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Preliminary communication

ALKENYL COMPLEXES OF IRIDIUM AND THEIR PROPERTIES AS CYCLOTRIMERIZATION CATALYSTS

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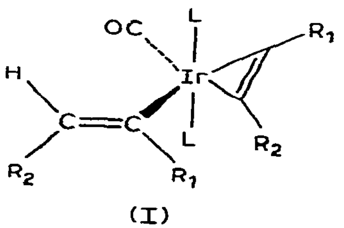
Summary

Reactions of activated, disubstituted acetylenes with $IrH(CO)(PPh_3)_3$ under various conditions give four-, five-, and six-coordinate alkenyliridium complexes. Some new, novel alkenyl metallocycles containing two different acetylenic units incorporated into the metallocyclopentadiene ring have also been prepared, and these are good catalysts for the cyclotrimerization of disubstituted acetylenes.

We have previously reported [1, 2] from this laboratory that activated, disubstituted acetylenes react with $IrH(CO)(PPh_3)_3$ to give σ-alkenyl-π-acetylene complexes of type I. In the case of $R_1 = R_2 = CN$, an X-ray study has also been reported [3]. Further investigations of the reactions of $IrH(CO)(PPh_3)_3$ with activated, disubstituted acetylenes have now shown that several additional alkenyliridium complexes, in addition to the σ-alkenyl-π-acetylene compounds, are formed in these reactions, and that some of these are effective catalysts for the cyclotrimerization of disubstituted acetylenes.



(I)

Reactions of $IrH(CO)(PPh_3)_3$ with disubstituted acetylenes are shown in Fig. 1. When hexafluorobutyne is bubbled through a CH_2Cl_2 solution of $IrH(CO)(PPh_3)_3$ at −20 °C, compound IIIa ($R_1 = R_2 = CF_3$; $\nu(C{\equiv}O)$[Nujol] 1977s, $\nu(C{\equiv}O)[CH_2Cl_2]$ 1997s, $\nu(C{=}C)$ 1610w) may be isolated. Dissolution of IIIa in

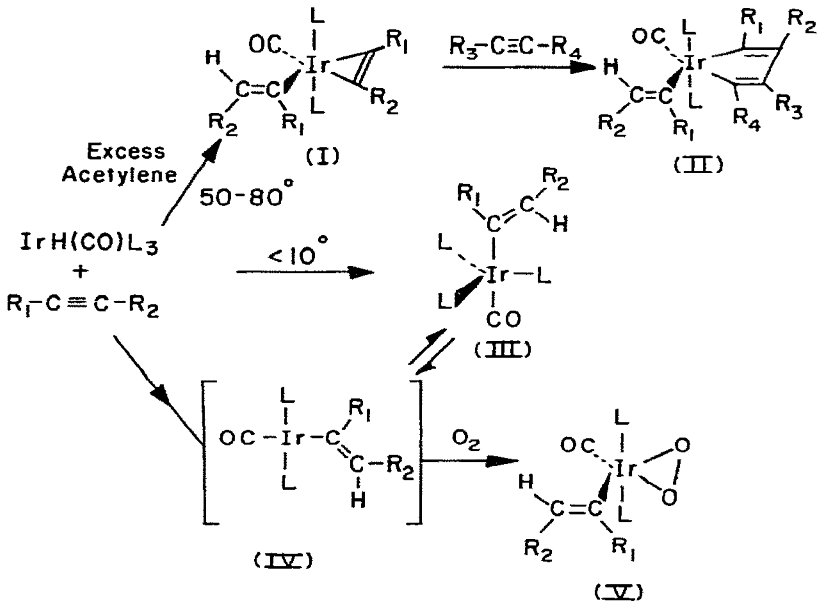
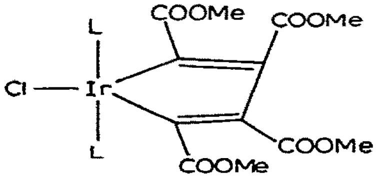
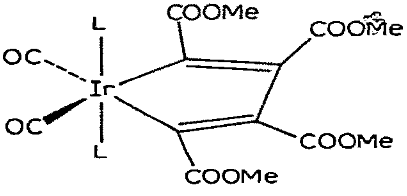


Fig. 1. Reactions of disubstituted acetylenes with $IrH(CO)L_3$ ($L = PPh_3$).

benzene at room temperature results in a transformation, as deduced from infrared spectral changes, presumably IIIa→IVa (IVa, $\nu(C\equiv O)$[benzene] 1974s), but on work-up in air the dioxygen adduct Va ($\nu(C\equiv O)$[Nujol] 1998s) is isolated. When $IrH(CO)(PPh_3)_3$ in slight excess is allowed to react with dimethylacetylenedicarboxylate at 0 °C, a strong absorption band at 1965 cm^{-1} assigned to IVb ($R_1 = R_2 =$ COOMe) is noted, but on work-up the compound isolated is again a dioxygen adduct, Vb ($\nu(C\equiv O)$[Nujol] 2007s). Reaction of ethylphenylpropiolate at room temperature with $IrH(CO)(PPh_3)_3$ gives a mixture of IIIc ($R_1 =$ Ph, $R_2 =$ COOEt, $\nu(C\equiv O)$[Nujol] 1972s, ν(COOEt) 1707s) which has been isolated as a solid, and IVc in solution ($\nu(C\equiv O)$ 1960s) but attempts to work up IVc again lead to a dioxygen adduct, Vc ($\nu(C\equiv O)$[Nujol] 1992s). Apparently the four-coordinate alkenyl complexes react avidly with oxygen and these have not as yet been obtained as the analytically pure solids. A compound of type V with tolan (Vd, $R_1 = R_2 =$ Ph, $\nu(C\equiv O)$ 2003s) has also been isolated.



(VI)



(VII)

At somewhat higher temperatures (50—80 °C) than those mentioned above, and with an excess of the disubstituted acetylene present, σ-alkenyl-π-acetylene complexes are formed [1]. These σ-alkenyl-π-acetylene complexes, I, react further with disubstituted acetylenes to give the novel metallocycles, II. Of particular interest are unsymmetrical metallocycles where two different acetylenes are incorporated into the metallocyclopentadiene ring. Thus, reaction of Ia ($R_1 = R_2 = CF_3$) with a slight excess of dimethylacetylenedicarboxylate at room temperature over a period of 15 h gives IIa ($R_1 = R_2 = CF_3$, $R_3 = R_4 =$ COOMe, ν(C≡O)[Nujol] 2072s, ν(COOMe) 1709s, 1729s, ν(C=C) 1614m). Reaction conditions (exclusion of light, freshly recrystallized Ia as starting material, and temperature) are very important in this reaction for a pure product (IIa) to be obtained in good yield. The ^{1}H NMR spectrum of IIa shows two COOMe proton signals (τ 6.60, 6.37) of equal intensity, and this suggests an unsymmetrical metallocyclopentadiene ring as shown in Fig. 1. Two additional metallocycles IIb ($R_1 = R_2 =$ COOMe, $R_3 = R_4 = CF_3$) and IIc ($R_1 = R_2 =$ COOMe, R_3 = Ph, R_4 = COOEt) have also been prepared.

The coordinatively saturated unsymmetrical metallocycles II are excellent catalysts for cyclotrimerization of disubstituted acetylenes. In a 1/1 stoichiometric reaction of IIa with dimethylacetylenedicarboxylate, the formation of $C_6(CF_3)_2(COOMe)_4$ suggests that metallocycle IIa, and not a decomposition product, is involved in the arene formation. The effectiveness of IIa as a catalyst may be compared with two metallocycles VI and VII, whose preparation and catalytic properties have been studied by Collman et al. [4]. Thus, in C_6D_6 at 80 °C with a 2 mole% concentration of IIa, there is a 70% conversion of dimethylacetylenedicarboxylate into $C_6(COOMe)_6$ after 8 h. With the same conditions complexes VI and VII provide only 11 and 5% conversions respectively after 8 h. With respect to the necessity of a vacant coordination position in the catalyst as stressed by Collman et al. (cf. VI and VII) the coordinatively-saturated metallocycle IIa is a much better catalyst than the coordinatively-unsaturated complex VI. Of course, it is possible that a coordinatively-unsaturated species derived from IIa, and not IIa itself, is the active catalyst. We have not recovered IIa from a catalyst system but do note that the intensity of ν(C≡O) is maintained throughout the course of the reactions and that the position of ν(C≡O) changes less than 10 cm^{-1} from that of IIa.

Comparing the catalytic properties of IIa and VII, one notes the significant enhancement of catalytic effectiveness when an alkenyl group is an auxiliary ligand in the catalyst instead of the chloride ion. We are extending our studies of the catalytic properties of these new alkenyliridium complexes, with emphasis on the mechanism of the cyclotrimerization process.

References

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