Preparation and *X*-Ray Crystallographic Determination of the Structure of the Platinacyclobutenone $[(C_6H_5)_3P]_2Pt[OC_3(C_6H_5)_2]$

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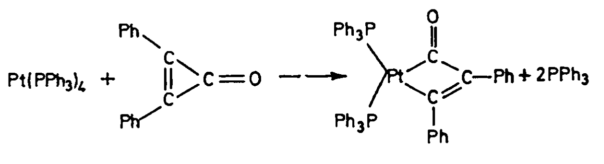
Summary The reaction of diphenylcyclopropenone with tetrakis(triphenylphosphine)platinum(0) is described, and the results of an *X*-ray crystallographic study of the product are reported.

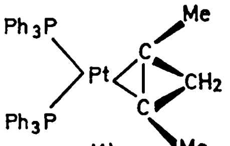
Several mechanisms have been suggested for the hydrocarboxylation of acetylenes to form αβ-unsaturated acids;[1] one invokes[2] the intermediacy of a metallacyclobutenone. The new complex reported here is the first authenticated example of a metallacyclobutenone.[3]



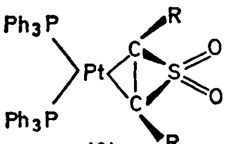
(1)

The reaction between $Pt(PPh_3)_4$ and diphenylcyclopropenone in dichloromethane at room temperature for 10 min gives the complex as yellow-orange needles in 60% yield, m.p. 158—160° (decomp.). A strong absorption at 1652 cm^{-1} is the only band observed in the 1500—2200 cm^{-1} region of the i.r. spectrum.

The crystals are monoclinic, $P2_1/c$, $a = 12{\cdot}56(4)$, $b = 11{\cdot}72(4)$, $c = 28{\cdot}34(9)$ Å, $\beta = 107{\cdot}5(9)^\circ$, $Z = 4$. Refinement on an isotropic model with 2029 diffractometer data yields an R value of 11%. The monomeric unit consists of a Pt^{II} central atom in quasi-square-planar co-ordination with two *cis*-PPh_3 ligands and a σ-bonded bidentate ligand derived from diphenylcyclopropenone (Figure). All bond lengths are within the range found for similar molecules.[4]



(1)



(2)

The most interesting feature of the molecule is its mode of formation *via* carbon–carbon bond cleavage. The metal atom has been inserted into a two-electron σ-bond of the three-membered carbon ring, forming a four-membered heterocyclic ring with two Pt–C σ-bonds of length 2·08(5) Å. The PtC_3 heterocyclic ring is nearly coplanar with the PtP_2 part. The dihedral angle between these two planes is *ca.* 11°, but none of the six atoms deviates from the leastsquares plane by more than 0·3 Å. This PtP_2C_3 portion defines the mean molecular plane. Both the C=C double bond and the remaining C–C single bond of the parent cyclopropenone retain their character, with bond lengths of 1·31(8) and 1·45(7) Å, respectively. The centroids of the two phenyl rings attached to the PtC_3 ring lie nearly in the plane of the molecule, with average C(phenyl)–C(heterocycle) bonds of 1·44(7) Å, while the planes of the phenyl rings are approximately perpendicular to the plane of the molecule. The oxygen atom lies 0·4 Å below the molecular plane, with a normal C=O bond distance of 1·21(7) Å. No interaction between the platinum and oxygen is expected due to the long distance, 2·95 Å, between these two atoms.

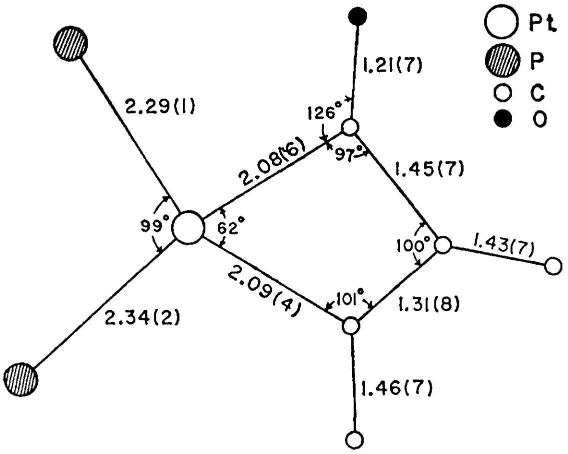


FIGURE *Structure of* $[(C_6H_5)_3P]_2Pt[OC_3(C_6H_5)_2]$. *Phenyl rings have been deleted for clarity.*

Cyclopropenone–metal complexes have been of interest since Orgel suggested that they might be intermediates in hydrocarboxylation reactions of acetylenes.[5] Simple MO considerations led to the suggestion that cyclopropenones should be capable of forming metal π-complexes analogous to those formed by cyclopentadienones and cycloheptatrienones.[6] Subsequently several cyclopropenone complexes were reported,[7] but in all cases, except one,[6] bonding to the metal appears to be *via* the oxygen atom. The ring-opening reaction, equation (1), illustrates a new way in which cyclopropenones may react with metal complexes. This mode of reactivity is in contrast to recently reported reactions of the related small ring compounds dimethylcyclopropene and thiiren 1,1-dioxides with $Pt(PPh_3)_2$ where the three-membered ring remains intact to give (**1**) and (**2**), respectively.[8]

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[2] C. W. Bird and E. M. Briggs, *J. Chem. Soc.* (*C*), 1967, 1265.

[3] It was tentatively suggested in a recent paper, R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2981 that the product obtained from irradiation of a mixture of *trans*-tricarbonylbis(trimethyl phosphite)ruthenium and 1 mol equiv. of hexafluorobutyne in hexane is a metalla-cyclobutenone.

[4] I. D. Brown and C. P. Weiss, 'Bond Index to the Determination of Inorganic Crystal Structures Published During 1970 (BIDICS-1970),' Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada.

[5] L. E. Orgel, *Chem. Soc. Special Publ.*, 1959, **13**, 93.

[6] D. A. Brown, *J. Inorg. Nuclear Chem.*, 1960, **13**, 212.

[7] C. W. Bird and E. M. Hollins, *Chem. and Ind.*, 1964, 1362; C. W. Bird and E. M. Briggs, *J. Chem. Soc.* (*A*), 1967, 1004; C. W. Bird, E. M. Briggs, and J. Hudec, *J. Chem. Soc.* (*C*), 1967, 1862; W. L. Fichteman, P. Schmidt, and M. Orchin, *J. Organometallic Chem.*, 1968, **12**, 249.

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