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RHODIUM COMPLEXES OF SOME CYCLO-OLEFINS

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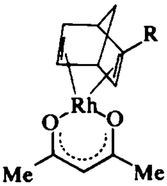
Abstract—Dicarbonyl(pentane-2,4-dionato)rhodium(I) does not form a complex with, or induce a skeletal rearrangement in, cycloheptatriene. 5-Exo-methylene-2-norbornene is present as an impurity in cycloheptatriene and is complexed by Rh(I) complexes as its endocyclic tautomer. Rhodium complexes of 1,3,5-cyclooctatriene, bicyclo [3.2.1] octa-2,6-diene, cyclooctatetraene, cyclooctatetraene epoxide, bicyclo [6.1.0] nonatriene and 9,9-dimethyl bicyclo [6.1.0] nonatriene are also reported.

Our interest[1] in rhodium complexes of cycloolefins was aroused by the report of an unusual rearrangement of 1,3,5-cycloheptatriene to a rhodium complex of norbornadiene (**1**; R = H) under the influence of the rhodium complex **2**.[2] At the time we began our reinvestigation of this reaction the concept of metal ions promoting orbital symmetry forbidden reactions was receiving much currency. The isomerisation of cycloheptatriene to (**1**; R = H) would, if valid, constitute an example of considerable importance in transition-metal promoted reactions. A number of mechanisms can be suggested for such a conversion and prompted repetition of the original work prior to a more detailed study.

It was found that considerable saving in time could be effected in the preparation of both (**1**; R = H) and **2**. Heating the complex **2** with excess cycloheptatriene in light petroleum (b.p. 60–80°) and monitoring the reaction by IR spectroscopy gave, on isolation of the product after 60 h, a yellow crystalline material m.p. 83–83·5° which clearly differed from the previously obtained complex (**1**; R = H). The reproducibility of the reaction was not very good but was improved by addition of a small quantity (*ca* 2% w/w of **2**) of **3** to the reaction mixture. Commonly, yields were in the range 14–18%, the maximum yield obtained being 24·5%. The mass spectrum, and microanalytical data for the new complex, showed it to be a rhodium acetylacetonate complex of a C_8H_{10} ligand. The NMR spectrum (Fig 1) showed, in addition to signals due to the acetylacetone moiety, two multiplets at τ 6·1 (3H) and 6·5 (2H), a singlet at τ 8·38 (3H) and a singlet showing evidence of fine splitting at τ 8·81 (2H). The signal at τ 8·38 indicated a C_7H_7—CH_3 ligand. A related complex could be prepared from **3** and commercial cycloheptatriene, although in much higher yield than when **2** was used. Spectral and analytical data supported the formula $(C_7H_7—CH_3)_2Rh_2Cl_2$.

The commercial synthesis of cycloheptatriene involves pyrolysis of norbornadiene and results in the formation of a number of by-products including benzene (by formal loss of carbene) and toluene.[3] To ascertain the role of impurities in the formation of the rhodium complexes a sample of cycloheptatriene was rigorously purified using a Nester-Faust spinning band fractionating column when it then failed to react with either **2** or **3**. An impurity in the cycloheptatriene was therefore implicated and the rearrangement of cycloheptatriene to (**1**; R = H) was clearly not occurring. Possible C_8H_{10} impurities, which were capable, either directly or on rearrangement, of giving rise to a C_7H_7—CH_3 ligand were therefore studied.

7-Methylcycloheptatriene **4** failed to give a complex with **3** and gave only a trace of an ill-defined product (<5%) with **2**. 1,3,5-Cyclooctatriene reacted, in boiling n-hexane, with **2** to give the complex **5** in almost quantitative yield. The NMR spectrum of **5** demonstrated that the organic ligand was still present in the monocyclic form with ligand proton signals at τ 4·26 (2H; uncomplexed double bond protons) and a multiplet at τ 5·52–6·18 (4H, protons of complexed double bonds). 1,3,5-Cyclooctatriene is known to be thermally equilibrated with its bicyc-



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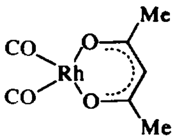

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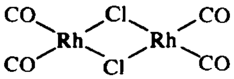

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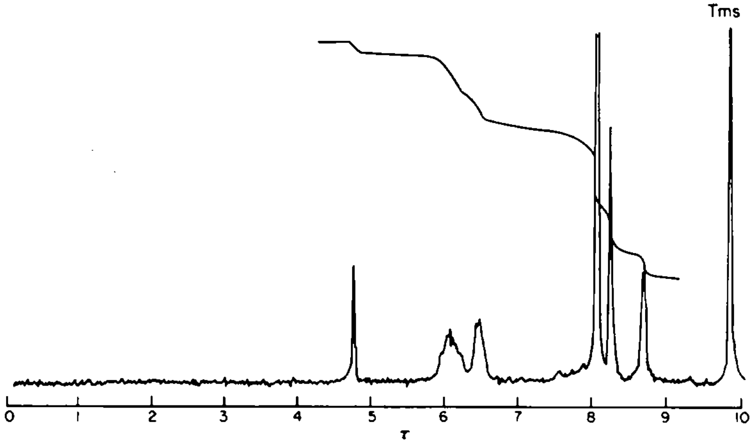


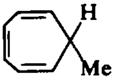
Fig 1. NMR spectrum (CCl_4) of 3-methylnorbornadiene (pentane-2, 4-dionato) rhodium (I).

lic valence tautomer **6** at *ca* 60°[4,5] but, as expected, no complex of **6** was obtained. A recent study of iron carbonyl complexes of related potentially valence tautomeric triene systems[6] reports isolation of complexes of both valence tautomers. Bicyclo [3.2.1] octa-2,6-diene also reacted readily with **2** but again the product (90%) was the complex **7** of the unrearranged ligand.

Finally the reaction of 5-*exo*-methylene-2-norbornene **8** with **2** was investigated. It was hoped that the 1,3-hydrogen shift generating 2-methylnorbornadiene would occur *in situ* since such metal complex-catalysed processes are well known.[7] The product from the reaction of **8** with **2** proved identical with the unknown complex obtained from commercial cycloheptatriene which therefore had the structure (**1**; R = Me). Confirmation of the presence of *ca* 5% of **8** or its endocyclic double bond isomer in commercial cycloheptatriene **7** was provided by GLC analysis. An independent reinvestigation[8] of the reaction of cycloheptatriene with **2** reached similar conclusions to our own but isolated (**1**; R = H) and not (**1**; R = Me). Presumably the source of cycloheptatriene accounts for the difference in results.[9]

The rhodium complex **9** of cyclooctatetraene, previously prepared by cleavage of di-μ-chlorodi(cyclooctatetraene) dirhodium in the presence of acetylacetone and potassium carbonate,[9] is more conveniently prepared by direct reaction of **2** with cyclooctatetraene. This complex was of interest because of the known valence tautomerism of cyclooctatetraene with the bicyclic tautomer **10**.[5] Although no thermal rearrangement involving the organic ligand of **9** was achieved, we found, despite the reported[10] thermal stability of **9**, that on heating at its melting point, cyclooctatetraene is liberated and the dirhodium complex **11**[10] is formed. A number of analogous reactions[11] involving cyclooctatetraene and platinum, cobalt or rhodium[10] have been reported.

Another potentially tautomeric system of much current interest[12] is the bicyclo [6.1.0] nonatriene system **12** and its oxa-analogue cyclooctatetraene epoxide **13**. Both these systems undergo thermal[12,13] and photochemical rearrangements[14] which, in the case of **12**, pose some interesting problems from or-



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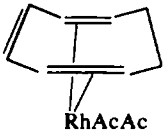

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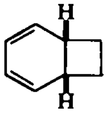

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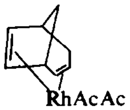

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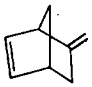

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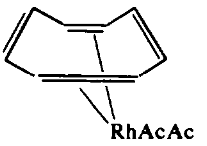

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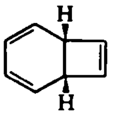

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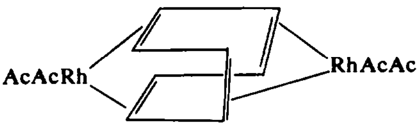

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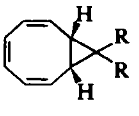

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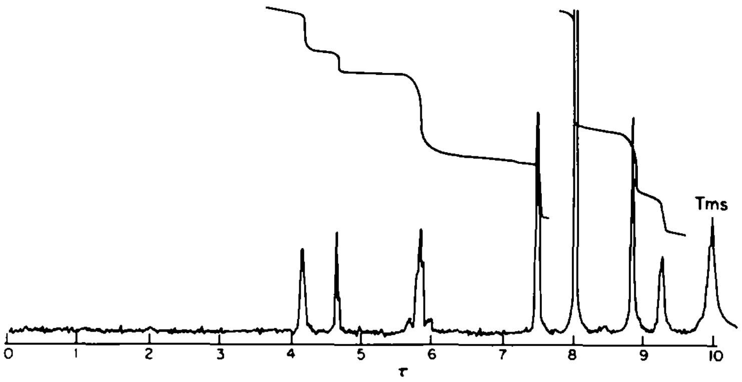
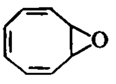


Fig 2. NMR spectrum (CCl_4) of 9,9-dimethylbicyclo [6. 1. 0] nona-2,4,6-triene (pentane-2, 4-dionato) rhodium (I).



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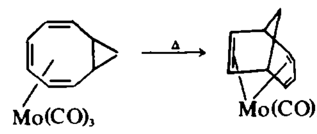

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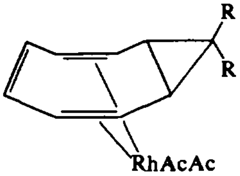

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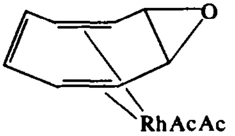

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bital symmetry considerations. The only report of rearrangement of a metal complex in these compounds involved the thermal rearrangement of **14** to **15**.[15] Reaction of the trienes (**12**; R = H or Me) and **13** with **2** occurred smoothly and gave the corresponding rhodium complexes (**16**; R = H or Me) and **17** in good yield. The NMR spectra provided in each case clear evidence for the presence of one uncomplexed double bond and for the presence of the unopened 3-membered ring (e.g. Fig 2). The thermal behaviour of the complexes (**16**; R = H or Me) and **17** in benzene solution was investigated by NMR (sealed tube). They were all essentially unchanged on heating at 200° and over this temperature no clean rearrangement occurred. The complexed ligand (**16**; R = H or Me) is thus more stable than the uncomplexed triene. However, rearrangement of (**12**; R = H or Me) and **13** could be induced catalytically using small amounts of **3**[16] and this will be discussed in a subsequent paper.

EXPERIMENTAL

M.p. determinations were carried out on a Kofler micro heating stage and are uncorrected. UV spectra were recorded for n-hexane solutions with a Unicam SP700 spectrometer and IR spectra for carbon tetrachloride solutions on a Unicam SP100 instrument. NMR spectra were measured for carbon tetrachloride solutions, either on a Perkin-Elmer RS10 60MHz or a Varian HA 100 instrument, using tetramethylsilane as internal reference (s, singlet; d, doublet; t, triplet; q, quartet, and m, multiplet). Alumina for chromatography was Spence type H and light petroleum had b.p. 60–80°.

Dicarbonyl (pentane 2,4-dionato)rhodium(I). A modification of the literature procedure[2] was employed. Tetracarbonyl-μ-dichlorodirhodium(I) (4·80 g) was added to a stirred solution of acetylacetone (12·0 ml) in redistilled light petroleum (400 ml, b.p. 60–80°) containing barium carbonate (16·0 g) and the mixture heated under reflux for 2 h. The barium carbonate was removed by filtration, washed with fresh redistilled light petroleum and the combined washings and filtrate evaporated to provide the product as green needles (5·65 g, 94·2%), m.p. 154–155° (lit[2] m.p. 155°).

2-Methylnorbornadiene (pentane-2,4-dionato) rhodium (I). (a) By reaction of dicarbonyl (pentane-2,4-dionato) rhodium (I) with commercial cycloheptatriene. Dicarbonyl (pentane-2, 4-dionato) rhodium (I) (300 mg) and redistilled commercial cycloheptatriene (3·0 ml, b.p. 114°) were heated to reflux in redistilled light petroleum (30 ml, b.p. 60–80°) to which had been added a trace (2–4 mg) of tetracarbonyl - μ - dichlorodirhodium (I) for 60 h under an atmosphere of nitrogen. The brown decomposition product formed (25·2 mg) was removed by filtration and washed with a little fresh, redistilled light petroleum. Evaporation of the combined filtrate and washings provided a brown oil (303 mg) which was dissolved in a little ether and percolated rapidly through a short (1·5 × 3·0 cm) column of alumina, eluting with more ether. Evaporation of the bright yellow eluate gave a yellow oil (195 mg) which rapidly crystallised. Trituration with a little ice-cold n-hexane and filtration afforded *3 - methylnorbornadiene (pentane-2, 4-dionato) - rhodium (I)*, as yellow needles (87·0 mg, 24·3%), m.p. 83·0–83·5°. (Found: C, 50·7; H, 5·45; $C_{13}H_{17}O_2Rh$ requires C, 50·65; H, 5·55%), λ_{max} (EtOH) 211(sh), 249, 272, 307(sh) and 382 nm (ε 15,110, 7,640, 8,410, 4,660 and 1,570) ν_{max} 929, 1031, 1265, 1368, 1392, 1428, 1519, 1577 and 2989 cm^{-1}, τ (C_6D_6) 4·86 (s, 1H, acetylacetone ring proton), 5·94 (m, 1H), 6·05 (m, 1H), 6·50 (m, 1H), 6·62 (m, 1H), 6·81 (m, 1H), 8·22 (s, 6H, acetylacetone methyls), 8·30 (s, 3H, ligand methyl), 9·20 (s with fine coupling, 2H methylene bridge protons), *m/e* (%): 309(6), 308 (M^+) (25), 209(8), 208(46), 207(7), 206(8), 182(7), 181(5), 168(8), 106(16), 105(7), 103(5), 100(66), 91(28), 85(64), 80(6), 79(8), 78(5), 77(6), 66(22), 44(11), 43(100), 42(6), 41(10); m*: 208. (*b*) *By reaction of dicarbonyl* (*pentane*-2, 4-*dionato*) *rhodium* (*I*) *with* 5 - *exo* - *methylene* - 2 - *norbornene*. Dicarbonyl (pentane-2, 4-dionato) rhodium (I) (400 mg) and 5 - *exo* - methylene - 2 - norbornene (2·0 ml) were heated to reflux in redistilled n-hexane (25 ml) containing a trace (*ca* 10 mg) of tetracarbonyl - μ - dichlorodirhodium (I) for 60 h. A quantity of suspended matter (30 mg) was removed by filtration and the light-amber solution evaporated to a brown oil (417 mg) which crystallised on standing. Trituration using several small amounts of cold n-hexane afforded yellow needles (115 mg, 47·8%), identical (m.p., mixed m.p., IR and NMR) with the product described in (a) above.

Di (3 - *methylnorbornadiene*) - μ - *dichlorodirhodium* (*I*). Tetracarbonyl - μ - dichlorodirhodium (I) (150 mg) and redistilled commercial cycloheptatriene (3·0 ml; b.p. 114°) were heated under reflux in redistilled n-hexane (30 ml) for 13 h under nitrogen. Suspended matter (18·6 mg) was removed by filtration and the filtrate evaporated to give a yellow oil (154 mg) which rapidly crystallised. Trituration with a little ice-cold ether provided *di* (3 - *methylnorbornadiene*) - μ - *dichlorodirhodium* (*I*) as yellow needles (130 mg, 69·3%), m.p. 145–147°. Satisfactory analytical data could not be obtained for this compound. λ_{max} 231, 302(infl) and 379 nm (ϵ 17,130, 3,670 and 2,460), ν_{max} ($CHCl_3$) 971, 1173, 1297, 1441 and 1464 cm^{-1}, τ 6·15 (m, 3H, olefinic protons), 6·50 (m, 2H, bridgehead protons), 8·39 (s, 3H, Me group), 8·83 (s with fine coupling, 2H, methylene bridge protons). *m*/*e* (%): 490(2·5), 488(3·5), 141(6), 128(4), 117(5), 115(4), 93(5), 92(13), 91(100), 85(6), 83(10), 80(8), 79(16), 78(20), 77(21), 66(25), 65(17), 63(7), 52(6), 51(13), 50(6); m*: 489, 453, 413, 383, 373, 346, 307, 165, 153.

Purfication of commercial cycloheptatriene. Commercial cycloheptatriene (Shell Chemical Co.) (160 ml) was distilled slowly through a Dufton fractionating column (30 cm) and the fraction b.p. 115–119° retained (95 ml). This was further fractionated using a Nester-Faust spinning-band column (24 inch) to provide a sample b.p. 117–118·5° (45 ml). A final fractionation on the spinning band column afforded pure cycloheptatriene, b.p. 118–118·5° (15 ml). GLC analysis of the product (12 ft × $\frac{1}{8}$ inch stainless-steel column containing 15% DC-710 silicone oil on Celite, 80–100 mesh at 100°) indicated a single substance.

GLC analysis of commercial cycloheptatriene before purification (2 metre × $\frac{1}{8}$ inch (O.D.) stainless-steel column packed with 15% polyethylene glycol 20M on silanized (HMDS) 90–100 mesh Chromosorb W at 100°) demonstrated the presence of 5-*exo*-methylene-2-norbornene or its *endo*cyclic isomer (*ca* 5·2%, r.t. 22 sec.).

1, 3, 5-*Cyclooctatriene* (*pentane*-2, 4-*dionato*) *rhodium* (*I*). Dicarbonyl (pentane-2, 4-dionato) rhodium (I) (300 mg) and 1,3,5-cyclooctatriene (600 mg)[18] were heated to reflux under nitrogen in redistilled n-hexane (25 ml) for 16 h. The solution was filtered (diatomite) to remove a faint turbidity and evaporated to give a yellow oil which rapidly crystallised. Trituration with a little cold n-hexane and filtration afforded 1, 3, 5-*cyclooctatriene* (*pentane*-2, 4-*dionato*) *rhodium* (*I*) (354 mg, 99·0%) as yellow needles, m.p. 128–129°, (Found: C, 50·6; H, 5·4. $C_{13}H_{17}O_2Rh$ requires C, 50·65; H, 5·55%), λ_{max} 207, 256 and 300 nm (ϵ 24,720, 11,400 and 5,060), ν_{max} 933, 1027, 1270, 1394, 1435, 1581, 2935 and 3001 cm^{-1}. τ 4·26 (split s, 2H, "uncoordinated" olefinic protons), 4·79 (s, 1H, acetylacetone ring proton), 5·52–6·18 (complex m, 4H), 7·35–7·70 (m, 2H), 8·12 (s superimposed on m, 8H, acetylacetone methyl groups, plus 2 ligand protons), *m*/*e* (%): 309(11), 308(M^+) (70), 306(10), 281(12), 280(100), 240(5), 238(7), 209(10), 208(30), 207(17), 206(25), 205(25), 204(13), 202(6), 196(30), 183(6·5), 182(66), 181(38), 180(20), 179(6), 168(21), 155(5), 154(10), 144(6), 142(9), 131(5), 130(8), 129(9), 115(8), 103(40), 100(6), 91(10), 85(8), 79(6), 78(18), 77(8), 51(6); m*: 51·7, 58·4, 137, 159·3, 180, 205, 208, 255 and 308.

Bicyclo [3, 2, 1] octa-2, 6-diene (pentane-2, 4-dionato) *rhodium* (*I*). Dicarbonyl (pentane-2, 4-dionato) rhodium (I) (300 mg) and bicyclo [3, 2, 1] octa-2, 6-diene (600 mg)[19] were heated to reflux in redistilled n-hexane (25 ml) under nitrogen for 35 h. Evaporation gave a yellow oil which rapidly crystallised. Trituration with a little ice-cold n-hexane and filtration provided *bicyclo* [3, 2, 1] *octa*-2, 6-*diene* (*pentane*-2, 4-*dionato*) *rhodium* (*I*), as yellow needles (323 mg, 90%), m.p. 173–174°, (Found: C, 50·85; H, 5·3. $C_{13}H_{17}O_2Rh$ requires C, 50·65; H, 5·55%), λ_{max} 218, 270, 300 and 386 nm; (ϵ 15,630, 8,920, 4,720 and 1,424), ν_{max} 930, 1025, 1269, 1395, 1435, 1582 and 2940 cm^{-1}. τ 4·80 (s, 1H, acetylacetone ring proton), 5·19 (m, 1H, C_1 bridgehead proton), 6·01 (m, 1H), 6·38 (m, 1H), 6·81 (m, 2H), 7·22 (m, 1H), 7·70 (m, 2H), 8·11 (s, 6H, methyl groups), 8·83 (t, 2H). *m*/*e*(%): 309(17), 308(M^+) (100), 280(16), 209(17), 208(98), 207(15), 206(23), 205(13), 204(7), 196(13), 183(7), 182(70), 181(34), 180(17), 169(5), 168(18), 154(6), 142(7), 130(5), 129(6), 107(5), 106(40), 105(25), 103(30), 100(40), 92(7), 91(70), 85(48), 82(5), 79(30), 78(60), 77(25), 66(7), 65(10), 53(6), 52(10), 51(17), 50(9); m*: 140·5, 159·3, 180·5, 205, 208, 255, 308.

Cyclooctatetraene (*pentane*-2, 4-*dionato*) *rhodium* (*I*). Dicarbonyl (pentane-2, 4-dionato) rhodium (I) (300 mg) and redistilled cyclooctatetraene (3·0 ml) were heated to reflux in redistilled light petroleum (b.p. 80–100°; 25 ml) under nitrogen for 19 h. Evaporation gave a yellow oil (368 mg) which quickly crystallised. Trituration with a little cold n-hexane and filtration provided the title compound as yellow needles (310 mg, 87·2%), m.p. 124–125° (resolidifies) (lit[9] m.p. 130°).

Di (*pentane*-2, 4-*dionato*) - μ - *cyclooctatetraenedirhodium* (*I*). Cyclooctatetraene (pentane-2, 4-dionato) rhodium (I) (100 mg) was heated to 130° in a sealed glass tube for 5 min. The tube was then opened and the colourless liquid condensate of cyclooctatetraene (IR and NMR identical with an authentic sample) removed. The crystalline residue was triturated in a little cold n-hexane and filtered to give the title compound (64 mg, 77%) as yellow needles, m.p. 247–249° (lit[9] m.p. 250°), M (mass spectrum) 508.

Bicyclo [6. 1. 0] *nona*-2, 4, 6-*triene* (*pentane*-2, 4-*dionato*) *rhodium* (*I*). Dicarbonyl (pentane-2, 4-dionato) rhodium (I) (600 mg) and bicyclo [6. 1. 0] nona-2, 4, 6-triene (600 mg)[20] were heated to reflux in redistilled n-hexane (15 ml) under nitrogen for 16 h. Evaporation gave a yellow oil (635 mg) which rapidly crystallised. Trituration with a little cold n-hexane and filtration afforded *bicyclo* [6. 1. 0] *nona*-2, 4, 6-*triene* (*pentane*-2, 4-*dionato*) *rhodium* (*I*), as yellow prisms (577 mg, 77·5%), m.p. 73–74°, (Found: C, 52·4; H, 5·2. $C_{14}H_{17}O_2Rh$ requires C, 52·5; H, 5·35%), λ_{max} 205, 302 and 361(sh) nm (ϵ 20,390, 4,860 and 1,110), ν_{max} 928, 960, 1027, 1270, 1393, 1437, 1582 and 3000 cm^{-1}, τ 4·35 (broad s, 2H, "uncoordinated" olefinic protons), 4·82 (s, 1H, acetylacetone ring proton), 5·87 (d, 4H, "coordinated" olefinic protons), 8·13 (s, 6H, methyl groups), 8·56 (m, 1H), 9·20 (m, 3H); *m*/*e* (%): 321(12), 320(M^+) (59), 277(5), 220(15), 219(74), 218(27), 217(100), 216(19), 215(8), 194(7), 193(10), 192(10), 191(20), 185(7), 181(5), 180(28), 172(5), 171(8), 168(8), 167(18), 166(8), 159(5), 158(7), 157(8), 156(6), 155(5), 154(6), 153(10), 152(6), 151(5), 145(12), 144(8), 143(18), 142(10), 141(40), 140(15), 139(10), 131(8), 130(20), 129(21), 128(22), 117(9), 116(33), 115(12), 114(38), 104(5), 103(84), 102(5), 100(5), 92(8), 91(45), 89(11), 85(13), 78(14), 76(5), 75(5), 74(5), 65(25), 63(20), 52(10), 51(17), 50(14); m*: 316, 285, 277, 275, 239, 215·5, 161, 150·5, 112·2.

9, 9-*Dimethylbicyclo* [6. 1. 0] *nona*-2, 4, 6-*triene* (*pentane*-2, 4-*dionato*) *rhodium* (*I*). Dicarbonyl (pentane-2, 4-dionato) rhodium (I) (0·518 g, 0·002 mole) and the nonatriene[21] (0·584 g, 0·004 mole) were heated under reflux in redistilled n-hexane (15 ml) under dry nitrogen for 22 h. Evaporation to half-volume gave on cooling 9, 9-*dimethylbicyclo* [6. 1. 0] *nona*-2, 4, 6-*triene* (*pentane*-2, 4-*dionato*) *rhodium* (*I*) as yellow needles (0·478 g, 59%) m.p. 137–137·5°, (Found: C, 55·4; H, 6·00; *m*/*e* 348(M$^+$), $C_{16}H_{22}O_2Rh$ requires: C, 55·2; H, 6·05%, M, 348), λ_{max} 228·5(sh), 303·5 and 352·5 nm, (ϵ 12,670, 4,360 and 1,460), ν_{max} 940, 990, 1032, 1208, 1274, 1394, 1448, 1542, 1596, 2920 and 3020 cm^{-1}, τ 4·31 (broad s, 2H), 4·80 (s, 1H), 5·95 (m, 4H), 7·58 (s, 3H, *syn*-Me), 8·11 (s, 6H), 8·90 (s, 3H, *anti*-Me), 9·31 (broad s, 2H).

Cyclooctatetraene oxide (*pentane*-2,4-*dionato*) *rhodium* (*I*). Dicarbonyl (pentane-2,4-dionato) rhodium (I) (300 mg) and cyclooctatetraene oxide (300 mg) were heated to reflux in redistilled n-hexane (25 ml) under nitrogen for 36 h. The solution was then filtered and evaporated to give a yellow crystalline residue. Trituration with cold n-hexane and filtration afforded cyclooctatetraene oxide (pentane-2, 4-dionato) rhodium (I) as yellow needles (244 mg, 65·1%), m.p. 156–157°, (Found: C, 48·4; H, 4·85. $C_{13}H_{15}O_3Rh$ requires C, 48·45; H, 4·7%), λ_{max} 205, 240 and 302 nm (ϵ 22,350, 9,880 and 4,970), ν_{max} 856, 937, 966, 1027, 1272, 1390, 1438, 1582 and 2999 cm^{-1}, τ 4·40 (broad s, 2H, "uncoordinated" olefinic protons), 4·72 (s, 1H, acetylacetone ring proton), 5·78 (broad s, 4H, "coordinated" olefinic protons), 7·11 (finely split s, 2H, bridgehead protons), 8·12 (s, 6H methyl groups), *m*/*e* (%): 323(7), 322(M$^+$) (35), 294(9), 293(22), 222(8), 209(16), 196(12), 195(24), 194(100), 193(20), 192(30), 181(12), 172(8), 169(11), 168(24), 167(8), 144(9), 143(6), 142(15), 141(10), 140(6), 131(7), 130(8), 129(10), 117(5), 115(24), 103(34), 100(9), 92(15), 91(100), 86(5), 85(12), 78(7), 77(5), 65(12), 57(16), 56(13), 51(7); m*: 322, 293, 268·5, 193, 190·5, 169·5, 149, 145·5, 128, 91, 68·4.

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