

1083. *Interaction of Fulvenes with Octacarbonyldicobalt and Dicarbonylchlororhodium.*

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$\alpha\alpha$ -Dialkylfulvenes interact with octacarbonyldicobalt to give a mixture of ring-substituted π -cyclopentadienyldicarbonylcobalt(I) compounds. However, $\alpha\alpha$ -diarylfulvenes (L) replace terminal carbon monoxide groups to give binuclear olefinic derivatives $L_2Co_2(CO)_6$; with dicarbonylchlororhodium, mononuclear complexes, $LRh(CO)_2Cl$, are obtained.

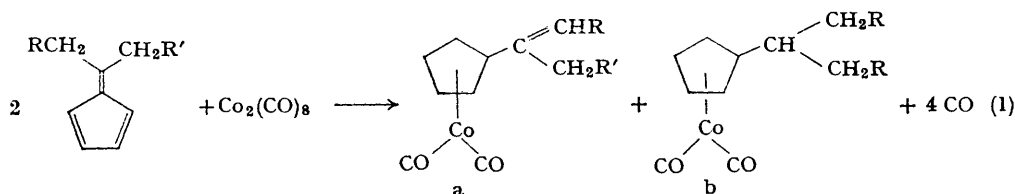
THE interaction of fulvenes with hexacarbonyls of molybdenum and tungsten leads to binuclear ring-substituted π -cyclopentadienylcarbonyls, the reaction being accompanied by hydrogen abstraction from the reaction medium or from excess of fulvene.¹ Using 6-alkylaminofulvenes,² hydrogen abstraction does not occur, and mononuclear ring-substituted π -cyclopentadienyltricarboxyls of molybdenum and tungsten, which have a zwitterionic structure, are obtained.² On the other hand, interaction of fulvenes with iron enneacarbonyl gives complexes in which the fulvenes are co-ordinated as olefinic ligands.³ In extension of these studies to cobalt and rhodium carbonyl compounds, both hydrogen abstraction, to give π -cyclopentadienyl compounds, and olefin-like co-ordination, depending on the circumstances, have been observed.

¹ E. W. Abel, A. Singh, and G. Wilkinson, *J.*, 1960, 1321.

² R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 801.

³ E. Weiss and W. Hübel, *Chem. Ber.*, 1962, **95**, 1186.

Interaction of $\alpha\alpha$ -dialkyl- and -diaryl-fulvenes with octacarbonyldicobalt. Alkylfulvenes react according to (1) to give a mixture of two π -cyclopentadienyldicarbonylcobalt derivatives with either unsaturated (a) or saturated side-chains (b):



Like the unsubstituted parent, π -C₅H₅Co(CO)₂,⁴ these compounds are air-sensitive dark-red liquids, distillable under vacuum and stable to *ca.* 140°. We have been unable to separate the two components by fractional distillation, chromatography on alumina, or vapour-phase chromatography due to their ready decomposition. However, the nature of the mixture has been demonstrated by infrared and nuclear magnetic resonance (n.m.r.) spectra of the mixtures and, in one case, by isolation of a pure sample of the saturated component. Thus, when the mixture (I) from the interaction of $\alpha\alpha'$ -dimethylfulvene and Co₂(CO)₈ was treated with hydrogen chloride in petroleum solution, the π -(isopropenylcyclopentadienyl)dicarbonylcobalt (Ia) adds hydrogen bromide and precipitates as a salt, leaving the π -(isopropylcyclopentadienyl)dicarbonylcobalt (Ib) in solution, from which it can be recovered pure. Other attempts at chemical separations, by shaking with silver nitrate solution, addition of bromine, or catalytic hydrogenation, led to decomposition.

The infrared (i.r.) spectra of all the mixtures (I)—(IV) show three terminal carbonyl stretching modes, and a C=C stretch at 1630 cm.⁻¹, in addition to typical ring absorption; for the pure π -(isopropylcyclopentadienyl)dicarbonylcobalt the spectrum is similar except for the absence of the 1630 cm.⁻¹ band. The n.m.r. spectra of the mixtures show two sets of characteristic π -cyclopentadienyl resonances in the 5 τ region with olefinic absorption of the side-chain in the 4 τ region. The mixture (I) has the simplest spectrum. There is a sharp doublet due to methyl at 8.90 τ ($J = 6.8$ c./sec.) and a quintet of CH resonances at 7.50 τ with the same splitting, proving the presence of the isopropyl group. At 8.05 τ there is an olefinic methyl group peak as a triplet through splitting by the olefinic protons ($J = 0.77$ c./sec.). The presence of the unsaturated isopropenyl group is shown by olefinic proton resonances at 4.81 and 4.85 τ , split mutually ($J = 2$ c./sec.), and by methyl ($J = 0.77$ c./sec.). The π -cyclopentadienyl protons account for two A₂B₂ sets at 5.08 and 5.15 τ . The pure isopropyl compound (Ib) had lines identical with those found in the mixture, and from the relative areas of the methyl-group resonances in the latter, it appears that the isopropyl and isopropenyl compounds occur in the mixture in a ratio of *ca.* 1:1.

The cyclohexyl-cyclohexenyl mixture also has a readily resolvable spectrum but the mixtures from ethylmethyl- and diethyl-fulvenes give very complicated spectra in the alkyl region, suggesting additional *cis-trans*-isomerism with respect to the double bond in the unsaturated component.

The formation of the 1:1 ratio of saturated and unsaturated components appears to be unaffected by a change of the solvent used for the reaction, from light petroleum to ethylene glycol dimethyl ether, or by use of a large excess of fulvene in light petroleum. This suggests that the simultaneous formation of equimolar ratios of the two compounds is probably due to a disproportionation involving a hydride transfer during the transition state of the reaction rather than a carbonium-ion mechanism involving hydrogen abstraction from the solvent. A similar disproportionation has been noted in the reaction of dimethylfulvene with

⁴ T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

but the presence of olefinic and phenyl-proton resonances as in (VIII) exclude any possible addition of hydrogen chloride to the co-ordinated hydrocarbon.

Prolonged interaction of (VIII) with hydrogen chloride leads to complete displacement of carbon monoxide and the formation of a crystalline complex of stoichiometry (fulvene)- RhCl_3 . This is diamagnetic and is presumably a halogen-bridged rhodium(III) species. Since it is insoluble even in acetone and water, it is probably polymeric in the solid. However, the apparent dimeric molecular weight in chloroform may suggest chloroform solvation rather than five-co-ordination, since the n.m.r. spectrum again indicates co-ordination of the fulvene through the exocyclic double bond.

EXPERIMENTAL

Microanalyses and molecular weights (Mechrolab Osmometer) were by the Microanalytical Laboratory, Imperial College. I.r. spectra were taken on a Grubb-Parsons Spectromaster and n.m.r. spectra, given as τ values (at 56.4 Mc./sec.), on a Varian 4310A instrument. Light petroleum had b. p. 60—80°. All reactions were carried out in a nitrogen atmosphere.

Dimethyl-, diethyl-, ethylmethyl-, and methyl-fulvenes,⁶ cyclohexylidenecyclopentadiene,⁷ $\alpha\alpha$ -diphenylfulvene,⁸ and $\alpha\alpha$ -bis-*p*-chlorophenylfulvene⁹ were made by published methods. $\alpha\alpha$ -Bis-*p*-tolylfulvene was prepared by Wheland and Mann's procedure⁹ from cyclopentadiene and bis-*p*-tolyl ketone in dioxan with sodium ethoxide as condensing agent, m. p. 105° (from ethanol) (Found: C, 92.8; H, 7.4. Calc. for $\text{C}_{20}\text{H}_{18}$: C, 92.95; H, 7.0%).

π -(*Isopropyl- and isopropenyl-cyclopentadienyl*)dicarbonylcobalt(I) (I) (1:1 Mixture).—To octacarbonyldicobalt (5.2 g., 0.015 mole) in light petroleum (80 ml.) was added dimethylfulvene (3.5 g., 0.033 mole) and the solution boiled for 6 hr. After cooling, it was passed through an alumina column which was washed with petroleum; the solvent was removed from the combined eluates to leave a dark-red oil which was distilled (46—48°/0.1 mm.) to give the product [4.1 g., 77% based on $\text{Co}_2(\text{CO})_8$]. It is miscible with all organic solvents but tends to decompose in chlorinated ones. Above 140°, decomposition occurs. The compound decomposes on exposure to air; ν_{max} . (CS_2 , CCl_4 , hexane): 2016s, 1952s, 1931m (CO), 1632w (C=C). N.m.r. data (liquid): 4.81, 4.85 (olefinic); 5.08, 5.15 ($\pi\text{-C}_5\text{H}_5$); 7.50 (CH); 8.05 (CH_3 olefinic); 8.90 (CH_3 aliphatic).

π -(*Isopropylcyclopentadienyl*)dicarbonylcobalt(I) (Ib).—Through a solution of the above mixture (3.1 g.) in light petroleum (25 ml.) at 0° was bubbled dry hydrogen bromide. After a few minutes, the excess of acid was swept out by nitrogen and the green precipitate collected. The solvent was removed from the filtrate and the residual oil distilled as above to give the complex (Found: C, 54.5; H, 4.7; Co, 26.4; O, 14.7%; *M* (benzene), 230. $\text{C}_{10}\text{H}_{11}\text{CoO}_2$ requires C, 54.1; H, 5.0; Co, 26.6; O, 14.4%; *M*, 222). The purity of the product was confirmed by n.m.r. and i.r. spectra, ν_{max} . (CCl_4 , CS_2 , hexane): 2959, 2915, 2857; 2016s, 1952s, 1931m (CO); 1470w, 1450w, 1440w, 1385w, 1384w, 1311w, 1302w, 1259m, 1131w, 1087m, 1015m, 917w, 885w, 815s, 800s, 614s. N.m.r. data (liquid): 5.08, 5.15 ($\pi\text{-C}_5\text{H}_5$); 7.50 (CH); 8.90 (CH_3 aliphatic).

Other Complexes Derived from Alkylfulvene and Octacarbonyldicobalt.—The mixture (II) was prepared in an analogous manner from ethylmethylfulvene (80%), b. p. 57—59°/0.1 mm. (Found: C, 56.6; H, 5.7%; *M* (benzene), 231. Calc. for $\text{C}_{11}\text{H}_{12}\text{CoO}_2$: C, 56.2; H, 5.1%; *M*, 235). The mixture (III) was prepared from diethylfulvene (60%), b. p. 64—65°/0.1 mm. (Found: C, 58.1; H, 5.7%; *M* (benzene), 250. Calc. for $\text{C}_{12}\text{H}_{14}\text{Co}_2\text{O}_2$: C, 57.8; H, 5.7%; *M*, 250).

The mixture (IV) was prepared from cyclohexylidenecyclopentadiene (50%), b. p. 106—107°/0.3 mm. (Found: C, 60.4; H, 5.5%; *M* (benzene), 256. Calc. for $\text{C}_{13}\text{H}_{14}\text{CoO}_2$: C, 59.8; H, 5.4%; *M*, 261). N.m.r. data (liquid): 3.91 (olefinic), 4.85, 5.19 ($\pi\text{-C}_5\text{H}_5$); 7.82 (CH_2 olefinic), 8.28 (CH_2 aliphatic).

Bis-($\alpha\alpha$ -diphenylfulvene)hexacarbonyldicobalt (V).—To a solution of octacarbonyldicobalt (1.2 g., 3.5 mmoles) in light petroleum (30 ml., 40—60°) was added $\alpha\alpha$ -diphenylfulvene (1.62 g., 7 mmoles) in light petroleum (40 ml.). After $\frac{1}{2}$ hr., light-brown needles began to appear; after 6 hr. these were collected and dried under nitrogen (2.1 g., 81%), decomposing at 76° (Found: C, 67.1; H, 4.2; Co, 15.2; O, 12.8. $\text{C}_{42}\text{H}_{28}\text{Co}_2\text{O}_6$ requires C, 67.5; H, 3.8; Co, 15.8; O, 12.8%). The compound is soluble in benzene, chloroform, and carbon disulphide. It can be stored under

⁶ G. Crane, C. E. Board, and A. L. Henne, *J. Amer. Chem. Soc.*, 1945, **67**, 1237.

⁷ E. P. Kohler and J. Kable, *J. Amer. Chem. Soc.*, 1935, **57**, 917.

⁸ J. Thiele and H. Balhorn, *Annalen*, 1908, **348**, 5.

⁹ G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, 1949, **17**, 264.

nitrogen or *in vacuo*, ν_{\max} . (CHCl_3 , CS_2): 2024vs, 1805s, 1592w, 1572w, 1488m, 1441m, 1397m, 1321w, 1179w, 1087w, 1073w, 1010w, 994w, 902w, 819w, 725m, 698s, 674s, 665m, 621m, 591w.

*Bis-(α -di-*p*-chlorophenylfulvene)hexacarbonyldicobalt (VI).*—Prepared as above from α -di-*p*-chlorophenylfulvene, this formed dark-brown *needles* (60%), decomposing at 68° (Found: C, 57.5; H, 4.3; Cl, 16.4; Co, 14.1; O, 11.0. $\text{C}_{42}\text{H}_{24}\text{Cl}_4\text{Co}_2\text{O}_6$ requires C, 57.1; H, 2.7; Cl, 16.0; Co, 13.3; O, 10.9%).

*Bis-(α -di-*p*-tolylfulvene)hexacarbonyldicobalt (VII).*—This was prepared as above, from α -di-*p*-tolylfulvene but under carbon monoxide to prevent decomposition (55%), decomposing at 76–78° (Found: C, 68.0; H, 4.8; Co, 15.4; O, 11.4. $\text{C}_{46}\text{H}_{36}\text{Co}_2\text{O}_6$ requires C, 68.8; H, 4.5; Co, 14.7; O, 12.0%). The compound is soluble in light petroleum.

α -Diphenylfulvenedicarbonylchlororhodium(I) (VIII).—A solution of diphenylfulvene (1.15 g., 5 mmoles) in light petroleum (b. p. 40–60°; 30 ml.) was added to sublimed dicarbonylchlororhodium (0.96 g., 2.5 mmoles) in light petroleum (b. p. 40–60°) and the mixture stirred for 48 hr. at room temperature when the dark-blue crystals of the *complex* were collected, washed, and dried *in vacuo* (1.2 g., 51%), decomposing at 141° (Found: C, 57.7; H, 4.0; Cl, 8.3; O, 6.6%; *M* (CHCl_3), 440. $\text{C}_{20}\text{H}_{14}\text{ClO}_2\text{Rh}$ requires C, 56.6; H, 3.3; Cl, 8.3; O, 7.5%; *M*, 425), ν_{\max} . (CHCl_3): 3067w, 2985w; 2062vs, 1984vs; 1613w, 1590w, 1567w, 1484w, 1439m, 1412w, 1376m, 1332m, 1311w, 1285w, 1176w, 1156w, 1075–1064w, 998w, 969w, 941m, 905w, 841m. N.m.r. data (CDCl_3): 3.56(2), 3.74(2) (olefinic); 2.76(10) (phenyl). N.m.r. data of $\text{C}_{18}\text{H}_{14}$ (CCl_4): 3.64(2), 3.82(2) (olefinic); 2.78(10) (phenyl).

*α -Di-*p*-tolylfulvenedicarbonylchlororhodium(I) (IX).*—This was prepared as for (VIII), but the solution was boiled in light petroleum for 24 hr., when the blue *crystals* were collected (55%), decomposing at 142–144° (Found: C, 58.9; H, 4.5; Cl, 8.4; O, 6.9%; *M* (CHCl_3), 460. $\text{C}_{22}\text{H}_{18}\text{ClO}_2\text{Rh}$ requires C, 58.4; H, 4.0; Cl, 7.8; O, 7.1%; *M*, 453). N.m.r. data (CDCl_3): 3.61(2), 3.80(2) (olefinic); 2.96(8) (phenyl); 7.62(3) (CH_3). N.m.r. data of $\text{C}_{20}\text{H}_{18}$ (CCl_4): 3.59(2), 3.87(2) (olefinic); 3.09(8) (phenyl); 7.74(3) (CH_3).

α -Diphenylfulvenemethyldicarbonylchloroiodorhodium(III) (X).—The complex (VIII) (0.212 g., 0.5 mmole) was shaken with methyl iodide (5 ml.), dissolving slowly to give a green solution. After 1 hr. the solvent was removed and the *complex* dried under nitrogen (*ca.* 100%) (Found: C, 42.0; H, 3.2; I, 20.8; O, 5.8. $\text{C}_{21}\text{H}_{17}\text{ClIO}_2\text{Rh}$ requires C, 44.5; H, 3.0; I, 22.4; O, 5.6%), ν_{\max} . (Nujol): 2058s, 1984s; other bands as starting material.

α -Diphenylfulvenedicarbonyldichlorohydridorhodium(III) (XI).—Through a solution of (VIII) (0.3 g.) in benzene (20 ml.) was passed hydrogen chloride until the blue solution just became brown. Rapid removal (by N_2) of excess of acid and addition to light petroleum (100 ml.) gave a yellow precipitate of the *complex* which was collected, washed with light petroleum and dried *in vacuo* (0.25 g., 76%), decomposing at 108° (Found: C, 51.0; H, 3.9; Cl, 15.3; O, 6.7. $\text{C}_{20}\text{H}_{15}\text{Cl}_2\text{O}_2\text{Rh}$ requires C, 52.1; H, 3.3; Cl, 15.4; O, 6.9%), ν_{\max} . (Nujol): 2128w, 2066s, 1976s; other bands as in starting material. N.m.r. data (CDCl_3): 4.26(2), 4.67(2) (olefinic); 2.70(10) (phenyl).

α -Diphenylfulvenetrichlororhodium.—Prepared as above, but passage of hydrogen chloride extended to *ca.* $\frac{1}{2}$ hr. the *complex* formed reddish-orange crystals which were collected, dried, and recrystallised from chloroform–benzene (0.18 g., 74%), decomposing *ca.* 200° (Found: C, 48.4; H, 3.8; Cl, 24.3%; *M* (CHCl_3), 822. $\text{C}_{36}\text{H}_{28}\text{Cl}_6\text{Rh}_2$ requires C, 49.2; H, 3.2; Cl, 24.2%; *M*, 879). It is insoluble in benzene, acetone, and water. It can be boiled in chloroform solution without decomposition. N.m.r. data (CDCl_3): 4.30(2), 4.75(2) (olefinic); 2.70(10) (phenyl).

We thank the Ethyl Corporation for financial support (to J. A.) and Dr. L. Pratt and Mr. J. F. Young for assistance.