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NOTE

Reactions between acetylenes and dodecacarbonyl triruthenium

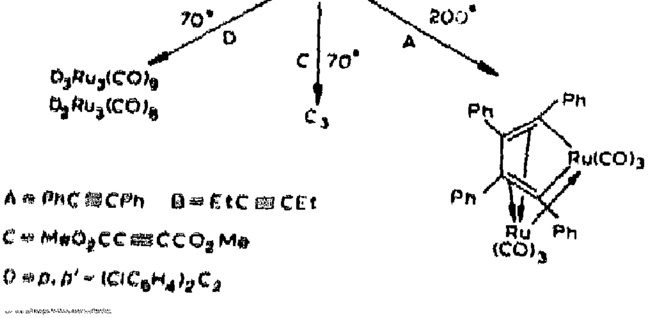
In a recent paper we reported[1] a convenient synthesis of dodecacarbonyl triruthenium. In this note we describe briefly reactions between this metal carbonyl and certain acetylenes.

In a typical experiment, a mixture of $Ru_3(CO)_{12}$ (250 mg, 0.39 mmole) and diphenylacetylene* (142 mg, 0.8 mmole) in hexane (25 ml) was refluxed for 18 h under nitrogen. Filtration afforded a dark purple-red crystalline material (35 mg 9%) ν(CO) (Nujol) 2018s, 1972s, 1944s and 1917s cm^{-1}. [Found: C, 56.6; H, 3.0; O, 12.7; mol. wt., 1091 (Mechrolab Osmometer). $C_{51}H_{30}O_9Ru_3$ calcd.: C, 56.2; H, 2.6; O, 13.2%; mol. wt., 1089.] The molecular formula indicates that the trinuclear ruthenium atom cluster present in the metal carbonyl has been retained in the diphenylacetylene derivative. A related triphenylphosphine complex $(Ph_3P)_3Ru_3(CO)_9$ has recently been reported[2,3].

At 200°, diphenylacetylene and dodecacarbonyl triruthenium in decalin gave as the principal product (47% yield) a yellow crystalline compound. [Found: C, 56.3; H, 2.5; O, 14.2; mol. wt., 711 (Mechrolab Osmometer). $C_{34}H_{20}O_6Ru_2$ calcd.: C, 56.2; H, 2.7; O, 13.2%; mol. wt., 726.] The infrared spectrum of this complex in the carbonyl stretching region showed bands (cyclohexane solution) at 2081 vs, 2041 vs, 2021 vs, 2006 (sh), 1996 vs and 1946 w cm^{-1}. This spectrum is very similar to that reported for the iron complex $(Ph_2C_2)_2Fe_2(CO)_6$ except that the bands in the spec-

CHART 1

REACTIONS OF SOME ACETYLENES WITH $Ru_3(CO)_{12}$



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* *Note added in proof.* The reaction between diphenylacetylene and dodecacarbonyl triruthenium has also been studied by Cetini *et al.*, (*Atti Accad. Sci. Torino*, in press).

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trum of the latter compound occur at about 20 cm^{-1} lower frequency[4]. The yellow ruthenium complex presumably has a structure similar to that of the iron analogues of type (acetylene)$_2$Fe$_2$(CO)$_6$; two diphenylacetylene molecules and an Ru(CO)$_3$ group forming a five membered heterocyclic ring system[5].

The above reactions, as well as those with some other acetylenes, are summarised in chart 1, the principal products only being indicated. The cyclopentadienone-ruthenium tricarbonyl complex obtained using 3-hexyne as the reactant has an infrared spectrum in the carbonyl stretching region [ν(CO), 2072, 2015, 1996 and 1649 cm^{-1} (CCl$_4$)] very similar to that of (tetraphenylcyclopentadienone)iron tricarbonyl [ν(CO), 2062, 2012, 1988 and 1642 cm^{-1}][4], in accord with the structure proposed.

The reaction between Ru$_3$(CO)$_{12}$ and *p,p'*-dichlorodiphenylacetylene (D) affords a dark red compound D$_3$Ru$_3$(CO)$_9$, ν(CO) (Nujol), 2021s, 1975s, 1968s, 1956(sh), and 1935m cm^{-1}. (Found: C, 47.6; H, 2.6; Cl, 16.8. $C_{51}H_{24}Cl_6O_9Ru_3$ calcd.: C, 47.2; H, 1.8; Cl, 16.4%.) This complex presumably has a structure similar to that of Ru$_3$(CO)$_{12}$, with one carbonyl group on each ruthenium atom being replaced by a *p,p'*-dichlorodiphenylacetylene group. A second reaction product obtained as orange crystals is formulated as D$_2$Ru$_3$(CO)$_8$ on the basis of its high resolution mass spectrum which besides showing a group of peaks between 1010 and 1025 (*m/e* ±2) [$C_{36}H_{16}{}^{35}Cl_4O_8{}^{102}Ru_3$ calcd.: 1022] shows successive loss of eight carbonyl groups, followed by loss of four chlorine atoms. In the carbonyl region of the infrared spectrum, bands occur (cyclohexane solution) at 2071s, 2032s, 2027vs, 2018s, 1978vs, 1883s, and 1863s cm^{-1}. The structure of this ruthenium complex is presumably similar to that of one or other of the two isomers of formula (PhC≡CPh)$_2$Fe$_3$(CO)$_8$ (*cf.* ref. 6), which are violet and black in colour. The black isomer has infrared bands at about 1850 cm^{-1} whereas the violet form does not[4]. On this basis it would appear that the complex D$_2$Ru$_3$(CO)$_8$ is analogous to the black compound (PhC≡CPh)$_2$Fe$_3$(CO)$_8$.

During the course of our work we have also studied the reaction between Ru$_3$(CO)$_{12}$ and (tetraphenylcyclobutadiene)palladium dibromide[7]. As expected, the complex (tetraphenylcyclobutadiene)ruthenium tricarbonyl is produced as yellow crystals, m.p. 217–219°, ν(CO) (cyclohexane), 2053vs, 1987vs, 1950w cm^{-1} (Found: C, 68.5; H, 3.7; O, 8.8; Ru, 18.2. $C_{31}H_{20}O_3Ru$ calcd.: C, 68.7; H, 3.7; O, 8.9; Ru, 18.6%.) The mass spectrum shows a group of peaks around *m/e* 542 (based on ^{102}Ru) corresponding to the parent ion, and peaks at around 514, 486 and 458 corresponding to (P–CO)$^+$, (P–2 CO)$^+$ and (P–3 CO)$^+$ ions, respectively. The infrared spectrum of the corresponding iron complex shows ν(CO) at 2037, 1965 and 1931 cm^{-1}, again these bands are about 20 cm^{-1} lower in frequency than those in the ruthenium derivatives.

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