

The First Example of a Cycloocta-1,3-diene Ligand Bound to Rhodium; Crystal Structures of $\text{Rh}(\eta^5\text{-C}_5\text{Ph}_5)\text{L}$ ($\text{L} = 1,3\text{-}$ or $1,5\text{-C}_8\text{H}_{12}$)

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Under reducing conditions $[\text{Rh}(\eta^5\text{-C}_5\text{Ph}_5)\text{Br}_2]_2$ reacts with either cycloocta-1,3- or -1,5-diene to give predominantly $\text{Rh}(\eta^5\text{-C}_5\text{Ph}_5)(1,3\text{-C}_8\text{H}_{12})$ **1** together with a small amount ($\leq 15\%$) of $\text{Rh}(\eta^5\text{-C}_5\text{Ph}_5)(1,5\text{-C}_8\text{H}_{12})$ **2**.

It is well established that the substituents on a cyclopentadienyl ligand can markedly influence the properties of metal complexes. We present herein a spectacular example involving the pentaphenylcyclopentadienyl ligand.

The structures of over 130 rhodium compounds containing a cyclooctadiene ligand have been determined;¹ hundreds of other rhodium cyclooctadiene complexes are known.² To our knowledge all contain the cycloocta-1,5-diene isomer and

none contain the more thermodynamically stable cycloocta-1,3-diene. This exclusive tendency to coordinate the 1,5-isomer is borne out by reports describing how cycloocta-1,3- or -1,4-diene when treated with rhodium compounds yields complexes containing cycloocta-1,5-diene.^{3,4} Most other group VIII metals resemble rhodium in commonly bonding to the 1,5-isomer although $\text{M}(1,3\text{-C}_8\text{H}_{12})\text{Cl}_2$ ($\text{M} = \text{Pd}$ or Pt)⁴ have been isolated and $\text{Co}(\text{C}_5\text{H}_5)(1,3\text{-C}_8\text{H}_{12})$ has been gener-

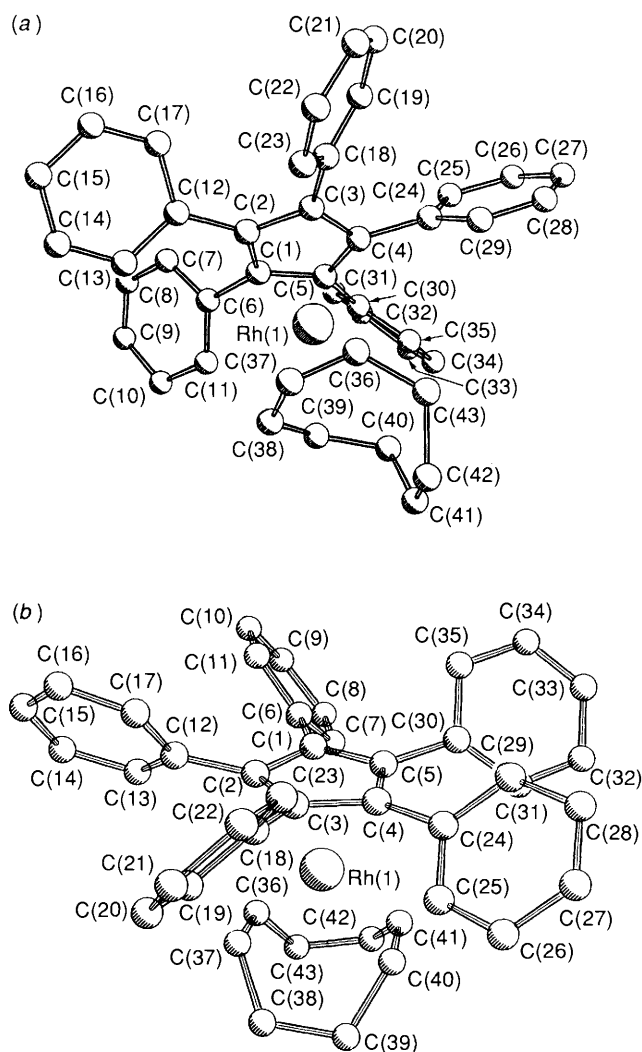


Fig. 1 Structure of (a) $\text{Rh}(\text{C}_5\text{Ph}_5)(1,3\text{-C}_8\text{H}_{12})$ **1**, (b) $\text{Rh}(\text{C}_5\text{Ph}_5)(1,5\text{-C}_8\text{H}_{12})$ **2**. Selected bond lengths (Å) and angles ($^\circ$): **1**, Rh–C(36) 2.119(26), Rh–C(37) 2.110(24), Rh–C(38) 2.103(22), Rh–C(39) 2.202(30), Rh–C_pplane 1.894, C(36)–C(37) 1.339(38), C(37)–C(38) 1.465(34), C(38)–C(39) 1.348(34); C(37)–C(36)–C(43) 127.3(26), C(36)–C(37)–C(38) 122.1(22), C(37)–C(38)–C(39) 122.6(23), C(38)–C(39)–C(40) 131.9(25), C(39)–C(40)–C(41) 113.1(31). **2**, Rh–C(36) 2.129(13), Rh–C(37) 2.051(14), Rh–C(40) 2.093(11), Rh–C(41) 2.110(10), Rh–C_pplane 1.928, C(36)–C(37) 1.318(19), C(37)–C(38) 1.515(21), C(38)–C(39) 1.485(24), C(40)–C(41) 1.327(20); C(43)–C(36)–C(37) 125.1(13), C(36)–C(37)–C(38) 125.8(11), C(37)–C(38)–C(39) 111.3(12), C(38)–C(39)–C(40) 114.2(11), C(39)–C(40)–C(41) 119.3(12), C(40)–C(41)–C(42) 128.0(13).

ated in solution.⁵ This contrasts, with the case of iron in which not only are there several examples of cycloocta-1,3-diene complexes *e.g.* $\text{Fe}(1,3\text{-C}_8\text{H}_{12})(\text{CO})_2(\text{PPh}_3)^6$ but $\text{Fe}(\text{CO})_5$ catalyses the isomerisation of the 1,5- to the 1,3-isomer.⁷

We report that when $[\text{Rh}(\text{C}_5\text{Ph}_5)\text{Br}_2]_2$ is stirred for 15 h at room temperature with cycloocta-1,3-diene in ethanol containing Na_2CO_3 , $\text{Rh}(\text{C}_5\text{Ph}_5)(1,3\text{-C}_8\text{H}_{12})$ **1** is formed together with *ca.* 7% of $\text{Rh}(\text{C}_5\text{Ph}_5)(1,5\text{-C}_8\text{H}_{12})$ **2**. The cycloocta-1,3-diene product is an orange-yellow air-stable solid, which shows no tendency to isomerise to the corresponding 1,5-compound when heated. When the reaction is repeated with cycloocta-1,5-diene, some (*ca.* 15%) $\text{Rh}(\text{C}_5\text{Ph}_5)(1,5\text{-C}_8\text{H}_{12})$ is formed but the major product is again **1**. A pure sample of $\text{Rh}(\text{C}_5\text{Ph}_5)(1,5\text{-C}_8\text{H}_{12})$ **2** was synthesized by treatment of $[\text{Rh}(1,5\text{-C}_8\text{H}_{12})\text{Cl}]_2$ with $\text{Li}(\text{C}_5\text{Ph}_5)$. Complex **2** shows no tendency to isomerise to the corresponding 1,3-complex when heated.

The crystal structures of both **1** and **2** (Fig. 1)[†] reveal that the unsaturated bonds of both cyclooctadiene ligands are extremely short *i.e.* mean C=C 1.343(36) and 1.322(19) Å, respectively; this compares with 1.341 Å in free cycloocta-1,5-diene⁸ and reflects the fact the C_5Ph_5 ligand is not a significant electron donor.⁹ The other bond lengths and angles are not significantly different from those in related structures *e.g.* $\text{Fe}(1,3\text{-C}_8\text{H}_{12})(\text{CO})_2(\text{PPh}_3)^6$ and $\text{Rh}(\text{C}_5\text{H}_5\text{CO}_2\text{Me})(1,5\text{-C}_8\text{H}_{12})$.¹⁰ There are no significant intramolecular interactions in either **1** or **2** and it is not apparent from the crystal structures as to why **1** should be unique in containing a stable rhodium-(1,3- C_8H_{12}) ligand. We note, however, that in certain solvents the cyclooctadiene prefers to bond in the 1,3-form in the 19-electron radical anion $\text{Co}(\text{C}_5\text{H}_5)(\text{C}_8\text{H}_{12})^-$ although in the neutral complex the 1,3- C_8H_{12} ligand rapidly isomerises to the 1,5-isomer.⁵ Given the known tendency of the C_5Ph_5 ligand to stabilise radical species¹¹ and the reducing conditions under which **1** is formed, we suggest that **1** results from a related 19-electron intermediate and that the unprecedented rhodium-(1,3- C_8H_{12}) is then trapped since interconversion between **1** and **2** clearly has an activation barrier greater than that for the $\text{Co}(\text{C}_5\text{H}_5)$ analogues. Electrochemical experiments are in progress to test these suggestions.

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- For details consult the Cambridge Crystallographic Data Centre.
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[†] Selected spectroscopic data: **1** δ_{H} (250 MHz, CDCl_3) 1.2 (2H, m, CH_2), 1.45 (2H, m, CH_2), 1.8 (2H, m, CH_2), 2.0 (2H, m, CH_2), 3.55 (2H, s, CH), 4.65 [2H, d, $J(\text{RhH})$ 5.0 Hz], 7.0 (25H, m, C_5Ph_5); δ_{C} (250 MHz, CD_2Cl_2) 134.9, 132.4, 127.5, 126.4, (Ph₅), 104.3 [C₅, d, $J(\text{RhC})$ 5.1 Hz], 84.5 [2C, d, $J(\text{RhC})$, 5.8 Hz, CH], 61.7 [2C, d, $J(\text{RhC})$ 17.8 Hz, CH], 28.7 (2C, s, CH_2), 25.4 (2C, s, CH_2). **2** δ_{H} (250 MHz, CDCl_3) 2.0 (4H, q, CH_2), 2.4 (4H, q, CH_2), 3.7 (4H, s, CH), 7.0 (25H, m, C_5Ph_5); δ_{C} (250 MHz, CD_2Cl_2) 135.0, 132.6, 127.7, 126.5 (Ph₅), 105.8 [C₅, d, $J(\text{RhC})$ 3.7 Hz], 74.8 [d, $J(\text{RhC})$ 14.4 Hz, CH], 32.5 (s, CH_2).

Crystal data: **1**, $\text{C}_{43}\text{H}_{37}\text{Rh}$; $M = 656.67$; crystallises from dichloromethane–hexane as orange-yellow plates. Orthorhombic, $a = 14.491(7)$, $b = 20.728(12)$, $c = 21.802(11)$ Å, $U = 6549(6)$ Å³; $D_c = 1.332$ g cm⁻³, $Z = 8$. Space group $Pbca$ (D_{2h}^{15} , No. 61). Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 5.40$ cm⁻¹, $F(000) = 2719.69$; $R = 0.0900$ (1596 reflections). **2**, $\text{C}_{43}\text{H}_{37}\text{Rh}$, $M = 656.67$; crystallises from dichloromethane–hexane as yellow plates (0.14 × 0.40 × 0.30 mm). Monoclinic, $a = 18.977(12)$, $b = 10.246(6)$, $c = 34.650(16)$ Å, $\beta = 109.75(4)^\circ$, $U = 6341(6)$ Å³; $D_c = 1.376$ g cm⁻³, $Z = 8$; space group $C2/c$ (C_{2h}^6 , No. 15); Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 5.58$ cm⁻¹, $F(000) = 2719.69$; $R = 0.0800$ (2872 reflections).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.