Reactions of Allene, 2,3-Dimethylbuta-1,3-diene, and Buta-1,3-diene with Bis(cyclo-octa-1,5-diene)-, Bis(ethylene)(trimethylphosphine)-, and Bis(ethylene)(tricyclohexylphosphine)-platinum; *X*-Ray Crystal Structures of η-Cyclo-octa-1,5-diene- and Bis(trimethylphosphine)-(1,4-*trans*-divinylbutane-1,4-diyl)platinum

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Reaction of allene or buta-1,3-diene with [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) gives (η-cyclo-octa-1,5-diene)(2,3-dimethylenebutane-1,4-diyl)platinum (1) and (η-cyclo-octa-1,5-diene)(1,4-*trans*-divinylbutane-1,4-diyl)platinum (2), respectively. The *trans* arrangement of the two vinyl groups in complex (2) has been confirmed by an *X*-ray diffraction study [monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.082(6)$, $b = 10.544(13)$, $c = 15.293(17)$ Å, and $\beta = 92.13(7)°$], but crystal twinning limits refinement to R 0.111 (R' 0.147). Displacement of co-ordinated cod from complex (2) with 2 mol equivalents of CNBu^t or PMe$_3$ affords $[\overline{\mathrm{Pt}\{\mathrm{CH(CH{=}CH_2)CH_2CH_2C}}\mathrm{H(CH{=}CH_2)}\}L_2]$ (L = CNBu^t or PMe$_3$). The structure of the trimethylphosphine complex has been identified by a single-crystal *X*-ray diffraction study. Crystals are triclinic, space group $P\bar{1}$, $a = 9.197(3)$, $b = 11.283(4)$, $c = 9.555(6)$ Å, $\alpha = 87.10(4)$, $\beta = 118.14(3)$, and $\gamma = 98.89(3)°$. Using 4 925 reflections collected at 213 K, refinement has converged at R 0.052 (R' 0.062). In contrast, treatment of (2) with 1 mol equivalent of PMe$_3$ gives (1-σ,6—8-η-*cis*-2-*trans*-6-octadienediyl)(trimethylphosphine)platinum, which is also formed from [Pt(C$_2$H$_4$)$_2$(PMe$_3$)] and excess of buta-1,3-diene. Reaction of [Pt(C$_2$H$_4$)$_2${P(C$_6$H$_{11}$)$_3$}] affords the corresponding C$_8$ complex. 2,3-Dimethyl- and 2,3-diphenyl-buta-1,3-diene react with [Pt(cod)$_2$] to give (η-cyclo-octa-1,5-diene)(2,3-dimethyl- and 2,3-diphenyl-but-2-ene-1,4-diyl)platinum respectively. The mechanistic implications of these observations are discussed.

ONE of the most thoroughly studied reactions in organometallic chemistry is the nickel-catalysed cyclo-dimerisation and -trimerisation of 1,3-dienes.[1] Whereas, cyclotrimerisation of buta-1,3-diene to cyclododeca-1,5,9-triene is the main reaction using [Ni(cod)$_2$] (cod = cyclo-octa-1,5-diene) as catalyst, the reaction can be modified by the addition of a tertiary phosphine or tertiary phosphite to give a system capable of cyclodimerising 1,3-dienes, which, in the case of buta-1,3-diene, affords *cis*-1,2-divinylcyclobutane, cyclo-octa-1,5-diene and 4-vinylcyclohex-1-ene, the distribution of these products being controlled by the reaction conditions and by the nature of the added ligand. Considerable progress has been made towards establishing a stepwise path for these reactions by the use of organic product analysis, the isolation of intermediates, and the use of model compounds.

With the development[2] of a practical synthesis of [Pt(cod)$_2$] the way was open for a study of its reaction with 1,3- and 1,2-dienes, there being a high expectation that stable complexes would be isolated from these reactions. Moreover, the formation and structures of the organoplatinum complexes might have a bearing on the mechanistic details of the catalytic nickel systems. We have reported[3] some aspects of this work in a preliminary communication.

RESULTS AND DISCUSSION

Initially the reaction of propa-1,2-diene (allene) with [Pt(cod)$_2$] was examined, it having been shown[1] previously that [Ni(cod)$_2$] catalyses the polymerisation and cyclo-oligomerisation of propa-1,2-diene and substituted 1,2-dienes. Addition (−20 °C) of [Pt(cod)$_2$] to a solution of propa-1,2-diene in hexane led to the rapid formation of a relatively stable, orange, crystalline complex (1), characterised by elemental analysis and n.m.r. spectroscopy. The ^{1}H and ^{13}C n.m.r. spectra (see Experimental section) showed chemical shifts and coupling constants consistent with the illustrated structure incorporating a 3,4-dimethyleneplatinacyclopentane ring system.† The presence of carbon–platinum σ bonds was confirmed by the appearance of a

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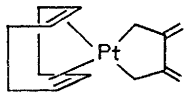
† The normal heterocyclic numbering scheme is used to describe the platinacyclo-pentanes and -pentenes described herein. In order to avoid cumbersome terminology, a different scheme (detailed in the Experimental section) is used for assigning n.m.r. spectral data.

[1] For a complete survey, see P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1975, vol. 2; also, C. R. Graham and L. M. Stephenson, *J. Amer. Chem. Soc.*, 1977, **99**, 7098.

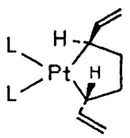
[2] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 3; *J.C.S. Dalton*, 1977, 271.

[3] G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1976, **98**, 3373.

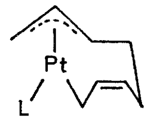
resonance in the ^{13}C spectrum at 33.5 p.p.m. with J(PtC) 725 Hz.[4] Although nickelacyclopentanes have been postulated [1] as intermediates in the nickel-catalysed cyclo-oligomerisation of propa-1,2-diene such species were not isolated. Thus the formation and characterisation of (1) is of considerable interest. However, a rhodium complex structurally similar to (1) has been isolated from the reaction of [Rh(acac)(C_2H_4)$_2$] (acac = pentane-2,4-dionate) with propa-1,2-diene.[5]



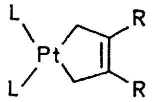
(1)



(2) L_2 = cod
(3) L = CNBu^t
(4) L = PMe$_3$



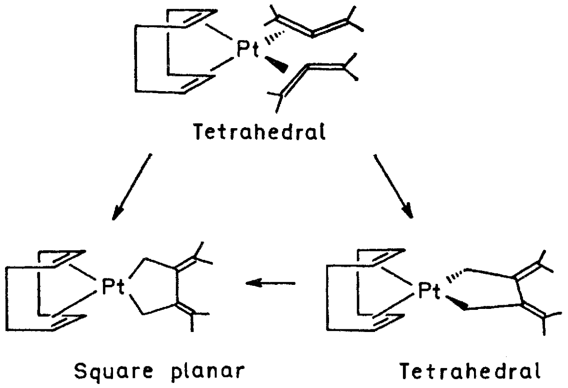
(5) L = PMe$_3$
(6) L = P(C_6H_{11})$_3$



(7) L_2 = cod, R = Me
(8) L_2 = cod, R = Ph
(9) L = CNBu^t, R = Me

It is interesting that in the formation of (1) there was no evidence for either 2,5- or 2,4-dimethyleneplatinacyclopentanes, the nickel analogues being the postulated precursors of 1,2- or 1,3-dimethylenecyclobutane.

It is suggested that in the reaction of propa-1,2-diene with [Pt(cod)$_2$] a tetrahedral [6] platinum(0) species is first formed containing co-ordinated cyclo-octa-1,5-diene and two molecules of η^2-bonded propa-1,2-diene. Then with a synchronous twisting to form a square-planar species, and the transfer of two electrons from filled platinum d orbitals, carbon–platinum and carbon–carbon σ-bond formation could occur (Scheme 1).



SCHEME 1

There is the less likely possibility that transfer of electrons (oxidation of platinum) takes place before twisting, yielding a tetrahedral platinum(II) species, which then rearranges to give the square-planar complex (1).

The reaction with buta-1,3-diene was next investigated. Solid [Pt(cod)$_2$] was added (−30 °C) to a saturated solution of buta-1,3-diene in hexane. A pale brown solution was formed from which, on warming to room temperature, was isolated, in high yield, a white crystalline complex (2). The latter was shown by elemental analysis and mass spectroscopy to have the composition $C_{16}H_{24}Pt$ corresponding to two butadiene molecules and one cyclo-octa-1,5-diene per platinum. The cyclo-octa-1,5-diene was readily displaced by t-butyl isocyanide or trimethylphosphine to give the crystalline complexes (3) and (4) respectively. Examination of the ^1H and ^{13}C n.m.r. spectra of these complexes clearly suggested that they contained a 2,5-divinylplatinacyclopentane ring system; however, the relative orientation, *i.e. cis* or *trans*, of the two vinyl groups could not be firmly established.

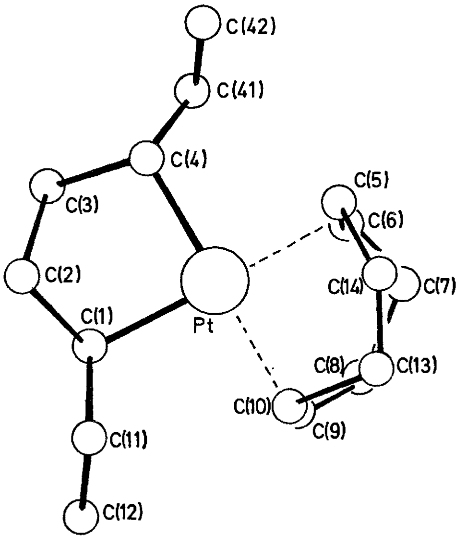


FIGURE 1 Molecular structure of complex (2)

Single-crystal X-ray diffraction studies were therefore undertaken in order to clarify this important structural feature. Data were first collected for the parent complex (2). However, although the crystals were twinned, the *trans* arrangement of the vinyl groups with respect to the five-membered ring was apparent (Figure 1). Table 1 gives internuclear distances and angles. The t-butyl isocyanide complex (3) was next investigated by X-ray diffraction and, although the *trans*-vinyl group arrangement was again confirmed, decomposition of the crystal during the X-ray data collection prevented refinement to better than R 0.126. Finally, attention was turned to the phosphine complex (4). With data collection at 213 K, the molecular configuration (Figure 2) was accurately established. Internuclear distances and angles are given in Table 2, and the molecular-packing diagram is shown in Figure 3.

Co-ordination around the platinum atom is essentially square planar with the usual distortion from 90° for the

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[4] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135.

[5] G. Ingrosso, A. Immirzi, and L. Porri, *J. Organometallic Chem.*, 1973, **60**, C35.

[6] N. Rösch and R. Hoffmann, *Inorg. Chem.*, 1974, **13**, 2656.

angle (82°) subtended at the metal by the two σ-bonded atoms C(1) and C(4). The corresponding angle in (2) is 84°. The five-membered ring is considerably puckered, with C(2) and C(3) located above and below the mean co-ordination plane of the platinum atom. The vinyl groups lie above and below this plane, with the bond lengths C(1)–C(11) and C(4)–C(41) at 1.48(1) Å being shorter than expected for a single carbon–carbon bond. In accord with some degree of delocalisation, the internuclear distances C(11)–C(12) and C(41)–C(42) are slightly longer than anticipated.

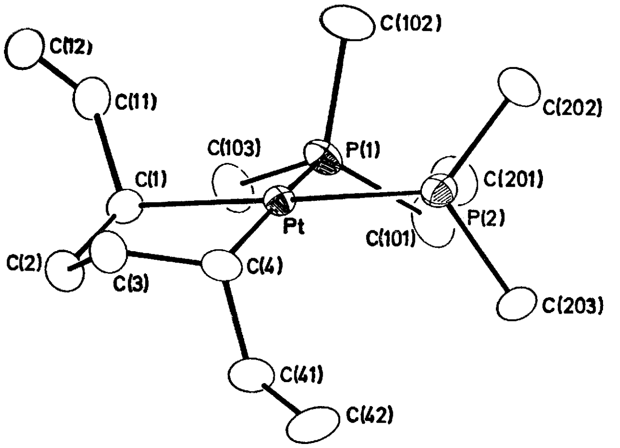

FIGURE 2 Molecular structure of complex (4)

TABLE 1

Internuclear distances (Å) and angles (°) in complex (2)

(*i*) Distances		(*ii*) Angles	
Pt–C(1)	2.10(4)	C(1)–Pt–C(4)	84(1)
Pt–C(4)	2.11(3)	C(1)–Pt–C(5,6) *	178(1)
Pt–C(5,6)	2.20(3)	C(4)–Pt–C(5,6)	96(1)
Pt–C(9,10) *	2.15(3)	C(1)–Pt–C(9,10)	95(1)
Pt–C(5)	2.32(3)	C(4)–Pt–C(9,10)	176(1)
Pt–C(6)	2.32(4)	C(5,6)–Pt–C(9,10)	85(1)
Pt–C(9)	2.25(4)		
Pt–C(10)	2.28(3)		
C(5)–C(6)	1.45(6)	C(14)–C(5)–C(6)	118(3)
C(6)–C(7)	1.35(5)	C(5)–C(6)–C(7)	134(4)
C(7)–C(8)	1.60(5)	C(6)–C(7)–C(8)	111(3)
C(8)–C(9)	1.39(5)	C(7)–C(8)–C(9)	119(3)
C(9)–C(10)	1.39(5)	C(8)–C(9)–C(10)	128(3)
C(10)–C(13)	1.57(5)	C(9)–C(10)–C(13)	120(3)
C(13)–C(14)	1.52(6)	C(10)–C(13)–C(14)	109(3)
C(14)–C(5)	1.61(5)	C(13)–C(14)–C(5)	119(3)
C(1)–C(11)	1.48(6)	Pt–C(1)–C(11)	119(3)
C(11)–C(12)	1.36(6)	Pt–C(1)–C(2)	109(2)
C(1)–C(2)	1.62(5)	Pt–C(4)–C(3)	108(2)
C(2)–C(3)	1.60(5)	Pt–C(4)–C(41)	112(2)
C(3)–C(4)	1.56(4)	C(1)–C(11)–C(12)	124(4)
C(4)–C(41)	1.47(5)	C(1)–C(2)–C(3)	104(3)
C(41)–C(42)	1.42(6)	C(2)–C(3)–C(4)	105(3)
		C(3)–C(4)–C(41)	105(3)
		C(4)–C(41)–C(42)	111(4)

* C(5,6) and C(9,10) designate the midpoint of the lines joining C(5) and C(6), and C(9) and C(10).

The vinyl groups are not symmetrically disposed with respect to Pt, C(1), and C(4), their positioning being almost certainly due to the relative arrangements of the methyl groups of the trimethylphosphine ligands. To produce an exactly symmetrical configuration by rotation of the vinyl groups about C(1)–C(11) or C(4)–C(41) would lead to even closer contacts between the methyl and vinyl hydrogen atoms which already show the shortest intramolecular separations.

TABLE 2

Internuclear distances (Å) and angles (°) in complex (4)

(*i*) Distances		(*ii*) Angles	
Pt–P(1)	2.306(2)	P(1)–Pt–P(2)	95.69(8)
Pt–P(2)	2.294(2)	P(1)–Pt–C(1)	91.5(2)
Pt–C(1)	2.142(8)	P(1)–Pt–C(4)	168.3(2)
Pt–C(4)	2.131(5)	P(2)–Pt–C(1)	172.4(1)
		P(2)–Pt–C(4)	91.3(2)
		C(1)–Pt–C(4)	82.1(3)
P(1)–C(101)	1.832(9)	C(101)–P(1)–C(102)	102.9(4)
P(1)–C(102)	1.827(8)	C(102)–P(1)–C(103)	101.1(4)
P(1)–C(103)	1.835(8)	C(103)–P(1)–C(101)	99.0(4)
P(2)–C(201)	1.820(7)	C(201)–P(2)–C(202)	98.9(3)
P(2)–C(202)	1.827(7)	C(202)–P(2)–C(203)	101.7(4)
P(2)–C(203)	1.838(10)	C(203)–P(2)–C(201)	103.4(4)
C(1)–C(11)	1.48(1)	Pt–C(1)–C(2)	110.5(5)
C(11)–C(12)	1.36(1)	Pt–C(1)–C(11)	105.7(5)
C(1)–C(2)	1.52(1)	C(2)–C(1)–C(11)	115.3(6)
C(2)–C(3)	1.52(1)	C(1)–C(11)–C(12)	126.8(6)
C(3)–C(4)	1.54(1)	C(1)–C(2)–C(3)	108.8(5)
C(4)–C(41)	1.48(1)	C(2)–C(3)–C(4)	109.3(5)
C(41)–C(42)	1.32(1)	Pt–C(4)–C(3)	108.8(5)
		C(3)–C(4)–C(41)	111.9(5)
		Pt–C(4)–C(41)	104.0(4)
		C(4)–C(41)–C(42)	128.1(6)

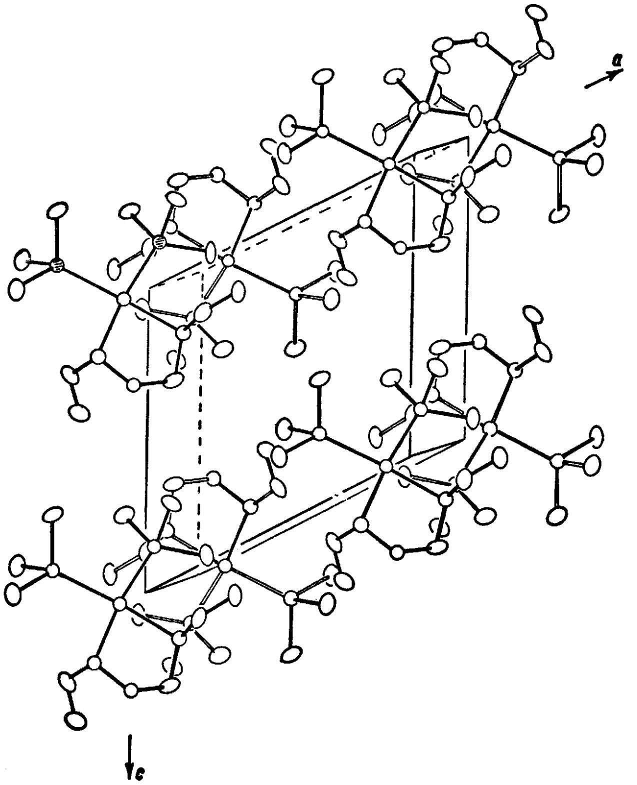

FIGURE 3 Molecular packing diagram of complex (4) viewed down the *b* axis

The Pt–P and Pt–C separations fall within ranges previously observed, namely 2.267(9)—2.331(5) [7] and

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[7] J. Browning and B. R. Penfold, *J. Cryst. Mol. Structure*, 1974, **4**, 335; M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1976, 759.

1.99(3)—2.15(2) Å,[8] respectively. The slight differences between Pt–P(1) and Pt–P(2), and between Pt–C(1) and Pt–C(4), are probably due to the orientation and packing effects, since the possibility of the acentric space group *P*1 was tested but found negative. The geometry of the trimethylphosphine ligands is normal.

In order to understand more fully these reactions, the reactions of buta-1,3-diene with the 16-electron systems $[Pt(C_2H_4)(PMe_3)_2]$ and $[Pt(C_2H_4)_2L][L = PMe_3$ or $P(C_6H_{11})_3]$ [9] were investigated. Buta-1,3-diene was bubbled through a slurry (−10 °C) of $[Pt(C_2H_4)(PMe_3)_2]$ in diethyl ether giving white crystals of (4). Reaction of buta-1,3-diene with $[Pt(C_2H_4)_2(PMe_3)]$ or $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ gave, respectively, the yellow crystalline complexes (5) and (6). The properties indicated that these complexes were octadienediyl(phosphine)platinum derivatives and, in agreement, treatment of (5) with PMe_3 afforded (4). Examination of the ^{13}C n.m.r. spectrum, and comparison of the ^1H spectrum with that reported [10] for the corresponding nickel species, showed that (5) and (6) were (1-σ,6—8-η-*cis*-2-*trans*-6-octadienediyl)-(trimethylphosphine)platinum and -(tricyclohexylphosphine)platinum, respectively.

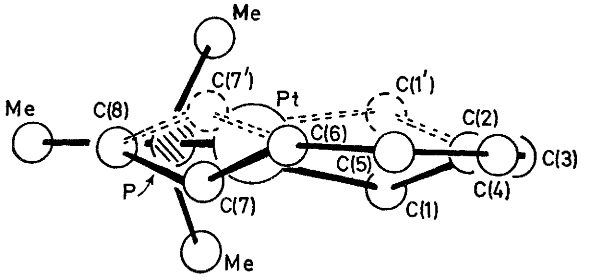
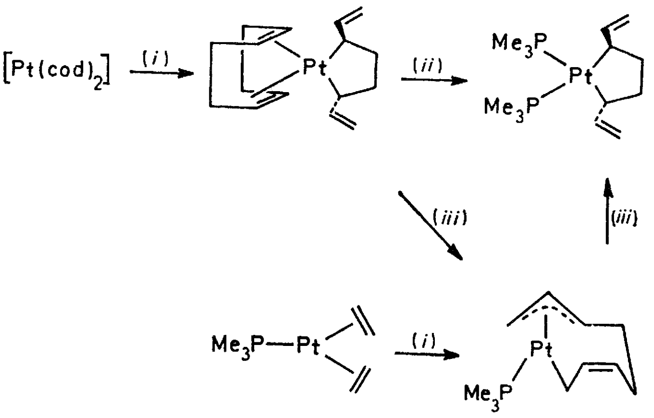


FIGURE 4 View of a molecule of complex (5) perpendicular to the crystallographic mirror plane

For complex (5) a ^{195}Pt chemical shift measured by the INDOR technique was observed at −796.7 p.p.m. [*J*(PtP) 4 194 Hz]. An *X*-ray crystallographic study was frustrated by disorder about a mirror plane (Figure 4); however, the η^3-allyl, σ-alkyl attachment of the C_8 chain to platinum was evident. In the case of the corresponding tricyclohexylphosphinenickel species, derived from isoprene and *cis*-penta-1,3-diene, there is unequivocal *X*-ray crystallographic evidence [11] for the σ,η^3-bonding mode for the C_8 chain. The interrelations and structures for the platinum system are summarised in Scheme 2.

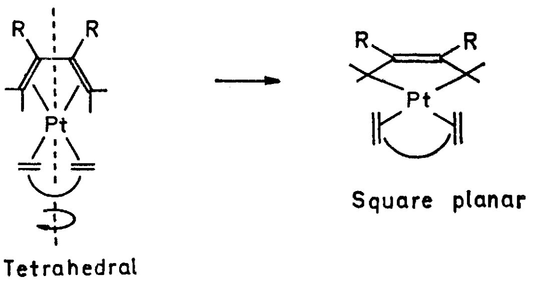
In striking contrast to the above reactions, where two buta-1,3-diene molecules link together to form a C_8 chain, reaction of 2,3-dimethylbuta-1,3-diene and 2,3-diphenylbuta-1,3-diene with $[Pt(cod)_2]$ gave the crystalline complexes (7) and (8) containing only one molecule of the reacting 1,3-diene. Replacement of the coordinated cyclo-octa-1,5-diene in (7) by Bu^tNC readily occurred to give (9). The ^{13}C n.m.r. spectra of these complexes all showed a chemical shift in the 30.9—40.7 p.p.m. region with a large (609—787 Hz) ^{195}Pt-^{13}C coupling characteristic [4] of a carbon atom σ-bonded to platinum, as required by the illustrated structures.



SCHEME 2 (*i*) $CH_2=CHCH=CH_2$; (*ii*) $2PMe_3$; (*iii*) PMe_3

In relation to the conformation adopted by the platinacyclopentene ring, it is interesting that the ^1H n.m.r. spectrum showed only a single sharp line with appropriate ^{195}Pt–^1H coupling for the $PtCH_2$ protons. On cooling to −90 °C there was no change in the line shape of this signal, implying the absence of pseudo-axial and equatorial environments, and hence a planar geometry for the platinacyclopentene ring.

The formation of (7) and (8) probably involves the initial formation of a tetrahedral species containing cyclo-octa-1,5-diene and the 1,3-diene as ligands (Scheme 3). Then, as suggested for the allene system, oxidative transfer of two electrons from platinum to the 1,3-diene with a concomitant twisting process could afford the square-planar platinacyclopentene structure. This transformation is particularly interesting in view of previous discussions [12] about the bonding in molecules such as (buta-1,3-diene)tricarbonyliron where emphasis has been placed on ferracyclopentene structures. It is reasonable to suggest that steric factors play an important role in inhibiting the formation of C_8 species of the type (2)—(4) observed with less-substituted 1,3-dienes.



SCHEME 3

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[8] R. Mason, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc. (A)*, 1970, 535; L. E. Smart, J. Browning, M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1777.

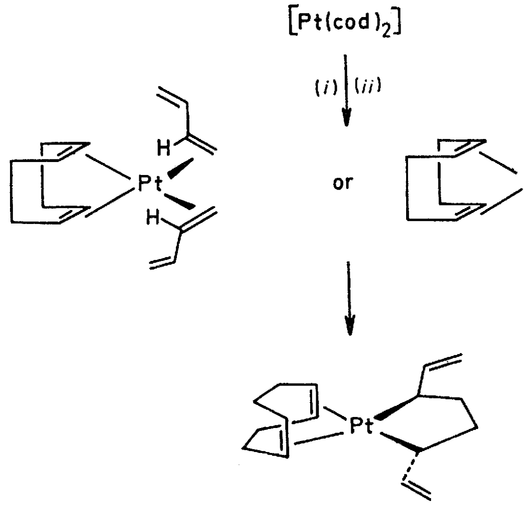
[9] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1975, 449.

[10] J. M. Brown, B. T. Golding, and M. J. Smith, *Chem. Comm.*, 1971, 1240.

[11] B. Barnett, B. Büssemeier, P. Heimbach, P. W. Jolly, C. Krüger, I. Tkatchenko, and G. Wilke, *Tetrahedron Letters*, 1972 1457.

[12] D. M. P. Mingos, *J.C.S. Dalton*, 1977, 20, 26, 31.

There remains the problem of attempting to provide explanations for the reactions summarised in Scheme 2, in particular the stereochemistry of the *trans*-2,5-divinylplatinacyclopentane ring system. As mentioned previously, there is a considerable body of evidence [1] to show that, in the nickel-catalysed dimerisation of buta-1,3-diene, open-chain C_8 species, one of which is isostructural with complex (5), play a key role. There is, however, the alternative possibility that a σ,η^3-C_8 intermediate is not traversed in the reaction between $[Pt(cod)_2]$ and buta-1,3-diene. It seems possible (Scheme 4) that one cyclo-octa-1,5-diene remains bonded to the platinum in the η^4 mode, leaving two co-ordination sites in a tetrahedral species to be occupied by two η^2-bonded buta-1,3-diene molecules. In the case of the 2,3-disubstituted buta-1,3-dienes perhaps a second molecule of 1,3-diene is unable to co-ordinate to the platinum. The postulated intermediate $[Pt(\eta^2\text{-}1,3\text{-}C_4H_6)_2(cod)]$ it thus ideally placed for direct formation of a divinylplatinacyclopentane ring *via* electron transfer from platinum to olefin π^* orbitals with concomitant twisting and Pt–C and C–C σ-bond formation. The reversible reaction $M(\eta^2\text{-}C_2H_4)_2 \rightleftharpoons \overline{M\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2}$ has been previously studied mainly in the context of olefin metathesis.[13-15]



SCHEME 4 (*i*) $+CH_2{=}CHCH{=}CH_2$; (*ii*) −cod

If the reaction does not proceed in this way (Scheme 4) then it is necessary for the remaining co-ordinated cyclo-octa-1,5-diene to adopt an η^2-bonding mode, thus allowing the formation of a trigonal intermediate $[Pt(\eta^2\text{-}1,3\text{-}C_4H_6)_2(\eta^2\text{-}1,5\text{-}C_8H_{12})]$. However, in the case of the reaction of $[PtL(C_2H_4)_2]$ [$L = PMe_3$ or $P(C_6H_{11})_3$] with an excess of buta-1,3-diene no such difficulty arises. As has been discussed [1] for the nickel system, the formation of a species $[Pt(\eta^2\text{-}1,3\text{-}C_4H_6)_2L]$ is a logical starting point for the reaction sequence. In spite of the plausibility of such an initial step it is important to note that no buta-1,3-diene complex of this type has been isolated either for the nickel or the platinum systems, implying that the next step readily occurs. This leaves uncertain the precise geometry of the three-co-ordinate complexes, but studies [9] with isostructural bis(ethylene) complexes have shown that a trigonal-planar geometry is preferred, and therefore in further discussion this geometry is assumed for the species $[Pt(\eta^2\text{-}1,3\text{-}C_4H_6)_2L]$.

Coupling of the two η^2-buta-1,3-diene molecules to form the C_8 chain has been discussed in terms of a concerted process,[16] and attempts [17] have been made to extend the Woodward–Hoffmann rules to this reaction. There are, however, difficulties [18] and our experiments do not clarify this problem; in particular it is not possible to distinguish between an initial reaction involving the formation of a 2,5-divinylmetallacyclopentane followed by subsequent rearrangement and conformational change, and the more generally accepted process in which C–C bond formation occurs remote from the metal.

In describing the nickel-catalysed formation of *cis*-divinylcyclobutane from buta-1,3-diene it has been assumed [1] that the immediate precursor of the cyclobutane, prior to a reductive-elimination reaction, is a *cis*-2,5-divinylnickelacyclopentane. Clearly the isolation of a *trans*-2,5-divinylplatinacyclopentane is at first sight unexpected. If as shown in Scheme 5 we consider the eight different ways two η^2-bonded buta-1,3-diene molecules could combine to form σ,η^3-C_8 intermediates,* it can be seen that two pairs of four interconverting C_8 conformational isomers can result. The isolation of (5) and (6) might suggest that the C_8 species with an unco-ordinated *trans*-2-olefin does not play a part, and that we need only consider the remaining four *cis*-2-olefin systems. However, the ease with which *syn–anti* exchange can occur suggests that such an assumption may not be valid. Thus, as illustrated, and depending on the conformation of the C_8 species preferred, access can be gained to either a *cis*- or *trans*-2,5-divinylcyclopentane. We suggest that the nature of the central metal, *i.e.* Ni or Pt, has such an effect on the relative energies of the C_8 conformations that in the case of the nickel system the *cis* geometry is adopted thus providing a path to *cis*-divinylcyclobutane, whereas with platinum the alternative *trans* path is energetically preferred.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on Varian Associates HA 100 and T 60 spectrometers at 100 and 60

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* In principle, η^3,η^3-C_8 species could be formed directly, but to simplify the argument, and because we have no direct information on this point, direct formation of the square-planar σ,η^3-C_8 species is assumed in agreement with the suggestion of Heimbach and his co-workers.[17]

[13] H. R. Fraser, P. H. Bird, S. A. Sezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 597.

[14] J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1976, **98**, 6529.

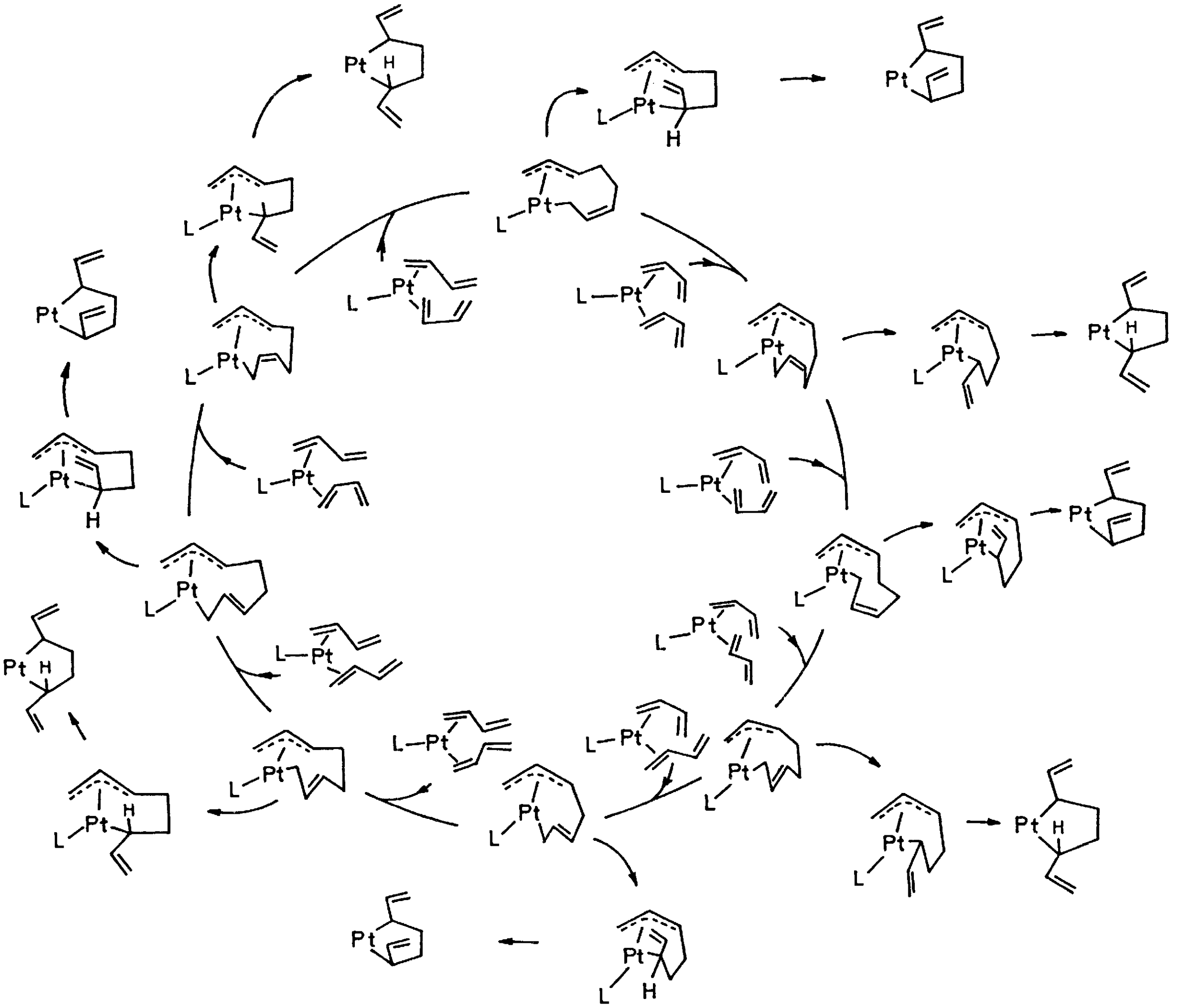
[15] R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, 1972, **94**, 2538; C. Biefeld, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, 1973, **12**, 2166.

[16] R. G. Pearson, *Chem. in Britain*, 1976, **12**, 160.

[17] H. Bucholz, P. Heimback, H. J. Hey, H. Selbeck, and W. Wiese, *Co-ordination Chem. Rev.*, 1972, **8**, 129; P. Heimbach, *Angew. Chem.*, 1973, **85**, 1035.

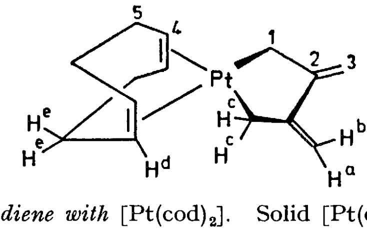
[18] F. Mango, *Co-ordination Chem. Rev.*, 1975, **15**, 109.

MHz, respectively. Carbon-13 n.m.r. spectra were obtained on a JEOL PFT-100 spectrometer at 25.15 MHz; chemical shifts are relative to internal $SiMe_4$. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer using Nujol mulls. Molecular weights were determined mass spectrometrically on an A.E.I. MS 902 spectrometer operating at 70 eV.* Reactions were conducted in a dry oxygen-free nitrogen atmosphere. Light petroleum refers to that fraction having b.p. 40—60 °C.



SCHEME 5 L = PMe_3. Among the intermediates, *cis–trans* isomerisation may be achieved *via* rotation about a C–C bond in a σ-bonded allyl species

Reactions.—Propa-1,2-*diene with bis*(*cyclo-octa*-1,5-*diene*)*platinum*. Propa-1,2-diene was slowly bubbled through hexane (20 cm^3) at −20 °C for 10 min. Solid [Pt(cod)$_2$] (0.30 g, 0.75 mmol) was added (−20 °C) to the resulting saturated solution with stirring. On warming to room temperature the solution became orange and a red solid was precipitated. After 1 h the volatile material was removed *in vacuo*, the residue extracted with light petroleum (20 cm^3), and the resulting orange solution filtered, reduced in volume, and cooled (−20 °C) to give pale orange crystals of (η-*cyclo-octa*-1,5-*diene*)(2,3-*dimethylenebutane*-1,4-*diyl*)-*platinum* (1) (50 mg, 17%) (Found: C, 44.6; H, 5.4. $C_{14}H_{20}Pt$ requires C, 43.9; H, 5.2%), $\nu_{max.}$(C=C) at 1 611m cm^{-1}. N.m.r. spectra: ^{1}H in C_6D_6, τ 4.55 [overlapping d of t, 2 H, H^a, J(H^{a}H^c) 1.7, J(H^{a}H^b) 2.5], 5.00 [overlapping d of t, 2 H, H^b, J(H^{b}H^c) 1.7, J(H^{a}H^b) 2.5], 5.50 [s, 4 H, H^d, J(PtH) 45], 7.10 [t, 4 H, H^c, J(PtH) 103, J(H^{a}H^c) = J(H^{b}H^c) 1.7 Hz], and 8.33 (s, 8 H, H^e); ^{13}C in C_6D_6, ^{1}H decoupled, 29.6 [C(5)], 33.5 [C(1), J(PtC^1) 725], 97.1 [C(4), J(PtC^4) 59], 101.2 [C(3), J(PtC^3) 82], and 162 p.p.m. [C(2), J(PtC^2) 0 Hz].



Buta-1,3-*diene with* [Pt(cod)$_2$]. Solid [Pt(cod)$_2$] (0.20 g, 0.5 mmol) was added (−30 °C) to a saturated solution of buta-1,3-diene in hexane (20 cm^3). A pale brown solution was formed which on warming to room temperature deposited a trace amount of an orange solid; stirring was continued for 2 h and then volatile material was removed *in vacuo*. The yellow residue was extracted with hexane (20 cm^3), and the extract filtered and concentrated (5 cm^3) to give on cooling (−20 °C) white crystals of (η-*cyclo-octa*-1,5-

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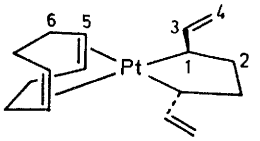
* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

diene)(1,4-trans-*divinylbutane*-1,4-*diyl*)*platinum* (2) (0.16 g, 76%), m.p. 110 °C (decomp.) (Found: C, 46.9; H, 6.0%; *M* 412. $C_{16}H_{24}Pt$ requires C, 46.7; H, 5.8%; *M* 412), $\nu_{max.}$ (C=C) at 1 608m cm^{-1}. N.m.r. spectra: ^1H in C_6D_6, τ 3.4—3.9 (m, 2 H, H^3), 4.9—5.6 (m, 8 H, $H^{4,5}$), 6.6—6.9 (m, 2 H, H^1), and 7.8—8.8 (m, 12 H, $H^{2,6}$); ^{13}C in C_6D_6, ^1H decoupled, 27.1 and 31.3 [C(6)], 39.7 [C(2), $J(PtC^2)$ 0], 56.6 [C(1), $J(PtC^1)$ 763], 100.3 and 101.0 [C(5), $J(PtC^5)$ 64 and 63], 105.6 [C(4), $J(PtC^4)$ 63], and 148.1 p.p.m. [C(3), $J(PtC^3)$ 41 Hz].

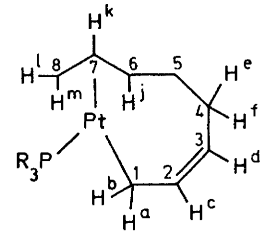


Complex (2) *with t-butyl isocyanide.* An excess of t-butyl isocyanide (0.2 cm^3) was added to a stirred solution of (2) (0.2 g, 0.5 mmol) in hexane (20 cm^3) at room temperature. An immediate reaction occurred and the volatile material was removed *in vacuo*. The residue was extracted with hexane (20 cm^3), and the extract was filtered, reduced in volume (5 cm^3), and cooled (−20 °C) to afford colourless crystals of (1,4-trans-*divinylbutane*-1,4-*diyl*)*bis*(*t-butyl isocyanide*)*platinum* (3) (0.2 g, 90%), m.p. 111—112 °C (decomp.) (Found: C, 45.7; H, 6.0; N, 5.8%; *M* 469. $C_{18}H_{30}N_2Pt$ requires C, 46.0; H, 6.4; N, 6.0%; *M* 469), $\nu_{max.}$ at 2 200(sh) 2 175s (NC), and 1 610s cm^{-1} (C=C). N.m.r. spectra: ^1H in C_6D_6, τ 2.9—3.5 (m, 2 H, H^3), 4.7—5.5 (m, 4 H, H^4), 6.2—6.5 (m, 2 H, H^1), 7.5—8.1 (m, 4 H, H^2), and 8.95 (s, 18 H, Bu^tN); ^{13}C in C_6D_6, ^1H decoupled, 29.7 [$(CH_3)_3C$], 38.6 [C(2), $J(PtC^2)$ 0], 46.2 [C(1), $J(PtC^1)$ 594], 58.4 [$(CH_3)_3CNC$], 102.7 [C(4), $J(PtC^4)$ 57], 152.4 [C(3), $J(PtC^3)$ 40 Hz], and 185.9 p.p.m. [$(CH_3)_3CNC$].

Complex (2) *with trimethylphosphine.* Trimethylphosphine (2 mmol) was condensed (−196 °C) into a tube containing (2) (0.2 g, 0.5 mmol) in hexane (20 cm^3). The reaction mixture was allowed to warm to room temperature with stirring. After 1 h the volatile material was removed *in vacuo*. The residue was extracted with hexane and the extract cooled (−20 °C) to give white crystals of (1,4-trans-*divinylbutane*-1,4-*diyl*)*bis*(*trimethylphosphine*)*platinum* (4) (0.18 g, 80%), m.p. 92—94 °C (decomp.) (Found: C, 37.4; H, 6.9. $C_{14}H_{30}P_2Pt$ requires C, 36.9; H, 6.6%), $\nu_{max.}$ (C=C) at 1 600s cm^{-1}. N.m.r. spectra: ^1H in C_6D_6, τ 3.1—3.7 (m, 2 H, H^3), 4.7—5.3 (m, 4 H, H^4), 6.5—6.9 (m, 2 H, H^1), 7.3—7.7 (m, 4 H, H^2), and 8.95 [d, 18 H, PMe, $^2J(PH)$ 10.0 Hz]; ^{13}C in C_6D_6, ^1H decoupled, 16.7 [C(5), PMe], 37.0 [C(2), $J(PtC^2)$ 0], 48.1 [C(1), $J(PtC^1)$ 584, $J(PC^1)$ (*cis*) 7.3, (*trans*) 93], 102.7 [C(4), $J(PtC^4)$ 55, $J(PC^4)$ 7.3], and 148.9 p.p.m. [C(3), $J(PtC^3)$ 60 Hz].

Buta-1,3-*diene with ethylenebis*(*trimethylphosphine*)-*platinum.* Trimethylphosphine (1.0 mmol) was condensed (−196 °C) into a solution of $[Pt(cod)_2]$ (0·5 mmol) in Et_2O (20 cm^3), which had been saturated with ethylene. The solution was warmed to room temperature and evaporated to dryness *in vacuo* yielding $[Pt(C_2H_4)(PMe_3)_2]$ as an off-white solid. This was slurried in Et_2O (20 cm^3) and buta-1,3-diene bubbled through the solution at −10 °C. After 1 h the volatile material was removed *in vacuo*, and the residue extracted with hexane (20 cm^3). On filtration and cooling (−20 °C) the extract afforded crystals of (4) (70 mg, 30%), identified by its i.r. spectrum.

Buta-1,3-*diene with bis*(*ethylene*)(*trimethylphosphine*)*platinum.* Buta-1,3-diene was bubbled through a solution of $[Pt(C_2H_4)_2(PMe_3)]$ (0.16 g, 0.5 mmol) in hexane (20 cm^3) cooled to −10 °C. After 20 min the reaction mixture was allowed to warm to room temperature and stirred for another 2 h. The volatile material was removed *in vacuo*, and the resulting off-white solid extracted with hexane (20 cm^3), and the extract filtered, concentrated, and cooled (−20 °C) to give pale yellow crystals of (1-σ, 6—8-η-cis-2-trans-6-*octadienediyl*)(*trimethylphosphine*)*platinum* (5) (0.12 g, 63%), m.p. 90—93 °C (decomp.) (Found: C, 35.3; H, 5.6. $C_{11}H_{21}PPt$ requires C, 34.8; H, 5.6%), $\nu_{max.}$ (C=C) at 1 615m cm^{-1}. N.m.r. spectra: ^1H in C_6D_6, ^{31}P decoupled, τ 3.85 [m, 1 H, H^c, $J(H^aH^c)$ 9.9, $J(H^bH^c)$ 7.6, $J(H^cH^d)$ 9.9, $J(H^eH^c) = J(H^fH^c)$ 1.2], 5.12 [m, 1 H, H^d, $J(H^cH^d)$ 9.9, $J(H^dH^e)$ 8.8, $J(H^dH^f)$ 7.2, $J(H^aH^d)$ 1.5], 6.40 (m, 1 H, H^k), 6.78 (complex d, 1 H, H^m), 7.18 [complex t, 1 H, H^a, $J(H^aH^c)$ 9.9, $J(H^aH^b)$ 8.3, $J(H^aH^d)$ 1.5], 7.65 [complex t, 1 H, H^b, $J(H^aH^b)$ 8.3, $J(H^bH^c)$ 7.6], 7.7—8.10 (complex m, 6 H), and 8.86 [d, 9 H, PMe, $^2J(PH)$ 9.8, $^3J(PtH)$ 40.6 Hz]; ^{195}Pt (INDOR), −796.7 p.p.m. [$J(PtP)$ 4 194 Hz]; ^{13}C in C_6D_6, ^1H decoupled, 4.4 [C(1), $J(PtC^1)$ 640, $J(PC^1)$ 5], 17.1 [PMe, $J(PC)$ 34, $J(PtC)$ 61], 25.2 [C(4) and C(5)], 49.9 [C(8), $J(PtC^8)$ 56], 64.4 [C(6), $J(PtC^6)$ 44, $J(PC^6)$ 36], 108.7 [C(7), $J(PtC^7)$ 32, $J(PC^7)$ 2], 112.6 [C(3), $J(PtC^3)$ 60], and 134.2 p.p.m. [C(2), $J(PtC^2)$ 78, $J(PC^2)$ 2 Hz].

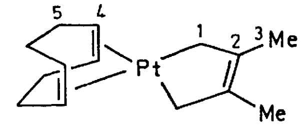


Buta-1,3-*diene with bis*(*ethylene*)(*tricyclohexylphosphine*)-*platinum.* A similar reaction between $[Pt(C_2H_4)_2\{P(C_6H_{11})_3\}]$ (0.27 g, 0.5 mmol) and excess of buta-1,3-diene in hexane (20 cm^3) gave from hexane (−20 °C) white crystals of (1-σ,6—8-η-cis-2-trans-6-*octadienediyl*)(*tricyclohexylphosphine*)*platinum* (6) (0.15 g, 52%) (Found: C, 55.1; H, 8.1. $C_{26}H_{45}PPt$ requires C, 53.5; H, 7.7%), $\nu_{max.}$ (C=C) at 1 610m cm^{-1}. N.m.r. spectra: ^1H in C_6D_6, τ 3.5 (complex q, 1 H, H^c), 4.70 (complex q, 1 H, H^d), 6.05 (m, 1 H, H^k), 6.55 (complex d, 1 H, H^m), and 7.0—9.0 (br, m); ^{13}C in C_6D_6, ^1H decoupled, 3.2 [C(1), $J(PtC^1)$ 651, $J(PC^1)$ 5], 24.7 [C(4) and C(5)], 26.9 [$P(C_6H_{11})_3$], 31.0 [$P(C_6H_{11})_3$], 49.7 [C(8), $J(PtC^8)$ 59], 66.0 [C(6), $J(PtC^6)$ 44, $J(PC^6)$ 34], 107.6 [C(7), $J(PtC^7)$ 29], 112.8 [C(3), $J(PtC^3)$ 64], and 135.1 p.p.m. [C(2), $J(PtC^2)$ 72 Hz].

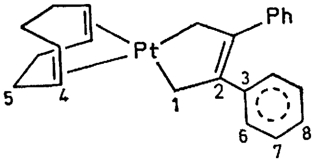
Complex (2) *with trimethylphosphine* (1 : 1).—Trimethylphosphine (0.5 mmol) was condensed (−196 °C) into a flask containing (2) (0.2 g, 0.5 mmol) in hexane. The reaction mixture was allowed to warm to room temperature with stirring. After 2 h the volatile material was removed *in vacuo*, the residue extracted with hexane (30 cm^3), and the extract filtered, concentrated, and cooled (−20 °C) to give white crystals of (5) (0.17 g, 90%), identical (i.r. and n.m.r. spectra) with that described above.

Complex (5) *with trimethylphosphine.* A solution of (5) (0.19 g, 0.5 mmol) in hexane (20 cm^3) was cooled to −196 °C and PMe_3 (0.5 mmol) condensed into the flask. Warming to room temperature followed by removal of volatiles and extraction with hexane gave from hexane (−20 °C) white crystals of (4) (0.16 g, 70%), identical (i.r. and n.m.r.) with that described above.

2,3-*Dimethylbuta*-1,3-*diene with* [Pt(cod)$_2$]. Solid [Pt(cod)$_2$] (0.2 g, 0.5 mmol) was added with stirring to a solution of 2,3-dimethylbuta-1,3-diene (0.5 cm^3, excess) in hexane (20 cm^3) at room temperature. A deep yellow solution was formed immediately. After 2 h the volatile material was removed *in vacuo*, and the deep yellow solid was extracted with hexane (20 cm^3), and the extract filtered, concentrated, and cooled (−20 °C) to give golden-yellow crystals of (*η-cyclo-octa*-1,5-*diene*)(2,3-*dimethylbut*-2-*ene*-1,4-*diyl*)*platinum* (7) (0.16 g, 84%), m.p. 95 °C (decomp.) (Found: C, 43.8; H, 6.0%; *M* 385. $C_{14}H_{22}Pt$ requires C, 43.6; H, 5.7%; *M* 385). N.m.r. spectra: ^{1}H in C_6D_6, τ 5.25 [s, 4 H, H^4, *J*(PtH) 40], 7.05 [s, 4 H, H^1, *J*(PtH) 92 Hz], 7.95 (s, 8 H, H^5), and 8.17 (s, 6 H, H^3); ^{13}C in $CDCl_3$, ^{1}H decoupled, 20.1 [C(3), *J*(PtC^3) 111], 29.6 [C(5)], 40.7 [C(1), *J*(PtC^1) 787], 96.8 [C(4), *J*(PtC^4) 52], and 136.4 p.p.m. [C(2), *J*(PtC^2) 0 Hz].



2,3-*Diphenylbuta*-1,3-*diene with bis*(*cyclo-octa*-1,3-*diene*)-*platinum*, [Pt(cod)$_2$]. A similar reaction of [Pt(cod)$_2$] (0.2 g, 0.5 mmol) with 2,3-diphenylbuta-1,3-diene (0.1 g, 0.5 mmol) in hexane gave white crystals of (*η-cyclo-octa*-1,5-*diene*)-(2,3-*diphenylbut*-2-*ene*-1,4-*diyl*)*platinum* (8) (0.23 g, 90%) (Found: C, 56.9; H, 5.4. $C_{24}H_{26}Pt$ requires C, 56.6; H, 5.1%). N.m.r. spectra: ^{1}H in $CDCl_3$, τ 2.96 (m, 10 H, C_6H_5), 4.95 [br, s with ^{195}Pt satellites, 4 H, H^4, *J*(PtH) 39], 6.80 [s, with ^{195}Pt satellites, 4 H, H^1, *J*(PtH) 86 Hz], and 7.64 (m, 8 H, H^5); ^{13}C in $CDCl_3$, ^{1}H decoupled 29.6 [C(5)], 37.5 [C(1), *J*(PtC^1) 766], 98.7 [C(4), *J*(PtC^4) 54], 125.4 [C(8)], 127.5 [C(7)], 128.8 [C(6)], 144.0 [C(3), *J*(PtC^3) 85], and 145.0 p.p.m. [C(2), *J*(PtC^2) 65 Hz].



Complex (7) *with t-butyl isocyanide*. An excess of Bu^{t}NC (0.2 cm^3) was added to a stirred solution of (7) (0.2 g, 0.5 mmol) in hexane (20 cm^3) at room temperature. The deep yellow solution immediately paled, and the volatile material was removed *in vacuo*. The resulting yellow solid was extracted with hexane (20 cm^3), the extract filtered, concentrated, and cooled (−20 °C) to give pale yellow crystals of (2,3-*dimethylbut*-2-*ene*-1,4-*diyl*)*bis*(*t-butyl isocyanide*)-*platinum* (9) (0.19 g, 85%), m.p. 85 °C (Found: C, 43.6; H, 6.5; N, 6.2%; *M* 443. $C_{16}H_{28}N_2Pt$ requires C, 43.3; H, 6.3; N, 6.3%; *M* 443), $\nu_{max.}$(NC) at 2 180s and 2 140s cm^{-1}. N.m.r. spectra: ^{1}H in C_6D_6, τ 6.82 [s, 4 H, H^1, *J*(PtH) 68 Hz], 8.95 (s, 6 H, H^3), and 9.05 (s, 18 H, Bu^{t}NC); ^{13}C in C_6D_6, ^{1}H decoupled, 21.4 [C(3), *J*(PtC^3) 96], 29.7 [(CH_3)$_3$-CNC], 30.9 [C(1), *J*(PtC^1) 609], 56.0 [(CH_3)$_3$*C*NC], and 136.2 p.p.m. [C(2), *J*(PtC^2) 46 Hz].

Crystal-structure Determinations.—Crystals of complex (4) grow as almost transparent prisms from diethyl ether, but become cloudy and darken to yellow on prolonged exposure to air. Accordingly, the crystal used for data collection, *ca*. 0.25 × 0.15 × 0.35 mm, was enclosed in a Lindemann glass capillary. Intensity data were collected at 213 K on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 60°$ using methods described earlier.[19] Of a total of 5 218 reflections, 4 925 were deemed independently observable for $I \geqslant 2\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measured intensity based on counting statistics. Only the observed data, corrected for Lorentz and polarisation effects and for *X*-ray absorption, were used in solution and refinement of the structure.

Crystal data. $C_{14}H_{30}P_2Pt$, $M = 455.5$, Triclinic, space group $P\bar{1}$, $a = 9.197(3)$, $b = 11.283(4)$, $c = 9.555(6)$ Å, $\alpha = 87.10(4)$, $\beta = 118.14(3)$, $\gamma = 98.89(3)°$, $U = 863.5(7)$ Å^3, $D_m = 1.74$, $Z = 2$, $D_c = 1.75$ g cm^{-3}, $F(000) = 444$, Mo-K_α *X*-radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-K_α) = 87.1 cm^{-1}.

Crystals of (2) grow from hexane as colourless prisms elongated along *a* in a twinned form. Twinning occurred in all the specimens examined, including those grown from different solvents. Intensity data were collected at 298 K in the range $2.9 \leqslant 2\theta \leqslant 50°$. Of a total of 2 868 reflections, 1 464 were deemed observable for $I \geqslant 2\sigma(I)$ after correction for Lorentz and polarisation effects.

Crystal data. $C_{16}H_{24}Pt$, $M = 411.5$, Monoclinic, space group $P2_1/n$, $a = 9.082(6)$, $b = 10.554(13)$, $c = 15.293(17)$ Å, $\beta = 92.13(7)°$, $U = 1\ 464(2)$ Å^3, $D_m = 1.86$, $Z = 4$, $D_c = 1.87$ g cm^{-3}, $F(000) = 792$, Mo-K_α *X*-radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-K_α) = 100.9 cm^{-1}.

Complexes (3) and (5) were also investigated at 220 K. For (3) 3 129 reflections met the criterion $I \geqslant 3\sigma(I)$, while for (5) 1 285 data were deemed observable for $I \geqslant 2\sigma(I)$.

Crystal data. $C_{18}H_{30}N_2Pt$ (3), $M = 469$, space group $P2_1/n$, $a = 9.032(13)$, $b = 12.204(15)$, $c = 18.923(20)$ Å, $\beta = 99.96(9)°$, $U = 2\ 054(4)$ Å^3, $D_m = 1.51$, $Z = 4$, $D_c = 1.52$ g cm^{-3}, $F(000) = 920$, Mo-K_α *X*-radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-K_α) = 67.9 cm^{-1}.

$C_{11}H_{21}PPt$ (5), $M = 379$, space group *Pnam*, $a = 15.979(15)$, $b = 9.017(24)$, $c = 8.992(7)$ Å, $U = 1\ 296(4)$ Å^3, $D_m = 1.93$, $Z = 4$, $D_c = 1.95$ g cm^{-3}, $F(000) = 720$, Mo-K_α *X*-radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-K_α) = 114.7 cm^{-1}.

Structure solutions and refinement. For (4) the molecular structure was solved from electron-density difference syntheses following location of the phosphorus and platinum atoms from a Patterson synthesis. Refinement was accomplished by blocked-matrix least squares, with all the non-hydrogen atoms having anisotropic thermal parameters. Weights were applied according to the scheme $1/w = \sigma(F_o) + \alpha(F_o)$, where $\alpha = 0.016$ and $\sigma(F_o)$ is the estimated standard deviation in $|F_{obs.}|$ based on counting statistics only. This gave a satisfactory weighting analysis with the refinement converging at *R* 0.052 (*R′* 0.062) for the 4 925 independent intensities with a mean shift-to-error ratio for the last cycles of 0.05 : 1 and a maximum of 0.25 : 1. The final electron-density difference synthesis showed some residual density around the platinum atom, but elsewhere no peaks >0.8 or < −0.6 e Å^{-3}.

Data for (2) were refined by full-matrix least squares, using anisotropic thermal parameters for the platinum atom only, and applying various tests to the data in an attempt to minimise errors arising from crystal twinning. The results in Table 1 correspond to a refinement (870 reflections) with $\sin\theta_{max.} = 0.45$ since the effect on the data of twinning was shown to increase with Bragg angle (θ). Refinement ceased at *R* 0.111 (*R′* 0.147) with a weighting scheme of $1/w = \sigma(F_o)$.

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[19] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

For both complexes (2) and (4), atomic scattering factors used were those of ref. 20 for Pt and P, ref. 21 for C, and ref. 22 for H. Corrections for the effects of anomalous dispersion were applied for Pt ($\Delta f' = -2.352$, $\Delta f'' = 8.388$) and P atoms ($\Delta f' = 0.090$, $\Delta f'' = 0.095$). The atomic co-ordinates are given in Tables 3 and 4, and equations of some least-squares planes in Tables 5 and 6. Observed and calculated structure factors for complexes (2) and (4) are listed in Supplementary Publication No. SUP 22331 (33 pp.).* Also deposited for complex (4) are final positional (fractional co-ordinates) and isotropic temperature parameters for the hydrogen atoms, bond lengths and angles involving hydrogen atoms, and anisotropic temperature parameters.

TABLE 3

Final positional (fractional co-ordinates) for complex (4)

Atom	x	y	z
Pt	0.146 86(2)	0.251 92(2)	0.018 96(2)
P(1)	0.404 5(2)	0.267 9(1)	0.241 3(2)
P(2)	−0.001 3(2)	0.166 9(1)	0.145 3(2)
C(101)	0.417 8(11)	0.326 1(7)	0.423 1(8)
C(102)	0.505 0(10)	0.133 6(7)	0.308 0(10)
C(103)	0.571 4(9)	0.374 3(7)	0.231 0(9)
C(201)	0.084 5(10)	0.051 8(6)	0.289 2(8)
C(202)	−0.210 5(9)	0.086 2(6)	0.023 9(9)
C(203)	−0.041 3(11)	0.274 6(6)	0.256 4(9)
C(1)	0.257 1(8)	0.321 5(5)	−0.127 6(7)
C(11)	0.335 0(9)	0.222 7(6)	−0.148 7(9)
C(12)	0.286 7(12)	0.160 5(7)	−0.286 0(10)
C(2)	0.127 7(9)	0.369 4(6)	−0.280 8(7)
C(3)	−0.039 9(9)	0.290 5(6)	−0.332 1(7)
C(4)	−0.077 1(8)	0.275 3(5)	−0.190 3(7)
C(41)	−0.124 3(8)	0.385 7(6)	−0.155 4(7)
C(42)	−0.257 5(10)	0.396 6(7)	−0.140 6(10)

TABLE 4

Final positional parameters (fractional co-ordinates) for complex (2)

Atom	x	y	z
Pt	0.257 0(2)	0.175 6(1)	1.039 1(1)
C(1)	0.247(6)	0.270(4)	0.918(3)
C(11)	0.319(5)	0.396(4)	0.911(2)
C(12)	0.244(6)	0.508(4)	0.907(2)
C(2)	0.289(4)	0.172(4)	0.841(2)
C(3)	0.215(5)	0.041(3)	0.868(2)
C(4)	0.280(4)	0.012(3)	0.962(2)
C(41)	0.193(4)	−0.092(3)	0.993(2)
C(42)	0.284(6)	−0.190(4)	1.029(3)
C(5)	0.352(4)	0.067(3)	1.160(2)
C(6)	0.195(5)	0.087(3)	1.172(3)
C(7)	0.117(4)	0.165(3)	1.222(2)
C(8)	0.076(4)	0.294(3)	1.173(2)
C(9)	0.173(4)	0.343(3)	1.113(2)
C(10)	0.326(4)	0.349(3)	1.120(2)
C(13)	0.410(5)	0.308(4)	1.207(2)
C(14)	0.464(5)	0.172(4)	1.198(2)

Data for complexes (3) and (5), treated as above, gave *R* 0.126 (*R′* 0.157) and *R* 0.062 (*R′* 0.054), respectively, but because in the former case the crystal underwent decomposition in the *X*-ray beam, even at 220 K, and in the latter the crystal was disordered, only the gross molecular structures were established (see Discussion section).

TABLE 5

Equations of least-squares planes for complex (4) in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates. Deviations (Å) of atoms from a plane are given in square brackets

Plane (1)

Pt, P(1), P(2), C(1), C(4)

$$-2.928x + 10.730y + 3.393z = 2.386$$

[Pt −0.05, P(1) 0.12, P(2) −0.10, C(1) −0.12, C(4) 0.15, C(11) −1.48, C(12) −2.47, C(41) 1.59, C(42) 2.15, C(2) 0.25, C(3) −0.28]

Plane (2)

Pt, P(1), P(2)

$$-3.431x + 10.740y + 3.203z = 2.262$$

Plane (3)

Pt, C(1), C(4)

$$-2.127x + 10.676y + 3.469z = 2.443$$

Plane (4)

C(1), C(11), C(12)

$$6.530x + 6.247y - 5.132z = 4.342$$

Plane (5)

C(4), C(41), C(42)

$$0.702x - 2.208y + 7.947z = -2.174$$

Dihedral angles (°)

Plane	(2)	(4)	(5)
(1)		70.6	86.8
(3)	10.3	67.6	83.3

TABLE 6

Equations of least-squares planes for complex (2) in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates. Deviations (Å) of atoms from a plane are given in square brackets

Plane (1)

Pt, C(1), C(4), C(516), C(910)

$$9.044x + 0.933y - 0.248z = 2.269$$

[Pt −0.04, C(1) −0.01, C(4) 0.03, C(516) −0.01, C(910) 0.03, C(11) 0.76, C(12) 0.19, C(41) −0.86, C(42) −0.13, C(3) −0.50, C(2) −0.01]

Plane (2)

Pt, C(516), C(910)

$$9.062x + 0.694y - 0.634z = 1.792$$

Plane (3)

Pt, C(1), C(4)

$$9.015x + 1.180y + 0.148z = 2.678$$

Plane (4)

C(1), C(11), C(12)

$$0.304x + 0.730y + 15.218z = 14.250$$

Plane (5)

C(4), C(41), C(42)

$$-0.530x + 4.547y + 13.796z = 13.182$$

Dihedral angles (°)

Plane	(2)	(4)	(5)
(1)		86.5	89.9
(3)	3.95	85.0	88.1

Computational work was carried out using the ' *X*-Ray ' system of programs at the University of London Computing Centre.[23]

We thank the S.R.C. for support.

[8/199 *Received, 7th February*, 1978]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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