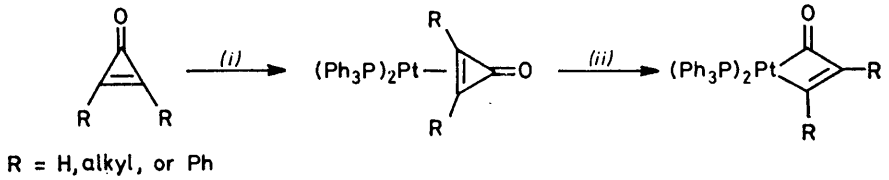
Carbon–Carbon Double-bond Cleavage in the Reactions of Diphenylcyclopropenone with Platinum(0) Complexes; Crystal and Molecular Structure of μ-2-Oxo-1,3-diphenylpropanediylidene-bis[bis(t-butyl isocyanide)platinum]

By **W. Eamon Carroll, Michael Green, Judith A. K. Howard, Michel Pfeffer,** and **F. Gordon A. Stone,***
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reaction of $[Pt_3(CNBu^t)_6]$ with diphenylcyclopropenone in toluene affords the yellow crystalline title complex $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNBu^t)_4]$, the structural identity of which has been established by a single-crystal *X*-ray diffraction study. The complex is monoclinic, space group $P2_1/n$, $Z = 4$, with unit-cell dimensions $a = 11.283(8)$, $b = 19.821(6)$, $c = 17.534(7)$ Å, and $\beta = 90.23(4)°$. Using 4 494 independent reflections, the refinement has converged to R 0.070 (R' 0.069). The molecule shows the unusual feature of ring opening at the carbon–carbon double bond of the cyclopropenone, the resulting C_3 fragment symmetrically bridging the two platinum atoms. Reaction between cyclo-octa-1,5-dienebis(methyl vinyl ketone)platinum and diphenylcyclopropenone at −50 °C yields an analogous complex $[Pt_2\{\mu\text{-}(PhC)_2CO\}(cod)_2]$ (cod = cyclo-octa-1,5-diene). Protonation of this species gives the cation $[Pt_2\{\mu\text{-}(PhC)_2C(OH)\}(cod)_2]^+$, while treatment with $CNBu^t$ or $P(OMe)_3$ leads to displacement of the cod ligands.

IN recent years there has been intense interest in transition-metal mediated reactions of organic molecules containing small rings.[1] Relevant to the results described herein are a number of reactions of cyclopropenones and cyclopropenylium cations. Thus, depending on the particular transition-metal substrate employed, cyclopropenylium cations can give metal complexes involving: (*i*) a symmetrical η^3-bonding mode, as in $[Ni(\eta\text{-}C_3Ph_3)(\eta\text{-}C_5H_5)]$;[2] (*ii*) unsymmetrical η^3, approaching η^2 co-ordination of the ring, as in $[Pt(\eta\text{-}C_3Ph_3)(PPh_3)_2][PF_6]$;[3] (*iii*) metallacyclobutenylium ion formation, resulting from ring opening, as in $[\overline{Ir\{C(Ph){\cdot}C(Ph){\cdot}C}(Ph)\}Cl(CO)(PMe_3)_2][BF_4]$;[4] and (*iv*) $\eta^3\text{-}C_3R_3\text{-}\mu$-bridge bonding, with ring opening, as in $[Pd_3\{\eta\text{-}C_3Ph(C_6H_4OMe\text{-}p)_2\}_2(acac)_2]$ (acac = acetylacetonate).[5]



SCHEME 1 (*i*) $[Pt(C_2H_4)(PPh_3)_2]$, −65 °C; (*ii*) −30 °C

The transition-metal chemistry of cyclopropenones is somewhat less developed. Reaction of cyclopropenones with certain metal carbonyls leads to decarbonylation and formation of acetylene-derived complexes,[6] while reactions with nickel(0) olefin complexes gives substituted quinones *via* catalytic dimerisation of the cyclopropenone.[7] However, cyclopropenones react with platinum(0) phosphine complexes to give metallacyclobutenones, *via* intermediate η^2 complexes (Scheme 1).[8,9]

We have recently discovered[10] a reactive triplatinum cluster complex $[Pt_3(CNBu^t)_6]$ which undergoes a remarkable reaction with hexakis(trifluoromethyl)benzene resulting in carbon–carbon bond cleavage.[11] It seemed appropriate to examine the reaction of the *triangulo*-triplatinum complex with cyclopropenones.

RESULTS AND DISCUSSION

Reaction of $[Pt_3(CNBu^t)_6]$ with diphenylcyclopropenone (2 : 3 mol ratio) in toluene solution produced a yellow crystalline complex (1).[12] The i.r. spectrum showed $\nu_{max.}(NC)$ at 2 168 and 2 140 cm^{-1}, consistent with a *cis*-$Pt(CNBu^t)_2$ fragment. A band at 1 556 cm^{-1} was assigned to a carbonyl group, much reduced in C–O bond order relative to that in diphenylcyclopropenone [$\nu_{max.}(CO)$ at 1 640 cm^{-1}].[13] The ^1H n.m.r. spectrum showed a phenyl resonance and a single sharp resonance attributable to Bu^t groups. Since the spectroscopic data and microanalyses did not allow assignment of a molecular structure for (1) a single-crystal *X*-ray

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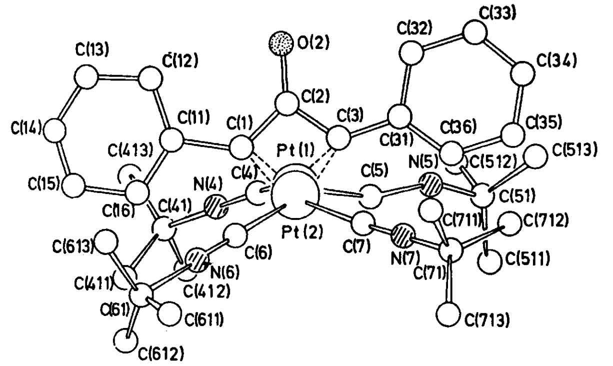
[13] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 1965, **87**, 1320.

diffraction study was undertaken which showed the molecule to be $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNBu^t)_4]$.

The molecule (Figure) contains two $[Pt(CNBu^t)_2]$ groups bridged transversely by a PhCC(O)CPh fragment formed by the hitherto unreported cleavage of the C=C bond of diphenylcyclopropenone. Internuclear distances and bond angles are given in Table 1. The C_3 ligand system lies almost perpendicular (89°) to the Pt–Pt vector and, indeed, the PhCC(O)CPh fragment forms an approximate, but non-crystallographic, mirror plane for the two $Pt(CNBu^t)_2$ moieties. The carbon atoms [C(1) and C(3)] originally forming the double bond now lie 2.18(2) Å apart, and equidistant from the two platinum atoms (mean Pt–C 2.11 Å). The bridgehead carbon, C(2), is similarly equidistant from the metal atoms but further removed at 2.50(2) Å. The opened C_3 fragment shows C–C separations [average 1.43(2) Å] commonly found in allyl complexes,[14] and the angle at the central carbon atom C(2) has increased to 99° from an acute angle which must be near 60° in diphenylcyclopropenone itself. The phenyl substituents are slightly bent towards C(2). The overall geometry of the bridging C_3 group in (1) bears a strong resemblance to that of the cyclopropenylium ion fragments in $[Pd_3\{\eta\text{-}C_3Ph(C_6H_4OMe\text{-}p)_2\}_2(acac)_2]$;[5] indeed the C–C separations and the non-bonded C(1)–C(3) distances are identical within experimental error. The recently reported[15] tetranuclear nickel complex $[\{Ni_2(\mu\text{-}C_3Cl_3)(\mu\text{-}Cl)(CO)_2\}_2]$ also contains ring-opened C_3 fragments. This complex is formed by treating $[Ni(CO)_4]$ with tetrachlorocyclopropene.



Molecular structure of the complex $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNBu^t)_4]$

TABLE 1

Internuclear distances (Å) and bond angles (°) (with estimated standard deviations in parentheses) for $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNBu^t)_4]$ (1)

(*a*) Bonds			
Pt(1)–Pt(2)	2.819(1)		
Pt(1)–C(1)	2.11(2)	Pt(2)–C(1)	2.13(2)
Pt(1)–C(2)	2.48(2)	Pt(2)–C(2)	2.50(2)
Pt(1)–C(3)	2.10(2)	Pt(2)–C(3)	2.10(2)
Pt(1)–C(4)	1.95(2)	Pt(2)–C(6)	1.94(2)
Pt(1)–C(5)	1.94(2)	Pt(2)–C(7)	1.94(2)
t-Butyl isocyanide ligands			
C(4)–N(4)	1.14(3)	C(6)–N(6)	1.16(3)
N(4)–C(41)	1.55(3)	N(6)–C(61)	1.62(4)
C(41)–C(411)	1.50(4)	C(61)–C(611)	1.54(5)
C(41)–C(412)	1.54(4)	C(61)–C(612)	1.37(5)
C(41)–C(413)	1.50(4)	C(61)–C(613)	1.54(5)
C(5)–N(5)	1.16(3)	C(7)–N(7)	1.18(2)
N(5)–C(51)	1.55(3)	N(7)–C(71)	1.50(3)
C(51)–C(511)	1.50(5)	C(71)–C(711)	1.55(4)
C(51)–C(512)	1.54(4)	C(71)–C(712)	1.52(4)
C(51)–C(513)	1.54(4)	C(71)–C(713)	1.47(5)
η^3-PhC·C(O)·CPh ligand			
C(1)–C(2)	1.41(2)	C(2)–O(2)	1.26(2)
C(1)–C(3)	2.18(2)	C(2)–C(3)	1.45(3)
C(1)–C(11)	1.52(3)	C(3)–C(31)	1.45(2)
C(11)–C(12)	1.40(3)	C(31)–C(32)	1.39(4)
C(12)–C(13)	1.49(4)	C(32)–C(33)	1.57(4)
C(13)–C(14)	1.37(4)	C(33)–C(34)	1.41(4)
C(14)–C(15)	1.36(4)	C(34)–C(35)	1.32(4)
C(15)–C(16)	1.43(4)	C(35)–C(36)	1.47(4)
C(16)–C(11)	1.41(3)	C(36)–C(31)	1.42(3)
(*b*) Angles			
C(1)–Pt(1)–C(3)	62.4(7)	C(1)–Pt(2)–C(3)	62.1(7)
C(1)–Pt(1)–C(4)	100.7(4)	C(1)–Pt(2)–C(6)	100.1(8)
C(3)–Pt(1)–C(5)	100.4(7)	C(3)–Pt(2)–C(7)	102.5(7)
C(5)–Pt(1)–C(4)	96.1(8)	C(6)–Pt(2)–C(7)	95.1(8)
t-Butyl isocyanide ligands			
Pt(1)–C(4)–N(4)	173(2)	Pt(2)–C(6)–N(6)	178(2)
C(4)–N(4)–C(41)	175(2)	C(6)–N(6)–C(61)	170(2)
N(4)–C(41)–C(411)	104(2)	N(6)–C(61)–C(611)	99(2)
N(4)–C(41)–C(412)	104(2)	N(6)–C(61)–C(612)	107(3)
N(4)–C(41)–C(413)	106(2)	N(6)–C(61)–C(613)	96(2)
C(411)–C(41)–C(412)	110(2)	C(611)–C(61)–C(612)	122(3)
C(411)–C(41)–C(413)	115(2)	C(611)–C(61)–C(613)	107(3)
C(412)–C(41)–C(413)	116(2)	C(612)–C(61)–C(613)	121(3)
Pt(1)–C(5)–N(5)	176(2)	Pt(2)–C(7)–N(7)	175(2)
C(5)–N(5)–C(51)	170(2)	C(7)–N(7)–C(71)	172(2)
N(5)–C(51)–C(511)	109(2)	N(7)–C(71)–C(711)	103(2)
N(5)–C(51)–C(512)	101(2)	N(7)–C(71)–C(712)	107(2)
N(5)–C(51)–C(513)	106(2)	N(7)–C(71)–C(713)	107(2)
C(511)–C(51)–C(512)	113(2)	C(711)–C(71)–C(712)	111(2)
C(511)–C(51)–C(513)	114(3)	C(711)–C(71)–C(713)	111(2)
C(512)–C(51)–C(513)	112(2)	C(712)–C(71)–C(713)	115(3)
η^3-PhC·C(O)·CPh ligand			
C(1)–C(2)–C(3)	99(1)		
C(1)–C(2)–O(2)	130(2)	C(3)–C(2)–O(2)	131(2)
C(2)–C(1)–C(3)	41(1)	C(2)–C(3)–C(1)	40(1)
Pt(1)–C(1)–C(2)	87(1)	Pt(2)–C(1)–C(2)	87(1)
Pt(1)–C(1)–Pt(2)	83.4(6)	Pt(1)–C(3)–Pt(2)	84.5(6)
Pt(1)–C(3)–C(2)	87(1)	Pt(2)–C(3)–C(2)	88(1)
Pt(1)–C(1)–C(11)	128(1)	Pt(2)–C(1)–C(11)	127(1)
Pt(1)–C(3)–C(31)	127(1)	Pt(2)–C(3)–C(31)	131(1)
C(1)–C(11)–C(12)	117(1)	C(3)–C(31)–C(32)	119(2)
C(1)–C(11)–C(16)	119(2)	C(3)–C(31)–C(36)	121(2)
C(16)–C(11)–C(12)	124(2)	C(36)–C(31)–C(32)	119(2)
C(11)–C(12)–C(13)	116(2)	C(31)–C(32)–C(33)	118(2)
C(12)–C(13)–C(14)	116(2)	C(32)–C(33)–C(34)	117(2)
C(13)–C(14)–C(15)	128(3)	C(33)–C(34)–C(35)	123(3)
C(14)–C(15)–C(16)	117(2)	C(34)–C(35)–C(36)	120(3)
C(15)–C(16)–C(11)	119(2)	C(35)–C(36)–C(31)	121(2)

The co-ordination around the platinum atoms in (1) is essentially square planar, planes being defined by Pt(1), C(1), C(3), C(4), and C(5), and by Pt(2), C(1), C(3), C(6), and C(7). The dihedral angle between these planes is 73° and these show dihedral angles of 55 and 52°, respectively, with respect to the mean plane [C(1), C(2), and C(3)] of the bridging ligand. However, a description in terms of square-planar co-ordination for platinum is perhaps somewhat oversimplified. Although the Pt–Pt separation [2.819(1) Å] is considerably longer than in other bridged diplatinum species (*ca.* 2.6 Å)[16] a weak

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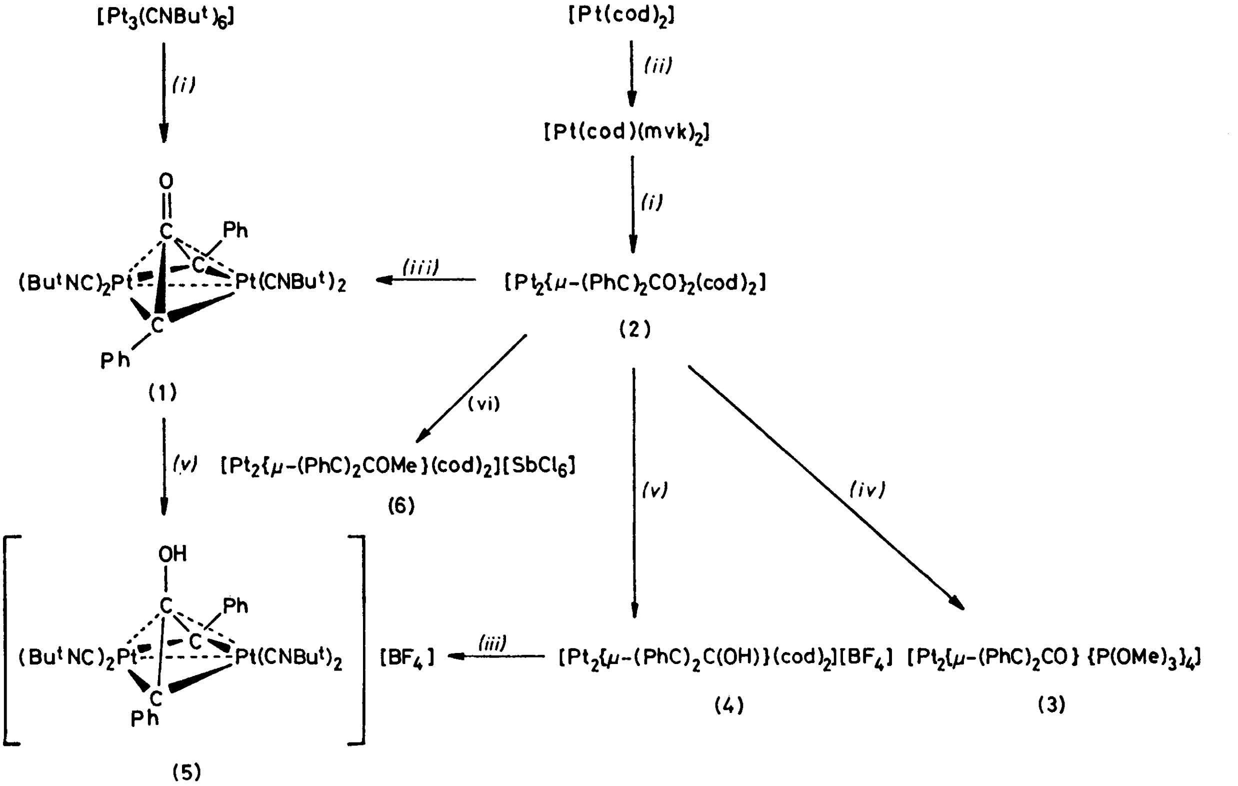
[15] R. G. Posey, G. P. Khare, and P. D. Frisch, *J. Amer. Chem. Soc.*, 1977, **99**, 4863.

[16] M. Green, J. A. K. Howard, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 278.

bonding interaction cannot be discounted. Moreover, although the mean Pt–C(2) distance [2.50(2) Å] exceeds the sum of the covalent radii [C(sp^2) 0.68 and Pt 1.31 Å] it may not be correct to describe it as non-bonding, particularly since the C(2)–O(2) distance (1.26 Å) is considerably lengthened over that found[17] in, for example, cyclopropanone (1.18 Å). We have referred earlier to the unusually low $\nu_{max.}$(CO) in the i.r. spectrum of (1). Additional evidence for interaction between C(2) and the platinum atoms is provided by the ^{1}H-decoupled ^{13}C n.m.r. spectrum, discussed below.



SCHEME 2 (*i*) Ph·C:C(Ph)·C:O; (*ii*) Me(CH$_2$:CH)C:O; (*iii*) CNBu^t; (*iv*) P(OMe)$_3$; (*v*) HBF$_4$; (*vi*) [OMe$_3$][SbCl$_6$]

Unfortunately no structural data on cyclopropenones appear to be available for correlation with the present study. However, results for two related systems are worthy of mention. The isoelectronic triphenylcyclopropenylium cation[18] has C–C three-membered ring separations of 1.37 Å, and since a zwitterionic form $Ph_2\overset{+}{C}_3$–$\overset{-}{O}$ of diphenylcyclopropenone is thought[19] to make a considerable contribution to the ground state it might be anticipated that C–C ring separations of at least this amount would be found in the ketone also. However, an *X*-ray crystallographic study[20] of the sulphur analogue Ph_2C_3S revealed a non-delocalised ring system with a C=C distance of 1.338 Å. Whatever the C–C bond orders of the C_3 ring of cyclopropenones it is remarkable that they are cleaved so easily by platinum(0) complexes.

Diplatinum complexes related to (1) can be prepared starting from bis(cyclo-octa-1,5-diene)platinum[21] (Scheme 2). Thus treatment of [Pt(cod)$_2$] with methyl vinyl ketone (mvk) affords a very reactive species formulated as [Pt(cod)(mvk)$_2$].[22] *In situ* reaction of the latter with diphenylcyclopropenone at −50 °C in 2 : 1 mol ratio gives the complex [Pt$_2${μ-(PhC)$_2$CO}(cod)$_2$] (2) in high yield. Complex (2) was fully characterised analytically and spectroscopically, and further evidence for its formulation comes from its ready reaction with t-butyl isocyanide to give (1). The cod ligands in (2) are also readily replaced by trimethyl phosphite affording complex (3). The ^{31}P (^{1}H-decoupled) n.m.r. spectrum of (3) is in complete accord with the structure proposed with a singlet signal ($\delta = -123.4$ p.p.m., relative to external H_3PO_4) with two sets of ^{195}Pt satellites corresponding to molecules having both one and two ^{195}Pt nuclei, the latter forming an [A(X)$_2$]$_2$ spin system. Analysis of the spectrum gave ^1J(PPt) 4 876, ^2J(PPt) 36, ^2J(PP) 36, ^3J(PP) 18, ^3J(PP′) 0, and J(PtPt) 1 977 Hz. The ^{195}Pt–^{195}Pt coupling constant is similar in magnitude to that found[23] in the ^{31}P spectrum of the

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[18] M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, 1966, **88**, 198.

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[20] L. L. Reed and J. P. Schaefer, *J.C.S. Chem. Comm.*, 1972, 528.

[21] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

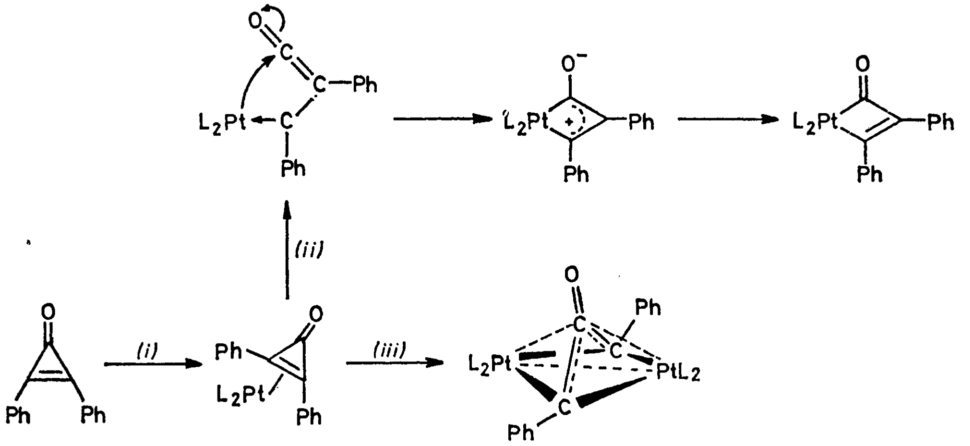
[22] M. Green, M. Pfeffer, and F. G. A. Stone, unpublished work.

[23] N. M. Boag, J. Browning, C. Crocker, P. L. Goggin, R. J. Goodfellow, M. Murray, and J. L. Spencer, *J. Chem. Res.*, 1978, (*S*) 228; (*M*) 2962.

triplatinum complex [{Pt(μ-CO)(PMeBu$^t_2$)}$_3$] (1 770 Hz) but considerably lower than that found for [Pt$_2${μ-(CF$_3$)$_2$CO}(cod)$_2$] (5 345 Hz),[16] where the Pt–Pt distance (2.585 Å) is considerably shorter than in (1) (2.819 Å).

The diplatinum complex (2) can be protonated (anhydrous tetrafluoroboric acid in diethyl ether) to give the salt (4). In the i.r., the $\nu_{max.}$(CO) band in (2) at 1 570 cm^{-1} is replaced by a broad $\nu_{max.}$(OH) band at 3 180 cm^{-1}. Subsequent reaction of (4) with CNBu^t gives (5), a species which can also be obtained by protonation of (1). Alkylation of (2) with [OMe$_3$][SbCl$_6$] affords the methoxy-derivative (6).

In order to gain further insight into the bonding of the bridging PhC•C(O)•CPh ligand to the platinum atoms in these complexes, ^{13}C n.m.r. measurements were made with particular reference to observing ^{195}Pt–^{13}C coupling constants. For the four complexes (1), (2), (4), and (5) coupling was observed between platinum and the three bridging carbon atoms. Although the signals were weak they were readily enhanced without shifting by addition of [Cr(acac)$_3$]. In all cases a quintet (1 : 8 : 18 : 8 : 1) splitting pattern was observed consistent with coupling to two identical platinum nuclei. Although the coupling constants *J*[PtC(2)] are lower than those for *J*[PtC(1,3)] (Table 2), their magnitude is such as to suggest bonding to the platinum atoms of the bridgehead carbon atoms. Thus in mononuclear allylplatinum species, such as [Pt(η-C$_3$H$_5$)(cod)]$^+$, coupling (*ca.* 46 Hz) between platinum and the central carbon of the allyl group is less than that (*ca.* 145 Hz) to the terminal carbons.[24]



SCHEME 3 (*i*) ' PtL$_2$ ' with L = PPh$_3$, CNBu^t, or L$_2$ = cod; (*ii*) L = PPh$_3$; (*iii*) ' PtL$_2$ ' with L = CNBu^t or L$_2$ = cod

TABLE 2

Carbon-13 chemical shifts and coupling constants for the PhC(1)•C(2)•(O)•C(3)Ph ligands [a]

Compound	δ C(1), C(3)	δ C(2)
(1) [Pt$_2${μ-(PhC)$_2$CO}(CNBu^t)$_4$] [b]	86.6 (342)	168.5 (125)
(2) [Pt$_2${μ-(PhC)$_2$CO}(cod)$_2$] [b]	108.8 (429)	155.9 (144)
(4) [Pt$_2${μ-(PhC)$_2$C(OH)}(cod)$_2$][BF$_4$] [c]	100.5 (394)	144.5 (119)
(5) [Pt$_2${μ-(PhC)$_2$C(OH)}(CNBu^t)$_4$][BF$_4$] [c]	80.4 (317)	155.6 (107)
PhC:C(Ph)•C:O [b]	124.1	155.9

[a] Hydrogen-1 decoupled, chemical shifts (p.p.m.) relative to SiMe$_4$, with coupling constants *J*(PtC) (Hz) in parentheses. [b] In CDCl$_3$. [c] In CD$_2$Cl$_2$.

Mechanistically it is interesting to compare the C=C double-bond cleavage observed in the present work with the earlier studies[8,9] involving phosphineplatinum(0) complexes (Scheme 1). By carrying out experiments at low temperatures it was shown[9] that the opening of the three-membered ring occurred *via* initial formation of an η^2 complex. A mechanism for subsequent rearrangement to a metallacyclobutenone has not been proposed but it is plausible to suggest that a carbenemetal complex is involved (Scheme 3). Such complexes have been invoked as intermediates in various metal-promoted reactions of small-ring organic molecules.[25-27] In the new reactions described herein, involving carbon–carbon double-bond cleavage, it is likely that the initial step also involves formation of an η^2 complex. The second step, however, might be attack by PtL$_2$ (L = CNBu^t or L$_2$ = cod) on the opposite side of the π complex so populating the antibonding orbitals of the C$_3$ system as to cause bond cleavage in the manner observed. It is unclear what factors control the two different reaction paths but an important feature must be the nature of the ligands CNBu^t or cod *versus* PR$_3$. In contrast to tertiary phosphines, perhaps the weaker donor ligands CNBu^t or cod are able to slow down the assumed conversion into a carbene complex, *via* the η^2 complex, so as to permit a second PtL$_2$ (L = CNBu^t or L$_2$ = cod) group to attack the bent σ orbitals of the C$_3$ ring. Concomitant Pt–Pt interaction and breaking of a formally bridging C=C bond could then occur. A similar step-

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[24] N. M. Boag, M. Green, J. L. Spencer, and F. G. A. Stone, unpublished work.

[25] R. Noyori, *Tetrahedron Letters*, 1973, 1691; R. Noyori, H. Kawauchi, and H. Takaya, *ibid.*, 1974, 1749.

[26] P. Binger and J. McMeeking, *Angew. Chem. Internat. Edn.*, 1974, **13**, 466.

[27] P. W. Jolly and G. Wilke, ' The Organic Chemistry of Nickel,' Academic Press, New York, 1975, vol. 2, ch. 1.

wise interaction of dibenzylideneacetone-palladium(0) or -platinum(0) with triarylcyclopropenylium bromides could account for formation of the complexes $[M_3(C_3R_3)_2Br_2]$ (M = Pd or Pt).[5]

The combination of a C=C double bond and bent C–C σ bonds in diphenylcyclopropenone leads us to suggest that this molecule behaves as a 'homo-diphenylacetylene' in reactions with $[Pt_3(CNBu^t)_6]$ or [Pt(cod)(mvk)$_2$]. We have recently reported[28] stepwise reactions of certain platinum(0) complexes with diphenylacetylene and other acetylenes which are strikingly similar to steps (*i*) and (*iii*) in Scheme 3, leading to formation of di- and tri-platinum species $[Pt_2(\mu\text{-ac})L_4]$ and $[Pt_3(\mu\text{-ac})_2L_4]$ (ac = acetylene). The ^{195}Pt–^{13}C coupling constants in these bridged acetylene complexes are very similar to those of the C(1) and C(3) bridging carbons listed in Table 2.

There has recently been much discussion of the role of metal clusters in the activation of multiple carbon–carbon bonds.[29] Initially we considered the possibility that in the reaction of $[Pt_3(CNBu^t)_6]$ with $Ph{\cdot}C{:}C(Ph){\cdot}C{:}O$ the cyclopropenone interacted directly with the cluster. However, we consider this to be unlikely in view of the similar chemistry observed with mononuclear [Pt(cod)(mvk)$_2$] which apparently can act as a source of the Pt(cod) moiety. We currently suspect that the reactivity of $[Pt_3(CNBu^t)_6]$ derives from its ability to act as a ready source of $[Pt(CNBu^t)_2]$.[11,30]

As an alternative route to complexes like (4), (5), or (6) we have considered attack on a mononuclear metallacyclobutenylium cation by a platinum(0) complex. Accordingly, the complex $[Pt\{C(Ph){:}C(Ph){\cdot}C{:}O\}(PPh_3)_2]$[8] was methylated with trimethyloxonium tetrafluoroborate giving $[Pt\{C(Ph){\cdot}C(Ph){\cdot}C{\cdot}OMe\}(PPh_3)_2][BF_4]$ (7) in high yield. Complex (7), however, did not react with $[Pt(C_2H_4)(PPh_3)_2]$ to give a diplatinum species analogous to (5) or (6). Failure of this reaction may be due to a number of factors.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra ($CDCl_3$ solutions) were recorded on a Varian Associates HA100 spectrometer with $SiMe_4$ (τ 10.00) as internal reference. Carbon-13 n.m.r. spectra were obtained ($CDCl_3$ or CD_2Cl_2 solutions) on a JEOL PFT-100 spectrometer at 25.1 MHz, were ^1H decoupled, and the shifts are relative to $SiMe_4$, positive values to high frequency. Coupling constants *J*(PtC) for the bridging ligand PhC·C(O)·CPh are given in Table 2. The assignments C(1), C(2), *etc.* refer to the carbon atoms in the Figure. The ^{31}P spectrum of complex (3) was also obtained on the JEOL PFT-100 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer using Nujol mulls. All the experiments were performed in a dry oxygen-free nitrogen atmosphere.

Diphenylcyclopropenone was prepared from dibenzyl ketone,[13] and [Pt(cod)$_2$] and $[Pt_3(CNBu^t)_6]$ by methods previously described.[10,21]

Syntheses.— μ-2-*Oxo*-1,3-*diphenylpropanediylidene-bis*[*bis*(*t-butyl isocyanide*)*platinum*], $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNBu^t)_4]$ (1). A solution of $[Pt_3(CNBu^t)_6]$ (0.27 g, 0.25 mmol) in toluene (15 cm^3) was treated dropwise with a toluene (15 cm^3) solution of diphenylcyclopropenone (0.08 g, 0.38 mmol). There was a rapid reaction, the initial red solution becoming yellow. After stirring for 1 h, solvent was removed *in vacuo*. Recrystallisation of the solid residue from dichloromethane–hexane afforded (1) as yellow *crystals* (0.29 g, 83%), m.p. 210 °C (decomp.) (Found: C, 45.3; H, 5.3; N, 6.0. $C_{35}H_{46}N_4OPt_2$ requires C, 45.3; H, 5.0; N, 6.0%), $\nu_{max.}$ at 2 168vs, 2 140vs, 1 584s, 1 568 (sh), 1 556s, 1 487s, 1 440s, 1 397w, 1 370s, 1 302w, 1 273vw, 1 263vw, 1 230m, 1 200s,br, 1 072w, 1 031w, 999w, 863w, 787m, 749m, 705s, 583m, 572m, 523m, 513m, and 452w cm^{-1}. N.m.r. spectra: ^1H, τ 8.70 (s, 36 H, Bu^t), 3.06 (m, 2 H, *p*-HC_6H_4), 2.82 (m, 4 H, *m*-$H_2C_6H_3$), and 1.92 (m, 4 H, *o*-$H_2C_6H_3$); ^{13}C, 30.0 [$(CH_3)_3CNC$], 56.4 [$(CH_3)_3CNC$], 86.6 [C(1) and C(3)], 123.0 [C(14) and C(34)], 126.8 [C(13), C(15), C(33), and C(35)], 129.0 [C(12), C(16), C(32), and C(36)], 148.5 [C(11) and C(31)], and 168.5 p.p.m. [C(2)].

μ-2-*Oxo*-1,3-*diphenylpropanediylidene-bis*[(η-*cyclo-octa*-1,5-*diene*)*platinum*], $[Pt_2\{\mu\text{-}(PhC)_2CO\}(cod)_2]$ (2). Bis-cyclo-octa-1,5-diene)platinum (0.62 g, 1.5 mmol) was added to a stirred diethyl ether (40 cm^3) solution of methyl vinyl ketone (5 cm^3, excess) at −20 °C. After 5 min the yellow solution was cooled to −50 °C and treated with diphenylcyclopropenone (0.16 g, 0.75 mmol). The mixture was warmed slowly to room temperature, during which time a yellow precipitate formed. After stirring (1 h) the mixture was filtered, washed with diethyl ether (2 × 20 cm^3) and hexane (20 cm^3), and dried *in vacuo*. Crystallisation from dichloromethane gave (2) as yellow *plates* (0.49 g, 80%), m.p. 206 °C (decomp.) (Found: C, 46.6; H, 4.6. $C_{31}H_{34}OPt_2$ requires C, 45.8; H, 4.2%), $\nu_{max.}$ at 3 030m,br 1 590m, 1 570vs, 1 508vw, 1 499vw, 1 484s, 1 438s, 1 412m, 1 368m, 1 330w, 1 302w, 1 229w, 1 214vw, 1 189vw, 1 175w, 1 155m, 1 070m, 1 029w, 1 020w, 990vw, 973m, 918w, 860m, 851m, 819w, 780s, 760m, 732m, 709s, 691m, 575s, and 460m cm^{-1}. N.m.r. spectra: ^1H, τ 7.80 (m, 8 H, CH_2), 7.64 (m, 8 H, CH_2), 5.56 [m, 4 H, CH=CH, *J*(PtH) 64], 4.84 [m, 4 H, CH=CH, *J*(PtH) 40 Hz], 2.94 (m, 6 H, C_6H_5), and 2.32 (m, 4 H, C_6H_5); ^{13}C, 30.2 (CH_2), 31.0 (CH_2), 91.6 [C=C, *J*(PtC) 99], 94.2 [C=C, *J*(PtC) 111 Hz], 108.8 [C(1) and C(3)], 125.3 [C(14) and C(34)], 127.0 [C(12), C(16), C(32), and C(36)], 128.0 [C(13), C(15), C(33), and C(35)], 143.7 [C(11) and C(31)], and 155.9 p.p.m. [C(2)].

Reactions of Complex (2).—(*a*) *With t-butyl isocyanide.* A suspension of complex (2) (0.05 g, 0.06 mmol) in diethyl ether (20 cm^3) was treated with excess of t-butyl isocyanide (0.2 cm^3, 2 mmol). After 10 min the resulting yellow solution was evaporated *in vacuo*, the residue dried, and crystallised from dichloromethane–light petroleum to give complex (1) in quantitative yield, its identity being confirmed from i.r. and ^1H n.m.r. spectra.

(*b*) *With trimethyl phosphite.* The complex $[Pt_2\{\mu\text{-}(PhC)_2CO\}\{P(OMe)_3\}_4]$ (3) was obtained quantitatively as bright yellow *crystals* using a similar method to that in (*a*) (Found: C, 29.6; H, 4.4. $C_{27}H_{46}O_{13}P_4Pt_2$ requires C, 29.7; H, 4.2%), $\nu_{max.}$(CO) at 1 549 cm^{-1}. Hydrogen-1 n.m.r.: τ 6.62 (m, MeO), 2.96 (m, C_6H_5), and 1.76 (m, C_6H_5).

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[28] N. M. Boag, M. Green, J. A. K. Howard, J. L. Spencer, R. F. D. Stansfield, F. G. A. Stone, M. D. O. Thomas, J. Vicente, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 930.

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[30] J. Fornies, M. Green, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1515.

(*c*) *With tetrafluoroboric acid.* A suspension of (2) (0.2 g, 0.25 mmol) in diethyl ether (20 cm^3) was treated with an excess of anhydrous HBF_4 (prepared by dissolving 40% aqueous acid in propionic anhydride). After 1 h the solvent was decanted and the pale cream solid washed (3×10 cm^3) with diethyl ether and dried *in vacuo*. Crystallisation from dichloromethane–hexane afforded pale cream *microcrystals* of $[Pt_2\{\mu\text{-}(PhC)_2C(OH)\}(cod)_2][BF_4]$ (4) (0.19 g, 86%) (Found: C, 40.8; H, 4.1. $C_{31}H_{35}BF_4OPt_2$ requires C, 41.3; H, 3.9%). N.m.r.: ^1H, τ 7.66 (m, 8 H, CH_2), 7.50 (m, 8 H, CH_2), 5.24 [m, 4 H, CH=CH, *J*(PtH) 40], 4.58 [m, 4 H, CH=CH, *J*(PtH) 48 Hz], 3.92 (br, 1 H, OH), and 2.54—2.50 (m, 10 H, C_6H_5); ^{13}C, 30.4 (CH_2), 31.2 (CH_2), 96.7 [C=C, *J*(PtC) 114], 97.5 [C=C, *J*(PtC) 116 Hz], 100.5 [C(1) and C(3)], 128.0, 128.1, and 129.5 [C(12)—C(16) and C(32)—C(36)], 137.8 [C(11) and C(31)], and 144.5 p.p.m. [C(2)].

Treatment of a suspension of (4) in diethyl ether with excess of $CNBu^t$ gave a white powder which was filtered off, dried *in vacuo*, and isolated as white *microcrystalline* $[Pt_2\{\mu\text{-}(PhC)_2C(OH)\}(CNBu^t)_4][BF_4]$ (5) (Found: C, 41.8; H, 5.1; N, 5.6. $C_{35}H_{47}BF_4N_4OPt_2$ requires C, 41.3; H, 4.6; N, 5.5%), $\nu_{max.}$(NC) at 2 200 and 2 182 cm^{-1}. N.m.r.: ^1H, τ 8.66 (s, 36 H, Bu^t), 5.52 (br, 1 H, OH), and 2.82—2.50 (m, 10 H, C_6H_5); ^{13}C, 30.0 [$(CH_3)_3CNC$], 58.2 [$(CH_3)_3CNC$], 80.4 [C(1) and C(3)], 126.4 [C(14) and C(34)], 128.3 [C(13), C(15), C(33), and C(35)], 129.8 [C(12), C(16), C(32), and C(36)], 141.8 [C(11) and C(31)], and 155.6 p.p.m. [C(2)].

(*d*) *With trimethyloxonium hexachloroantimonate*(V). A solution of (2) (0.1 g, 0.13 mmol) in dichloromethane (15 cm^3) was treated with $[OMe_3][SbCl_6]$ (0.1 g, 0.25 mmol). The orange-red mixture produced was stirred vigorously for 1 h. The solution was decanted into diethyl ether (50 cm^3) in which the product precipitated. Crystallisation from dichloromethane gave orange *needles* of $[Pt_2\{\mu\text{-}(PhC)_2COMe\}(cod)_2][SbCl_6]$ (6) (0.05 g, 35%) (Found: C, 33.0; H, 3.5. $C_{32}H_{37}Cl_6OPt_2Sb$ requires C, 33.0; H, 3.7%).

Crystal-structure Determination of $[Pt_2\{\mu\text{-}(PhC)_2CO\}(CNBu^t)_4]$ (1).—Complex (1) crystallised from toluene as yellow prisms and that used for data collection was of dimensions *ca.* $0.4 \times 0.15 \times 0.15$ mm and enclosed in a Lindemann glass capillary. Intensity data were collected at room temperature on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 50°$ based on methods described earlier.[31] Of a total of 7 996 reflections, 4 494 were deemed independently observable according to the criterion $I \geqslant 2\sigma(I)$, 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 the solution and refinement of the structure.

Crystal data. $C_{35}H_{46}N_4OPt_2$, $M = 928.9$, Monoclinic, space group $P2_1/n$, $F(000) = 1\,792$, $a = 11.283(8)$, $b = 19.821(6)$, $c = 17.534(7)$ Å, $\beta = 90.23(4)°$, $U = 3\,920$ Å^3, $D_m = 1.59$, $Z = 4$, $D_c = 1.58$ g cm^{-3}, Mo-K_α *X*-radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 75.54 cm^{-1}.

Structure solution and refinement. The molecular structure (Figure) was solved from electron-density difference syntheses, following location of the two platinum atoms from a Patterson synthesis. In the final stages of full-matrix least-squares refinement only the platinum atoms were given anisotropic thermal parameters. Hydrogen-atom contributions were not included. The observed high thermal activity of the methyl carbon atoms in the t-butyl isocyanide ligands is characteristic.[10] There was also indication of thermal disorder in one phenyl ring [C(33) and C(34)] but since its origin is not definable the high thermal parameters are presented as refined.

TABLE 3

Final positional (fractional co-ordinate) parameters, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt(1)	−0.007 62(6)	0.181 24(3)	0.064 06(4)
Pt(2)	−0.003 70(6)	0.169 75(3)	0.224 28(4)
C(1)	0.857 8(16)	0.193 4(8)	0.146 0(9)
C(11)	0.732 9(18)	0.165 1(9)	0.145 0(10)
C(12)	0.639 8(22)	0.211 8(11)	0.146 9(12)
C(13)	0.517 3(27)	0.183 6(15)	0.145 9(16)
C(14)	0.508 5(26)	0.114 7(16)	0.145 5(15)
C(15)	0.597 9(28)	0.068 6(14)	0.140 8(15)
C(16)	0.716 3(23)	0.094 7(12)	0.141 6(13)
C(2)	0.893 7(17)	0.261 7(9)	0.151 5(10)
O(2)	0.831 9(13)	0.315 0(7)	0.151 6(7)
C(3)	1.020 9(15)	0.252 1(8)	0.151 1(9)
C(31)	1.108 1(17)	0.305 8(9)	0.152 6(10)
C(32)	1.071 9(28)	0.371 9(16)	0.141 2(16)
C(33)	1.168 8(20)	0.428 4(10)	0.136 4(11)
C(34)	1 287 3(30)	0.408 9(17)	0.150 3(17)
C(35)	1.320 1(25)	0.345 4(15)	0.161 3(15)
C(36)	1 230 2(24)	0.291 6(12)	0.163 2(13)
C(4)	0.918 9(18)	0.115 1(10)	−0.003 5(10)
N(4)	0.866 2(16)	0.076 0(8)	−0.042 1(9)
C(41)	0.788 5(25)	0.029 1(13)	−0.087 8(15)
C(411)	0.765 9(28)	−0.027 1(16)	−0.032 4(17)
C(412)	0.871 2(30)	0.004 6(16)	−0.151 8(18)
C(413)	0.680 2(27)	0.067 0(14)	−0.112 3(15)
C(5)	1.130 2(18)	0.198 1(9)	0.000 6(10)
N(5)	1.215 9(17)	0.209 6(9)	−0.033 7(10)
C(51)	1.316 0(28)	0.230 8(15)	−0.089 2(16)
C(511)	1.394 1(34)	0.171 3(17)	−0.104 6(20)
C(512)	1.243 6(27)	0.253 9(14)	−0.159 5(16)
C(513)	1.380 6(28)	0.289 7(16)	−0.049 8(17)
C(6)	0.924 8(20)	0.094 6(11)	0.277 7(12)
N(6)	0.882 3(18)	0.048 6(10)	0.308 3(11)
C(61)	0.816 6(34)	−0.019 3(19)	0.337 1(21)
C(611)	0.881 0(34)	−0.028 1(18)	0.413 9(22)
C(612)	0.827 1(36)	−0.065 6(20)	0.279 5(22)
C(613)	0.696 0(35)	0.014 1(19)	0.354 3(20)
C(7)	1.137 7(17)	0.172 6(9)	0.287 5(10)
N(7)	1.219 2(16)	0.175 9(8)	0.330 2(9)
C(71)	1.313 4(25)	0.187 2(13)	0.389 6(14)
C(711)	1.242 2(29)	0.212 2(16)	0.459 6(18)
C(712)	1.395 9(29)	0.242 0(16)	0.359 9(17)
C(713)	1.368 7(37)	0.121 5(22)	0.404 3(22)

TABLE 4

Equations of some least-squares planes in the form $Ax + By + Cz = D$, where *x*, *y*, and *z* are fractional co-ordinates: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): C(1), C(2), C(3)

$$-0.047x - 1.366y + 17.492z = 2.250$$

[O(2) 0.07]

Plane (2): Pt(1), C(1), C(3), C(4), C(5)

$$-5.174x + 14.165y - 9.229z = -3.090$$

[C(2) 0.80, O(2) 1.88]

Plane (3): Pt(2), C(1), C(3), C(6), C(7)

$$-4.912x + 12.223y + 11.528z = -0.188$$

[C(2) 0.76, O(2) 1.71]

Angles (°) between planes: (1)–(2) 55; (1)–(3) 52; (2)–(3) 73

Weightings, applied according to the scheme $1/w = \sigma^2(F) + 0.025F$, gave a satisfactory analysis. Refinement converged to *R* 0.070 (*R'* 0.069), with a mean shift-to-error

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

ratio of 0.05 : 1 and a maximum of 1.65 : 1 in the last cycle of refinement. An electron-density synthesis showed no peaks >0.9 or <-0.9 e Å^{-3}, except in the regions of the suspect atoms C(33) and C(34) with $|\rho_{\text{max.}}| = 1.6$ e Å^{-3}. The atomic scattering factors used were those of ref. 32 for Pt, and ref. 33 for C, N, and O. Corrections for the effects of anomalous dispersion were applied for the Pt atoms ($\Delta f' = -2.352$, $\Delta f'' = 8.388$). Computational work was carried out using the ' *X*-RAY ' system of programs at the University of London Computing Centre. The atomic co-ordinates are given in Table 3 and equations of some least-squares planes in Table 4. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22302 (20 pp.).*

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

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