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Preliminary communication

THE REACTION OF ALLENE WITH β-DIKETONATOIRIDIUM(I) COMPLEXES: FORMATION AND CRYSTAL STRUCTURE OF A NEW IRIDOCYCLOPENTANE DERIVATIVE

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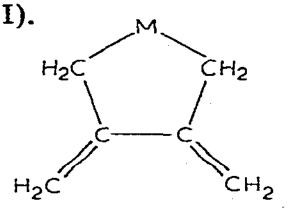
Summary

The reaction of allene with (Acac)Ir(η-C_8H_{14})$_2$ at −78°C yields new iridium(III) derivatives containing the 3,4-dimethyleneiridocyclopentane moiety. One of these complexes has been studied by X-ray diffraction.

It was recently shown [1,2] that allene can enter into an oxidative coupling reaction giving compounds characterized by the presence of the 3,4-dimethylene-metallocyclopentane moiety (I).



M = transition metal

(I)

This is of interest since compounds of this type have been postulated [2-5] as intermediate species in some catalytic and stoichiometric reactions of allene with transition metal derivatives. We have isolated new complexes of iridium(III) containing the moiety (I) (M = Ir) and we describe below their preparations and structures.

When a suspension of (Acac)Ir(η-C_8H_{14})$_2$** in liquid allene is allowed to react at −78°, the solid dissolves in about 30 min to give a clear solution from which a pale yellow microcrystalline precipitate (II) is obtained in high yield

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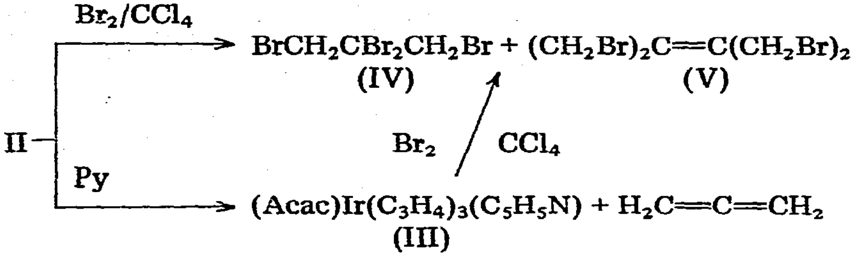
**Acac = acetylacetonato; C_8H_{14} = cyclooctene.

on adding cold pentane. Since this compound is unstable at temperatures above −20°C, elemental analysis and molecular weight measurements could not be carried out. Its structural assignment rests on a low temperature IR spectrum and on the reactions outlined in Scheme 1.

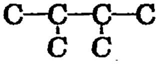
SCHEME 1



The IR spectrum of II (nujol mull, −30°C) reveals that the acetylacetonato group is bonded to iridium by the two oxygen atoms [ν(C═O) 1580 cm^{-1}; ν(C═C) 1510 cm^{-1}]. Two bands of medium intensity at 1710 and 1690 cm^{-1} and a broad, strong absorption centered at 685 cm^{-1}, indicate [6] that in II at least two allene molecules are coordinated to iridium by one double bond. Treatment of a suspension of II in heptane at −30°C with pyridine gave a stable yellow-greenish compound of formula $(Acac)Ir(C_3H_4)_3(C_5H_5N)$ (III) in high yield with evolution of allene.

At least one of the three allene molecules of III is coordinated to iridium by one of its double bonds since the IR spectrum (KBr) shows two bands at 1770 and 855 cm^{-1} [6]. Both II and III react with bromine in carbon tetrachloride (Scheme 1) to give unidentified inorganic compounds and a mixture of 1,2,2,3-tetrabromopropane (IV) and tetrabromomethylethylene (V), (authentic NMR spectra).

The NMR spectra showed that the mixtures obtained from II and III contained IV and V in molar ratios of 2:1 and 1:1, respectively.

The formation of 1,2,2,3-tetrabromopropane confirms the presence of coordinated allene in the complexes II and III [8]. Assuming that no coupling between allene molecules occurs during the reaction of II and III with Br_2, the results also suggest [1,7] that both complexes contain an allene dimer containing the skeleton  $\mathrm{C{-}\underset{\mathrm{C}}{\underset{|}{C}}{-}\underset{\mathrm{C}}{\underset{|}{C}}{-}C}$, from which tetrabromomethylethylene is formed. This was confirmed by the X-ray diffraction study of a single crystal of III. The X-ray intensities were measured with a Philips PW 1100 diffractometer using graphite-monochromated Mo-K_α radiation and the structure was solved by Patterson and Fourier methods and refined by anisotropic least-squares down to a value of 0.071 for the conventional R index. The crystal data of III (racemic form) are: a = 9.248(1), b = 18.547(5), c = 10.853(1) Å, β 96.53(1)°; space group $P2_1/c$; Z = 4.

As shown in Fig. 1, in the distorted octahedral coordination the acetylacetonato group and the allene dimer act as chelating ligands with a *pseudo*-

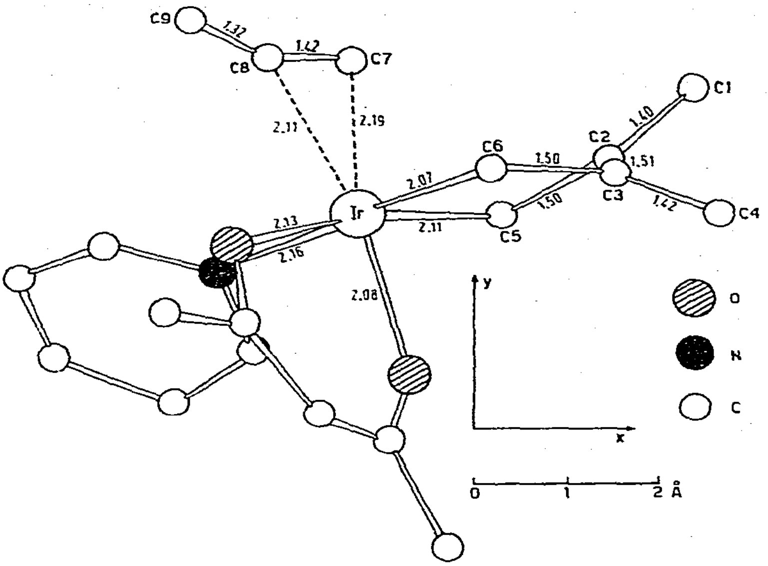
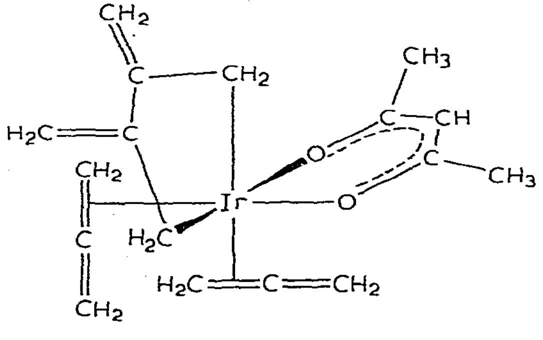


Fig. 1. Projection of the structure of the complex III.

FAC configuration relative to each other. The coordination around the iridium atom is completed by one of the double bonds of the allene molecule and by the pyridine molecule.

As in the case of a known rhodium complex [9], the allene dimer is not planar, and the internal rotation angle C(1)—C(2)—C(3)—C(6) is 37.5° (1°). The allene molecule is bent with coordination symmetry C_s and the angle C(7)—C(8)—C(9) is 151.3° (3°). This coordination geometry is close to that of the first excited (triplet) state of allene [10]. The results strongly support the structure shown for II.

The high thermal instability of II can be associated with a ready loss of the coordinated allene molecules and the formation of coordinatively unsaturated complexes.



(II)

Acknowledgement

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