

# Formation and Molecular Structure of ( $\eta^5$ -Cyclopentadienyl)-( $\eta^4$ -cyclobuta-[I]phenanthrene)rhodium: a Cyclobutadiene-Metal Complex Derived from the Intramolecular Cyclodimerization of an Acyclic Diacetylene

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**Summary** Interactions of the diacetylene 2,2'-bis(phenylethynyl)biphenyl with the metal carbonyls [ $(\eta^5\text{-C}_5\text{H}_5)\text{-Co}(\text{CO})_2$ ], [ $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ ], and [ $\text{Fe}(\text{CO})_5$ ] proceed *via* intramolecular cyclodimerization to form the respective  $\eta^4$ -1,2-diphenylcyclobuta-[I]phenanthrene complexes in each case; for the rhodium analogue, a cyclobutadiene-type structure containing a unique trapezoidal  $\eta^4\text{-C}_4$ -ring has been unequivocally established by means of *X*-ray diffraction techniques.

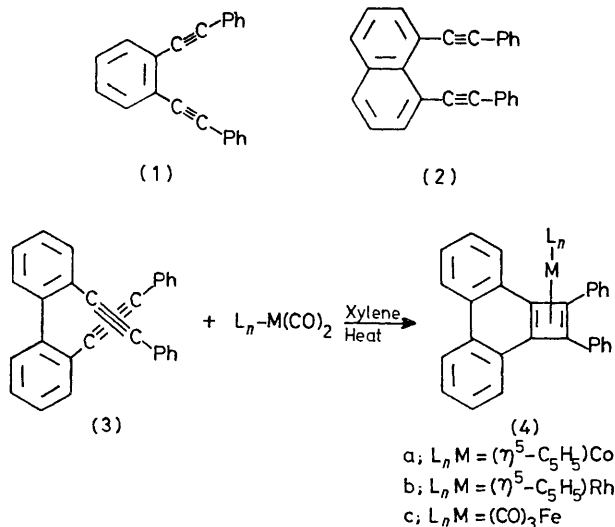
INTERACTIONS of acetylenes and metal carbonyls have been the subject of considerable research in recent years, both in terms of a clearer understanding of the various catalytic processes involved that frequently lead to new and unique organic systems, and also in terms of the structural elucidation of resulting novel organometallic products.<sup>1</sup> In contrast to mono-acetylenes, reactions of diacetylenes (diynes) and metal carbonyls have only recently begun to receive attention. Thus, reactions of acyclic diacetylenes 1,2-bis(phenylethynyl)benzene (**1**) and 1,8-bis(phenylethynyl)naphthalene (**2**) with [ $\text{Fe}(\text{CO})_5$ ], for example, have been shown to produce intermolecular-derived cyclobutadiene-iron-ferrole<sup>2</sup> and intramolecular-derived cyclopentadienone products,<sup>3</sup> respectively.

We now report the first examples of the intramolecular cyclodimerization of a related acyclic diacetylene, 2,2'-bis(phenylethynyl)biphenyl (**3**), with metal carbonyls to form cyclobutadiene-metal complexes (**4**),<sup>†</sup> and also the preliminary results of an *X*-ray diffraction study on the rhodium analogue (**4b**) which serves to establish unequivocally its structure as ( $\eta^5$ -cyclopentadienyl)( $\eta^4$ -1,2-diphenylcyclobuta-[I]phenanthrene)rhodium. Independent studies concerning the reaction of (**3**) and  $(\text{Ph}_3\text{P})_3\text{RhCl}$  have indicated that both  $\eta^4$ -cyclobutadiene and rhodiacyclic complexes were produced; the structures of these products were largely inferred from their chemical reactions.<sup>4</sup>

The cyclobutadiene-metal complexes (**4a-c**) are produced as the major products in moderate yields from the reactions of (**3**) with  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ ,  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ , and  $\text{Fe}(\text{CO})_5$ , respectively, in refluxing xylene. The products were characterized by satisfactory C, H, and metal analyses as well as by spectroscopic data: [(**4a**),  $\tau$  5.63 (s,  $\eta^5\text{-C}_5\text{H}_5$ ) and 1.5-3.0 (m, ArH), *m/e* 478 ( $M^+$ ); (**4b**),  $\tau$  4.85 (d,  $J_{\text{Rh-H}}$  1 Hz,  $\eta^5\text{-C}_5\text{H}_5$ ) and 1.7-2.5 (m, ArH), *m/e* 522 ( $M^+$ ); (**4c**), *m/e* 494 ( $M^+$ ), 466 ( $M - \text{CO}$ )<sup>+</sup>, 438 ( $M - 2\text{CO}$ )<sup>+</sup>, and 410 ( $M - 3\text{CO}$ )<sup>+</sup>]. All cyclobutadiene-metal complexes (**4a-c**) are air-stable, both in the solid state and for short periods in solution.

In order to provide conclusive evidence for the unusual structures of these products, and to obtain accurate bond distance and bond angle data for complexes of this type, a single-crystal *X*-ray diffraction study of (**4b**) was undertaken. *Crystal data*:  $\text{C}_{33}\text{H}_{23}\text{Rh}$ , space group  $P\bar{1}$ ;  $a = 10.023(1)$ ,  $b = 11.146(3)$ ,  $c = 22.314(4)$  Å,  $\alpha = 101.26(2)$ ,  $\beta = 97.53(1)$ ,  $\gamma = 96.55(1)^\circ$ ;  $U = 2398.7$  Å<sup>3</sup>;  $D_m = 1.45(2)$ ,  $D_c = 1.46$  g cm<sup>-3</sup>,  $Z = 4$ . Crystal was a sphere, 0.55 mm diameter mounted approximately along 056 direction,  $\mu = 7.16$  cm<sup>-1</sup>. 8081 reflections were observed of a total of 8818 measured, Mo- $K_\alpha$  (graphite monochromator) radiation, final  $R(F) = 0.036$ .

The most notable structural features of (**4b**) are: (a) the existence of a ( $\eta^4\text{-C}_4$ )Rh species, as opposed to a rhodiacyclic structure of the type determined by Müller *et al.*<sup>5</sup> for a similarly derived complex; (b) the fusion of the two acetylenes to give rise to a cyclobuta-[I]phenanthrene derivative in spite of steric hindrance at H(17) and H(18), and ring strain associated with the C(6), C(7)···C(12), C(13) portion of the molecule (see Figure). There are two independent molecules in the asymmetric unit and, being



<sup>†</sup> It has been briefly mentioned in a footnote (ref. 3a) that a reaction between (**3**) and [ $\text{Fe}(\text{CO})_5$ ] gives a cyclobutadiene complex, but details are not available.

nearly identical, we will give details for only one which is shown in the Figure. ‡

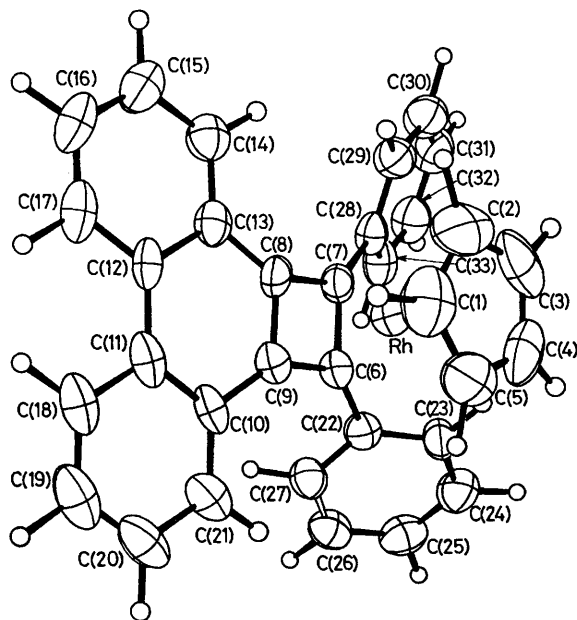


FIGURE. The molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_{28}\text{H}_{18})]$ : C(6)–C(7), 1.484(8); C(7)–C(8), 1.487(8); C(8)–C(9), 1.442(8); C(6)–C(9), and 1.479(7) Å;  $\angle$ C(6)–C(7)–C(8), 88.3(4);  $\angle$ C(7)–C(8)–C(9), 91.4(4);  $\angle$ C(8)–C(9)–C(6), 90.2(4); and  $\angle$ C(9)–C(6)–C(7), 90.1(4)°.

In our opinion, the most interesting data are as follows. (a) The  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}$  fragment is similar to that described by Cash *et al.*<sup>6</sup> for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^4\text{-C}_4\text{Ph}_4)]$ , in that the distance between the Rh–( $\text{C}_5$ -ring centroid) is 1.882 Å (*cf.* 1.868 Å in ref. 6). The Rh–( $\text{C}_4$ -ring centroid) distance is 1.858 Å (*cf.* 1.828 Å in ref. 6). (b) While the cyclobutadiene

ring in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^4\text{-C}_4\text{Ph}_4)]$  is a square (within  $< 2$  e.s.d.'s), the corresponding ring in (4b) is definitely trapezoidal (see distances in the Figure caption). This also implies that the six-membered ring C(8)⋯C(13) contains a high double bond contribution at C(8)–C(9). Such an observation is of great interest when compared to the structure and theoretical calculations in phenanthrene itself. For example, the X-ray and neutron diffraction studies of Okaya *et al.*<sup>7</sup> have shown that this bond in phenanthrene is nearly an isolated double bond (1.358 Å) in accordance with the theoretical predictions of Coulson (1.378 Å).<sup>8</sup> In the case of (4b) this bond is 1.442(8) and 1.447(8) Å in the two independent molecules present in our crystal. Thus, they are longer than the value found in phenanthrene,<sup>7</sup> longer than an aromatic bond, but shorter than the C–C bonds reported<sup>8</sup> for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^4\text{-C}_4\text{Ph}_4)]$  [mean 1.470(4) Å], in which the cyclobutadiene ring has none of the constraints that our fused ring system contains. (c) The phenanthrene ring in (4b) is planar, the largest deviation of an atom from the least-squares plane of the phenanthrene species being 0.08 Å. (d) There is a folding at the C(8)–C(9) bond such that the plane of the phenanthrene ring and the plane of the cyclobutadiene ring make an angle of 7°, the folding being away from the  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}$  fragment, like the phenyl rings in  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\eta^4\text{-C}_4\text{Ph}_4)]$ .<sup>6</sup> (e) The two phenyl substituents in (4b) also bend out of the  $\text{C}_4$ -plane and away from the  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}$  unit. Thus, C(22) and C(28) are, respectively, 0.27 and 0.20 Å out of the plane of the cyclobutadiene ring, the ring being exactly planar (largest deviation from planarity being 0.003 Å).

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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.

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