Synthesis of Di-rhodium Complexes Containing s-*cis*-Bridging 1,3-Diene Ligands: *X*-Ray Crystal and Molecular Structure of μ-(η^4-Cyclohexa-1,3-diene)-μ-carbonyl-bis-(η^5-indenyl)dirhodium(*Rh–Rh*)

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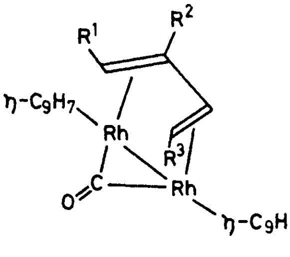
Summary Reaction of $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$ with buta-1,3-diene, *trans*-penta-1,3-diene, isoprene, *trans*, *trans*-hexa-2,4-diene, cyclopentadiene, and cyclohexa-1,3-diene affords the stable complexes $[Rh_2(\mu\text{-}CO)(\mu\text{-}1,3\text{-}diene)(\eta^5\text{-}C_9H_7)_2]$; an *X*-ray crystallographic study of the cyclohexa-1,3-diene complex shows that the diene is more weakly held than in mononuclear systems.

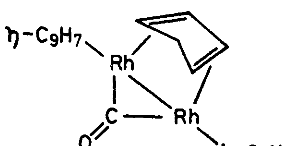
THE chemistry of 1,3-dienes co-ordinated to one metal centre is highly developed.[1,2] In contrast very little is known about the comparative behaviour of s-*cis*-1,3-dienes bonded to adjacent metal centres, although there is currently[3] considerable general interest in the reactions of organic ligands co-ordinated to more than one metal site. Metal-cluster complexes containing 1,3-dienes are rare, and in those cases where the compounds have been structurally characterised, non-cyclic dienes either bond to *one* metal centre or adopt a *transoid* geometry to span *two* metal sites,[4] thus making a comparison with the mononuclear systems difficult. Clearly, an s-*cis* conformation is demanded if the diene is contained within a small ring system; unfortunately, however, the only structural authentication[5] of such a cyclic diene bridging two metal centres, in the compound μ-(5-cyclopentadienylcyclopentadiene)-bis-(η-cyclopentadienylplatinum)(*Pt–Pt*), involves relatively large errors on molecular parameters involving the ligands, thus precluding a meaningful discussion of the nature of the bonding. In this paper we describe the synthesis and, in one case, an accurate structural characterisation of complexes in which two bonded rhodium atoms are bridged by s-*cis*-1,3-diene ligands.

We have previously noted[6] that in refluxing heptane dicarbonyl(η^5-indenyl)rhodium is transformed selectively into tri-(μ_2-carbonyl)-tri-(η^5-indenyl)-*triangulo*-trirhodium.

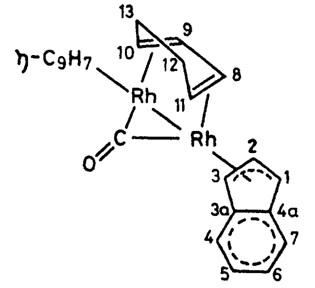
Whereas this cluster reacts with ethylene to form the mononuclear complex [Rh(C_2H_4)(CO)(η^5-C_9H_7)], reaction (60 °C, 1 h, toluene) with buta-1,3-diene, *trans*-penta-1,3-diene, isoprene, *trans,trans*-hexa-2,4-diene, cyclopentadiene, and cyclohexa-1,3-diene affords in good yield (60—80%) the red crystalline complexes (**1**)—(**6**)† with general molecular formula [Rh_2(μ-CO)(μ-diene)(η^5-C_9H_7)$_2$]. In order to define the molecular geometry of these molecules a single-crystal *X*-ray diffraction study was undertaken with the cyclohexadiene complex (**6**).



(1); $R^1 = R^2 = R^3 = H$
(2); $R^1 = Me$, $R^2 = R^3 = H$
(3); $R^1 = R^3 = H$, $R^2 = Me$
(4); $R^1 = R^3 = Me$, $R^2 = H$



(5)



(6)

Crystal data: $C_{25}H_{22}ORh_2$, $M = 544{\cdot}26$, monoclinic, space group $P2_1/c$, $a = 11{\cdot}137\,6(14)$, $b = 10{\cdot}658\,4(12)$, $c = 17{\cdot}175(6)$ Å, $\beta = 97{\cdot}81(2)°$, $U = 2020{\cdot}0$ Å^3, $Z = 4$, $D_c = 1{\cdot}80$ g cm^{-3}, $F(000) = 1\,096$ electrons, μ(Mo-$K_{\bar{\alpha}}$) = 14·9 cm^{-1}. Data were collected on an Enraf–Nonius CAD 4 diffractometer to $\theta_{max} = 30°$ using graphite-monochromated Mo-$K_{\bar{\alpha}}$ radiation ($\bar{\lambda} = 0{\cdot}710\,69$ Å). Of 5 877 independent measured intensities, 5 154 [$F \geqslant 1{\cdot}5\,\sigma(F)$] were retained to solve (*via* Patterson and difference Fourier syntheses) and refine (*via* full-matrix least-squares) the structure to *R* 0·036.‡

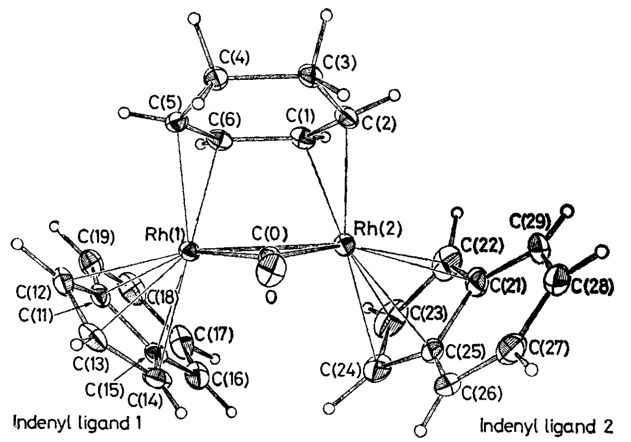
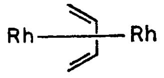


FIGURE. Perspective view of a molecule of compound (**6**), showing the crystallographic numbering. Some important bond lengths: Rh(1)–Rh(2) 2·646 2(6), Rh(1)–C(O) 1·960(3), Rh(2)–C(O) 1·980(3), C(O)–O 1·172(4), Rh(1)–C(5) 2·187(3), Rh(1)–C(6) 2·147(3), Rh(2)–C(1) 2·133(3), Rh(2)–C(2) 2·160(3), C(5)–C(6) 1·396(5), C(6)–C(1) 1·466(5), C(1)–C(2) 1·395(5), Rh(1)–C(11) 2·399(3), Rh(1)–C(12) 2·227(3), Rh(1)–C(13) 2·201(3), Rh(1)–C(14) 2·197(3), Rh(1)–C(15) 2·394(3), Rh(2)–C(21) 2·335(4), Rh(2)–C(22) 2·216(4), Rh(2)–C(23) 2·241(4), Rh(2)–C(24) 2·238(4), and Rh(2)–C(25) 2·344(4) Å.

The molecular structure (Figure) clearly establishes that, in the solid state, the cyclohexa-1,3-diene ligand bridges the two rhodium atoms, and that of two limiting[7] geometries for such a bridging system the arrangement (A) is preferred over arrangement (B). The diene plane [C(5)C(6)C(1)C(2)] is oblique to a plane through the Rh_2CO fragment (dihedral angle *ca.* 19°) and the saturated residue –C(4)H_2C(3)H_2– is *syn* with respect to the carbonyl bridge. Within the cyclic diene, which is in the boat conformation, there is a *ca.* 14° folding angle about the C(2) . . . C(5) vector.

(A)



(B)

The indenyl ligands adopt an *anti*-orientation, and both show some degree of distortion from η^5- towards η^3-co-ordination, a feature which has been invoked[6] to explain the higher reactivity of η^5-indenyl complexes compared to analogous cyclopentadienyl complexes. A convenient measurement of this distortion is Δ, the 'slip' parameter§ of the metal atom across the bonded face. In compound (**6**) the slip is more marked in the case of indenyl ligand 1 (Figure) ($\Delta_1 = 0{\cdot}226$, $\Delta_2 = 0{\cdot}121$ Å), and it is Rh(1) that is favoured in slight asymmetric bridging by the carbonyl

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† Representative spectroscopic data: (**1**) [ν_{CO}(CH_2Cl_2) 1 783 cm^{-1}], (**2**) [ν_{CO} 1 785 cm^{-1}], (**3**) [ν_{CO} 1 765 cm^{-1}], (**4**) [ν_{CO} 1 819 cm^{-1}], (**5**) [ν_{CO} 1 744 cm^{-1}], (**6**) [ν_{CO} 1 788 cm^{-1}; ^{13}C n.m.r. ($CDCl_3$, 30 °C) δ, 230·7 (t, CO, J_{RhC} 109 Hz), 124 (s, C-4,7′), 122·6 (s, C-4′,7), 120·5 (s, C-5,6′), 118·6 (s, C-6,5′), 114·9 (s, C-4a′,3a), 111·9 (s, C-4a,3a′), 95·9 (t, C-2,2′, J_{RhC} 5·9 Hz), 81·7 (t, C-1′,3, J_{RhC} 4·9 Hz), 76·1 (t, C-1,3′, J_{RhC} 3·9 Hz), 54·9 (apparent t, AA′X system, C-8,9, J_{RhC} 9·5 Hz), 46·4 (apparent d of d, AA′X system, C-10,11, J_{RhC} 16·6, $J_{Rh'C}$, 1·3 Hz), and 21·2 (s, C-12,13) p.p.m.; numbering as in formula (**6**), primed numbers referring to the second η-C_9H_7 group].

‡ 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.

§ Δ is defined as the shortest distance from the perpendicular of the η^5-bonded face to the metal atom. See D. M. P. Mingos, M. I. Forsyth, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363.

group [Rh(1)–C(O) 1·960(3), Rh(2)–C(O) 1·980(3) Å]. These molecular distortions are reflected in a relatively short Rh–Rh distance of 2·646 Å.

In the case of the complexes containing acyclic 1,3-dienes it was thought possible that the Rh–Rh bond could lengthen so as to accommodate a bridging s-*trans*-bonded 1,3-diene as observed in the complex [$Os_3(CO)_{10}$(s-*trans*-C_4H_6)]. However, comparison of the n.m.r. parameters for the series of complexes (**1**)—(**6**) with those reported for the osmium system suggests that the dirhodium complexes (**1**)—(**4**) also contain bridging *cis*-1,3-diene ligands. Clearly the Os_3 system unlike the Rh_2 complexes is unable to adapt to the geometrical contraint of a μ-*cis*-1,3-diene.

Structural studies on mononuclear 1,3-diene complexes[8] typically reveal that C(inner)–C(outer) is somewhat longer than C(inner)–C(inner), reversing the trend for unco-ordinated dienes and implying significant interaction between both sets of frontier orbitals (ligand H.O.M.O. → metal L.U.M.O., and metal H.O.M.O. → ligand L.U.M.O.); indeed, the extent of this reversal in C–C bond lengths may be taken as indicative of the total strength of the metal–ligand bond. In compound (**6**), however, C(1)–C(6) is 1·466(5) Å, whilst C(5)–C(6) and C(1)–C(2) are *still significantly shorter*, being 1·396(5) and 1·395(5) Å, respectively.

We may therefore conclude that the metal–diene bonding in (**6**) is relatively weak. Clearly, the fact that the diene bridges a di-metal centre makes an important contribution to the long C(inner)–C(inner) distance observed, and thus it is likely that similarly weak metal–diene bonding is a feature of other dinuclear complexes with s-*cis*-bridging 1,3-diene ligands. The possibility that this difference might be reflected in the chemistry of these compounds is being investigated.

The ^{13}C n.m.r. spectra of complexes (**1**)—(**6**) showed ^{103}Rh coupling to the carbons of the co-ordinated 1,3-diene, thus confirming the stability of the complexes in solution. In the room temperature spectrum of, for example, complex (**6**) the olefinic carbon signals appear as AA′X systems owing to coupling to the two ^{103}Rh nuclei. The appearance of two ^{103}Rh–^{13}C coupling constants of 16·6 and 1·3 Hz in the resonance due to the 'outer' olefinic carbons shows that at room temperature the 1,3-diene does not rotate about an axis perpendicular to the Rh–Rh vector. This contrasts with the low activation energy observed[9] for 'rotation' of a 1,3-diene co-ordinated to one metal centre.

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