_{18})$] (II) in methanol containing hydrobromic acid was heated under reflux it gave (IV) (14% yield) and [$PtBr_4$]$^{2-}$, isolated as the tetraphenylarsonium salt (43% yield). We tentatively propose that the hmdb ligand in [$PtBr_2(C_{12}H_{18})$] (II) undergoes ring contraction and attack to give a complex of the ligand (V; X = Br or OMe) which then undergoes breakdown to give (IV). Hexamethyl Dewar benzene has been shown to undergo breakdown to give (V) in the presence of acid.[15]

When treated with sodium methoxide in methanol [$PtX_2(C_{12}H_{18})$] (X = Cl or Br) is converted into a yellow dehydro-hmbd complex [$Pt_2X_2(\mu\text{-}C_{12}H_{17})_2$] in 70—80% yield. The complexes are binuclear in benzene (see Table 1). The far-i.r. spectrum of the chloro-complex (Table 2) shows a strong band at 316 cm^{-1}, absent from the spectrum of the corresponding bromide and therefore assigned to a terminal platinum–chlorine stretching frequency. The complexes [$Pt_2X_2(\mu\text{-}C_{12}H_{17})_2$] (X = Cl or Br) are recovered unchanged after treatment with

TABLE 4

N.m.r. [a] and i.r. data for the complexes [$PtX_2C_{10}H_{16})$]

X	τ_1	τ_3	τ_3	τ_4	ν(C=C) (cm^{-1})	ν(Pt–Cl) (cm^{-1})
Br	7·82 J_{Pt} 38	8·51 J_{Pt} 12	9·03d J_4 6·5	6·88q J_3 6·5	1488s	
Cl [b]	7·78 J_{Pt} 20	8·54 J_{Pt} 10	9·04d J_4 6·5	6·65q J_3 6·5	1490s	333s, 312s

[a] Recorded in $CDCl_3$; protons identified as in structure (III).
[b] N.m.r. data taken from ref. 20.

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triphenylphosphine, isoquinoline, thallium(I) acetylacetonate, or sodium cyclopentadienide and this confirms the far-i.r. evidence that a bridging platinum–chlorine system is not present. The i.r. spectrum of $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ shows two medium bands at 1497 and 1570 cm^{-1}, characteristic of two C=C stretching frequencies lowered by co-ordination to the platinum atom. The corresponding bromo-complex gave two medium bands at 1475 and 1567 cm^{-1}. $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ reacts with hydrogen chloride to give $[PtCl_2(C_{12}H_{18})]$ (I) in 39% yield. The ^1H n.m.r. spectrum of $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ in $CDCl_3$ (Table 3) indicates the presence of five non-equivalent methyl groups per platinum atom (each resonance has accompanying satellites due to coupling with ^{195}Pt). The four resonances in the region τ 6·30—7·50 are attributed to the remaining two protons of the $C_{12}H_{17}$ ligand. The bromo-complex has a similar spectrum (see Table 3).

The structure of $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ has been determined by *X*-ray diffraction analysis and is shown in (VI; X = Cl).[13,16] A dehydrohexamethyl Dewar benzene (pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl) ligand bridges two platinum atoms, being co-ordinated *via* a σ-bond from the methylene carbon atom to one platinum and to the other *via* the two π-olefin bonds. The platinum–olefin bonds *trans* to the chlorines and *trans* to the σ-bonded carbon atoms are different; hence two C=C stretching frequencies are observed. The presence of a bridging allylic system in the dehydrohexamethyl Dewar benzene complex is noteworthy and the allyl (C_3H_5) group itself has been shown to bridge between two platinum atoms in $[Pt_2(C_3H_5)_2(acac)_2]$ and $[Pt_4Cl_4(C_3H_5)_4]$.[17-19]

The ^1H resonances in the n.m.r. spectrum of $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ are assigned as in Table 3 with the numbering of protons as in (VIa). The protons of type *a* and *b* give a complex pattern which we have not analysed.

Treatment of $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ with sodium iodide in acetone gave the iodo-complex $[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ (VII). The ^1H n.m.r. and i.r. spectra of the iodo-complex are completely different from those of the complexes $[Pt_2X_2(\mu\text{-}C_{12}H_{17})_2]$ (VI; X = Cl or Br). The i.r. spectrum contains a weak band at 1681 cm^{-1} characteristic of an unco-ordinated carbon–carbon double-bond in hmdb. The ^1H n.m.r. spectrum in $CDCl_3$ contains seven sets of resonances, of relative intensities 1 : 1 : 3 : 3 : 3 : 3 : 3, and resembles the spectra of the palladium(II) complexes of similar composition. $[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ readily undergoes bridge-splitting reactions with ligands L to give mononuclear complexes of the type $[PtI(\pi\text{-}C_{12}H_{17})L]$ (VIII). Thus $[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ has an iodo-bridged π-allylic structure (VII; X = I), in which the $C_{12}H_{17}$ ligand is bonded to the metal in a completely analogous way to that observed in $[Pd(acac)(C_{12}H_{17})]$. We have designed a $C_{12}H_{17}$ ligand bonded in this way as π-$C_{12}H_{17}$ in order to distinguish it from the bridging $C_{12}H_{17}$ of (V) which we have called μ-$C_{12}H_{17}$. The assignment of resonances in the n.m.r. spectrum of (VII), made on the basis of chemical shifts and relative intensities, is given in Table 5 with the numbering shown in (VIIa). The very broad platinum satellites observed only for proton *a* in $[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ have also been noted in the n.m.r. spectra of other allylic platinum(II) complexes.[18] Nuclear magnetic double resonance studies on $[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ (VII) at 90 MHz show that the apparent doublet at τ 8·51 (τ_3) is not caused by any spin–spin interaction, but that the doublet observed for proton *a* is due to coupling with proton *b*. The band width of the broad resonance observed at τ 7·46 due to proton *b* is not reduced when any one of five methyl resonances is irradiated. To explain these results, we tentatively suggest that $[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ exists in solution as approximately equal amounts of two isomers; *i.e.*, *cis*- and *trans*-forms with respect to the allylic ligands. We further suggest that steric factors cause the rate of interchange between the two forms to be sufficiently slow, such that the separate resonances due to protons of types *b* or 3 are not averaged out. The interchange could occur *via* a rotation of the allylic ligand. $[Pt_2Cl_2(2\text{-methylallyl})_2]$ shows two such isomers at −65° in $CDCl_3$ solution.[18]

$[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ reacted with thallium(I) acetylacetonate or sodium cyclopentadienide to give mononuclear complexes of the type $[PtQ(\pi\text{-}C_{12}H_{17})]$ (IX; Q = acac or C_5H_5). The ^1H n.m.r. spectra (Table 5) of these compounds show sharp platinum satellites for protons of types *a*, *b*, and 3. In the cyclopentadienyl complex, satellites are observed for methyl protons of types 1 and 4 (VIa). An *X*-ray diffraction study of $[Pt(acac)(\pi\text{-}C_{12}H_{17})]$ shows it to be isomorphous with the corresponding palladium(II) analogue.[20] Treatment of $[Pt(acac)(\pi\text{-}C_{12}H_{17})]$ with hydrogen chloride in diethyl ether gave the chloro-bridged complex $[Pt_2Cl_2(\pi\text{-}C_{12}H_{17})_2]$ (VII; X = Cl). The action of lithium bromide on $[Pt_2Cl_2(\mu\text{-}C_{12}H_{17})_2]$ in acetone gave $[Pt_2Br_2(\pi\text{-}C_{12}H_{17})_2]$. The n.m.r. spectra (Table 5) of $[Pt_2X_2(\pi\text{-}C_{12}H_{17})_2]$ (VII; Cl or Br) are similar to the corresponding palladium(II) analogues. The two low field doublets are assigned to protons *a* and *b*. Platinum satellites for these types of protons are only observed for X = Br. We tentatively suggest that these compounds, like the corresponding iodide, exist in solution as a mixture of *cis*- and *trans*-isomers. The far-i.r. spectrum of $[Pt_2Cl_2(\pi\text{-}C_{12}H_{17})_2]$ contains absorption bands at 272 and 238 cm^{-1}, absent from the spectrum of the corresponding bromide and therefore assigned to the bridging platinum–chlorine stretching frequencies.

$[Pt_2X_2(\pi\text{-}C_{12}H_{17})_2]$ (X = Cl or I) reacts with typical bridge-splitting ligands (L) to give mononuclear complexes of the type $[PtX(C_{12}H_{17})L]$ (VIII; where L = PPh_3, $AsPh_3$, isoquinoline, or pyridine). The assignment of the asymmetric structure (VIII) to these complexes where L = PPh_3 or $AsPh_3$ is confirmed by the

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[19] G. Raper and W. S. McDonald, *J.C.S. Dalton*, 1972, 265.

[20] J. F. Malone and W. S. McDonald, unpublished work.

n.m.r. spectra (Table 5), in which protons of types *a′* and *b′* (VIIIa) absorb at higher τ-values and the methyl protons of type 3 at lower τ-value than in the corresponding halogeno-bridged complexes. With bipyridyl $[Pt_2I_2(\pi\text{-}C_{12}H_{17})_2]$ gives $[Pt(bipy)(\pi\text{-}C_{12}H_{17})]^+I^-$ (X). The n.m.r. spectra (Table 5) of the complexes $[PtI(\pi\text{-}C_{12}H_{17})L]$ (L = pyridine or isoquinoline) in $CDCl_3$ contain two pairs of doublets of different relative intensities in the region τ 6·00—7·50. The remainder of the spectra are not assigned owing to considerable overlap of the resonances. The low field pair of doublets are assigned to protons $H_{a''}$ and $H_{b''}$ in structure (VIIIb) where these protons are *trans* to the ligand L. The high field pair of doublets are assigned to protons $H_{a'}$ and $H_{b'}$ in structure (VIIIa; X = I) which are *trans* to the iodide ligand. Molecular weight measurements on these complexes in benzene indicate no dissociation into the iodo-bridged dimer. Addition of an excess of the amine has no effect on the n.m.r. spectra of the allylic ligand.

TABLE 5

N.m.r. data for compounds of the type $[Pt_2X_2(\pi\text{-}C_{12}H_{17})_2]$, $[PtQ(\pi\text{-}C_{12}H_{17})]$, and $[PtX(\pi\text{-}C_{12}H_{17})L]$, measured at 4° in $CDCl_3$ unless stated otherwise. Resonances are singlets unless stated otherwise; d = 1 : 1 doublet; q = partially resolved quartet; qt = 1 : 1 : 1 : 1 quartet; br = broad (width at half-height given in parentheses). Coupling constants, *J*-values (±0·2) measured in Hz. J_a = coupling constant with proton of type *a* (similarly for J_b, $J_{a'}$, *etc.*). J_P (±0·2) = coupling with phosphorus. J_{Pt} (±0·5) = coupling with ^{195}Pt. Protons identified as shown in structures (VIIa), (VIIIa), (VIIIb).

									Comments Other assignments
$[Pt_2X_2(\pi\text{-}C_{12}H_{17})_2]$									
X		τ_a	τ_b	τ_3	τ_5	τ_6 [a,b]	τ_1	τ_4 [a]	
Cl		6·17d J_b 3·0	7·43d J_a 3·0	8·73	8·28q	8·43q	8·73	8·73	*c*
Br		6·23d J_b 3·0 J_{Pt} 40	7·45d J_a 3·0 J_{Pt} 84	8·67	8·29q	8·44q	8·72	8·77	*d*
I		6·28d J_b 3·0 J_{Pt} 35	7·46m,br (9)	8·49 8·53	8·29q	8·43q	8·68	8·80	*e*
$[PtQ(\pi\text{-}C_{12}H_{17})]$									acac ligand
Q									τ_4 τ_{Me}
acac		6·24d J_b 3·0 J_{Pt} 43	7·42d J_b 3·0 J_{Pt} 92	8·78 J_{Pt} 16·5	8·27q	8·42q	8·78	8·81	4·56 8·07 J_{Pt} 7·0 8·12
C_5H_5		5·93d J_b 2·2 J_{Pt} 71	7·29d J_a 2·2 J_{Pt} 111·5	8·67 J_{Pt} 60·5	8·30q	8·47q	8·81 J_{Pt} 7	9·09 J_{Pt} 4	$\tau_{C_5H_5}$ = 4·13 J_{Pt} 22·5
$[PtX(\pi\text{-}C_{12}H_{17})L]$									
X	L	$\tau_{a'}$	$\tau_{b'}$						
I	$AsPh_3$	6·79d $J_{b'}$ 3·0	7·52d $J_{a'}$ 3·0	8·20	8·24	8·43	8·43	9·01	
Cl	PPh_3	7·52qt $J_{b'}$ 3·5 J_P 2·0 J_{Pt} 32	7·67qt $J_{a'}$ 3·5 J_P 2·0 J_{Pt} 75	8·28d J_P 6·0	8·25	84·9	8·49	8·94	*d*
I	PPh_3	7·19qt $J_{b'}$ 3·5 J_P 1·5	7·41d,br $J_{a'}$ 3 (3)	8·20d J_P 9·0	8·24q	8·44	8·44	9·03	*f*
I	PPh_3	7·11qt $J_{b'}$ 3·5 J_P 1·7	7·44d,br $J_{a'}$ 3 (3)	8·01d J_P 6·0	8·40q	8·60q	8·14	8·93	In benzene *f*
$[Pt(\pi\text{-}C_{12}H_{17})(C_{10}H_8N_2)]I$		5·81d $J_{b'}$ 3·0	6·51d $J_{a'}$ 3·0	8·45	8·14q	8·36q	8·66	8·92	

$[PtI(\pi\text{-}C_{12}H_{17})L]$					
L	$\tau_{a'}$	$\tau_{b'}$	$\tau_{a''}$	$\tau_{b''}$	
Pyridine	6·25d $J_{b'}$ 3·5	7·41d $J_{a'}$ 3·5	6·10d $J_{b'}$ 2·5	7·23d $J_{a''}$ 2·5	*g*
Isoquinoline	6·20d $J_{b'}$ 3·5	7·34d $J_{a'}$ 3·5	6·08d $J_{b''}$ 2·0	7·20d $J_{a''}$ 2·0	*h*

[a] Definite assignments to τ_5 and τ_6 or to τ_1 and τ_4 could not be made. [b] Long-range coupling between the methyl groups of types 5 and 6 caused mutual splitting into 1 : 3 : 3 : 1 quartets with $J_{5,6}$ *ca.* 1 Hz. Often only the two central peaks of the quartet were resolved. [c] Platinum satellites not observed probably due to broadness and limited solubility of the compound in $CDCl_3$. [d] Platinum satellites for τ_a and τ_b very broad. [e] Very broad platinum satellites observed only for τ_a. [f] Platinum satellites not observed. Spectrum also contains a band at τ 6·92 (2·5) [in benzene at τ 6·85 (3·0)]. [g] Platinum satellites not observed. Ratio *a″* : *a′* = 0·82. Resonances due to methyl groups complex and occur in the region τ 8·32—9·33. [h] Platinum satellites not observed. Ratio *a″* : *a′* = 0·66. Resonances due to methyl groups complex and occur in the region τ 8·23—9·36.

EXPERIMENTAL

M.p.s or decomposition points were determined on a Kofler hot-stage block and are corrected. Analytical data and physical properties are presented in Table 1.

Dichloro(hexamethylbicyclo[2,2,0]*hexa*-2,5-*diene)platinum*(II), (I).—*Method* 1. Hexamethylbicyclo[2,2,0]hexa-2,5-diene (1·7 ml) was added to a solution of di-μ-chlorodichlorobis(ethylene)diplatinum(II) (1·59 g) in ethanol (13 ml). The solution was then put aside at 0° for 24 h when the residue was filtered off and washed with diethyl ether. Recrystallisation from dichloromethane–methanol (charcoal) gave the required *product* as colourless prisms (1·47 g).

Method 2. Hexamethylbicyclo[2,2,0]hexa-2,5-diene (4·0 ml) was added to a solution of sodium chloroplatinite(II) (4·0 g) in ethanol (10 ml) containing concentrated hydrochloric acid (0·2 ml). After 45 min at 20° the solution was put aside at 0° for 2 days. The precipitate was filtered off and washed with diethyl ether and then water. Recrystallisation from dichloromethane–methanol (charcoal) gave the required product (1·01 g), with an identical i.r. spectrum with that of the product prepared by Method 1.

Dibromo(hexamethylbicyclo[2,2,0]*hexa*-2,5-*diene)platinum*(II), (II).—A solution of dichloro(hexamethylbicyclo[2,2,0]hexa-2,5-diene)platinum(II) (0·38 g) and lithium bromide (1·0 g) in acetone (20 ml) was shaken for 10 min. The solvent was then removed under reduced pressure, the residue washed with water and dried *in vacuo* (over P_2O_5). Recrystallisation from dichloromethane–methanol gave the required product as pale yellow prisms (0·27 g).

Di-iodo(hexamethylbicyclo[2,2,0]*hexa*-2,5-*diene)platinum*(II), (II).—This was similarly prepared in 73% yield by metathesis from the dichloride with sodium iodide. It gave *yellow prisms* from dichloromethane–methanol.

Dichloro-di-μ-(pentamethylbicyclo[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl)-diplatinum*(II).—*Method* 1. A suspension of dichloro(hexamethylbicyclo[2,2,0]hexa-2,5-diene)platinum(II) (0·165 g) and anhydrous sodium carbonate (0·5 g) in methanol (3 ml) was shaken at room temperature for 1·5 h and then set aside at 0°. After 3 days the residual solid was filtered off and extracted with dichloromethane. Addition of methanol to this extract gave the required *product* as yellow prisms (0·08 g).

Method 2. Dichloro(hexamethylbicyclo[2,2,0]hexa-2,5-diene)platinum(II) (0·7 g) was suspended in sodium methoxide–methanol solution (12 ml; 0·3M). After 10 min the resulting clear dark yellow solution was put aside at −10° for 3 days. This gave the required product (0·45 g) identical with that formed by Method 1.

Dibromodi-μ-(pentamethylbicyclo[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl)-diplatinum*(II), (VI).—Dibromo(hexamethylbicyclo-[2,2,0]hexa-2,5-diene)platinum(II) (0·29 g) was suspended in a sodium methoxide–methanol solution (4 ml; 0·3M). The resulting solution was set aside at −10° for 3 days when the required *product* had separated from the solution as yellow prisms (0·19 g).

Action of Triphenylphosphine on Dichloro(hexamethylbicyclo[2,2,0]*hexa*-2,5-*diene)platinum*(II).— Triphenylphosphine (0·037 g; 2 mol per mol Pt) was added to a suspension of dichloro(hexamethylbicyclo[2,2,0]hexa-2,5-diene)platinum(II) (0·03 g) in chloroform (1 ml). *cis*-Dichlorobis(triphenylphosphine)platinum(II) separated out as white microcrystals (0·045 g), m.p. 275—290°. The i.r. spectrum of the product was identical with that of an authentic sample. Removal of the solvent under reduced pressure gave hexamethylbenzene (0·008 g).

Action of Hydrogen Chloride (1·0 *Mol*) *on Dichloro-di-μ-(pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl)-diplatinum*(II).—A solution of dichloro-di-μ-(pentamethylbicyclo-[2,2,0]hexa-2,5-dien-2-ylmethyl)-platinum(II) (0·08 g) in benzene (10 ml) was treated with a solution of hydrogen chloride in diethyl ether (0·23 ml; 0·955M). After 2 days at 20° dichloro(hexamethylbicyclo[2,2,0]hexa-2,5-diene)-platinum(II) (0·034 g) had separated and was identified by its i.r. and n.m.r. spectra.

Dichloro(pentamethylcyclopenta-1,3-*diene)platinum*(II), (III).—Hexamethylbicyclo[2,2,0]hexa-2,5-diene (6 ml) was added to a suspension of potassium chloroplatinite(II) (2·0 g) in methanol (40 ml) containing stannous chloride dihydrate (0·25 g) and concentrated hydrochloric acid (7 ml) and the mixture refluxed for 6 h. The solution was washed with light petroleum (b.p. 40—60°, 50 ml), and then evaporated down under reduced pressure to a small volume (*ca.* 5 ml). Ethanol (15 ml) was added and the solution cooled to −10°. After 24 h the resulting solid was filtered off, washed with water and diethyl ether to give the product as pale yellow prisms (1·51 g), decomposing at 200—210°.

Dibromo(pentamethylcyclopenta-1,3-*diene)platinum*(II), (IV).—A solution of dichloro(pentamethylcyclopenta-1,3-diene)platinum(II) (0·41 g) in acetone (20 ml) and dichloromethane (10 ml) containing lithium bromide (1·0 g) was refluxed for 1 h. The solvent was removed under reduced pressure, the residue washed with water and dried *in vacuo* (over P_2O_5). Recrystallisation from dichloromethane–light petroleum (b.p. 40—60°) gave the *product* as yellow prisms (0·23 g).

Action of Hydrobromic Acid on Dibromo(hexamethylbicyclo[2,2,0]*hexa*-2,5-*diene)platinum*(II).—A suspension of dibromo(hexamethylbicyclo[2,2,0]hexa-2,5-diene)platinum(II) (0·3 g) in methanol (30 ml) containing concentrated hydrobromic acid (6 ml) was refluxed under a nitrogen atmosphere for 7 h. The solution was concentrated to a small volume under reduced pressure and after cooling to 0° the precipitate of hexamethylbenzene (0·05 g) was filtered off. The filtrate was added to water (50 ml) and extracted with dichloromethane (2 × 20 ml). The organic extract was dried ($MgSO_4$) and the solvent removed under reduced pressure. Recrystallisation from dichloromethane–light petroleum (b.p. 40—60°) gave dibromo(pentamethylcyclopenta-1,3-diene)platinum(II) (0·04 g) as pale yellow prisms. The i.r. spectrum was identical to that of an authentic sample. Addition of tetraphenylarsonium chloride (0·3 g) in methanol–water (1 : 1, 20 ml) to the aqueous solution gave bistetraphenylarsonium tetrabromoplatinate(II) (0·32 g) as pale yellow prisms.

*Di-μ-iodo-bis(α,*2,3-*η-pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl)diplatinum*(II), (VII).—A solution of dichlorodi-μ-(pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) (0·297 g) in acetone (30 ml) and dichloromethane (8 ml) was refluxed with an excess of sodium iodide (1·6 g) for 2 h. The solvent was removed under reduced pressure and the residue washed with water, dried *in vacuo* (over P_2O_5), and recrystallised from dichloromethane–methanol to give the required *product* as pale yellow prisms (0·243 g).

*Di-μ-bromo-bis(α,*2,3-*η-pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl)diplatinum*(II), (VII).—This was similarly prepared from dichlorodi-μ-(pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) by metathesis with lithium bromide and formed *yellow prisms* (59%) from dichloromethane–methanol.

*Cyclopentadienyl(α,*2,3-*η-pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl)platinum*(II), (IX).—Di-μ-iodo-bis(α,2,3-η-pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) (0·128 g) suspended in dry tetrahydrofuran (10 ml) under nitrogen was treated with a tetrahydrofuran solution of sodium cyclopentadienide (0·25 ml; 1·07M; 1·0 mol per mol Pt) to give a red solution which was evaporated to dryness under reduced pressure. The solid was extracted with light petroleum (b.p. 30—40°), the solvent was removed under reduced pressure, and the residue sublimed at 55° and 5×10^{-2} mmHg onto a cold finger (0°) to give the *product* as yellow microprisms (0·061 g).

Acetylacetonato(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*platinum*(II), (IX).—A solution of di-μ-iodo-bis(α,2,3-η-pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) (0·135 g) in warm benzene (10 ml) was treated with a solution of thallium(I) acetylacetonate (0·095 g; 1·1 mol per mol Pt) in warm benzene (15 ml). After shaking the mixture for 45 min the thallium(I) iodide was filtered off, the solvent removed under reduced pressure, and the residue recrystallised from the minimum amount of light petroleum (b.p. 40—60°) at −10° to give the *product* as colourless prisms (0·101 g).

Action of Hydrogen Chloride on Acetylacetonato(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*platinum*(II).—A solution of hydrogen chloride in diethyl ether (3·8 ml; 0·1M; 1·0 mol per mol Pt) was added to a solution of acetylacetonato(α,2,3-η-pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)platinum(II) (0·162 g) in diethyl ether (5 ml). Di-μ-chloro-bis(α,2,3-η-pentamethylbicyclo[2,2,0]-hexa-2,5-dien-2-ylmethyl)diplatinum(II) separated out on standing at 20° as *colourless prisms* (0·118 g).

Iodo(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*pyridineplatinum*(II), (VIII).—Pyridine (0·05 ml) was added to a solution of di-μ-iodo-bis(α,2,3-η-pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) (0·1 g) in dichloromethane (2 ml). Addition of diethyl ether (6 ml) gave the *product* as colourless prisms (0·07 g).

Iodo(*isoquinoline*)(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*platinum*(II), (VIII).—This complex was prepared similarly from di-μ-iodo-bis(α,2,3-η-pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) (0·093 g) and isoquinoline as *pale yellow prisms* (0·045 g).

2,2′-*Bipyridyl*(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*platinum*(II) *Iodide*, (X).—This complex was prepared similarly from di-μ-iodo-bis(α,2,3-η-pentamethylbicyclo[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) (0·12 g) and 2,2′-bipyridyl as *yellow prisms* (0·14 g).

Preparation of Halogeno(*allyl*)*platinum*(II) *Complexes with Tertiary Phosphines or Arsines by Bridge-splitting Reactions.*—*Chloro*(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*triphenylphosphineplatinum*(II), (VIII). Triphenylphosphine (0·034 g; 1 mol per mol Pt) was added to a solution of di-μ-chloro-bis(α,2,3-η-pentamethylbicyclo-[2,2,0]hexa-2,5-dien-2-ylmethyl)diplatinum(II) (0·050 g) in benzene (3 ml). Addition of light petroleum (b.p. 40—60°, 6 ml) gave the *product* as colourless prisms (0·050 g). The following compounds were prepared similarly from the corresponding bridged halogeno(allyl)platinum(II) complexes: *Iodo*(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*triphenylphosphineplatinum*(II), as pale yellow prisms (50%); *iodo*(α,2,3-η-*pentamethylbicyclo*[2,2,0]*hexa*-2,5-*dien*-2-*ylmethyl*)*triphenylarsineplatinum*(II), as pale yellow prisms (55%).

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