The Synthesis and Reactions of Some Cyclopentadienylplatinum Complexes. Crystal Structure of $[Pt_2\{\mu\text{-}C(Ph)C(Ph)C(O)\}(\eta\text{-}C_5H_5)_2]$ †

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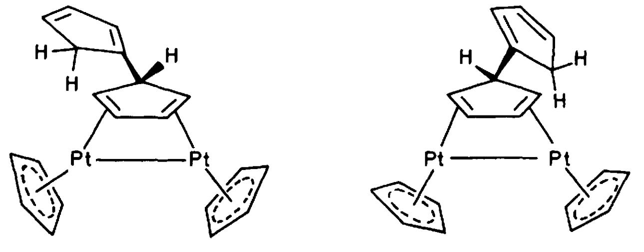
Treatment of di-μ-chloro-dichlorobis(η-ethylene)diplatinum with $Mg(C_5H_5)_2$ affords the compounds $[Pt(\eta\text{-}C_2H_4)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$ and $[Pt_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$. Reaction between $[NBu^n{}_4]_2[Pt_2Cl_4(CO)_2]$ and $Mg(C_5H_5)_2$ affords $[Pt_2(CO)_2(\eta\text{-}C_5H_5)_2]$ in good yield, as well as the compound $[Pt(CO)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$. Protonation of $[Pt(\eta\text{-}C_2H_4)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$ yields the salt $[Pt(\eta\text{-}C_2H_4)(\eta^2\text{-}C_5H_6)(\eta\text{-}C_5H_5)][BF_4]$. Reaction of $[Pt(\eta\text{-}C_2H_4)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$ with $PhC{\equiv}CPh$ affords (η-cyclopentadienyl)(σ: 2—3-η-2,3-diphenylbicyclo[2.2.1]hepta-2,5-dien-7-yl) platinum. The compound $[Pt_2(CO)_2(\eta\text{-}C_5H_5)_2]$ on treatment with $PhC{\equiv}CPh$ in the presence of Me_3NO gives $[Pt_2\{\mu\text{-}C(Ph)C(Ph)C(O)\}(\eta\text{-}C_5H_5)_2]$, and on similar treatment with $Bu^tC{\equiv}CBu^t$ and Me_3NO affords $[Pt_2(\mu\text{-}Bu^tC_2Bu^t)(\eta\text{-}C_5H_5)_2]$. The complex $[Pt_2\{\mu\text{-}C(Ph)C(Ph)C(O)\}(\eta\text{-}C_5H_5)_2]$ was structurally characterised by a single crystal *X*-ray diffraction study. The metal–metal bond [Pt–Pt 2.590(1) Å] is bridged by the C(Ph)=C(Ph)–C(O) ligand, in such a manner that the terminal carbon atoms are each σ-bonded to one platinum centre, while the C(Ph)=C(Ph) fragment is η^2-co-ordinated to the other. Both metal atoms carry C_5H_5 ligands, but one is asymmetrically bound. The n.m.r. data (^{1}H, ^{31}C-{^{1}H}, and ^{195}Pt-{^{1}H}) for the new compounds are reported and discussed, and this information used to suggest mechanisms for the dynamic behaviour of $[Pt(\eta\text{-}C_2H_4)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$, $[Pt_2(CO)_2(\eta\text{-}C_5H_5)_2]$, and $[Pt(\eta\text{-}C_2H_4)(\eta^2\text{-}C_5H_6)(\eta\text{-}C_5H_5)]^+$.

The chemistry of the cyclopentadienyl derivatives of the Group 8 metals is highly developed with the exception of that of platinum.[1] At an early stage in the exploitation of cyclopentadienylmetal chemistry, Fischer *et al.*[2] isolated the potentially interesting compound $[Pt_2(CO)_2(\eta\text{-}C_5H_5)_2]$ but in very low yield (*ca.* 6%). They also noted [3] the formation of a dinuclear species in which a 1,3-diene ligand apparently bridged two platinum atoms.[4] Evidently further synthetic and structural studies in this area were worthwhile and we were led to using bis(cyclopentadienyl)magnesium [5] as a reagent for preparing cyclopentadienylplatinum compounds.



endo *exo*

(2)

Results and Discussion

Treatment of a tetrahydrofuran (thf) solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_2H_4)_2]$ [6] with bis(cyclopentadienyl)magnesium at 0 °C affords two platinum complexes, (1) and (2), separable by column chromatography.

Compound (1), obtained in good yield (48%), was characterised by microanalysis and by mass and n.m.r. spectroscopy as $[Pt(\eta\text{-}C_2H_4)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$, a compound in which C_5H_5 groups are both σ and η^5 co-ordinated to platinum. Variable-temperature ^{1}H and ^{13}C-{^{1}H} n.m.r. studies revealed that (1) undergoes dynamic behaviour in solution, consistent with two processes taking place; the limiting low-temperature spectra being observed at −65 °C. The two mechanisms (Scheme 1) which account for the data involve rotation of the C_2H_4 ligand about an axis through the platinum atom and perpendicular to the C=C bond [$\Delta G^\ddagger$ *ca.* 56 kJ mol^{-1} for $T_c = 294$ K (ref. 7)], and movement of the metal atom around the σ-bonded C_5H_5 ligand *via* a succession of [1,5]-sigmatropic shifts. That the ethylene ligand in (1) sits perpendicular to the plane defined by C^1, Pt, and the centroid of the η^5-C_5H_5 ring (Scheme 1) is shown by the ^{1}H–^{1}H coupling constants [8] derived from the low-temperature ^{1}H spectrum, and the equivalence of the signals for the ^{13}C nuclei of the C_2H_4 group at low temperature.

After 3 h at 80 °C, a benzene solution of (1) showed three additional ^{195}Pt resonances at δ −1 066, −1 092, and −2 017 p.p.m. The last peak is attributable to the diplatinum compound (2), discussed below. The relationship between the signal of (1) (δ −963) and those at −1 066 and −1 092 p.p.m. closely parallels that observed (see below) between the ^{195}Pt n.m.r. shifts for $[Pt(CO)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$ (3) and two vinyl isomers with which it equilibrates. Hence we suggest that the resonances which appear at δ −1 066 and −1 092 when benzene solutions of (1) are warmed are also due to vinylplatinum species (Scheme 1), formed by [1,5]-H-shift processes.

Compound (2), formed in the reaction between $[Pt_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_2H_4)_2]$ and $Mg(C_5H_5)_2$, was identified (analysis, mass, and n.m.r. spectroscopy) as the previously observed diene-bridged diplatinum complex $[Pt_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$.[3,4] The ^{1}H and ^{13}C-{^{1}H} n.m.r. data indicated that (2) existed as equal amounts of the *exo* and *endo* isomers which differ only in the configuration of the C_5H_5 substituent on the μ-C_5H_5 ligand.

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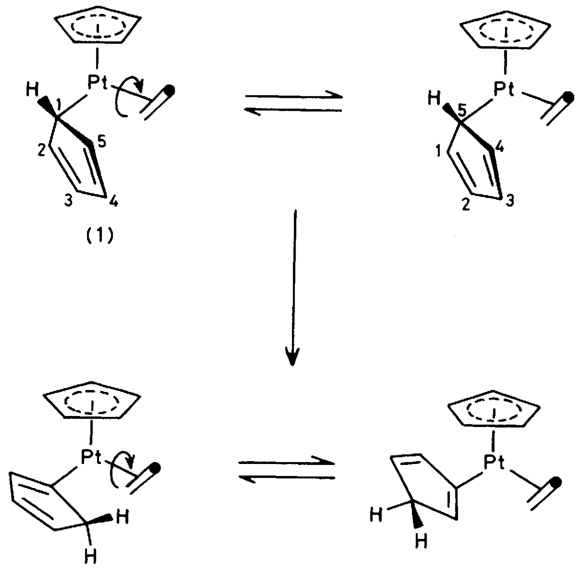
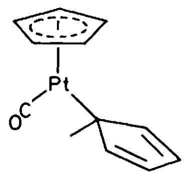
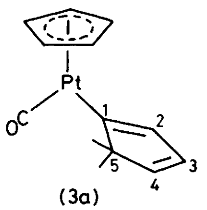
† μ-[η^2-1,2-Diphenyl-3-oxopropene-1,3-diyl-$C^{1,3}$(Pt^1)$C^{1,2}$(Pt^2)]-bis-(η-cyclopentadienylplatinum) (*Pt–Pt*).

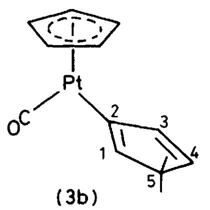
Supplementary data available (No. SUP 23721, 22 pp.): observed and calculated structure factors, hydrogen atom co-ordinates, thermal parameters. See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

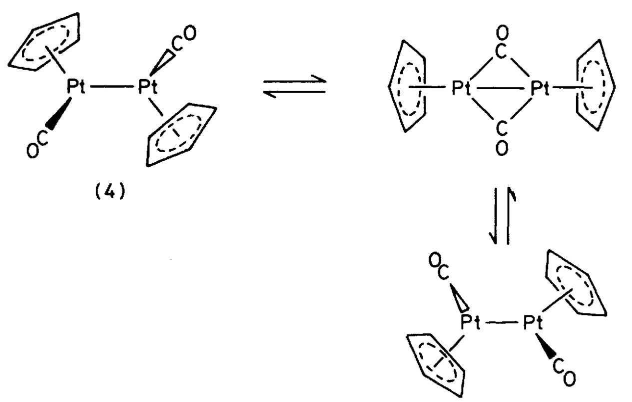


Scheme 1.

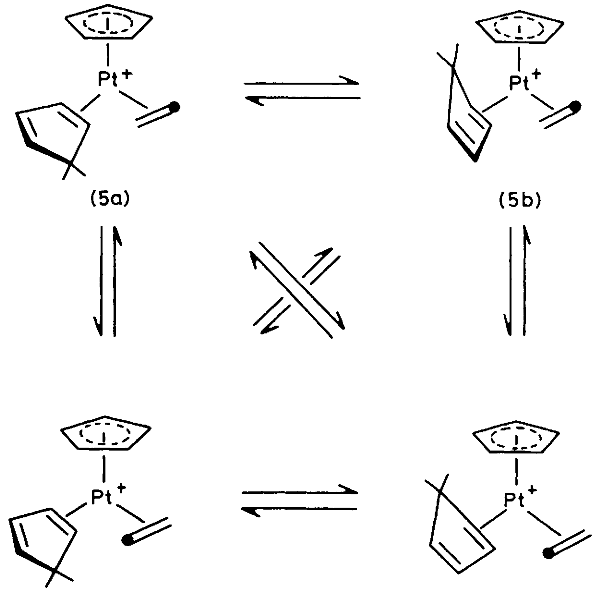

(3)


(3a)


(3b)



Scheme 2.



Scheme 3.

The reaction between $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ [9] and $Mg(C_5H_5)_2$ was next examined, and when carried out in thf at 0 °C afforded a mixture of $[Pt(CO)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$ (3) (*ca.* 8%) and $[Pt_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (4) (*ca.* 50%). The latter complex has previously only been obtained in low yield.[2] Compound (3) is structurally related to (1) and shows (n.m.r. data) a similar movement of the metal atom about the σ-bonded C_5H_5 ligand. A high yield (70%) synthesis of (3) is possible by treating a thf solution of (1) with CO (5×10^6 Pa, 25 °C).

By n.m.r. spectroscopy ($^{195}Pt\text{-}\{^1H\}$, ^1H, and selective decoupling experiments), compound (3) was observed to slowly convert to its vinyl isomer (3a) in solution, which in turn equilibrates with the other vinyl isomer (3b) [*cf.* the behaviour of $SiCl_2Me(C_5H_5)$ [10]]. From considerations discussed elsewhere,[11-13] coupling between ^{195}Pt nuclei and the olefinic protons of (3a) and (3b) can be taken to have positive sign. Thence $^1H\text{-}\{^1H\}$ selective decoupling experiments showed that the coupling between ^{195}Pt and the aliphatic protons was positive in (3a) but negative in (3b). These signs support the assignments of the structures of these vinyl isomers which could form from (3) by successive [1,5]-H-shifts. As expected,[14] (3a) and (3b) have very similar ^{195}Pt chemical shifts (δ −1 220 and −1 254 p.p.m., respectively) which are not far removed from that (δ −1 038) for (3).

The ^1H n.m.r. spectrum of compound (4) has been previously reported,[15] and the data for our product were in agreement. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (4) showed a signal for the $\eta\text{-}C_5H_5$ ligands at δ 91.9 p.p.m. with apparently equal coupling (12 Hz) to both ^{195}Pt sites.

The efficient synthesis of (4) from $[NBu^n_4]_2[Pt_2Cl_4(CO)_2]$ made it possible to prepare samples with ^{13}C enrichment (*ca.* 75%) of the CO ligands. The $^{13}C\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ spectra of the enriched material closely resembled those observed for enriched samples of the dianions $[Pt_2X_4(CO)_2]^{2-}$ (X = Cl or Br).[9] Thus, the room-temperature spectra showed prominent broad features at *ca.* $\pm\frac{1}{2}[^1J(PtC)]$ consistent with intramolecular CO site-exchange, which presumably proceeds *via* a CO bridged intermediate (Scheme 2), in a similar manner to that suggested [9] for the anions $[Pt_2X_4(CO)_2]^{2-}$. To obtain well resolved spectra, measurements were made at *ca.* −80 °C, and the various parameters, including *J*(PtPt), evaluated (Experimental section) as described elsewhere.[9] Splitting of the inner lines as a consequence of the term $^3J(^{13}C^{13}C)$ was not resolved (<10 Hz) so this coupling was assumed to be zero. Interestingly, the CO carbon isotope effect on $\delta(^{195}Pt)$ is larger than in $[Pt_2X_4(CO)_2]^{2-}$, *viz.* 1.25 compared with 0.8 p.p.m.

As stated above, the C_2H_4 ligand in (1) can be displaced by CO. It was also found that (1) could be protonated (HBF_4–propionic anhydride mixture) to give the salt $[Pt(\eta\text{-}C_2H_4)(\eta^2\text{-}C_5H_6)(\eta\text{-}C_5H_5)][BF_4]$ (5). The n.m.r. data for this salt showed that the cation undergoes dynamic behaviour in solution. Evidently both the C_2H_4 and the C_5H_6 groups rotate about axes through the platinum atom and the midpoints of the η^2-bonded C=C group (Scheme 3). There was no evidence for the platinum atom ' switching ' back and forth between the two olefinic co-ordination sites of the C_5H_6 ligand. On cooling to −75 °C the dynamic processes were frozen out, and the

Table 1. Internuclear distances (Å) and angles (°) for $[Pt_2\{\mu\text{-}C(Ph)C(Ph)C(O)\}(\eta\text{-}C_5H_5)_2]$ (7), with estimated standard deviations in parentheses

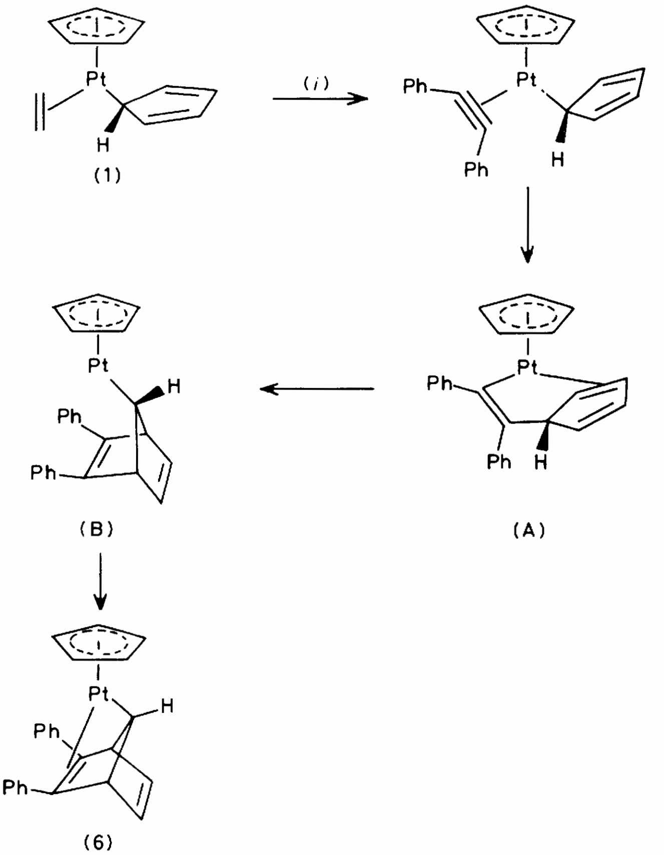
(*a*) Distances *

Pt(1)–Pt(2)	2.590(1)	Pt(1)–C(08)	2.28(2)	Pt(2)–C(01)	2.30(3)	C(1)–C(2)	1.46(4)
Pt(1)–C(1)	2.03(2)	Pt(1)–C(09)	2.29(2)	Pt(2)–C(02)	2.20(3)	C(2)–C(3)	1.53(4)
Pt(1)–C(2)	2.15(3)	Pt(1)–C(010)	2.28(2)	Pt(2)–C(03)	2.24(2)	C(1)–C(11)	1.47(3)
Pt(1) · · · C(3)	2.61(3)	Pt(2)–C(1)	2.04(3)	Pt(2)–C(04)	2.37(2)	C(3)–O(3)	1.17(3)
Pt(1)–C(06)	2.28(3)	Pt(2)–C(3)	2.02(3)	Pt(2)–C(05)	2.41(2)	C(2)–C(21)	1.48(3)
Pt(1)–C(07)	2.28(3)	Pt(2) · · · C(2)	2.63(3)				

(*b*) Angles

Pt(1)–C(1)–Pt(2)	79.0(7)	Pt(1)–C(1)–C(11)	128(1)	C(2)–C(3)–O(3)	130(3)
Pt(1)–C(2)–Pt(2)	64.6(6)	C(11)–C(1)–C(2)	131(2)	C(2)–C(3)–Pt(2)	95(1)
Pt(1)–C(3)–Pt(2)	66.6(7)	C(21)–C(2)–C(1)	129(2)	C(2)–C(1)–Pt(1)	74(1)
Pt(1) · · · C(3)–O(3)	140(2)	C(1)–C(2)–C(3)	100(2)	C(21)–C(2)–Pt(2)	173(1)
Pt(2)–C(3)–O(3)	135(2)	C(3)–C(2)–C(21)	129(2)	C(21)–C(2)–Pt(1)	122(1)

* C–C distances for C_5H_5 and C_6H_5 rings were constrained to 1.42 and 1.39 Å, respectively.



Scheme 4. (*i*) PhC_2Ph, $-C_2H_4$

resulting spectrum suggested the presence of two isomers of relative proportions 1 : 5 [(5a) and (5b), respectively, Scheme 3]. In the intermediate temperature range, a coalescence temperature of −40 °C was observed for ethylene rotation ($\Delta G^{\ddagger}_{T_c}$ *ca.* 49 kJ mol^{-1}), and an approximate coalescence temperature of −50 °C for η^2-C_5H_6 rotation. It should be noted (Scheme 3), however, that an envelope flip (*endo* $\rightleftarrows$ *exo*) of the CH_2 unit of the C_5H_6 ligand, which would produce the corresponding enantiomers, cannot be ruled out as an alternative to C_5H_6 rotation.

Reactions of (1) and (4) with PhC≡CPh were also investigated. At 70 °C, (1) affords compound (6) (Scheme 4), a product corresponding to a formal (4 + 2) π addition of the alkyne to the platinum substituted C_5H_5 ring. The illustrated structure is proposed on the basis of the ^1H and ^{13}C-$\{^1H\}$ n.m.r. data. Formation of (6) is related to the earlier observed reactions between nickelocene and the alkynes $C_2(CO_2Me)_2$ [16] and $CF_3C_2CF_3$ [17] which afford products with similar structures. However, PhC_2Ph is not a reactive dienophile, and it is unlikely that a platinum substituent could activate a cyclopentadiene ring so that it would undergo a Diels–Alder reaction with diphenylacetylene. The pathway shown in Scheme 4 for the formation of (6) thus seems more likely. An initial displacement of C_2H_4 by PhC_2Ph could be followed by 'insertion' of the alkyne into the C–Pt σ bond to give the 18-electron vinyl species (A). This intermediate could then undergo an intramolecular insertion reaction to give (B), which on collapsing would yield the 18-electron product (6).

The diplatinum complex (4) does not react thermally with PhC_2Ph. However, treatment of (4) with PhC_2Ph in the presence of Me_3NO affords a crystalline product (7), the i.r. spectrum of which showed a strong band at 1 681 cm^{-1}, suggestive of a ketonic CO group. The structural identity of (7) was established by a single-crystal *X*-ray diffraction study, data from which are summarised in Table 1. The molecule is shown in the Figure, which also illustrates the atom-numbering scheme.

Compound (7) is a diplatinum species. The Pt–Pt separation [2.590(1) Å] corresponds to that expected for a single bond, and may be compared with those found in $[Pt_3(\mu\text{-}CO)_3\{P(cyclo\text{-}C_6H_{11})_3\}_3]$ [2.654(2) Å],[18] $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$ [2.632(2) Å],[19] $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ [2.624(1) Å],[20] $[Pt_2\{\mu\text{-}C(CF_3)_2O\}(cod)_2]$ (cod = cyclo-octa-1,5-diene) [2.585(1) Å],[21] and compound (2) [2.581(4) Å]. Each platinum carries an η^5-cyclopentadienyl ligand. The metal–metal bond is spanned by a C(Ph)C(Ph)C(O) group derived from one CO and one PhC_2Ph molecule. The bridging organic group is η^2-bonded to Pt(1) *via* the olefinic link C(1)–C(2) [1.46(4) Å], and is σ-bonded to Pt(2) *via* the ketonic carbon C(3) and the 'olefinic' carbon C(1). The distances between C(1), C(2), and C(3) and the platinum atoms to which they are bonded are all within the range [1.99(3)—2.15(2) Å] found previously for carbon–platinum σ bonds.[22] However, the Pt(1) · · · C(3) and the Pt(2) · · · C(2) distances in (7) (Table 1) are non-bonding.

It is interesting to relate the bridging C(Ph)C(Ph)C(O) group in (7) with the bridging C(Ph)C(O)C(Ph) ligand in the compound $[Pt_2\{\mu\text{-}C(Ph)C(O)C(Ph)\}(CNBu^t)_4]$.[23] However, in the latter there is no Pt–Pt bond, and the bonding mode of

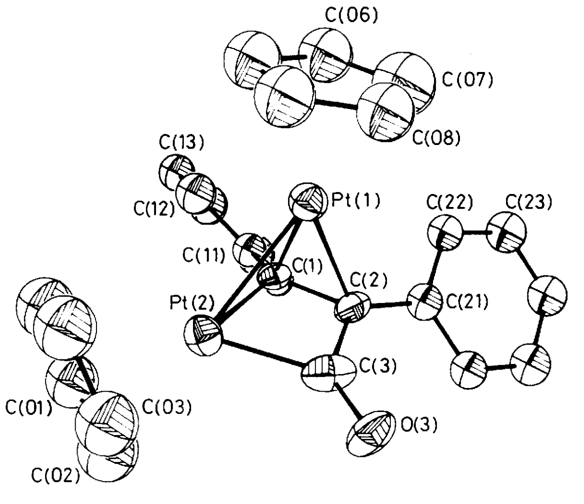


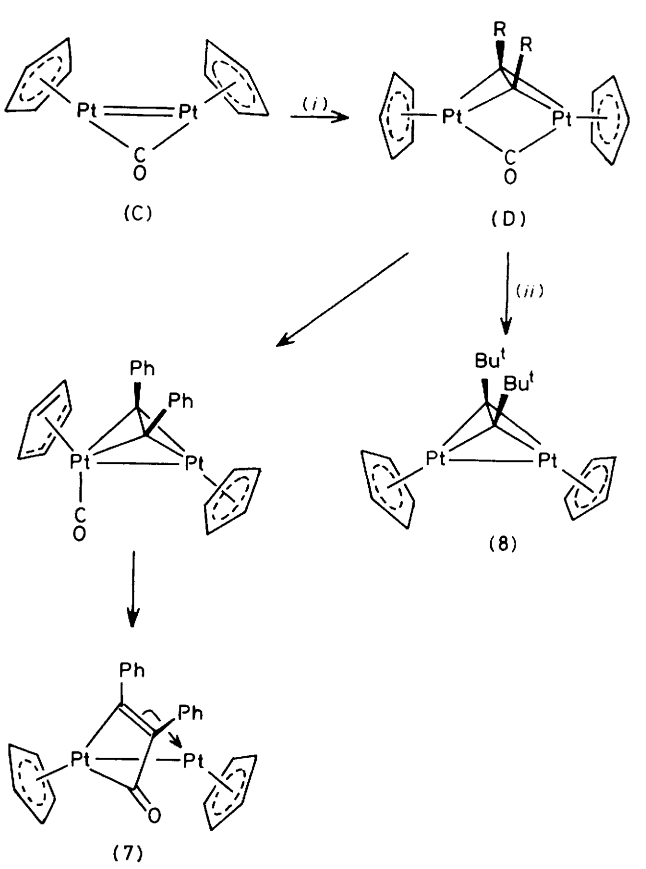
Figure. Molecular structure of $[Pt_2\{\mu\text{-}C(Ph)C(Ph)C(O)\}(\eta\text{-}C_5H_5)_2]$ (7) with the atom-numbering scheme

the C_3 bridge is very different. More relevant to (7) is the compound $[W_2\{\mu\text{-}C(CO_2Me)C(CO_2Me)C(O)\}(CO)_4(\eta\text{-}C_5H_5)_2]$, which also contains a metallacyclobutene ring.[24]

Although both cyclopentadienyl ligands in (7) are η^5-bonded to the platinum atoms there is an indication of asymmetry in the attachment of the C_5H_5 group to Pt(2). Shorter Pt–C separations are observed for the ring-carbon atoms C(02) and C(03) lying more nearly *trans* to the Pt–Pt vector, and longer distances for those [C(01), C(04), and C(05)] more *transoid* to the C_3 ligand system.

A complex related to (7), and to the ditungsten species mentioned above, is the diruthenium compound $[Ru_2\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(O)C(Ph)C(Ph)\}(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$.[25] In the latter the C(Ph)C(Ph)C(O) fragment adopts a different bonding mode in bridging the two metal centres. It was proposed [25] that in forming the diruthenium compound by u.v. irradiation of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in the presence of PhC≡CPh, homolytic fission of the Ru–Ru bond occurs, and that the metallacyclobutenone ring is formed at one metal centre before interaction occurs with a second $Ru(CO)_2(\eta\text{-}C_5H_5)$ moiety. It is unlikely that a similar sequence of reactions occurs in the formation of (7). Treatment of (3) with Me_3NO probably leads to loss of one co-ordinated CO as CO_2, and formation of the unsaturated species (C) (Scheme 5), related to $[Co_2(CO)_7]$. As in the reactions of $[Co_2(CO)_8]$ with alkynes, a transversely bridged complex (D) would be expected to form with PhC≡CPh. In order to form the platinacyclobutenone ring system it would be necessary for one C_5H_5 ligand to slip to an η^3-bonding mode so as to accommodate a change from bridging to terminal mode for the CO group. A carbonyl ' insertion ' reaction would then afford (7) directly. It follows that the whole process takes place at a dimetal centre.

This proposal is supported by the observation that reaction of (3) with Me_3NO in the presence of Bu^{t}C≡CBu^t gives the diplatinum compound (8), isostructural with the well known dinickel complexes $[Ni_2(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ (R = alkyl or aryl).[26] Thus it is possible that (8) is formed by a competitive reaction pathway available to an intermediate isostructural with (D) (Scheme 5), which simply extrudes CO to establish a Pt–Pt bond.



Scheme 5. (*i*) + RC$_2$R (R = Ph or Bu^t); (*ii*) −CO

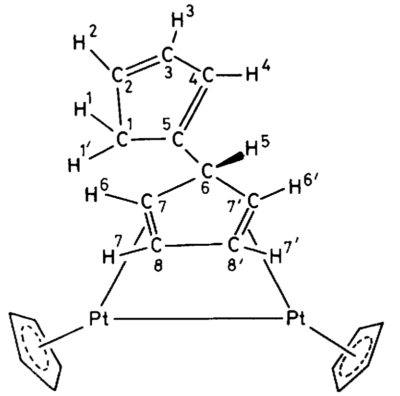
Experimental

The ^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H}, and ^{195}Pt-{^{1}H}, n.m.r. spectra were measured in [^{2}H$_1$]chloroform, unless otherwise stated, on JEOL PS-100, FX 90Q, or FX 200 spectrometers, as appropriate. Data given are for room-temperature measurements unless otherwise indicated and coupling constants are in Hz. Carbon-13 chemical shifts are relative to $SiMe_4$ with positive values to high frequency of the reference. The ^{195}Pt shifts are measured to high frequency of $\Xi({}^{195}Pt)$ = 21.4 MHz. Tris(acetylacetonato)chromium(III) was added to reduce ^{13}C relaxation times. All molecular weights were obtained by mass spectroscopy using an A.E.I. MS 902 instrument, and i.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents. Light petroleum refers to that fraction of b.p. 30—40 °C.

Reaction of Di-μ-chloro-dichlorobis(η-ethylene)diplatinum with Bis(cyclopentadienyl)magnesium.—A solution of $Mg(C_5H_5)_2$ (0.55 g, 3.57 mmol) in thf (5 cm^3) was added dropwise (10 min) with stirring (0 °C) to an ethylene-saturated thf (20 cm^3) solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_2H_4)_2]$ (1.0 g, 1.7 mmol). After 2 h, solid alumina (*ca.* 10 g) was added, and the solvent removed *in vacuo*. The residue was transferred to an alumina-packed chromatography column (10 × 2.5 cm), charged with light petroleum. Elution with light petroleum–diethyl ether (20 : 1) afforded an orange band. Removal of solvent gave orange *crystals* of $[Pt(\eta\text{-}C_2H_4)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)]$ (1) (0.58 g, 48%) (Found: C, 41.1; H, 4.1%; *M*, 353. $C_{12}H_{14}Pt$ requires C, 40.8; H, 4.0%; *M*, 353); m.p. 28 °C. N.m.r.: ^{1}H (at −65 °C in [^{2}H$_6$]acetone), δ 6.48 (m, 2 H, CH), 6.15 [m, 2 H, CH, *J*(PtH) 19], 5.31 [s, 5 H, C_5H_5, *J*(PtH) 14], 2.73 [s, 1 H, CH, *J*(PtH) 165], 3.36 [2 H, *J*(PtH) 84] and 2.14 [2 H, *J*(PtH) 70] {[AX]$_2$ spin system, C_2H_4, *J*(AA′) ≃ *J*(XX′) 7.2, *J*(AX) 11.4, and *J*(AX′) 1.3}; ^{1}H (at 70 °C in [^{2}H$_6$]benzene), δ 5.79 [s, 5 H,

C_5H_5, J(PtH) 41], 4.79 [s, 5 H, C_5H_5, J(PtH) 14], and 2.63 [s, 4 H, C_2H_4, J(PtH) 77]; ^{13}C-{^{1}H} (at −80 °C in [$^{2}H_2$]dichloromethane–CH_2Cl_2), δ 143.5 [CH, J(PtC) 51], 122.1 [CH, J(PtC) 32], 94.5 [C_5H_5, J(PtC) 17], 32.2 [C_2H_4, J(PtC) 300], and 27.9 p.p.m. [CHPt, J(PtC) 686]; ^{13}C-{^{1}H} ([$^{2}H_6$]benzene), δ 94.5 [C_5H_5, J(PtC) 16] and 32.0 p.p.m. [C_2H_4, J(PtC) 304]; ^{195}Pt-{^{1}H} ([$^{2}H_6$]benzene), δ −963 p.p.m.

Further elution of the chromatography column with light petroleum–diethyl ether (3 : 2) afforded the green crystalline compound [$Pt_2(\mu\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2$] (2) [3] (0.32 g, 34%) (Found: C, 37.3; H, 3.5%; M, 650. Calc. for $C_{20}H_{20}Pt_2$: C, 36.9; H, 3.1%; M, 650). N.m.r.: ^{1}H ([$^{2}H_6$]benzene), isomer (2a), δ 6.52 [m, 1 H, H^2, $J(H^2H^4)$ 1, $J(H^2H^{1,1'})$ 1.5, $J(H^2H^3)$ 5], 6.36 [m, 1 H, H^3, $J(H^3H^4)$ 2, $J(H^3H^2)$ 5, $J(H^3H^{1,1'})$ 1.5], 5.97 (br, m, 1 H, H^4), 5.65 [s, 5 H, C_5H_5, J(PtH) 14, J(PtH) 9], 4.78 [part of $(AB)_2$ subspectrum, 2 H, H^6 and $H^{6'}$ or H^7 and $H^{7'}$, J(PtH) 85], 4.11 [s, 1 H, H^5, J(PtH) 41], 3.30 [part of $(AB)_2$ subspectrum, 2 H, H^7 and $H^{7'}$ or H^6 and $H^{6'}$, J(PtH) 83], and 2.76 (m, 2 H, H^1 and $H^{1'}$); isomer (2b) 6.47 [m, 1 H, H^3, $J(H^3H^4)$ 2, $J(H^3H^2)$ 5.5, $J(H^3H^1)$ 2], 6.25 [m, 1 H, H^2, $J(H^2H^4)$ 1, $J(H^2H^1)$ 1.5, $J(H^2H^3)$ 5.5], 6.21 (br, m, 1 H, H^4), 5.66 [s, 5 H, C_5H_5, J(PtH) 14, J(PtH) 9], 4.69 [part of $(AB)_2$ subspectrum, 2 H, H^6 and $H^{6'}$ or H^7 and $H^{7'}$ J(PtH) 85], 4.07 [s, 1 H, H^5, J(PtH) 41], 3.90 [part of $(AB)_2$ subspectrum, 2 H, H^7 and $H^{7'}$ or H^6 and $H^{6'}$, J(PtH) 83], and 2.78 (m, 2 H, H^1 and $H^{1'}$); ^{13}C-{^{1}H}, isomer (2a), δ 151.8 [C^5, J(PtC) 73], 133.5, 130.4, 124.3 (C^2, C^3, C^4), 90.7 [C_5H_5, J(PtC) 13, J(PtC) 7], 58.7 [C^6, J(PtC) 34], 48.0 [C^7 and $C^{7'}$ or C^8 and $C^{8'}$, J(PtC) 398], 40.9 (C^1), and 40.5 p.p.m. [C^8 and $C^{8'}$ or C^7 and $C^{7'}$, J(PtC) 190, ^{2}J(PtC) 66]; isomer (2b), δ 154.7 [C^5, J(PtC) 76], 132.5, 132.2, 124.9 (C^2, C^3, C^4), 90.7 [C_5H_5, J(PtC) 13, J (PtC) 7], 58.1 [C^6, J(PtC) 32], 48.9 [C^7 and $C^{7'}$ or C^8 and $C^{8'}$, J(PtC) 398], 40.6 (C^1), and 40.1 p.p.m. [C^8 and $C^{8'}$ or C^7 and $C^{7'}$, J(PtC) 191, J(PtC) 66]; ^{195}Pt-{^{1}H} ([$^{2}H_6$]benzene), isomer (2a) and isomer (2b), δ −2 016 p.p.m.



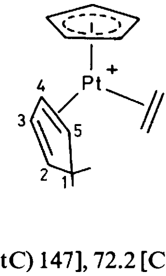
endo

Reaction of [$NBu^n{}_4$]$_2$[$Pt_2Cl_4(CO)_2$] *with* $Mg(C_5H_5)_2$.—A solution of $Mg(C_5H_5)_2$ (1 mmol) in thf (10 cm^3) was added dropwise with stirring (0 °C) to a suspension of [$NBu^n{}_4$]$_2$[$Pt_2Cl_4(CO)_2$] (1.07 g, 1 mmol) in the same solvent (100 cm^3). The yellow solid slowly dissolved to give a dark red solution. After 1 h, volatile material was removed *in vacuo*, and the residue extracted with hexane. Reduction of the volume of the extracts to *ca.* 5 cm^3 and cooling gave red needles of [$Pt_2(CO)_2(\eta\text{-}C_5H_5)_2$] (4)[2] (0.23 g), see below. The supernatant liquid was chromatographed on alumina (0 °C), using hexane as eluant, affording a yellow *oil*, [$Pt(CO)(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)$] (3) (0.03 g, 8%); $\nu_{max.}$ (CO) 2 035vs and 1 985vw cm^{-1} (hexane). N.m.r.: ^{1}H (at −70 °C in [$^{2}H_6$]acetone), δ 6.55 (m, 2 H, CH), 6.25 [m, 2 H, CH, J(PtH) 20], 5.96 [s, 5 H, C_5H_5, J(PtH) 13], and 5.24 [s, br, 1 H, σ-PtCH, J(PtC) 198]; ^{1}H (at 60 °C in [$^{2}H_6$]acetone), δ 6.11 [s, 5 H, J(PtH) 13] and 5.71 [s, 5 H, J(PtH) 44]; ^{13}C-{^{1}H} (at −70 °C in [$^{2}H_6$]acetone), δ 162.1 [CO, J(PtC) 2 494], 143.8 [CH, J(PtC) 45], 123.0 [CH, J(PtC) 34], 94.8 [C_5H_5, J(PtC) 11], and 12.1 p.p.m. [PtCH, J(PtC) 614]; ^{195}Pt-{^{1}H} (in [$^{2}H_6$]benzene), δ −1 038 p.p.m.

A [$^{2}H_6$]benzene solution of (3) slowly converted into isomer (3a) {n.m.r.: ^{1}H, δ 6.69 [m, H^3, J(PtH) 5], 6.54 [m, H^2, J(PtH) 60], 6.53 [m, H^4, J(PtH) 18] [with spin decoupling of CH_2 groups, couplings were found as $J(H^2H^3)$ 2.0, $J(H^2H^4)$ 1.1, and $J(H^3H^4)$ 5.4], 3.03 [q, 2 H, CH_2, J(HH) all *ca.* 1.3, J(PtH) 9], and 5.30 [s, 5 H, C_5H_5, J(PtH) 13]; ^{195}Pt-{^{1}H}, δ −1 220 p.p.m.} and isomer (3b) {n.m.r.: ^{1}H, δ 6.69 [m, H^3, J(PtH) 22], 6.41 [m, H^4, J(PtH) 6], 6.34 [m, H^1, J(PtH) 54] [with spin decoupling of CH_2 groups, couplings were found as $J(H^1H^3)$ 1.1, $J(H^1H^4)$ 2.0, and $J(H^3H^4)$ 5.1], 3.09 [q, 2 H, CH_2, J(HH) all *ca.* 1.6, J(PtH) 15], and 5.36 [s, 5 H, C_5H_5, J(PtH) 13]; ^{195}Pt-{^{1}H}, δ −1 254 p.p.m.}.

Further elution with hexane yielded a red band which was collected. Solvent was evaporated *in vacuo*, and the residue recrystallised (0 °C) from diethyl ether–hexane to give red crystals of [$Pt_2(CO)_2(\eta\text{-}C_5H_5)_2$] (4) (0.05 g, overall yield 48%) [Found: C, 25.4; H, 1.8%; M, 576. Calc. for $C_{12}H_{10}O_2Pt_2$: C, 25.0; H, 1.8%; M, 576]; $\nu_{max.}$(CO) 2 019s, 1 999vs, and 1 959vw cm^{-1} (hexane) [lit.[2] 2 020s and 1 996vs cm^{-1} (cyclo-C_6H_{12})]. N.m.r.: ^{13}C-{^{1}H} (^{13}C enriched at −80 °C in C_6H_5Me), δ 164.1 [CO, ^{1}J(PtC) ±2 446, ^{2}J(PtC) ∓102]; ^{195}Pt-{^{1}H} (at −80 °C in C_6H_5Me), δ −2 140 p.p.m. [J(PtPt) 9 400 ± 70].

Protonation of Compound (1).—Complex (1) (0.35 g, 0.99 mmol) was dissolved in propionic anhydride (5 cm^3) and treated with an excess of HBF_4 [1 cm^3 of 40% aqueous HBF_4 in $(EtCO)_2CO$ (7 cm^3); *ca.* 6 mmol]. After 5 min, the mixture was added to diethyl ether (100 cm^3) with vigorous stirring. Solvent was decanted from the yellow precipitate which was washed with diethyl ether (2 × 20 cm^3), and dried *in vacuo* to give yellow *microcrystals* of [$Pt(\eta\text{-}C_2H_4)(\eta^2\text{-}C_5H_6)(\eta\text{-}C_5H_5)$][$BF_4$] (5) (0.41 g, 93%) (Found: C, 32.6; H, 3.4. $C_{12}H_{15}BF_4Pt$ requires C, 32.7; H, 3.4%); m.p. 140 °C (decomp.). N.m.r.: ^{1}H ([$^{2}H_3$]nitromethane), δ 6.60 (m, 1 H, CH), 6.46 (m, 1 H, CH), 6.03 [s, 5 H, C_5H_5, J(PtH) 17], 5.79 [m, 1 H, CH, J(PtH) 89], 5.02 [m, 1 H, CH, J(PtH) 78], and 3.52 [m, 6 H, C_2H_4 and CH_2, J(PtH) 53]; ^{13}C-{^{1}H} ([$^{2}H_6$]acetone), δ 138.8 [C^2 or C^3, J(PtC) 38], 134.0 [C^3 or C^2, J(PtC) 44], 100.5 [C_5H_5, J(PtC) 26], 81.6 [C^4 or C^5, J(PtC) 147], 72.2 [C^5 or C^4, J(PtC) 239], 51.2 [C_2H_4, J(PtC) 204], and 43.2 p.p.m. [C^1, J(PtC) 29]; ^{13}C-{^{1}H} (at −75 °C in [$^{2}H_6$]acetone), isomer (5a), δ 140.1 [C^2 or C^3, J(PtC) 32], 128.4 [C^3 or C^2, J(PtC) 42], 98.1 [C_5H_5, J(PtC) 20], 75.4 [C^4 or C^5, J(PtC) 148], 62.9 [C^5 or C^4, J(PtC) 230], 51.3 (C_2H_4), 50.5 (C_2H_4), and 39.7 p.p.m. (C^1); isomer (5b), δ 137.1 [C^2 or C^3, J(PtC) 34], 136.1 [C^3 or C^2, J(PtC) 44], 100.8 [C_5H_5, J(PtC) 27], 82.1 [C^4 or C^5, J(PtC) 147], 75.1 [C^5 or C^4, J(PtC) 252], 50.1 [C_2H_4, J(PtC) 194], 49.8 [C_2H_4, J(PtC) 182], and 44.1 p.p.m. [C^1, J(PtC) 30].

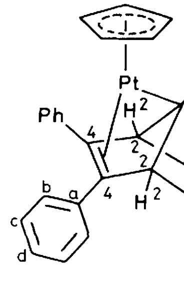


Reaction of Complex (1) *with Diphenylacetylene*.—A solution

Table 2. Atomic positional (fractional co-ordinates) parameters for complex (7) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	0.321 98(9)	−0.016 30(8)	0.247 73(6)	C(24)	0.369 5(14)	−0.234 9(9)	−0.085 5(10)
Pt(2)	0.079 10(10)	0.019 86(8)	0.248 68(6)	C(25)	0.250 9(14)	−0.262 2(9)	−0.056 9(10)
O(3)	0.070(2)	−0.192 6(2)	0.205 1(11)	C(26)	0.198 7(14)	−0.210 2(9)	0.013 6(10)
C(3)	0.113(3)	−0.114(2)	0.197(2)	C(21)	0.265 0(14)	−0.130 9(9)	0.055 4(10)
C(1)	0.194(2)	0.028(2)	0.141 9(14)	C(01)	−0.075(3)	0.139 2(15)	0.252 6(12)
C(2)	0.208(3)	−0.077(2)	0.130(2)	C(02)	−0.123(3)	0.044 9(15)	0.271 8(12)
C(12)	0.252 5(15)	0.198 1(11)	0.112 5(8)	C(03)	−0.060(3)	0.012 9(15)	0.357 7(12)
C(13)	0.268 1(15)	0.276 7(11)	0.053 1(8)	C(04)	0.027(3)	0.087 4(15)	0.391 5(12)
C(14)	0.238 5(15)	0.265 9(11)	−0.042 4(8)	C(05)	0.017(3)	0.165 5(15)	0.326 5(12)
C(15)	0.193 4(15)	0.176 4(11)	−0.078 6(8)	C(06)	0.527(3)	0.042 0(15)	0.267 2(13)
C(16)	0.177 8(15)	0.097 9(11)	−0.019 2(8)	C(07)	0.532(3)	−0.061 7(15)	0.269 9(13)
C(11)	0.207 4(15)	0.108 7(11)	0.076 4(8)	C(08)	0.470(3)	−0.093 5(15)	0.348 0(13)
C(22)	0.383 6(14)	−0.103 6(9)	0.026 8(10)	C(09)	0.427(3)	−0.009 5(15)	0.393 5(13)
C(23)	0.435 8(14)	−0.155 6(9)	−0.043 7(10)	C(010)	0.462(3)	0.074 3(15)	0.343 6(13)

of (1) (0.25 g, 0.71 mmol) and diphenylacetylene (1.0 g, 5.6 mmol) in toluene (2 cm^3) was heated at 70 °C for 16 h. The solvent was removed *in vacuo* and the residue chromatographed on an alumina column (20 × 2 cm). Elution with toluene–light petroleum (1 : 1) afforded a yellow band which was collected and rechromatographed. Elution with light petroleum removed unreacted PhC≡CPh. Further elution with light petroleum–dichloromethane (9 : 1) gave a yellow band. Removal of solvent *in vacuo*, followed by crystallisation of the residue from light petroleum gave yellow *crystals* of [Pt(σ : η^2-$C_7H_5Ph_2$)(η-C_5H_5)] (6) (0.1 g, 30%) (Found: C, 57.0; H, 4.1%; *M*, 503. $C_{24}H_{20}Pt$ requires C, 57.3; H, 4.0% *M*, 503); m.p. 140 °C. N.m.r.: ^{1}H, δ 7.11 (s, 10 H, Ph), 6.83 [t, 2 H, H^3, $|J(H^3H^2) + J(H^3H^{2'})|$ 2, J(PtH^3) 7.5], 5.71 [s, 5 H, C_5H_5, J(PtH) 14], 3.94 [d of t, 2 H, H^2, $|J(H^2H^3) + J(H^2H^{3'})|$ 2, $J(H^2H^1)$ 2.8, J(PtH) 31], and 2.30 [t, 1 H, H^1, $J(H^1H^2)$ 2.8, J(PtH) 94]; ^{13}C-{^{1}H}, δ 146.7 [C^3, J(PtC) 156], 140.8 [C^a, J(PtC) 43], 129.0 [C^b, J(PtC) 40], 127.6 (C^c), 125.9 (C^d), 91.2 [C_5H_5, J(PtC) 9], 67.9 [C^2, J(PtC) 120], 63.7 [C^4, J(PtC) 268], and 2.8 p.p.m. [C^1, J(PtC) 518]; ^{195}Pt-{^{1}H} ([^{2}H$_6$]benzene), δ 748 p.p.m.



Reaction of Compound (4) *with* PhC≡CPh.—Freshly sublimed Me_3NO (0.038 g, 0.5 mmol) was added to a stirred solution of (4) (0.144 g, 0.25 mmol) and diphenylacetylene (0.178 g, 1 mmol) in dry acetone (25 cm^3). The mixture was stirred at room temperature for 12 h, the colour changing from red to dark green. Volatile material was removed *in vacuo*, and the residue extracted with hexane. The volume of the solvent was reduced *in vacuo* to *ca.* 3 cm^3, and the solution cooled (−20 °C), affording yellow-brown *crystals* of [Pt_2{μ-C(Ph)-C(Ph)C(O)}(η-C_5H_5)$_2$] (7) (0.065 g, 36%) (Found: C, 41.6; H, 3.2; $C_{25}H_{20}OPt_2$ requires C, 41.3; H, 2.8%); $\nu_{max.}$ (CO) 1 681vs cm^{-1} (Nujol). N.m.r.: ^{1}H, δ 7.6—7.0 (m, 10 H, Ph), 3.93 [s, 5 H, C_5H_5, ^2J(PtH) 19, ^3J(PtH) 2], and 3.85 [s, 5 H, C_5H_5, ^2J(PtH) 15, ^3J(PtH) 1.5]; ^{13}C-{^{1}H}, δ 161.7 [CO, ^1J(PtC) 678, ^2J(PtC) 79], 131.0—127.1 (Ph), 107.7 [*C*Ph, J(PtC) 806, J(PtC) 601], 92.5 [C_5H_5, ^1J(PtC) 81, ^2J(PtC) 10], 90.7 [C_5H_5, ^1J(PtC) 39, ^2J(PtC) 34], and 72.5 p.p.m. [*C*Ph, ^1J(PtC) 159, ^2J(PtC) 35]; ^{195}Pt-{^{1}H}, δ −1 128 and −1 413 p.p.m. [J(PtPt) 9 005].

Reaction of Compound (4) *with* Bu^{t}C≡CBu^t.—In a similar manner to that above, (4) (0.144 g, 0.35 mmol) was treated with Me_3NO (0.5 mmol) and Bu^{t}C≡CBu^t (1 mmol) in acetone (25 cm^3). The hexane extract was chromatographed on an alumina packed column. Elution with hexane–diethyl ether (3 : 1) afforded a brown band. Solvent was removed *in vacuo* and the residue recrystallised (0 °C) from hexane–diethyl ether to give yellow-brown *crystals* of [Pt_2(μ-Bu^tC_2Bu^t)(η-C_5H_5)$_2$] (8) (0.064 g, 39%) (Found: C, 36.8; H, 4.4%; *M*, 658. $C_{20}H_{28}Pt_2$ requires C, 36.5; H, 4.3%; *M*, 658). N.m.r.: ^{1}H, δ 5.73 [s, 10 H, C_5H_5, J(PtH) 18] and 1.14 [s, 18 H, Bu^t, J(PtH) 2.5]; ^{13}C-{^{1}H}, δ 89.9 [*C*Bu^t, J(PtC) 476], 88.5 [C_5H_5, J(PtC) 31], 32.5 [Bu^t, J(PtC) 31], and 27.9 p.p.m. (*C*Me$_3$); ^{195}Pt-{^{1}H}, δ −1 745 p.p.m.

Crystal Structure Determination.—Crystals of (7) were grown from dichloromethane. Preliminary investigations showed that a reduction in the temperature of the sample caused a phase change, and accompanying degradation of the crystals. Diffracted intensities were, therefore, measured at 298 K on a Nicolet $P2_1$ four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 50°$, according to previously described methods.[27,28] Of the total 1 582 reflections, 1 492 had $I \geqslant 2\sigma(I)$ and only these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects. The latter were estimated by an empirical method, since the irregular morphology of the sample (mean radius 0.07 mm) defied accurate indexing and measurement.

Crystal data. $C_{25}H_{20}OPt_2$, $M = 726.6$, Monoclinic, $a = 10.463(4)$, $b = 13.678(7)$, $c = 14.457(8)$ Å, $\beta = 95.36(2)°$, $Z = 4$, $D_c = 2.35$ g cm^{-3}, $U = 2\ 060(1)$ Å^3, $F(000) = 1\ 336$, space group $P2_1/n$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 130.7 cm^{-1}.

Structure solution and refinement for (7). The structure was solved and all non-hydrogen atoms located by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were included at calculated positions (C–H 0.96 Å), and anisotropic thermal parameters were employed for the Pt and C(1)–O(3) chain of atoms only. Refinement by blocked-cascade least squares led to *R* 0.045 (*R'* 0.054) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.0009|F_o|^2]^{-1}$ giving a reasonable weight analysis. The final electron-density difference synthesis showed disturbing residual peaks *ca.* 3 e Å^{-3}, in the close neighbourhood of the metal atoms doubtless due to the inadequacy of the absorption correction. Scattering factors were from ref. 29. All computations were carried out on an Eclipse S230 (Data General) computer with the SHELXTL system of programs.[30] Atom co-ordinates are listed in Table 2.

Acknowledgements

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