coupling constant and asymmetry parameter respectively. The value for the coupling constant is much smaller than that (570 kc/s) estimated by Brown and Ladd for the quadrupole coupling constant of the ^{7}Li nucleus in a toluene solution of ethyllithium[8]. The relatively large values of the coupling constant and asymmetry parameter for ethyllithium show that the small coupling constant for methyllithium is due to the cancelling out of large field gradients of opposite signs. Thus although a qualitative rationalisation of the difference between the two compounds presents no difficulty, a quantitative explanation on the basis of a simple model is not likely to be very successful. This task would be much simplified if the orientation of the field gradient axes in ethyllithium could be determined, however, the problem of growing a large single crystal of this compound is considerable.

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PRELIMINARY NOTES

Reactions of acetylenes with noble-metal halides.

III*. Tetra-substituted cyclopentadienonerhodium chlorides

In connection with our interest in the reactions of acetylenes with palladium(II) halides[1], we have also studied some reactions of acetylenes with a complex of another d^8 ion, rhodium(I) dicarbonyl chloride dimer (I).

Reaction of (I) with a large excess of diphenylacetylene (II, R = C_6H_5) in refluxing benzene gave two soluble products and an insoluble polymer. The soluble materials were separated by chromatography on Florisil to give hexaphenylbenzene (V, R = C_6H_5; 9%) and orange-red 2,3,4,5-tetraphenylcyclopentadienonerhodium chloride (tetracyclonerhodium chloride) (III, R = C_6H_5) in 47% yield. The insoluble brown polymer, obtained in 12% yield, was identified by analysis and infra-red

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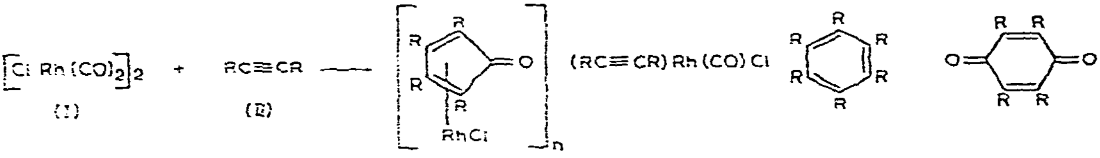
* Parts I and II of this series are entitled "Reactions of Palladium Compounds with Acetylenes" and are quoted in ref. 1.

spectrum as a diphenylacetylene complex of rhodium carbonyl chloride (IV, R = C_6H_5).

Tetracyclonerhodium chloride (III, R = C_6H_5) was characterized by analysis, NMR spectrum, the similarity of its infra-red spectrum to that of the known tetracycloneiron tricarbonyl[2] in the 6–16 μ region and by an independent synthesis. Molecular weight measurements in chloroform indicated that it is a dimer in this solvent and is presumably chlorine-bridged.

Tetracyclone and (I) on refluxing in benzene gave, after chromatography of the soluble product, a 30% yield of (III). In addition an insoluble yellow material crystallized out of solution during the reaction. This material, a polymer of [(tetracyclone)Rh(CO)Cl] obtained in 57% yield, was smoothly converted into (III, R = C_6H_5) on refluxing in xylene for a short time. When (I) and tetracyclone were heated in a larger volume of solvent, or for a longer time, yields of the polymer greatly decreased, sometimes to zero, with consequent increase in the amount of (III, R = C_6H_5) produced directly.



(III) (IV) (V) (VI)

3-Hexyne (II, R = C_2H_5) reacted similarly with (I) in refluxing benzene to give an insoluble blue (3-hexyne)rhodium carbonyl chloride polymer (IV, R = C_2H_5) in 47% yield. On chromatography of the benzene-soluble product a 40% yield of tetraethylcyclopentadienone rhodium chloride (III, R = C_2H_5) and a small amount (8%) of an organic compound, identified as 2,3,5,6-tetraethyl-*p*-benzoquinone (VI, R = C_2H_5) were obtained. None of the expected hexaethylbenzene (V, R = C_2H_5) was formed in this reaction. The complex (III, R = C_2H_5), in contrast to the tetracyclone complex, was a trimer in solution.

One other acetylene, hexafluoro-2-butyne, had previously been shown by Dickson and Wilkinson[3] to be oligomerized by rhodium(I) complexes. On reaction of this acetylene with carbon monoxide in the presence of (I) they obtained 2,3,4,5-tetrakis(trifluoromethyl)cyclopentadienone; no metal complexes were identified here but a substituted cyclopentadienone and a substituted benzene complex were obtained from this acetylene and cyclopentadienylrhodium dicarbonyl. The oligomerization of acetylenes with rhodium (I) complexes thus appears to be a general reaction.

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