Oxidative Addition of Triarylcyclopropenium Bromides to Pd^0 and Pt^0 Compounds: the Synthesis and *X*-Ray Structure of $Pd_3\{\mu\text{-}[\eta^3\text{-}C_3(Ph)(p\text{-}MeOC_6H_4)_2]_2\}(acac)_2]$(*Pd–Pd–Pd*)

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Summary Dibenzylideneacetone (dba)–palladium(0) and –platinum(0) complexes $[M_2(dba)_3]$solv. react with triarylcyclopropenium bromides to give the ring-opened trinuclear complexes, $[M_3(C_3R_3)_2Br_2]$; the pentanedionato-derivative of one, $[Pd_3\{C_3Ph(p\text{-}MeOC_6H_4)_2\}(acac)_2]$, has been shown by *X*-ray crystallography to have a bent Pd–Pd–Pd skeleton with η^3-C_3R_3 ligands bridging each pair of palladium atoms such that the C_3 plane intersects the Pd–Pd bond.

THE dibenzylideneacetone (dba) complexes of Pd^0 and Pt^0, $[M_2(dba)_3]$.solvent,[1] undergo oxidative addition with allylic and benzylic halides to give products of the type $[M(R)X]_n$, where R is an η^3-allylic ligand.[2] We now report the extension of these reactions to triarylcyclopropenium salts where an entirely novel type of complex is formed.

Addition of an excess of bis(*p*-methoxyphenyl)phenyl cyclopropenium bromide (Ia) to a dichloromethane solution of $[Pd_2(dba)_3]$.$CHCl_3$ caused immediate reaction with a change in colour from maroon to amber. A brown solid $[Pd_3Br_2\{C_3Ph(p\text{-}MeOC_6H_4)_2\}_2]$,† was isolated (60% yield) which on reaction with Tl(acac) (acac = pentane-2,4-dionato) gave the bis(pentanedionato) complex (IVa) (58%). Exactly analogous reactions occurred for platinum and for the

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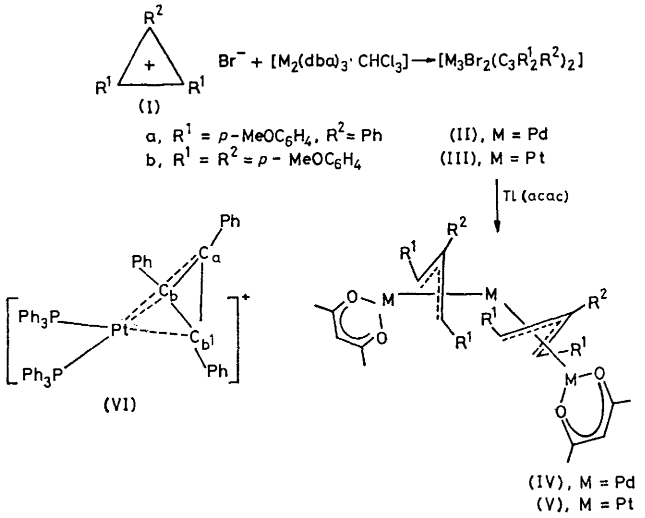
† All new complexes gave satisfactory elemental analyses and molecular weights.



(I)

a, R^1 = p-MeOC_6H_4, R^2 = Ph (II), M = Pd

b, R^1 = R^2 = p-MeOC_6H_4 (III), M = Pt

(VI)

(IV), M = Pd

(V), M = Pt

tris-(p-methoxyphenyl)cyclopropenium bromide (Ib). The X-ray crystal structure of complex (IVa) was determined.

Crystal data: $C_{56}H_{52}O_8Pd_3$, $M = 1172{\cdot}23$, monoclinic, $a = 14{\cdot}99(1)$, $b = 21{\cdot}88(2)$, $c = 18{\cdot}98(2)$ Å, $\beta = 90{\cdot}51(1)°$, $U = 6227$ Å^3, $Z = 4$, space group $C2/c$ (C^6_{2h}, No. 15). Three dimensional X-ray data were collected with the crystal mounted along the b-axis, using Mo-$K\alpha$ radiation (graphite monochromator) and a Stoe STADI-2 diffractometer. 2259 independent reflections were collected with $I_{\text{obs}} \geqslant 3\sigma(I_{\text{obs}})$; the structure was solved using Patterson and Fourier methods. Block diagonal least-squares refinement using anisotropic temperature factors for the palladium atoms, isotropic temperature factors for all other atoms, and with the phenyl carbon atoms treated as groups of fixed geometry has reduced R to 0·076.‡

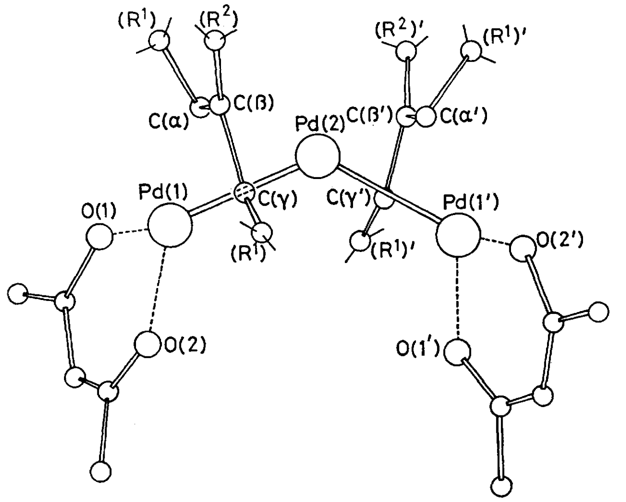


Figure. The structure of complex (IVa); for clarity, hydrogen atoms, the p-methoxyphenyl substituents (R^1) at C(α) and C(γ), and the phenyl (R^2) at C(β) are omitted.

The complex (IVa) has a crystallographic two-fold axis passing through the central palladium [Pd(2)] which relates the primed and unprimed atoms in the Figure. The Pd(1)–Pd(2)–Pd(1′) framework is bent (127°) in the middle, Pd(1) and Pd(1′) are each chelated to a pentanedionato-ligand, and two η^3-$C_3R^1_2R^2$ ligands bridge Pd(1)–Pd(2) and Pd(1′)–Pd(2) such that the plane of the C_3 ligand intersects the Pd–Pd bond. The Pd(1)–Pd(2) bond distance [2·663(2) Å] lies well within the range of reported Pd–Pd bond lengths (2·531—2·699 Å),[3] but Pd(1) ··· Pd(1′) (4·28 Å) is not bonding.

The η^3-$C_3R^1_2R^2$ ligands have C(α) and C(γ) closer to Pd(1) [2·01(2) and 2·01(2) Å] than to Pd(2) [2·13 and 2·12(2) Å] and C(β) closer to Pd(2) [2·31(2) Å] than to Pd(1) [2·55(2) Å]. The bridging ligands have p-methoxyphenyl substituents at C(α) and C(γ) and the phenyl at C(β), and the p-methoxyphenyl substituents are bent slightly towards the phenyl [angle R^1–C(α or γ)–C(β) = 130 or 131°]. The C–C distances in the η^3-C_3 ligand are normal for C(α)–C(β) [1·42(3) Å] and C(β)–C(γ) [1·43(3) Å] but there is essentially no bond between C(α) and C(γ) [2·18 Å]; the angle C(α)–C(β)–C(γ) has also opened to 100°. The dihedral angle formed by the plane of the η^3-C_3 unit and the plane Pd(1)–O(1)–O(2) is 151°.

The similarity of the ^{1}H and ^{13}C n.m.r. spectra of (IVa), (IVb), (Va), and (Vb) shows that the η^3-tris(p-methoxyphenyl)palladium and the η^3-bis(p-methoxyphenyl) (phenyl)- and tris(p-methoxyphenyl)-platinum complexes have the same structure. These spectra also show differentiation between C(α) (and its substituents) and C(γ) (and its substituents) as well as showing that the pentanedionato-ligands also have no plane of symmetry. For example, the ^{1}H n.m.r. spectrum of (IVa) (in $CDCl_3$) shows resonances at δ 1·77 and 1·98 (2 × s, acac Me) 3·75 and 3·79 (2 × s, OMe), 5·16 (s, acac CH), and 6·5—8·0 (m, Ph), while that of (Vb) shows resonances at δ 1·78 and 1·91 (2 × s, acac Me), 3·70, 3·72, and 3·75 (3 × s, OMe), 5·32 (s, acac CH), and 6·4—7·8 (m, ArH).

The triarylcyclopropenium ligand has been found (i) to co-ordinate symmetrically (η^3- to one Ni$^{\text{II}}$),[4] (ii) to ring open forming a planar metallacyclobutenium ion (with one Ir$^{\text{III}}$),[5] and (iii), to co-ordinate asymmetrically in the η^3-form to one Pt$^{\text{II}}$ as in (VI).[6]

In the last compound (VI), although Pt–C_a (2·48 Å) is greater than Pt–C_b (2·09 Å) and C_b–C_{b^1}, (1·58 Å) is greater than C_a–C_b (1·39 Å), there is obviously still bonding between C_b and C_{b^1}.[6] The relationship between (IVa) and (VI) is clear; the co-ordination of another metal atom to the C_3 ligand causes ring opening to occur because extra electron density is being accepted by the ligand.

This ring-opening does not appear to be easily reversed in the complexes (IV) or (V); however, while they are rigid on the ^{1}H n.m.r. time-scale at +32 °C, on heating the tris-p-methoxyphenyl-palladium complex (IVb) in nitrobenzene for example, coalescence between the α- and the γ-methoxy groups as well as coalescence of the acac methyls is observed. The fact that one of the methoxy groups (on the β-p-methoxyphenyl) does not coalesce with the others below the decomposition point (130 °C) indicates that the three p-methoxyphenyl groups and hence the carbons α, β, and γ do not all become equivalent. Therefore ring closure does not occur. The dynamic process which is observed

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

($\Delta G^{\ddagger} = 18{\cdot}2$ kcal mol^{-1}) is probably a racemisation involving a twisting of the (η^3-C_3R_3)(acac)Pd(1) groups about their bonds to Pd(2).

We thank the S.R.C. for support, I.C.I. Ltd. for a grant towards the purchase of chemicals, and the University of Sheffield for a Junior Research Fellowship (to P.M.B.).

(*Received*, 17*th December* 1976; *Com.* 1372.)

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