Alkyne Complexes of Platinum. Part 6.[1] The Synthesis of Compounds containing Platinacyclopenta-2,4-diene and Diplatinacyclohexa-2,5-diene Rings

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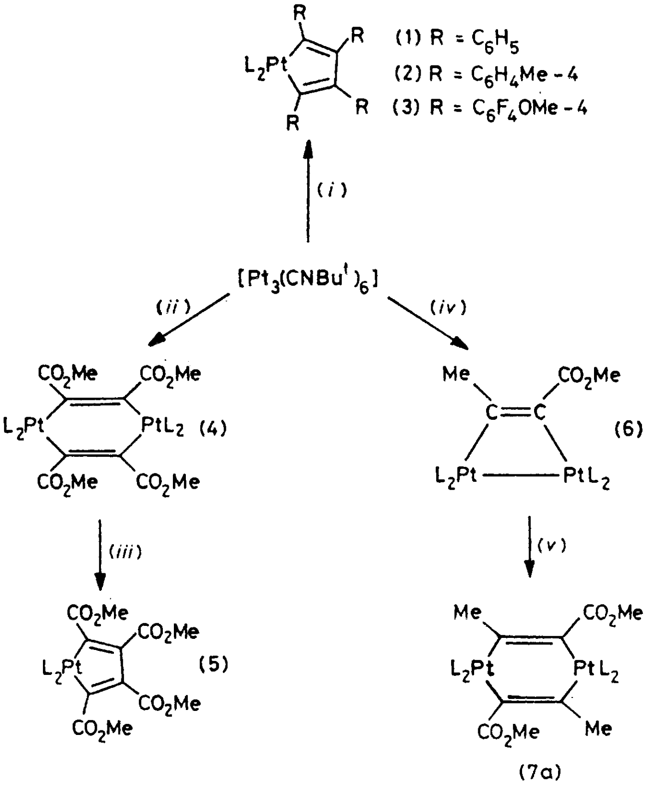
The triplatinum compound $[Pt_3(CNBu^t)_6]$ reacts with the alkynes $RC\equiv CR$ (R = Ph, C_6H_4Me-4, or C_6F_4OMe-4) in toluene at 100 °C to give platinacyclopenta-2,4-diene complexes $[Pt\{C(R)=C(R)C(R)=C(R)\}(CNBu^t)_2]$, and with $C_2(CO_2Me)_2$ at 40 °C to afford the diplatinacyclohexa-2,5-diene compound $[Pt\{C(CO_2Me)=C(CO_2Me)PtC(CO_2Me)=C(CO_2Me)\}(CNBu^t)_4]$. Bis(cyclo-octa-1,5-diene)platinum reacts with $RC\equiv CR$ (R = C_6F_4OMe-4 or CO_2Me) to afford the compounds $[Pt\{C(R)=C(R)C(R)=C(R)\}(cod)]$ (cod = cyclo-octa-1,5-diene). The unsymmetrical alkyne $MeC\equiv CCO_2Me$ reacts at 25 °C with $[Pt_3(CNBu^t)_6]$ to give $[Pt\{C(Me)=C(CO_2Me)PtC(Me)=C(CO_2Me)\}(CNBu^t)_4]$, and with $[Pt(cod)_2]$ to yield a mixture of platinacyclopentadiene isomers $[Pt\{C(R^2)=C(R^3)C(R^4)=C(R^5)\}(cod)]$ ($R^2 = R^4 = Me$, $R^3 = R^5 = CO_2Me$; $R^2 = R^5 = CO_2Me$, $R^3 = R^4 = Me$). At 100 °C in toluene, the compound $[Pt(RC_2R)(cod)]$ (R = C_6F_4OMe-4) affords $[Pt\{C(R)=C(R)C(R)=C(R)\}(cod)]$, whereas in acetone at ambient temperatures it is slowly converted into $[Pt\{C(R)=C(R)PtC(R)=C(R)\}(cod)_2]$. The latter in hot toluene affords the platinacyclopenta-2,4-diene derivative and platinum metal. Moreover, treatment of $[Pt\{C(R)=C(R)PtC(R)=C(R)\}(CNBu^t)_4]$ (R = CO_2Me) with $C_2(CO_2Me)_2$ affords $[Pt\{C(R)=C(R)C(R)=C(R)\}(CNBu^t)_2]$ in high yield. Hydrogen-1 and ^{13}C n.m.r. data for the new compounds are reported, and the observed interconversion of the various metallacycles is discussed.

THE ability of low-valent transition-metal complexes to react with alkynes to afford products containing metallacyclopenta-2,4-diene rings $MC(R)=C(R)C(R)=C(R)$ has long been known, and such species have been implicated in the catalytic trimerisation of alkynes.[2] The earliest examples of such metallacycles emerged from studies on reactions of iron carbonyls with alkynes,[3] but the majority have been prepared by employing rhodium,[4-6] iridium,[7] palladium,[8,9] and ruthenium [10,11] complexes as precursors. Two other classes of metallacycle have been obtained *via* reaction of alkynes with low-valent metal complexes, and these are illustrated by *cis,trans,cis*-$[M\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}L_2]$ [M = Ni, L = $P(OMe)_3$ or $AsMe_2Ph$; M = Pt, L = PEt_3 or L_2 = dppe] [dppe = 1,2-bis(diphenylphosphino)ethane],[12] and $[Ir\{C(CF_3)=C(CF_3)IrC(CF_3)=C(CF_3)\}(NO)_2(PPh_3)_2]$.[13] Reaction of hexakis(trifluoromethyl)benzene with $[Pt_3(CNBu^t)_6]$ or $[Pt(trans\text{-}PhCH=CHPh)(PMe_3)_2]$ affords the *cis,cis,cis*-$[Pt\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}L_2]$ (L = $CNBu^t$ or PMe_3)[14] complexes in which the seven-membered ring adopts a different stereochemistry from that found in the products from the reaction with $CF_3C\equiv CCF_3$.[12] With an excess of $CF_3C\equiv CCF_3$, $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) forms a triplatinum spiro-complex containing a dimetallacyclobutene and a 1,4-dimetallacyclo-2,5,7-triene ring system.[15] A diplatinum compound $[Pt\{C(CF_3)=C(CF_3)PtC(CF_3)=C(CF_3)\}(cod)_2]$ with a dimetallacyclohexa-2,5-diene ring analogous to the above iridium compound has also been prepared.[15] Although metallacycloheptatriene compounds have been invoked [2] as possible intermediates in the catalytic cyclo-tetramerisation of alkynes, the role of the dimetallacyclohexa-2,5-diene species in catalytic reactions has not hitherto been considered. Herein we present evidence that the latter species as well as dimetallacyclobutene complexes may well be involved in pathways to metallacyclopenta-2,4-dienes.

RESULTS AND DISCUSSION

We have previously reported that the triplatinum complex $[Pt_3(CNBu^t)_6]$ reacts at room temperature with three equivalents of $PhC\equiv CPh$ to give the η^2-alkyne compound $[Pt(PhC_2Ph)(CNBu^t)_2]$ in high yield.[16] However, if this reaction is carried out with excess of the alkyne under more vigorous conditions the platinacyclopenta-2,4-diene compound (1) (Scheme 1) is obtained, characterised by microanalysis (Table 1) and by n.m.r. spectroscopy (Table 2). Clearly the pathway to (1) involves initial formation of $[Pt(PhC_2Ph)(CNBu^t)_2]$, the transformation from a metallacyclopropene to a metallacyclopentadiene system with excess of alkyne being well delineated.[2,7] The ^{13}C n.m.r. spectrum of (1) establishes the structure. A resonance at δ 155.4 p.p.m. may be assigned to the two carbon atoms σ bonded to platinum, because this signal shows ^{195}Pt satellites with $J(PtC)$ of 880 Hz.[17] The remaining two carbon atoms of the penta-2,4-diene ring give rise to a resonance at 159.3 p.p.m., with $J(PtC)$ 111 Hz. Complexes (2) and (3) were prepared in a similar manner to (1), by treating $[Pt_3(CNBu^t)_6]$ with the alkynes 4,4'-$MeC_6H_4C\equiv CC_6H_4Me$ and 4,4'-$MeOC_6F_4C\equiv CC_6F_4OMe$, respectively.

In order to produce (1)—(3) at a reasonable rate it was necessary to heat the reactants. In contrast, [$Pt_3(CNBu^t)_6$] and $MeO_2CC{\equiv}CCO_2Me$ react at room temperature to give the diplatinacyclohexa-2,5-diene complex (4) (Scheme 1). The presence of two platinum atoms in (4) was clearly demonstrated by the pattern of signals in the ^{13}C n.m.r. spectrum (Table 2). Both the olefinic and the carboxyl carbon atoms show double $^{195}Pt{-}^{13}C$ satellites on their respective resonances. Dimetallacyclohexadiene complexes such as (4) have hitherto been rare; however, *X*-ray crystallographic studies on the above mentioned [$Ir\{C(CF_3){=}C(CF_3)IrC(CF_3){=}C(CF_3)\}(NO)_2(PPh_3)_2$] and [$Pt\{C(CF_3){=}C(CF_3)PtC(CF_3){=}C(CF_3)\}(cod)_2$] have confirmed the nature of these species and revealed a ' boat ' conformation for the dimetalla-ring system.[13,15,18]



SCHEME 1 Reactions of [$Pt_3(CNBu^t)_6$] with alkynes; L = $CNBu^t$. (*i*) $RC{\equiv}CR$ in toluene at 100 °C; (*ii*) $C_2(CO_2Me)_2$ in thf at 25 °C; (*iii*) excess $C_2(CO_2Me)_2$ in thf at 40 °C; (*iv*) $MeC{\equiv}CCO_2Me$ in toluene–light petroleum at 25 °C for 0.5 h; (*v*) in toluene–light petroleum after 8 h

Complex (4) reacts with excess of $MeO_2CC{\equiv}CCO_2Me$ under mild conditions to give the platinacyclopentadiene compound (5) (Scheme 1). It is interesting to note that the violet complex [$Fe_3\{\mu\text{-}(\sigma\text{-}PhC_2Ph)_2\}(CO)_8$], obtained from [$Fe_3(CO)_{12}$] and $PhC{\equiv}CPh$ and which contains a diferracyclohexa-2,5-diene ring, rearranges in boiling benzene to a black isomer having a ferracyclopentadiene ring system.[19-21]

Compounds (1)—(5) are all derived from symmetrically substituted alkynes, and it was of interest to investigate a reaction of [$Pt_3(CNBu^t)_6$] with an unsymmetrical alkyne. Treatment of the triplatinum compound with three equivalents of $MeC{\equiv}CCO_2Me$ afforded after 0.5 h a pale yellow precipitate of the diplatinacyclobutene complex (6).[22] Further reaction afforded a diplatinacyclohexa-2,5-diene complex (7), in high yield. There are three isomeric forms of (7): that shown, (7a) (Scheme 1), [$Pt\{C(CO_2Me){=}C(Me)PtC(Me){=}C(CO_2Me)\}(CNBu^t)_4$] (7b), and [$Pt\{C(Me){=}C(Me)PtC(CO_2Me){=}C(CO_2Me)\}(CNBu^t)_4$] (7c). The ^1H and ^{13}C n.m.r. spectra (Table 2), with double ^{195}Pt satellites on the acetylenic methyl resonance, do not distinguish between the isomers. However, measurement of the ^{195}Pt n.m.r. spectrum revealed only one signal at δ 362 p.p.m., thus eliminating structure (7b). Isomer (7c) is most unlikely to be formed, hence structure (7a) is assigned to the product.

Earlier we have reported [16] reactions of [$Pt(cod)_2$] with alkynes which give two types of product [$Pt(alkyne)_2$] and [$Pt(alkyne)(cod)$]. We now describe reactions of [$Pt(cod)_2$] with alkynes which afford metallacycles. With excess 4,4'-$MeOC_6F_4C{\equiv}CC_6F_4OMe$ and $MeO_2CC{\equiv}CCO_2Me$, the compound [$Pt(cod)_2$] affords the platinacyclopenta-2,4-diene complexes (8) and (9) (Scheme 2). As in the corresponding reactions between [$Pt_3(CNBu^t)_6$] and these alkynes, the ring system with the CO_2Me substituents forms most readily. Compounds (8) and (9) react with $CNBu^t$ to give (3) and (5), respectively, and these species were characterised in the usual manner (Tables 1 and 2). Thus the five-membered ring system in (9) was readily identified from the ^{13}C n.m.r. spectrum by the two resonances at δ 154.8 p.p.m. [J(PtC) 1 096] and 148.7 [J(PtC) 84 Hz].

Interestingly, ^1J(PtC) for the ring-carbon atoms bound directly to platinum in (9) is *ca.* 200 Hz greater than that found for these carbon atoms in (1) and (2) (Table 2). This difference evidently arises from the bonding properties of the cod ligand in (9) since in the ^{13}C n.m.r. spectrum of the isocyanide complex (5), ^1J(PtC) is 893 Hz, a similar value to that found in the spectra of (1) and (2). This pattern of $^{195}Pt{-}^{13}C$ coupling has been observed previously among the complexes [$Pt(PhC_2Ph)L_2$] (L = PR_3 or $CNBu^t$, L_2 = cod).[16]

In order to establish whether a reaction between [$Pt(cod)_2$] and an alkyne to give metalla-ring compounds was regioselective the behaviour of $MeC{\equiv}CCO_2Me$ was investigated. Examination of the ^{13}C n.m.r. spectrum of the mixture obtained using excess of $MeC{\equiv}CCO_2Me$ revealed the presence of two isomeric platinacyclopentadienes in *ca.* 2 : 1 proportions. The major isomer * observed in solution was assigned the head-to-tail structure (10a) on the basis of the character of the

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* Crystallisation afforded only the minor isomer, and in approximately 50% yield. This is a larger yield than would have been expected from the n.m.r. observations on the product mixture in solution, and implies that rearrangement of metallacyclopentadienes can occur. Preliminary results on the system [$Pt_3(CNBu^t)_6$]–$Pr^iC{\equiv}CH$ have shown that isomerisation occurs in polar solvents.

TABLE 1

Analytical [a] and physical data for the complexes

Complex	M.p. (θ_c/°C)	Colour	Yield (%)	Analysis (%) C	H	N
(1) [b]	325 (decomp.) [c]	Orange	90	63.7 (63.6)	5.6 (5.3)	4.0 (3.9)
(2)	186	Orange	74	64.8 (65.2)	6.3 (6.0)	3.6 (3.6)
(3)	224—226	Yellow-green	2 [d]	44.8 (44.5)	2.7 (2.7)	2.5 (2.3)
(4) [e]	>174 (decomp.)	White	57	38.1 (38.2)	5.0 (5.6)	5.4 (5.6)
(5)	133—134	Yellow-green	81	40.7 (40.9)	4.8 (4.7)	4.4 (4.3)
(7)	96—98 (decomp.)	Pale yellow	93	38.5 (39.1)	5.5 (5.4)	5.5 (5.7)
(8)	253—255	Yellow-green	55	44.8 (45.0)	2.3 (2.3)	
(9)	154	Yellow-green	68	40.8 (40.9)	4.2 (4.1)	
(10)	138	Yellow	48	43.1 (43.3)	5.0 (4.8)	
(14)	210—212	Pale yellow	67	41.8 (42.0)	2.9 (2.7)	
(15)	>300	Pale yellow	73	41.6 (42.0)	3.0 (3.2)	3.8 (3.8)

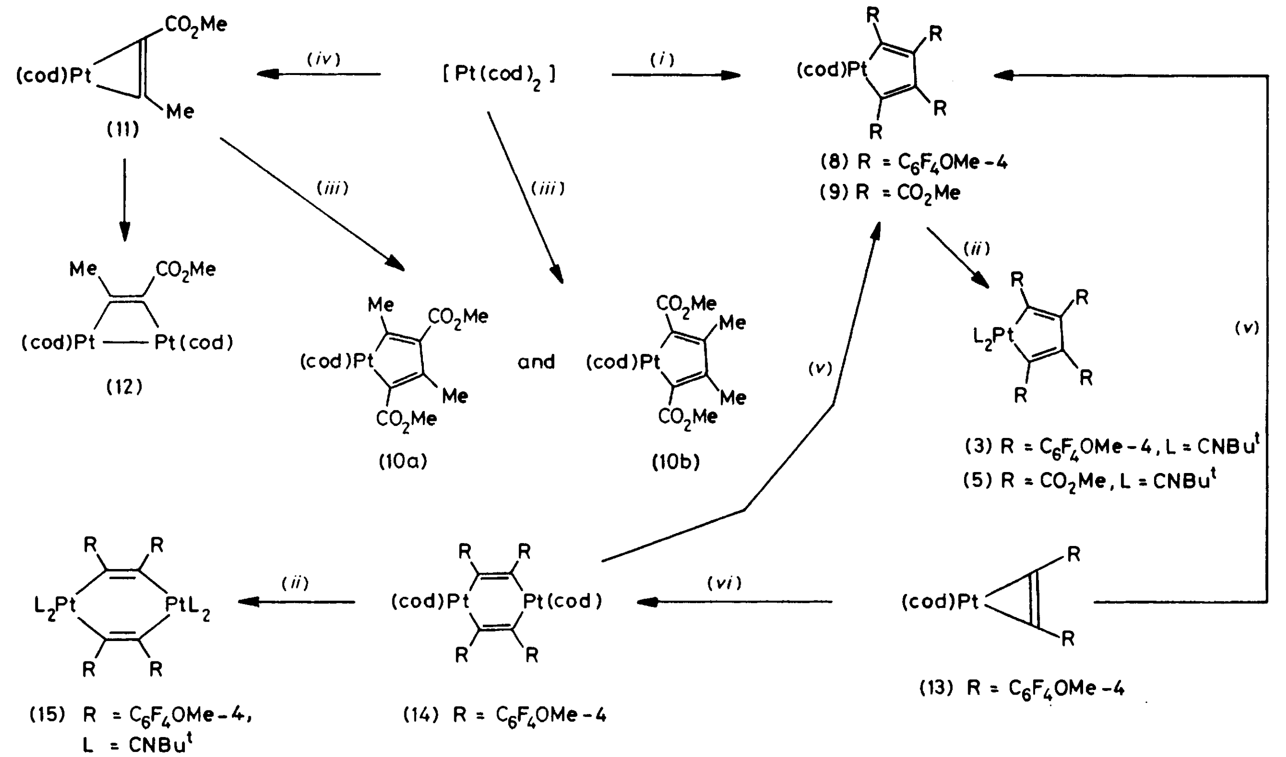
[a] Calculated values are given in parentheses. [b] *M* (osmometric), 721 (718). [c] Turns yellow >210 °C. [d] 85% yield from (8) and CNBu^t. [e] *M* (osmo metric), 1 181 (1 007).

TABLE 2

Hydrogen-1 and carbon-13 n.m.r. data [a]

Complex	^{1}H [b]	^{13}C [c]
(1)	2.98—3.28 (m, 20 H, Ph), 8.88 (s, 18 H, Bu^t)	159.3 [*C*=CPt, ^{2}J(PtC) 111], 155.4 [C=*C*Pt, ^{1}J(PtC) 880], 152.5 [α-C (Ph), *J*(PtC) 53], 141.6 [α-C (Ph), *J*(PtC) 73], 130.6 [β-C (Ph)], 128.3 [β-C (Ph), *J*(PtC) 21], 126.7 [γ-C (Ph)], 126.1 [γ-C (Ph)], 124.0 [δ-C (Ph)], 122.9 [δ-C (Ph)], 57.0 (*C*Me$_3$), 29.5 (Me)
(2)	3.13 [m, AA′BB′, 8 H, C$_6$H$_4$, ^{3}J(HH) 8], 3.40 (s, 8 H, C$_6$H$_4$), 7.82 [s, 6 H, Me, ^{7}J(PtH) 5.5], 7.96 (s, 6 H, Me), 8.89 (s, 18 H, Bu^t)	159.0 [*C*=CPt, ^{2}J(PtC) 116], 155.0 [C=*C*Pt, ^{1}J(PtC) 882], 149.8 [α-C (C$_6$H$_4$Me), *J*(PtC) 53], 138.8 [α-C (C$_6$H$_4$Me), *J*(PtC) 73], 132.6 [δ-C (C$_6$H$_4$Me)], 131.4 [δ-C (C$_6$H$_4$Me)], 130.4 [β-C (C$_6$H$_4$Me)], 128.3 [β-C (C$_6$H$_4$Me), *J*(PtC) 26], 127.4 [γ-C (C$_6$H$_4$Me)], 126.8 [γ-C (C$_6$H$_4$Me)], 56.7 (*C*Me$_3$), 29.4 (C*Me*$_3$), 21.1 (Me), 20.9 (Me)
(3)	6.02 (m, 6 H, OMe), 6.05 (m, 6 H, OMe), 8.67 (s, Bu^t)	
(4)	6.39 (s, 12 H, OMe), 8.51 (s, 36 H, Bu^t)	174.8 [*C*O$_2$Me, *J*(PtC) 114, 49], 154.3 [*C*O$_2$Me, *J*(PtC) 850, 17], 130.8 [*C*NBu^t, ^{1}J(PtC) 980], 56.8 (*C*Me$_3$), 51.1 (OMe), 30.0 (C*Me*$_3$)
(5)	6.26 (s, 6 H, OMe), 6.31 (s, 6 H, OMe), 8.41 (s, 18 H, Bu^t)	175.3 [*C*O$_2$Me, *J*(PtC) 58], 165.8 [*C*O$_2$Me, *J*(PtC) 93], 154.3 [C=*C*Pt, ^{1}J(PtC) 893], 148.5 [*C*=CPt, ^{2}J(PtC) 84], 130 [t, *C*NBu^t, ^{1}J(NC) 17, ^{1}J(PtC) 1 044], 58.3 (*C*Me$_3$), 51.3 (OMe), 51.1 (OMe), 30.0 (Me)
(7) [d,e]	6.37 (s, 6 H, OMe), 7.59 [s, 6 H, Me, ^{3}J(PtH) 56, ^{4}J(PtH) 11], 8.53 (s, 36 H, Bu^t)	174.3 (CO$_2$Me), 171.1, 171.0 (*C*Me, *C*O$_2$Me), 56.5 (*C*Me$_3$), 56.3 (*C*Me$_3$), 50.2 (OMe), 32.3 [Me, *J*(PtC) 98, 110], 30.2 (C*Me*$_3$), 30.1 (C*Me*$_3$)
(8)	5.18 [s, 4 H, CH, ^{2}J(PtH) 42], 5.96 (m, 6 H, OMe), 6.03 (m, 6 H, OMe), 7.55 (s, br, 8 H, CH$_2$)	
(9)	4.46 [s, 4 H, CH, ^{2}J(PtH) 46], 6.25 (s, 6 H, OMe), 6.30 (s, 6 H, OMe), 7.49 (s, br, 8 H, CH$_2$)	172.2 [*C*O$_2$Me, *J*(PtC) 70], 165.1 [*C*O$_2$Me, *J*(PtC) 107], 154.8 [C=*C*Pt, ^{1}J(PtC) 1 096], 148.7 [*C*=CPt, ^{2}J(PtC) 98], 108.8 [CH, ^{1}J(PtC) 66], 51.7 (OMe), 51.4 (OMe), 30.3 (CH$_2$)
(10) [f]	4.71 [s, 4 H, CH, ^{2}J(PtH) 42], 6.30 (s, 6 H, OMe), 7.59 (s, 8 H, CH$_2$), 8.27 [s, 6 H, Me, ^{4}J(PtH) 8]	[g] 174.3 [*C*O$_2$Me, *J*(PtC) 84], 168.1 [*C*O$_2$Me, *J*(PtC) 128], 164.9 [C=*C*Pt, ^{1}J(PtC) 1 085], 156.1 [*C*=CPt, *J*(PtC) 103], 149.4 [*C*=CPt, *J*(PtC) 159], 145.3 [C=*C*Pt, ^{1}J(PtC) 1 113], 109.4 [CH, ^{1}J(PtC) 44], 102.5 [CH, ^{1}J(PtC) 73], 51.0 (OMe), 30.2 (CH$_2$), 30.1 (CH$_2$), 22.6 [Me, *J*(PtC) 96], 17.1 [Me, *J*(PtC) 79] [h] 173.7 [*C*O$_2$Me, *J*(PtC) 76], 157.4 [*C*=CPt, ^{2}J(PtC) 99], 145.8 [C=*C*Pt, ^{1}J(PtC) 1 070], 105.4 [CH, ^{1}J(PtC) 66], 50.7 (OMe), 30.4 (CH$_2$), 17.4 [Me, *J*(PtC) 85]
(14)	4.32 [m, br, 4 H, CH, ^{2}J(PtH) 36], 5.22 [m, br, 4 H, CH, ^{2}J(PtH) 36], 5.98 (m, 12 H, OMe), 7.41 (s, br, 8 H, CH$_2$), 7.76 (s, br, 8 H, CH$_2$)	
(15)	6.06 (s, 12 H, OMe), 8.58 (s, 36 H, Bu^t)	

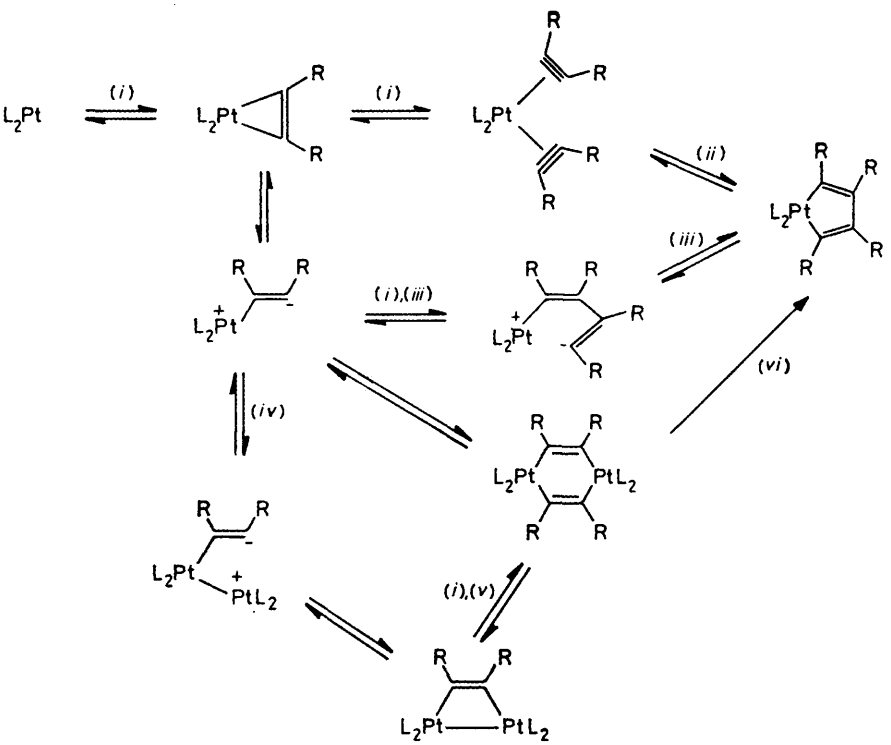
[a] Measured in [^{2}H$_1$]chloroform at 25 °C, coupling constants in Hz. [b] Chemical shifts in τ. [c] Hydrogen-1 decoupled, chemical shifts in p.p.m. to high frequency of SiMe$_4$, resonances are singlets unless otherwise stated. [d] Toluene solvate with ^{1}H resonances at τ 2.8 and 7.64, and ^{13}C signals at δ 138.6, 128.9, 128.2, 125.3, and 21.4 p.p.m. [e] Platinum-195 n.m.r. ([^{2}H$_1$]chloroform, −20 °C), δ 362 p.p.m. [f] Platinum-195 n.m.r. {[^{2}H$_1$]chloroform, −30 °C, to high frequency of $\Xi(^{195}\text{Pt}) = 21.4$ MHz}, δ 519 [major isomer, (10a)], 478 p.p.m. [minor isomer, (10b)]. [g] Major isomer (10a), as determined from measurement of n.m.r. spectrum (see text). [h] Minor isomer (10b).



SCHEME 2 Formation of (cyclo-octa-1,5-diene)platinum–cyclopenta-2,4-diene and –cyclohexa-2,5-diene complexes. (*i*) RC≡CR (R = C_6F_4OMe-4, in toluene at 100 °C; R = CO_2Me, in thf at 40 °C); (*ii*) $CNBu^t$; (*iii*) excess $MeC{\equiv}CCO_2Me$ in thf at −30 °C and then at 25 °C; (*iv*) equimolar $MeC{\equiv}CCO_2Me$ in $[^2H_1]$chloroform at −40 to −30 °C; (*v*) in toluene at 100 °C; (*vi*) in acetone, rearrangement slow at 25 °C

^{13}C n.m.r. signals, *viz.* the expected resonances for pairs of non-equivalent CO_2Me and Me ring-substituents, and four peaks for the ring-carbon atoms. The minor isomer had a less complicated spectrum and is assigned structure (10b) since calculations [23] suggest that if the reaction were controlled entirely by electronic factors this isomer would be expected to be the only product. In order to shed light on the mode of formation of (10), synthesis of the isomers was monitored by ^{195}Pt n.m.r. spectroscopy, employing an equimolar mixture of $[Pt(cod)_2]$ and $MeC{\equiv}CCO_2Me$ in $[^2H_1]$chloroform at −40 °C, followed by slowly warming to −30 °C. Initially, a single ^{195}Pt resonance was observed at δ 756 p.p.m. which can be ascribed to the η^2-complex (11) (Scheme 2). After 0.5 h at −30 °C the intensity of this signal decreased and resonances assignable to four other ^{195}Pt environments appeared. Two peaks seen at δ 696 and 650 p.p.m., respectively, were related by a ^{195}Pt–^{195}Pt coupling (7 000 ± 50 Hz) which suggested the presence of a molecule with a strong Pt–Pt bond,[24] as would be expected for a diplatinacyclobutene complex $[Pt_2\{\mu\text{-}(\sigma\text{-}MeC_2CO_2Me)\}(cod)_2]$, (12).[25] The other two resonances at 519 and 478 p.p.m. are due to the isomers (10a) and (10b), respectively. The relative 2 : 1 proportions of these two species were the same as when the reaction was conducted at ambient temperatures. After 3 h at −30 °C the signal ascribed to (11) had further decreased in intensity. On warming to 0 °C, decomposition of the transient species (11) and (12) occurred. Possible steps in the formation of (10) from $[Pt(cod)_2]$ are discussed later, in the context of the above observations, and in relation to results described below concerning formation of other platinacycles (Scheme 3).

When a toluene solution of $[Pt(4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)(cod)]$ (13)[16] was heated at 100 °C it decomposed to give a black solid, presumably platinum, and the platinacyclopentadiene complex (8) (Scheme 2). In other experiments solutions of (13) in $[^2H_6]$acetone were allowed to stand at room temperature and the ^1H n.m.r. spectrum measured at intervals. After several days, bands due to another complex were observed but these were not the resonances of compound (8). Conversion into the new species was complete after two weeks, and by carrying out the process on a larger scale the new compound was isolated and characterised as the diplatinacyclohexadiene complex (14). It was also observed that the diplatinacyclobutene complex $[Pt_2\{\mu\text{-}(\sigma\text{-}4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)\}(cod)_2]$ [22] reacted with a mol equivalent of the alkyne to give (14) but at a slower rate than the synthesis of the complex *via* dimerisation of (13). The ^1H n.m.r. (Table 2) showed a 1 : 1 cod : alkyne ratio as well as two cod C*H* environments, and one O*Me* environment. The two C*H* signals would arise through the aforementioned boat configuration of the dimetallacyclohexadiene ring. It was of interest that following removal of the yellow crystals of (14), obtained from (13)



SCHEME 3 Formation of organo-platinum and diplatinum cyclic compounds (L_2 = cod or L = $CNBu^t$). (*i*) $RC{\equiv}CR$; (*ii*) for unsymmetrical alkynes, *e.g.* $MeC{\equiv}CCO_2Me$, this step would be electronically controlled to produce the ring-isomer with the electron-withdrawing substituents on the carbon atoms σ bonded to the metal [see ref. 23 and formation of (10b) (see text)]; (*iii*) for unsymmetrically substituted alkynes this pathway will produce the platinacyclopenta-2,4-diene isomer, *e.g.* (10a), with a head-to-tail arrangement of substituent groups (see refs. 27—29); (*iv*) $+PtL_2$; (*v*) with electrophilic alkynes this reaction path may be slow; (*vi*) $- PtL_2$

in acetone, examination of the ^1H n.m.r. spectrum of the supernatant liquid revealed the presence of signals due to (8). Treatment of this supernatant liquid with $CNBu^t$ afforded compound (3). However, reaction of (14) with $CNBu^t$ afforded complex (15), which showed only one Bu^t resonance in its ^1H n.m.r. spectrum, as expected from the structure proposed. These studies on (8), (13), and (14) suggest that the three species are intimately related, with (8) being thermodynamically the most stable. In accord with this, when a sample of (14) was heated at 100 °C in toluene, compound (8) was formed in 90% yield together with some black material, evidently platinum.

The conversion of (6) into (7a) (Scheme 1), the synthesis of (14) from $[Pt_2\{\mu\text{-}(\sigma\text{-}4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)\}(cod)_2]$, and the possible involvement of (12) in the formation of (10) (Scheme 2) are of interest in view of the report[26] that alkynes can insert into the metal–metal bond of $[Pd_2Cl_2(\mu\text{-}dppe)_2]$. However, we referred above to the fact that (14) forms more slowly from the diplatinacyclobutene precursor than it does from (13). This suggests that diplatinacyclobutene complexes might convert to diplatinacyclohexadiene compounds not *via* direct addition of alkyne to the metal–metal bond but *via* an alternative pathway involving dissociation into the species PtL_2 (L = $CNBu^t$ or L_2 = cod) and $L_2\overset{+}{Pt}C(R){=}\bar{C}(R)$. Dimerisation of the latter would afford a diplatinacyclohexadiene complex as observed, while capture of PtL_2 by the alkyne molecule would give an η^2-alkyne complex which in its dipolar form, $L_2\overset{+}{Pt}C(R){=}\bar{C}(R)$, could afford additional diplatinacyclohexadiene complex. We have previously demonstrated[27,28] that the compound $[Pt(C_2F_4)(cod)]$ dimerises in solution to give the diplatinaoctafluorocyclohexane complex $[Pt_2(\mu\text{-}CF_2CF_2)_2(cod)_2]$ and it seems likely that this process proceeds *via* the intermediacy of a dipolar species $(cod)\overset{+}{Pt}CF_2\bar{C}F_2$.[29] Formation of (14) from (13) could occur in the same manner, so that in some instances formation of the diplatinacyclohexadiene complexes does not require diplatinacyclobutene species as intermediates.

The various organoplatinum cyclic compounds described herein can evidently be formed *via* alternative pathways in some cases, the nature of the products depending on the alkyne involved. Scheme 3 summarises probable steps involved in metallacycle formation, based on the experimental results obtained.

EXPERIMENTAL

The instrumentation used, and experimental methods employed, were as described earlier.[16] I.r. bands were recorded as Nujol mulls. Light petroleum refers to that fraction b.p. 30—40 °C. The compounds $[Pt(cod)_2]$,[30] $[Pt_3(CNBu^t)_6]$,[31] and $[Pt(4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)(cod)]$[16]

were prepared as previously described. Analytical and other data on the new compounds are given in Table 1.

Preparation of Platinacyclopenta-2,4-*diene Complexes*.—(*a*) A toluene solution (30 cm^3) of [$Pt_3(CNBu^t)_6$] (0.50 g, 0.46 mmol) and diphenylacetylene (0.62 g, 3.45 mmol) was heated at 100 °C for 3 d. On cooling, orange *crystals* of [$Pt\{C(Ph)=C(Ph)C(Ph)=C(Ph)\}(CNBu^t)_2$] (1) (0.40 g) were obtained; $\nu_{max.}$ (NC) at 2 220vs and 2 190 cm^{-1}. Removal of solvent *in vacuo* from the mother-liquor, and washing the residue with light petroleum (2 × 10 cm^3) and diethyl ether (5 cm^3), afforded a further 0.20 g of complex (1).

(*b*) A toluene solution (15 cm^3) of [$Pt_3(CNBu^t)_6$] (0.30 g, 0.28 mmol) and 4,4′-$MeC_6H_4C{\equiv}CC_6H_4Me$ (0.38 g, 1.83 mmol) was heated at 100 °C (15 h). After filtration, and removal of solvent *in vacuo*, the residue was extracted with diethyl ether (30 cm^3) and the extract filtered through Celite (1 × 2 cm). Cooling to −20 °C gave orange *crystals* of [$Pt\{C(C_6H_4Me)=C(C_6H_4Me)C(C_6H_4Me)=C(C_6H_4Me)\}(CNBu^t)_2$] (2) (0.15 g); $\nu_{max.}$ (NC) at 2 200vs and 2 155vs cm^{-1}. Addition of light petroleum (20 cm^3) to the mother-liquor, followed by reduction in volume *in vacuo* and cooling, gave a further 0.20 g of (2), slightly contaminated with free 4,4′-$MeC_6H_4C{\equiv}CC_6H_4Me$.

(*c*) (i) A toluene solution (15 cm^3) of [$Pt_3(CNBu^t)_6$] (0.075 g, 0.069 mmol) and 4,4′-$MeOC_6F_4C{\equiv}CC_6F_4OMe$ (0.28 g, 0.545 mmol) was heated at 100 °C for 60 h. The solution was then cooled to room temperature, filtered, and cooled to −20 °C, affording yellow-green *needles* of the complex [$Pt\{C(C_6F_4OMe)=C(C_6F_4OMe)C(C_6F_4OMe)=C(C_6F_4OMe)\}(CNBu^t)_2$], (3) (5 mg). The supernatant was taken to dryness in *vacuo*, redissolved in diethyl ether (4 cm^3), and cooled (−20 °C), affording crystals of unchanged 4,4′-$MeOC_6F_4C{\equiv}CC_6F_4OMe$.

(ii) Addition of $CNBu^t$ (0.2 cm^3) to a chloroform (3 cm^3) solution of complex (8) (0.045 g, 0.042 mmol), followed by addition of light petroleum gave yellow-green *needles* of (3) (0.04 g).

(*d*) (i) A tetrahydrofuran (thf) solution (30 cm^3) of $MeO_2CC{\equiv}CCO_2Me$ (0.2 g, 2.1 mmol) and compound (4) (0.50 g, 0.5 mmol) was heated at 40 °C for 60 h. The mixture was then passed through a short alumina column, reduced in volume to *ca*. 5 cm^3, and the supernatant liquid decanted from the precipitate which formed. The latter was washed with diethyl ether (2 × 3 cm^3) and light petroleum (3 × 3 cm^3), affording yellow-green *crystals* of the complex [$Pt\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C(CO_2Me)\}(CNBu^t)_2$] (5) (0.27 g, 84%), identified by i.r. and ^{1}H n.m.r. spectroscopy.

(ii) A thf solution (20 cm^3) of compound (9) (0.13 g, 0.25 mmol) was treated with excess $CNBu^t$ (0.1 cm^3). After 3 h the solution was reduced *in vacuo* to *ca*. 5 cm^3, and hexane (10 cm^3) added. The resultant precipitate was washed with diethyl ether (2 × 2 cm^3) and hexane (2 × 4 cm^3), and recrystallised from diethyl ether–hexane to give yellow-green *crystals* of (5) (0.13 g); $\nu_{max.}$ at 2 218vs (NC), 2 208vs (NC), and 1 710vs, br (CO) cm^{-1}.

(*e*) The compounds [$Pt(cod)_2$] (0.05 g, 0.12 mmol) and 4,4′-$MeOC_6F_4C{\equiv}CC_6F_4OMe$ (0.10 g, 0.26 mmol) were heated in toluene at 100 °C for 90 h. All solvent was removed *in vacuo*, the residue redissolved in toluene and filtered. On cooling to −20 °C yellow-green *crystals* of the complex [$Pt\{C(C_6F_4OMe)=C(C_6F_4OMe)C(C_6F_4OMe)=C(C_6F_4OMe)\}(cod)$] (8) (0.07 g) were obtained.

(*f*) A thf solution (30 cm^3) of [$Pt(cod)_2$] (0.41 g, 1 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (0.57 g, 4 mmol) was heated at 40 °C for 30 h. The volume of solution was reduced *in vacuo* (5 cm^3), and hexane (10 cm^3) added. The precipitate which formed was washed with hexane (3 × 3 cm^3), and crystallised from thf–diethyl ether to give green-yellow *crystals* of [$Pt\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C(CO_2Me)\}(cod)$] (9) (0.40 g); $\nu_{max.}$ (CO) at 1 723vs, 1 708vs, and 1 690vs cm^{-1}.

(*g*) A thf solution (20 cm^3) of $MeC{\equiv}CCO_2Me$ (0.2 g, 2 mmol) at −30 °C was treated portion-wise with [$Pt(cod)_2$] (0.205 g, 0.5 mmol). The mixture was stirred at −30 °C (2 h) and at 25 °C (4 h). Volatile material was removed *in vacuo* and chromatography on alumina, eluting with diethyl ether-light petroleum (1 : 1), gave a solution which on concentration to *ca*. 10 cm^3 yielded yellow *microcrystals* of (10b) [$Pt\{C(CO_2Me)=C(Me)C(Me)=C(CO_2Me)\}(cod)$], (0.12 g); $\nu_{max.}$ (CO) at 1 680vs cm^{-1}.

Preparation of Diplatinacyclohexa-2,5-*diene Complexes*.—(*a*) A suspension of [$Pt_3(CNBu^t)_6$] (0.35 g, 0.32 mmol) in a mixture of toluene (10 cm^3) and light petroleum (7 cm^3) was treated at 25 °C with $MeC{\equiv}CCO_2Me$ (94 mg, 0.96 mmol) in light petroleum (5 cm^3). After 30 min the colour of the solution faded and a flocculent pale yellow precipitate formed. Stirring was continued for 8 h, affording a somewhat heavier precipitate. The supernatant liquid was removed, and the solid washed with light petroleum (2 × 3 cm^3) and dried *in vacuo* to give yellow *microcrystals* of the complex [$Pt\{C(Me)=C(CO_2Me)PtC(Me)=C(CO_2Me)\}(CNBu^t)_4$]·$\frac{1}{2}C_6H_5Me$, (7a) (0.427 g, 93%).

(*b*) The compound [$Pt_3(CNBu^t)_6$] (0.15 g, 0.138 mmol) was added to a thf solution (15 cm^3) of $MeO_2CC{\equiv}CCO_2Me$ (0.13 g, 0.92 mmol). After 3 h the volume of the solution was reduced *in vacuo* to *ca*. 2 cm^3, and the resultant precipitate was washed with diethyl ether (2 × 2 cm^3) and hexane (3 × 4 cm^3). Recrystallisation from thf–hexane afforded white *crystals* of [$Pt_2(\mu\text{-}MeO_2CC_2CO_2Me)_2(CNBu^t)_4$] (4) (0.11 g); $\nu_{max.}$ at 2 215vs (NC), 2 192vs (NC), and 1 685vs (CO) cm^{-1}.

(*c*) An acetone solution (5 cm^3) of [$Pt(4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)(cod)$] (13) (0.342 g, 0.5 mmol) was allowed to stand for 2 weeks. Addition of light petroleum afforded bright yellow *crystals* of [$Pt_2(\mu\text{-}4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)_2(cod)_2$] (14) (0.227 g). The supernatant liquid was reduced *in vacuo* to an oil, and dissolved in dichloromethane (4 cm^3). Addition of $CNBu^t$ (0.2 cm^3) followed by light petroleum afforded yellow-green *crystals* of the complex (3) [$Pt\{C(C_6F_4OMe)=C(C_6F_4OMe)C(C_6F_4OMe)=C(C_6F_4OMe)\}(CNBu^t)_2$] (0.049 g).

(*d*) A dichloromethane solution (3 cm^3) of complex (14) (0.05 g, 0.037 mmol) was treated with $CNBu^t$ (0.15 cm^3). The yellow colour was discharged, and addition of light petroleum afforded very pale yellow crystals of [$Pt_2(\mu\text{-}4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)_2(CNBu^t)_4$] (15) (0.041 g); $\nu_{max.}$ (NC) at 2 192s and 2 167s cm^{-1}.

Conversion of [$Pt(4,4'\text{-}MeOC_6F_4C_2C_6F_4OMe)(cod)$] (13) *into Compound* (8).—A toluene solution (15 cm^3) of (13) (0.68 g, 1 mmol) was heated at 100 °C for 24 h. The dark liquid produced was filtered through alumina (1 × 2 cm), and the resultant solution evaporated *in vacuo*. The residue was crystallised from toluene (−20 °C) affording *crystals* of compound (8) (0.105 g, 20%), identified by i.r. and ^{1}H n.m.r. spectroscopy.

Conversion of Compound (14) *into* (8).—A toluene solution

(10 cm^3) of (14) (0.05 g, 0.036 mmol) was heated (100 °C, 24 h) and the dark product filtered through alumina (1 × 2 cm). Solvent was removed *in vacuo*, and the residue crystallised from dichloromethane–light petroleum affording needles of compound (8) (0.018 g, 92%), identified by ^{1}H n.m.r. and i.r. spectroscopy.

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