Ring Opening of Cyclobutenedione Derivatives with Zerovalent Platinum

By E. Roger Hamner, Raymond D. W. Kemmitt,* and Martin A. R. Smith
(*Chemistry Department, The University, Leicester,* LE1 7RH)

Summary trans-Stilbenebis(triphenylphosphine)platinum(0) and other platinum(0) compounds ring open cyclobutenedione derivatives *via* metal-olefin intermediates to give platinacyclopentenedione complexes; only olefin complexes are formed with tetrakis(triphenylphosphine)-palladium(0) except with benzocyclobutenedione which undergoes ring-opening.

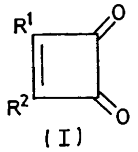
Significant differences have been observed between the photochemistry of cyclobutenediones and benzocyclobutenediones.[1] We find, however, that their organoplatinum chemistry is similar and that platinum(0) complexes effect unsymmetrical ring opening of these systems to provide a general synthesis of platinacyclopentenedione complexes. The cyclic diones (Ia)—(Ic) readily react with *trans*-stilbenebis(triphenylphosphine)platinum(0) or tetrakis(triphenylarsine)platinum(0) in chloroform or benzene solution to yield the air-stable crystalline complexes (II).

Table

Complex		I.r. data[a]	N.m.r. data[b]					
			H			Me (or OMe)		
		ν(CO) region/cm^{-1}	δ	*J*(Pt–H)	*J*(P–H)	δ	*J* (Pt–Me)	*J* (P–Me)
(IIa)	L=Ph$_3$P	1658(vs), 1667(sh)	9·20	21·5	17·0 (*trans* P)			
	L=Ph$_3$As	1657(vs), 1677(s)	9·40	21·5	8·5 (*cis* P)			
(IIb)	L=Ph$_3$P	1652(vs), 1660(s), 1684(w)				2·75		
(IIc)	L=Ph$_3$P	1650(sh), 1659(vs)				3·25 3·70		
	L=Ph$_3$As	1657(vs)				3·51 3·90		
(IIIa)	L=Ph$_3$P	1723(vs)	4·75	48·8	6·7[c,d]			
	L=Ph$_3$As	1724(vs)	5·00	57·5				
(IIIb)	L=Ph$_3$P	1692(s), 1721(vs)				1·48	11·5	5·6 (*trans* P) 4·5 (*cis* P)
	L=Ph$_3$As	1693(sh), 1706(sh) 1720(vs)				1·60	13·0	
(IIIc)	R^2=H	1708(sh), 1724(vs)	5·55		1·7 (*trans* P) 0 (*cis* P)			
	R^2=Me	1691(s), 1721 (vs)				1·44		6·3[c]

[a] I.r. spectra taken as Nujol mulls between KBr or NaCl plates. Accurate to ± 3 cm^{-1}. The free ligands have ν(CO) values in the range 1800—1720 cm^{-1}. W. Ried and A. H. Schmidt, *Angew. Chem. Internat. Edn.*, 1972, **11**, 997; S. Cohen and S. G. Cohen, *J. Amer. Chem. Soc.*, 1966, **88**, 1533. [b] 100 MHz spectra in CDCl$_3$. Shifts are in p.p.m. downfield of Me$_4$Si. Coupling constants in Hz. [c] Apparent triplet spectra arising from ABX or ABX$_3$ (A, B=P, X=H) systems in which $J(AB) >> |J(AX) - J(BX)|$. Observed $J = \frac{1}{2}|J(AX) + J(BX)|$. This is confirmed by observation of AB quartets in the proton decoupled ^{31}P spectra. [d] ^{31}P data (CH$_2$Cl$_2$, 40·5 MHz). $J(P_AP_B)$ 34 Hz; $J(PtP_A)$ 4194 Hz, $J(PtP_B)$ 4072 Hz; δ_A +114·7, δ_B +112·4 p.p.m. [*vs* ext. P(OMe)$_3$].

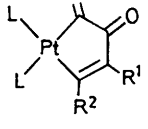
The structures of these complexes follow from microanalytical data, their i.r. spectra which exhibit strong carbonyl stretching frequencies in the region 1680—1650 cm^{-1} and their ^{1}H n.m.r. spectra (Table). The magnitude of the values of *J*(P–H) for the ring opened product prepared from 1-phenylcyclobut-1-ene-2,3-dione strongly supports a structure in which the –CH–CO– bond of the four membered ring has been cleaved. Conjugation of the phenyl group with the cyclobutenedione ring presumably inhibits cleavage of the –C(Ph)–CO– bond and this effect may well influence the point of cleavage in the reaction with (Ib), although the present data does not preclude the alternative isomer. Unsymmetrical ring cleavage of benzocyclobutenedione by platinum(0) systems has previously been reported.[2] In diethyl ether (Ia) reacts with Pt(*trans*-stilbene)(PPh$_3$)$_2$ and Pt(AsPh$_3$)$_4$ to form precipitates of the intermediate olefin complexes (IIIa). These complexes



(I)

a; R^1= Ph, R^2= H
b; R^1= Ph, R^2= OMe
c; R^1= R^2=OMe
d; R^1= Ph, R^2=Me

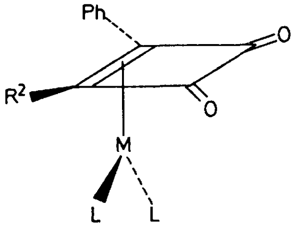
exhibit carbonyl stretching frequencies in the range 1730—1690 cm^{-1} in contrast to the complexes (II), (Table). In chloroform solution the complexes (IIIa) re-arrange slowly to the ring opened isomers and it is therefore apparent that these carbon-carbon bond cleavage reactions occur *via* intermediate olefin complexes as has been observed in the related ring opening reactions of cyclopropenones.[3] However, it is apparent from the present studies that olefin complexes derived from the four-membered ring diones are more stable to ring opening than those formed with cyclopropenones which readily ring open even at low temperatures.[3] No intermediate olefin complexes can be isolated



(II)

L= PPh$_3$ or AsPh$_3$
a; R^1=Ph, R^2=H
b; R^1=Ph, R^2=OMe
c; R^1=R^2=OMe

with the cyclic diones (Ib) and (Ic) and the observation that these diones undergo rapid ring opening suggests that the presence of electron withdrawing substituents facilitate C–C bond cleavage in these systems. Further support for this effect is provided by the observation that (Id) only forms olefin complexes of type (IIIb) which do not ring open even in solution over long periods. Recent studies on the reactions of cyano substituted cyclopropanes also suggest that electron withdrawing groups facilitate C–C bond cleavage by platinum(0).[4]



a; M=Pt, R_2=H, L=PPh_3 or $AsPh_3$
b; M=Pt, R_2=Me, L=PPh_3 or $AsPh_3$
c; M=Pd, R_2=Me or H, L=PPh_3

(III)

Experiments with $Pd(PPh_3)_4$ show that the cyclobutenediones (Ia)–(Id) are not ring opened by palladium(0) but do form isolable olefin complexes (IIIc) in some instances. This is consistent with the lower nucleophilicity of palladium (0) and decreased tendency for palladium (0), as compared to platinum(0), to undergo oxidative addition. However, we do find that $Pd(PPh_3)_4$ does ring expand benzocyclobutenedione [$\nu(CO)$ of complex = $1638\ \text{cm}^{-1}$]. In studies with cyclopropenones and $Pd(PPh_3)_4$ neither intermediate olefin nor ring opened products have been reported.[3]

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[1] O. L. Chapman, C. L. McIntosh, and L. L. Barber, *Chem. Comm.*, 1971, 1162.

[2] J. A. Evans, G. F. Everitt, R. D. W. Kemmitt, and D. R. Russell, *J.C.S. Chem. Comm.*, 1973, 158.

[3] J. P. Visser and J. E. Ramakers-Blom, *J. Organometallic Chem.*, 1972, **44**, C63.

[4] M. Lenarda, R. Ros, M. Graziani, and U. Belluco, *J. Organometallic Chem.*, 1974, **65**, 407; D. J. Yarrow, J. A. Ibers, M. Lenarda, and M. Graziani, *J. Organometallic Chem.*, 1974, **70**, 133.