Reaction of 1,2-Benzocyclobutadienequinone with Zerovalent Platinum: Preparation and Structure of (1,1-Bistriphenylphosphine)platinabenzocyclopentenedione

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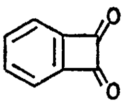
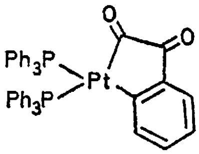
Summary The reaction of tetrakis(triphenylphosphine)-platinum with 1,2-benzocyclobutadienequinone (**1**) effects an unsymmetrical opening of, and insertion of $Pt(PPh_3)_2$ into, the four-membered ring of (**1**) to give two conformers of the title compound, whose crystal structures have been determined.

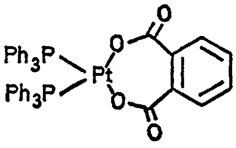
Our interest in the oxidative addition reaction of *o*-quinones to various metal complexes[1] has led us to investigate the organometallic chemistry of 1,2-benzocyclobutadienequinone, (**1**).[2]



(**1**)



(**2**)



(**3**)

The cyclic dione (**1**) reacts with Pt(PPh$_3$)$_4$ in benzene at room temperature to produce a deep-red solution. Addition of ethanol to the solution induces formation of deep-red crystals (**2a**), [65%, m.p. 205—212° (decomp.); ν(CO) 1640sh, 1660s, 1686m cm^{-1}; λ_{max} (Nujol mull) 506br nm], and deep-blue crystals (**2b**), [5%, m.p. 190—205° became red, 205—212° (decomp.); ν(CO) 1647s, 1692w cm^{-1}; λ_{max} (Nujol mull) 562br nm], both having the same molecular formula. *X*-Ray structure determinations have shown that the red and blue crystals contain conformers of the same molecular species (**2**), which is the result of insertion of Pt(PPh$_3$)$_2$ into the (C$_6$H$_4$)C–C(O) bond of the cyclic dione (**1**).

Crystal data: (**2a**) $C_{44}H_{34}O_2P_2Pt$, $M = 851{\cdot}9$, red monoclinic crystals, $a = 11{\cdot}79$, $b = 22{\cdot}27$, $c = 15{\cdot}64$ Å, $\beta = 122{\cdot}0°$, $U = 3481$ Å^3; $Z = 4$, space group $P2_1/c$; $R = 0{\cdot}057$ for 3961 reflections with $I/\sigma(I) \geqslant 3$. (**2b**) blue triclinic crystals, $a = 9{\cdot}740$, $b = 9{\cdot}797$, $c = 19{\cdot}61$ Å, $\alpha = 99{\cdot}9$, $\beta = 96{\cdot}9$, $\gamma = 105{\cdot}6°$, $U = 1749$ Å^3; $Z = 2$, space group $P\bar{1}$ assumed; $R = 0{\cdot}050$ for 3999 reflections with $I/\sigma(I) \geqslant 3$, from a Stoe Weissenberg automatic diffractometer.

The principal difference between conformers (**2a**) and (**2b**) occurs in the angles of twist of the two carbonyl groups about the connecting C–C bond. Details of molecular geometry will be presented elsewhere.

The relative amounts of (**2a**) and (**2b**) which can be isolated can be affected by the presence of excess of triphenylphosphine. Thus recrystallisation of the red form from chloroform–ethanol in the presence of triphenylphosphine affords (**2b**). Recrystallisation of the blue form in the absence of free phosphine affords the more stable red form (**2a**).

Treatment of (**1**) with both Pt(PMePh$_2$)$_4$ and Pt(AsPh)$_4$ affords similar ring-opened products. These reactions of (**1**) with zerovalent platinum complexes, which involve the unsymmetrical opening of the four-membered ring, contrast with the photolysis of (**1**) which leads to symmetrical cleavage of the ring.[3] In the presence of oxygen, (**1**) and Pt(PPh$_3$)$_4$ gave the carboxylate complex (**3**), [90%, m.p. 171 (decomp.); ν(CO$_2$)$_{asym}$ 1640 cm^{-1}] which may also be obtained by the addition of phthalic acid to Pt(PPh$_3$)$_4$.

Diphenylcyclopropenone has been shown to undergo a similar insertion reaction of Pt(PPh$_3$)$_2$ into a σ-bond of the three-membered carbon ring.[4]

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