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Preliminary communication

THE REACTION OF ALLENE WITH β-DIKETONATOIRIDIUM(I) COMPLEXES: FORMATION AND CRYSTAL STRUCTURE OF A NEW BIS-η-ALLYLIC DERIVATIVE OF IRIDIUM(III)

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Summary

The reaction of allene with (Hfacac)Ir(η-$C_8H_{14})_2$ to give a new bis-η-allylic complex of iridium(III) containing an allene tetramer is described; the X-ray structure of this compound is reported.

As a part of a systematic study of the reactions of allene with transition metal complexes [1-4], we have examined the reaction of allene with iridium(I) compounds into which there has been little investigation [5].

We describe below the preparation and the structure of a new iridium(III) complex in which an allene tetramer is bonded to iridium by two η-allylic groups.

When allene is bubbled through a pentane solution of (Hfacac)Ir(η-$C_8H_{14})_2$ ** at room temperature, a fast reaction occurs as indicated by a rapid change in colour from reddish-violet to light red. From the solution a compound of stoichiometry (Hfacac)Ir$(C_3H_4)_4$ (yield 60%) (I) can be obtained as red crystals by cooling to —30°C.

I is thermally stable and remains unchanged in air for prolonged periods. Its IR spectrum (KBr) reveals that the β-diketonato group is bonded to iridium by the two oxygen atoms, as indicated by the bands due to ν(C⎓O) and to ν(C⎓C) which appear at 1630 and 1550 cm^{-1}, respectively. Catalytic hydrogenation of I under mild conditions gives metallic iridium and a mixture

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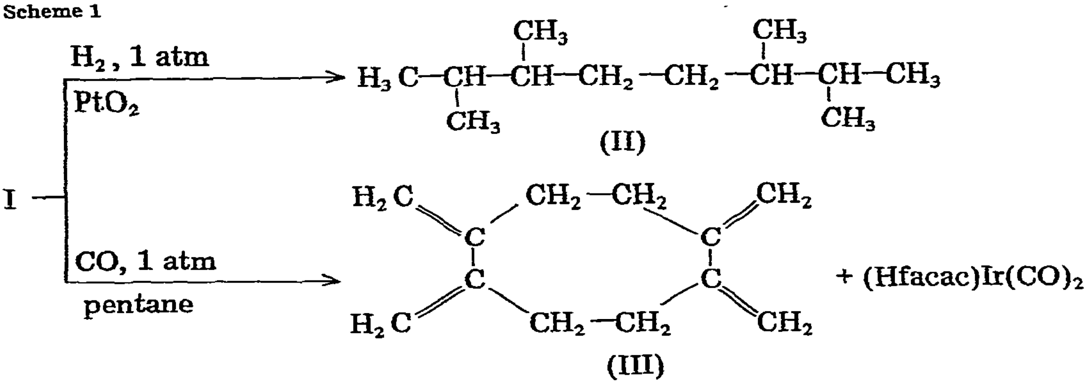
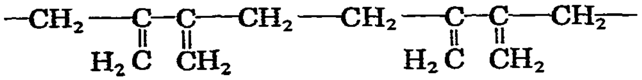
[**] Hfacac = 1,1,1,5,5,5-hexafluoroacetylacetonato; C_8H_{14} = cyclooctene.

of products, in which 2,3,6,7-tetramethyloctane (II) predominates (95%, by GLC). Treatment of I with CO at room temperature gives 1,2,5,6-tetramethylenecyclooctane (III) and $(Hfacac)Ir(CO)_2$ (Scheme 1).

Scheme 1



These findings are consistent [1] with the presence in I of the 2,3,6,7-tetramethyleneoctane-1,8-diyl group (IV).



$$-CH_2-\underset{\underset{H_2C}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2-CH_2-\underset{\underset{H_2C}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}-CH_2-$$

(IV)

The X-ray examination of a single crystal of I reveals that both ends of the group IV are bonded to iridium in an η-allylic fashion (Fig. 1). The X-ray

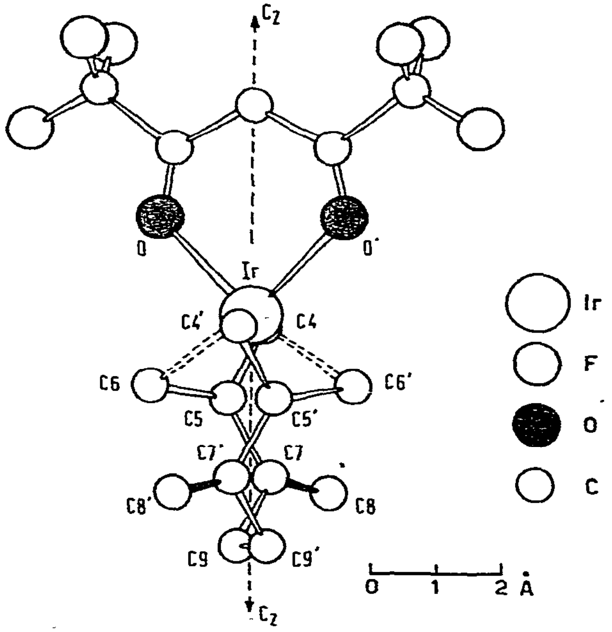


Fig.1. Projection of the structure of the complex I.

intensities (graphite-monochromated Cu-K_α radiation) were measured with a Philips PW 1100 diffractometer and the structure was solved by Patterson and Fourier methods. The least-squares refinement, using anisotropic temperature parameters, led to a final value of 0.064 for the conventional R-index. The crystal data are: a = 9.850(2), b = 21.452(8), c = 8.583(2) Å, β 96.91(2)°; space group $C2/c$; Z = 4 units $IrO_2C_{17}H_{17}F_6$ per cell. As shown in Fig. 1, the C_2 molecular symmetry is retained in the crystal and the coordination polyhedron around the iridium atom can be described as a very distorted octahedron if the η-allylic groups are regarded as bidentate ligands.

The four atoms O, O′, C(6), and C(6′) have an approximately square-planar arrangement, while the Ir—C(4) and Ir—C(4′) bond axes deviate by about 21° from the axial direction and form an angle of 168.7°. The coordination bond lengths are: Ir—C(4) = 2.21(1) Å, Ir—C(5) = 2.15(1) Å, Ir—C(6) = 2.11(1) Å, and Ir—O = 2.136(8) Å. These bond-lengths reveal unambiguously that the two equivalent η-allylic groups are asymmetrically bonded to the iridium atom, as observed for bis-η-allylic complexes of rhodium(III) having a C_2 symmetry [1,3,6-8].

The conformation of the hydrocarbon ligand is very close to that described for a similar rhodium complex [3], with a value of 20° for the torsion angle C(4)—C(5)—C(7)—C(8).

These results illustrate the analogy between some rhodium and iridium derivatives as in terms of their reactions with allene. Furthermore the reaction described appears to provide an easy route to di-η-allylic complexes of iridium(III).

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