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NOTE

SUBSTITUTED CYCLOPENTADIENONE–RUTHENIUM TRICARBONYL COMPLEXES

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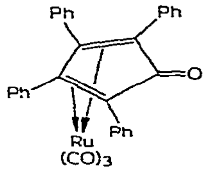
Recent communications[1,2] have described the reactions of several acetylenes with triruthenium dodecacarbonyl. One of the products isolated from the reaction with diphenylacetylene was tetraphenylcyclopentadienone–ruthenium tricarbonyl (I), which is described as a deep yellow solid, m.p. 135–137° (decompn.)[1].



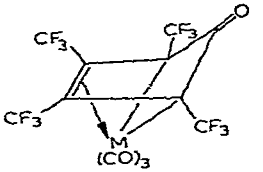
(I)

We have prepared this complex in 85% yield by the reaction of tetracyclone with $Ru_3(CO)_{12}$ in refluxing benzene. So prepared, the complex forms pale yellow crystals, m.p. 180–183° (decompn.), and it has been characterised as the cyclopentadienone complex by analysis, and by infrared and mass spectrometry.

The carbonyl region of the infrared spectrum shows three bands typical of an $M(CO)_3$ group at 2081, 2026, and 2005 cm^{-1} [*cf.* the analogous iron complex[3], with ν(CO) at 2060, 2015, and 1988 cm^{-1}]. The other bands in the spectrum, however, do not all agree with those found by other workers in similar solvents[1]. Thus we find bands at 1657 and 1601 cm^{-1}, which can probably be assigned to the ketonic CO and C=C stretching frequencies. The former band shifts from 1657 cm^{-1} in carbon disulphide solution, to 1633 cm^{-1} in chloroform, whereas other bands are affected by only a few cm^{-1}. This suggests that this band is associated with the ketonic carbonyl group, the shift being caused by some hydrogen bonding effect. In the iron complex, this band is reported[3] at 1642 cm^{-1}.

The mass spectrum of the ruthenium complex shows a parent ion, and peaks arising by loss of *four* carbonyl groups, characteristic of dienone complexes[4], and also a strong peak due to $Ph_4C_5O^+$. These facts suggest that either this complex can exist in two different crystal forms, or that the Italian workers have isolated an isomeric complex, $(Ph_2C_2)_2Ru(CO)_4$, from their reaction.

In the thermal reaction between hexafluoro-2-butyne and iron pentacarbonyl[5], the sole product was found to be tetrakis(trifluoromethyl)cyclopentadienone–iron tricarbonyl (IIa), shown to have this structure by an X-ray study[6]. The similar reaction with triruthenium dodecacarbonyl gives the analogous complex (IIb), as shown by analysis and its spectral properties.



(IIa) M = Fe
(IIb) M = Ru

The infrared spectrum of (IIb) shows two strong terminal ν(CO) at 2130 and 2072 cm^{-1}, with a shoulder at 2036 cm^{-1} [*cf.* complex (IIa), ν(CO) at 2133 vs, 2083 vs, 2040 (sh) cm^{-1}][5], and the strengths and positions of the other bands in the spectrum agree with those observed in (IIa). In particular, there are strong bands at 1719 and 1705 cm^{-1}, arising from the ketonic CO and the coordinated double bond; as with complex (IIa), it is not possible in this case to assign these two bands more specifically.

Irradiation of a mixture of the carbonyl and the acetylene gives a complex mixture of products, in which complex (IIb) was identified by its infrared spectrum. Evidently the UV irradiation results in further reaction, either of the acetylene with the carbonyl, or with complex (IIb). The metal–metal bond absorption in $Ru_3(CO)_{12}$ occurs at 391 mμ[7]; this is sufficiently close to the irradiating wavelength (366.5 mμ) for it to be likely that fission of the metal–metal bonds occurs on irradiation, to give $Ru(CO)_4$ fragments.

EXPERIMENTAL

Tetraphenylcyclopentadienone–ruthenium tricarbonyl

A mixture of tetracyclone (576 mg, 1.5 mmoles) and $Ru_3(CO)_{12}$ (321 mg, 0.5 mmole) in benzene (25 ml) was refluxed in nitrogen for a total of 18 h. Solvent was removed, and the residue was recrystallised from a pentane/benzene mixture to give yellow or yellow-brown crystals. These were extracted with pentane, and the extract was cooled to give very pale yellow crystals of the complex (I) (725 mg, 85%), m.p. 180–183° (decompn.) (Found: C, 67.41; H, 3.44; mol.wt. (mass spectrometry), 570. $C_{32}H_{20}O_4{}^{102}Ru$ calcd.: C, 67.33; H, 3.51%; mol.wt., 570.)

IR spectrum: ν(CO) 2081 vs, 2026 vs, 2005 vs cm^{-1} (cyclohexane); 2079 vs, 2027 vs, 2007 vs cm^{-1} (CCl_4); 2081 vs, 2030 vs, 2012 vs cm^{-1} ($CHCl_3$); other bands at 3080 w, 3055 m, 3045 w, 3020 w, 2915 w, 2840 vw, 1801 vw, 1657 s, 1601 w, 1309 vw, 1280 vw, 1198 w, 1183 w, 1154 vw, 1116 w, 1071 w, 1028 m, 1006 w, 914 vw, 839 w, 803 m, 768 m, 750 s, 732 m, 703 s, 698 s, 640 w cm^{-1} (CS_2).

Reaction between hexafluoro-2-butyne and $Ru_3(CO)_{12}$

Hexafluoro-2-butyne (320 mg, 2 mmoles) was condensed on to $Ru_3(CO)_{12}$ (200 mg, 0.3 mmole) in cyclohexane (20 ml) in a Carius tube. The tube was sealed, and heated at 135° for 40 h. After removal of solvent and sublimation (70°/0.1 mm) of the residue, extraction of the sublimate with pentane left a yellow solid, which was resublimed to give the white complex (IIb) (45 mg, 10%), m.p. 154° (Found: C, 26.9; H, 0.0; F, 42.4; mol.wt. (mass spectrometry), 538. $C_{12}F_{12}O_4Ru$ calcd.: C, 26.8; H, 0.0; F, 42.4%; mol.wt. (^{102}Ru), 538.)

IR spectrum (cyclohexane): 2130 vs, 2072 vs, 2036 sh [ν(CO)], 1719 s, 1705 s [ν(ring-CO) and ν(C=C)], 1400 m, 1341 w, 1200 s, 1141 m, 986 vw, 851 m, 647 vw, 625 m cm^{-1}.

The residue after sublimation consisted of white crystals of a trimer of the acetylene (Found: mol.wt. (mass spectrometry), 486. $C_{12}F_{18}$ calcd.: mol.wt., 486.)

The same complex was formed using benzene as a solvent in a similar reaction. The complex is soluble in benzene and chloroform, but insoluble in pentane. With acetone or methanol, red solutions are formed.

Irradiation (41 h) of a mixture of $Ru_3(CO)_{12}$ (500 mg, 0.8 mmole) and hexafluoro-2-butyne (800 mg, 5 mmoles) in benzene (20 ml) gave, besides unreacted carbonyl, a small amount of yellow solid, whose IR spectrum indicated it to be a mixture of complex (IIb) with other carbonyl-containing products. The small amounts obtained precluded any further investigation.

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