

600. Dicarboxyl- β -diketonato- and Related Complexes of Rhodium(I).

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The reaction of tetracarbonyl- μ -dichlorodirrhodium(I) with acetylacetone and other β -diketones in presence of base leads to monomeric ato-complexes of the general formula (β -diketone)Rh(CO)₂. The carbon monoxide groups can be replaced by olefins and in part by triphenyl-phosphine, -arsine, and -stibine.

ENOLIZABLE β -diketones usually react with metal carbonyls causing complete loss of carbon monoxide, and in this way β -diketonato-complexes of iron(III),¹ chromium(III), and molybdenum(III)² have been obtained. However, we find that tetracarbonyl- μ -dichlorodirrhodium(I) reacts with various β -diketones in presence of barium carbonate without loss of carbon monoxide, affording monomeric complexes such as dicarbonyl(pentane-2,4-dionato)rhodium(I), (CO)₂Rh(C₅H₇O₂).

This last complex reacts immediately with excess triphenylphosphine or triphenylarsine (L) to give yellow complexes, L(CO)Rh(C₅H₇O₂); however, triphenylstibine affords a red, diamagnetic six-co-ordinate complex (Ph₃Sb)₃(CO)Rh(C₅H₇O₂) which is a non-electrolyte in acetone. The carbon monoxide groups can be completely substituted by olefins. Thus, (CO)₂Rh(C₅H₇O₂) reacts immediately with cyclo-octa-1,5-diene, yielding the yellow cyclo-octa-1,5-diene(pentane-2,4-dionato)rhodium(I), the existence of which has been mentioned³ as a product of the reactions between the halogen-bridged olefin complex (C₈H₁₂RhCl)₂ and acetylacetone, but refluxing in petroleum (60—80°) is required when bicyclo[2,2,1]hepta-2,5-diene (norbornadiene) is used. No evidence for displacement of carbon monoxide was obtained when butadiene, 1,4-diphenylbutadiene, or 2,5-dimethylhexa-2,4-diene were used under similar refluxing conditions.

Cycloheptatriene reacts slowly with dicarbonyl(pentane-2,4-dionato)rhodium to give a single yellow crystalline product. The infrared spectrum shows no bands attributable to an unco-ordinated double bond as observed in C₇H₈Fe(CO)₃,⁴ and the high-resolution nuclear magnetic resonance spectrum again differs from that of this iron complex and of cycloheptadienetricarbonyliron⁴ or the cycloheptatriene tricarbonyls of molybdenum and tungsten.⁵ Both the infrared and n.m.r. spectra are, in fact, closely similar to those of the norbornadiene(pentane-2,4-dionato)rhodium complex. In view of this similarity and the similarity in melting point of both the norbornadiene and cycloheptatriene complexes, together with the fact that there is no depression of melting point of a mixture of the two compounds, it appears that both compounds are identical and that in forming the metal complex the triene has undergone isomerisation.

The interaction of 3-allylpentane-2,4-dione and [Rh(CO)₂Cl]₂ gave two products, one of which was the expected monomeric orange-yellow, somewhat petroleum-soluble dicarbonyl-(3-allylpentane-2,4-dionato)rhodium, (CO)₂Rh(C₈H₁₁O₂). The other was red and insoluble in organic solvents with stoichiometry (CO)₄Rh₂(C₈H₁₁O₂)Cl; its infrared spectrum showed three strong carbon monoxide stretching frequencies but no band in the 1600 cm.⁻¹ region expected for a free C=C stretch. The compound reacted immediately, losing carbon monoxide, with excess of cyclo-octa-1,5-diene, and from the reaction mixture could be isolated both bis(cyclo-octa-1,5-diene)- μ -dichlorodirrhodium³ and cyclo-octa-1,5-diene-(3-allylpentane-2,4-dionato)rhodium, identified by comparison with authentic samples. Since the red compound can also be obtained from the interaction of [Rh(CO)₂Cl]₂ and (CO)₂Rh(C₈H₁₁O₂) it seems likely that the red complex is a binuclear species of type (I).

¹ Reihlen, Gruhl, and von Hessing, *Annalen*, 1929, **472**, 283; Hieber, *Sitzungsber. Akad. Wiss. Heidelberg*, 1929, **3**, 3.

² Dunne and Cotton, *Inorg. Chem.*, 1963, **2**, 263; Goan, Huether, and Podall, *ibid.*, 1963, **2**, 1078, and references therein.

³ Chatt and Venanzi, *J.*, 1957, 4735.

⁴ Burton, Pratt, and Wilkinson, *J.*, 1961, 594.

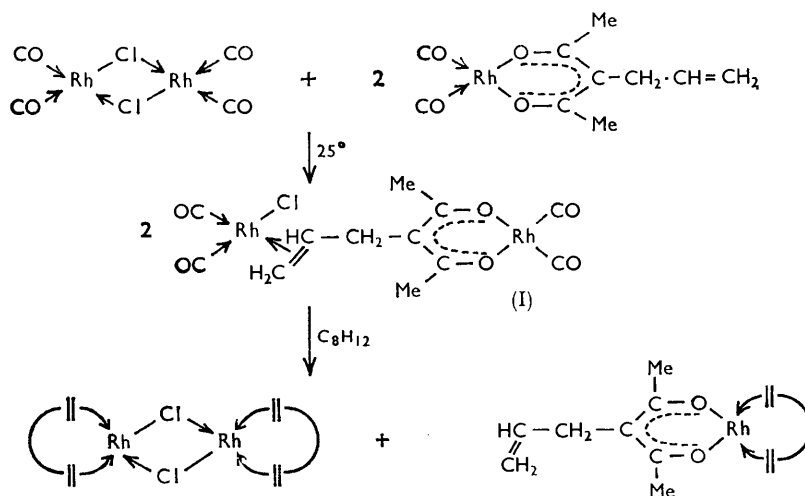
⁵ Bennett, Pratt, and Wilkinson, *J.*, 1961, 2037.

[1964]

and Related Complexes of Rhodium(I).

3157

These reactions are summarised in the diagram. The monomeric complex $(\text{CO})_2\text{Rh}(\text{C}_8\text{H}_{11}\text{O}_2)$ shows odd behaviour in that, when its orange-yellow solutions are evaporated rapidly, a reddish solid is obtained, whereas on slow evaporation orange-yellow crystals result; both forms dissolve to give the same species in solution. The red form shows slight differences in the position of some bands in the infrared (solid-state) spectrum with two additional weak bands at 1701 and 1724 cm^{-1} . It is probable that the more stable orange-yellow substance is the normal 3-allylacetylacetonate but that the red form contains a proportion of the isomeric species in which the double bond of the allyl group is co-ordinated to the metal leaving an unco-ordinated keto-group.



Infrared and Nuclear Magnetic Resonance Spectra.—The infrared spectra of the petroleum-soluble dicarbonyl- β -diketonato-complexes in the carbon monoxide stretching region show no great variation except for a shift of 10 – 20 cm^{-1} to higher frequencies with strongly electronegative trifluoromethyl substituents on the ring. There is no appreciable shift with phenyl substituents ($<4\text{ cm}^{-1}$), presumably owing to conjugation effects which, by making back-donation from the metal atom to the carbon monoxide ligand more difficult, thus cancel out the effect of the greater electronegativity of the phenyl-group compared to alkyl-group substituents. Shifts to lower frequencies are found in the monocarbonyls containing triphenylphosphine and triphenylarsine, as expected.

The proton resonance spectra show sharp signals characteristic of the β -diketone ring, no splitting due to coupling to ^{103}Rh through oxygen being observed. There are large variations in the line position of the central hydrogen atom of the β -diketone ring, from τ 3.62 to 4.93 [cf. for $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Rh}(\text{III})$, τ 4.65].⁶ The lowest values occur with trifluoromethyl and phenyl substituents and the highest values where the carbon monoxide groups are replaced by olefin ligands, as expected. Similar, but smaller, changes are observed for the τ values of methyl substituents on the ring, ranging from τ 7.75 for dicarbonyl-(1,1,1-trifluoropentane-2,4-dionato)rhodium to 8.25 for norbornadiene(pentane-2,4-dionato)rhodium [cf. for $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Rh}$, τ 7.89].⁶

EXPERIMENTAL

Microanalyses and molecular weights (Mechrolab osmometer) were by the Microanalytical Laboratory, Imperial College. Infrared spectra (in cm^{-1}) were taken on Perkin-Elmer Infracord and Grubb-Parsons grating Spectromaster instruments. Nuclear magnetic resonance spectra

⁶ Collman, in "Reactions of Coordinated Ligands and Homogeneous Catalysis," *Advances in Chemistry Series No. 37*, American Chemical Society, Washington, D.C., 1963, pp. 78–97.

were taken on a Varian Associates 4300 spectrometer at 56.4 Mc./sec., using conventional methods (τ values from internal tetramethylsilane reference).

Reactions were carried out under nitrogen initially. Tetracarboxyl- μ -dichlorodirrhodium(I) was prepared by the action of carbon monoxide on rhodium trichloride hydrate (Johnson, Matthey and Co.) at ca. 100°. ⁷

Dicarboxyl(pentane-2,4-dionato)rhodium(I).—Tetracarboxyl- μ -dichlorodirrhodium(I) (2.40 g.), acetylacetone (6 ml.), and barium carbonate (8 g.) were refluxed in petroleum (b. p. 60–80°; 200 ml.) with stirring for ca. 1 week. Vacuum-concentration of the green filtered solution gave needles which showed red-green dichroism of the *compound*, m. p. 155° (2.9 g.) [Found: C, 32.3; H, 2.8; O, 24.8%; *M*, 253 (benzene). C₇H₇O₄Rh requires C, 32.5; H, 2.7; O, 24.8; *M*, 258]. From the mother-liquor an additional small quantity of the compound was recovered by evaporation followed by vacuum-sublimation at ca. 90°; at higher temperatures a small quantity of trisacetylacetonatorrhodium(III), identical with an authentic specimen, was recovered.

The dicarboxyl sublimates with slight decomposition at 90° in a vacuum. It is soluble in acetone, benzene, and chlorinated solvents, giving green solutions; it is sparingly soluble in methanol, ether, and aliphatic hydrocarbons, and, with slight decomposition, in carbon disulphide. It can be stored for several months in air without change. If a toluene solution of the complex containing excess of acetylacetone is refluxed for ca. 5 days, disproportionation occurs, a mirror of rhodium being formed together with trisacetylacetonatorrhodium(III). Attempts to brominate the ring in (CO)₂RhC₅H₇O₂ using *N*-bromosuccinimide in chloroform led to complete decomposition at room temperature. Equally unsuccessful were attempts to acetylate the complex with acetic anhydride-dichloromethane-boron trifluoride etherate and to add bromine or iodine in carbon tetrachloride. ν_{\max} . (carbonyl region) in petroleum (b. p. 40–60°), grating, 2083s, 2066w, 2015s, 1987w; in CCl₄ and CS₂ 2990w, 2911w, 1553s, 1513s, 1429m, 1374m, 1276m, 1193w, 1126w, 1019m, 933w, 782m; n.m.r. (in CCl₄) τ 4.48 (area 1, central proton), 7.89 (area 6, methyl groups).

Dicarboxyl(1,1,1-trifluoropentane-2,4-dionato)rhodium(I).—Tetracarboxyl- μ -dichlororhodium(I) (0.38 g.) and 1,1,1-trifluoropentane-2,4-diene (2.0 ml.) were refluxed with excess of barium carbonate in petroleum (b. p. 60–80°) for ca. 24 hr. The filtered solution was evaporated in a vacuum without heating and the residual *compound* purified by vacuum-sublimation at 70°, to give wine-red crystals (0.43 g., 94%), m. p. 110–111° [Found: C, 27.0; H, 1.3%; *M*, 330 (benzene). C₇H₄F₃O₄Rh requires C, 26.90; H, 1.28%; *M*, 312]. The solubility properties are similar to those of the acetylacetonate. ν_{\max} . (carbonyl region) in petroleum (b. p. 40–60°), grating, 2094s, 2079w, 2027s, 1997w; in CCl₄ and CS₂: 3145w, 2959w, 2933w, 1608s, 1527m, 1439m, 1362m, 1300s, 1225m, 1198s, 1156s, 1143s, 951w, 867w; n.m.r. (in CCl₄) τ 3.98 (1), 7.75 (3, CH₃).

Dicarboxyl(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I).—This was prepared as the trifluoroacetylacetonate, from [Rh(CO)₂Cl]₂ (0.38 g.) and C₇H₂F₆O₂ (2.0 ml.). By sublimation at room temperature on to an ice-cooled probe, dark red needles of the *compound* were obtained, m. p. 71–74° (Found: C, 22.3; H, 0.4. C₇HF₆O₂Rh requires C, 22.9; H, 0.3%), soluble in ether and hydrocarbons; ν_{\max} . (carbonyl region) in petroleum (b. p. 40–60°), grating, 2103s, 2088w, 2041s, 2028w; in Nujol: 1609s, 1262m, 1535m, 1451s, 1359w, 1344m, 1256vs, 1231vs, 1168vs, 1155vs, 1106s, 951w, 816s, 747m, 686m, 620w, 601m, 533w, 488m, 476w; n.m.r. (in CCl₄) τ 3.52.

Dicarboxyl(4-phenylbutane-1,4-dionato)rhodium(I).—This was prepared from [Rh(CO)₂Cl]₂ (0.27 g.) and 4-phenylbutane-2,4-dione (0.23 g.) with excess of barium carbonate for ca. 3 hr. in refluxing petroleum (b. p. 60–80°; 10 ml.). The filtered solution was chromatographed twice on alumina in petroleum (b. p. 60–80°); recovery and crystallisation from petroleum gave the red *compound*, m. p. 100–101° (0.07 g.) (Found: C, 44.6; H, 2.7. C₁₂H₉O₄Rh requires C, 45.0; H, 2.8); ν_{\max} . (carbonyl region), grating in petroleum, 2085s, 2072w, 2015s, 1988w; n.m.r. (in CCl₄) τ 2.11–2.30 and 2.58–2.71, two asymmetric quartets, total relative area 5 (phenyl group); τ 3.82 (area 1), τ 7.84 (area 3, methyl group).

Tetracarboxylchloro(3-allylpentane-2,4-dionato)dirrhodium.—(a) Excess of barium carbonate, [Rh(CO)₂Cl]₂ (1.15 g.), and 3-allylpentane-2,4-dione (1.0 ml.) in petroleum (b. p. 60–80°; 100 ml.) were shaken for ca. 3 days. After evaporation of the filtered solution the red residue was washed with petroleum (b. p. 30–40°) until the washings were colourless; the washings were worked up as described below. The residual red *polymeric compound*, m. p. 152° (decomp.)

⁷ McCleverty and Wilkinson, *Inorg. Synth.*, **8**, in the press.

(0.5 g.) (Found: C, 29.2; H, 2.8; Cl, 7.0; O, 20.0. $C_{12}H_{11}ClO_6Rh_2$ requires C, 29.3; H, 2.3; Cl, 7.2; O, 19.5%), is insoluble in hydrocarbons, acetone, and chloroform; ν_{max} . (Nujol and hexachlorobutadiene mulls) 3062vw, 2998vw, 2963vw, 2928vw, 2092w, 2072s, 2016s, 1996s, 1965w, 1565s, 1450s, 1359s, 1345m, 1300w, 1278w, 1244w, 1212w, 1159w, 1114w, 1018w, 970w, 924w, 269w, 803w.

(b) The orange-yellow allylacetonate (see below) and tetracarbonyl- μ -dichlorodirrhodium(I) in stoichiometric amounts (ca. 0.1 g.) were dissolved in petroleum (b. p. 60–80°; 20 ml.). After 1 week, the solvent was removed and the residue washed with petroleum (b. p. 30–40°; 3 × 5 ml.). The product was identical with that obtained in (a) according to infrared spectra and m. p.

Dicarbonyl-(3-allylpentane-2,4-dionato)rhodium(I).—The concentrated petroleum washings referred to above were chromatographed on alumina, elution being with petroleum (b. p. 30–40°). Rapid vacuum-evaporation of the solution leaves a red solid but slow evaporation gives an orange-yellow product. On shaking or trituration under petroleum, the red changes into the orange-yellow form and the latter can be re-converted into the red form by dissolution and rapid evaporation. The orange-yellow compound has m. p. 78–80° [Found: C, 39.9; H, 4.0; O, 21.2%; *M*, 304 (benzene). $C_{10}H_{11}O_4Rh$ requires C, 40.3; H, 3.7; O, 21.5%; *M*, 298]; ν_{max} . (Nujol mull) (red form) 2062s, 1996s, 1965sh, 1724w, 1701w, 1639w, 1563s, 1451s, 1414w, 1355s, 1348w, 1282m, 1261w; (yellow form) 2062s, 2004s, 1976w, 1639w, and remainder same as red form; (in CCl_4) additional bands at 3084w, 3067w, 3007w, 2979sh, 2965m, 2937w; n.m.r. (in CCl_4) τ 7.87 (6.0, methyl groups), 6.99, complex (2.3), 4.92 (3.2), vinyl group.

Bicyclo[2,2,1]hepta-2,5-diene(pentane-2,4-dionato)rhodium.—The dicarbonyl acetylacetonate (0.4 g.) and norbornadiene (5 ml.) in benzene (20 ml.) were refluxed for ca. 24 hr. After removal of the gelatinous norbornadiene polymer formed in the reaction the solution was evaporated. Chromatography on alumina and elution with methylene chloride affords yellow needles of the compound, m. p. 175–177° (0.4 g.) [Found: C, 49.3; H, 5.1; O, 10.9%; *M* (benzene) 290. $C_{12}H_{15}O_2Rh$ requires C, 49.0; H, 5.1; O, 10.9%; *M*, 293.9], insoluble in petroleum but soluble in acetone, ether, and chlorinated hydrocarbons; ν_{max} . (Nujol and hexachlorobutadiene mulls) 3069w, 3041m, 3000s, 2950s, 2924sh, 2913s, 2849m, 2837w, 1570s, 1558s, 1591s, 1456m, 1441m, 1427m, 1383s, 1351m, 1300m, 1264m, 1245w, 1200w, 1168m, 1152w, 1099w, 1067w, 1024m, 992w, 940m, 932; n.m.r. (in CCl_4) τ 4.84, relative area 1, central ring proton; 6.20, area 6, complex, norbornadiene ring protons; 8.16, area 6, sharp, CH_3 groups of acetylacetonate; 8.81, area 2, norbornadiene bridgehead protons.

The same complex, m. p. and mixed m. p. 176–177° was obtained when cycloheptatriene (1.5 ml.) and the dicarbonylacetylacetonate (0.3 g.) were refluxed in petroleum (b. p. 60–80°; 30 ml.) for 2 days [Found: C, 48.7; H, 5.2; O, 10.8%; *M* (benzene) 295].

Cyclo-octa-1,5-diene(pentane-2,4-dionato)rhodium.—This was prepared from the dicarbonyl acetylacetonate (0.1 g.) and the diene (2.0 ml.) in petroleum (b. p. 30–40°; 10 ml.). After 30 min. at room temperature the solution was evaporated. Extraction of the residue with petroleum (b. p. 40–60°), concentration, and crystallisation gave yellow crystals, m. p. 125–128° (decomp.), identical with original material³ (Found: C, 50.6; H, 6.1; O, 10.4. Calc. for $C_{13}H_{19}O_2Rh$: C, 50.4; H, 6.2; O, 10.3%); n.m.r. (in CCl_4) τ 7.27–8.37 complex and 8.12, sharp, total area 14, from methylene protons of diene and two methyl groups; 6.03, broad (ca. 1.3 c./sec.), area 4, co-ordinated olefinic protons; 4.79, area 1, sharp, central proton on acetylacetonate-ring.

Cyclo-octa-1,5-diene-(3-allylpentane-2,4-dionato)rhodium.—On addition of excess of olefin (ca. 2 ml.) to the dicarbonyl complex (0.5 g.), carbon monoxide was lost immediately; after brief shaking and removal of unused diene, crystallisation from petroleum (b. p. 40–60°) gave yellow crystals of the compound, m. p. 76–77° (0.44 g.) (Found: C, 54.7; H, 7.2; O, 9.3. $C_{16}H_{23}O_2Rh$ requires C, 54.9; H, 6.6; O, 9.1%), soluble in petroleum, ether, methylene chloride, benzene, and acetone.

Carbonyltriphenylphosphine(pentane-2,4-dionato)rhodium.—The dicarbonyl (0.2 g.) in benzene (10 ml.) was added to triphenylphosphine (0.8 g.) in benzene (10 ml.). After carbon monoxide evolution ceased the benzene was removed, the residue was washed twice with ether and chromatographed on alumina using chloroform eluant; crystallisation gave the yellow compound, decomp. ca. 175° (0.14 g.) (Found: C, 58.4; H, 4.5. $C_{24}H_{22}O_3PRh$ requires C, 58.6; H, 4.5%). It is soluble in acetone, benzene, chloroform and methylene chloride but sparingly soluble in methanol and carbon tetrachloride (with which it reacts), and insoluble in petroleum and ether;

ν_{\max} . (Nujol) 1980s, 1938w, 1568s, 1517s, 1481s, 1434s, 1312w, 1271m, 1193w, 1185w, 1163w, 1116w, 1092m, 1068w, 1027m, 997m, 993w, 924w, 852w, 794m, 755m, 750m, 700s, 695s, 616w.

Carbonyltriphenylarsine(pentane-2,4-dionato)rhodium.—This was prepared similarly, from the dicarbonyl (0.13 g.) and triphenylarsine (0.69 g.) in benzene, but with chromatography using methylene chloride–benzene (3 : 1) and crystallisation from ether, to give the yellow *compound*, m. p. 185–188° (decomp.) (0.08 g.) (Found: C, 53.4; H, 4.1. $C_{24}H_{22}AsO_3Rh$ requires C, 53.8; H, 4.1%). It reacts at once with carbon tetrachloride and carbon disulphide, giving orange and red solutions, respectively; ν_{\max} . (carbonyl region) in petroleum (b. p. 40–60°) 1976.

Carbonyltris(triphenylstibine)(pentane-2,4-dionato)rhodium.—To the dicarbonyl (0.2 g.) in ether (40 ml.) was added triphenylstibine (1.0 g.) in ether (10 ml.). After removal of solvent from the orange solution the residue was chromatographed on alumina using dichloromethane. After concentration, addition of ether gave the red *complex* (0.26 g.) which was purified by dissolving it in ether and removing the latter slowly in a vacuum, to leave red crystals, decomp. 154–156° [Found: C, 54.5; H, 4.2; O, 3.7%; M (acetone), 1176. $C_{56}H_{52}O_3RhSb_3$ requires C, 54.2; H, 4.2; O, 3.8%; M , 1240]. The compound gives a non-conducting solution in acetone. It reacts with carbon tetrachloride. The n.m.r. spectrum of a saturated acetone solution showed only phenyl-group resonances and the substance is too insoluble in petroleum for a carbonyl frequency to be observed; ν_{\max} . (Nujol) 1969s, 1570w, 1475m, 1376m, 1299w, 1261w, 1179w, 1157w, 1065m, 1020m, 997m, 729s, 694s, 656w, 545w.

We thank the Ethyl Corporation for financial support (F. B.); Johnson, Matthey, and Co. Ltd. for the loan of rhodium; and Shell Chemical Co. Ltd. for gifts of olefins.

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[Received, November 16th, 1963.]