Journal of Organometallic Chemistry, 129 (1977) 117—120
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ALKENYLOXYCARBONYL DERIVATIVES OF IRIDIUM(I)

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(Received September 6th, 1976)

Summary

The compounds obtained by reaction of 2-alkenols with tricarbonylbis(triphenylphosphine)iridium cation in basic medium, are alkenyloxycarbonyl derivatives, in which the alkenyloxycarbonyl moiety is chelated through a σ and a η bond.

During work on iridium alkoxy carbonyls [1], we observed though did not report, that the compound obtained from allyl alcohol was different in type from those obtained from saturated alcohols, since it contained only a single terminal CO group. We have now studied such complexes more extensively and have concluded that the product from allyl alcohol is again an alkoxy carbonyl derivative, but with one coordination position occupied by a η bond between the metal and the ethylene bond:

$$\underline{Ir(CO)L_2COOCH_2CH=}CH_2$$
$$L = PPh_3 \qquad (I)$$

Compound I was obtained quantitatively, as a mixture of two isomers, from two reactions:

$$[Ir(CO)_3L_2]^+ + CH_2{=}CH{-}CH_2OH + OH^- \rightarrow I + CO + H_2O$$

$$[Ir(CO)_2L_3]^+ + CH_2{=}CH{-}CH_2OH + OH^- \rightarrow I + L + H_2O$$

The isomers were separated by crystallisation from different solvents: Ia m.p. 160°C; Ib m.p. 175°C. Although both compounds may be distinguished through their IR spectra (Table 1), each has only a single band attributable to a terminal

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TABLE 1

ANALYTICAL DATA FOR ALKENYLOXYCARBONYL DERIVATIVES OF IRIDIUM

No.	Compound	M.p. (°C)	Analysis found (calcd.) (%)			IR		
			Mol.wt.	C	H	ν(CO)	ν(CO(OR))	ν(COC)
Ia	$Ir(CO)L_2COOCH_2-CH=CH_2$	160	828(829)	60,18(59,3)	4,40(4,22)	2010	1660	945
Ib	$Ir(CO)L_2COOCH_2CH=CH_2$	175	(829)	59,8(59,3)	4,35(4,22)	2010	1660	950, 960, 970
II	$Ir(CO)_2L_2COOCH_2CH=CH_2$	165	880(857)	59,48(58,8)	3,54(4,08)	2060, 2000	1665	980, 990, 1090, 1100
III	$Ir(CO)_2L_2COOCH_3$	110	790(831)	58,48(57,8)	3,96(3,97)	1945, 1998	1640	1050
IV	$Ir(CO)L_2COOCH_2=CH-C_6H_5$	159	898(905)	59,70(62,30)	3,95(4,31)	2020	1660	935, 950
V	$Ir(CO)_2L_2COOCH_2CH_2CH_3$	137	850(859)	59,80(58,8)	4,37(4,32)	1995, 1940	1640	1040, 1050

CO stretching mode and a single CO ester group mode. This is different from compounds derived from aliphatic alcohols which in all cases give two terminal CO stretching bands. The evidence that these new compounds have structures with a chelating allyl is as follows:
(1) If there were no η bond the compound would be four-coordinate, in contrast with saturated alcohol derivatives of this series, which are without exception five-coordinate. There are no bands attributable to hydride hydrogen atoms in the NMR spectrum.
(2) Bands attributable to $\nu(C{=}C)$ stretching fall at 1360 cm^{-1} for both isomers, compared to $\nu(C{=}C)$ 1645 cm^{-1} in allyl alcohol. A shift of this size is characteristic of the formation of η bonds by platinum group metals [2].
(3) Compound I cannot be transesterified, even by prolonged boiling with saturated alcohols. However, if the reaction is carried out in an atmosphere of CO, I is transesterified, presumably via initial addition of CO with opening of the η ring:

$$\mathrm{I + CO \rightleftharpoons Ir(CO)_2L_2\,COOCH_2{-}CH{=}CH_2}$$

(II)

$$\mathrm{II + CH_3OH \rightarrow Ir(CO)_2L_2\,COOCH_3 + CH_2{=}CH{-}CH_2OH}$$

Compound II may be isolated by treating a benzene solution of I with CO, and is stable in solution only in the presence of CO. There is a slow conversion II → I, even in the solid state. Compound I could also be obtained from a more accessible starting product, namely the commercially available *trans*-carbonylchlorobis(triphenylphosphine)iridium, by treatment of the latter with CO in the presence of potassium hydroxide and excess of allyl alcohol:

$$\mathrm{Ir(CO)ClL_2 + KOH + CO + CH_2{=}CH{-}CH_2OH \rightarrow I + KCl + H_2O}$$

As alkoxycarbonyl compounds are readily formed by cationic carbonyl derivatives, the equilibrium:
$\mathrm{Ir(CO)ClL_2 + 2\,CO \rightleftharpoons [(Ir(CO)_3L_2]^+Cl^-}$ probably occurs, and is shifted to the right as a result of the nucleophilic attack by the alcohol on the carbonyl group. The derivatives of cinnamic and propargyl alcohol, which will be described elsewhere, have also been prepared by this method. The same reaction occurs with saturated alcohols and this constitutes a convenient way of abtaining alkoxycarbonyl compounds of this series.

Experimental

Compound I was prepared in several ways, as follows.

I. (a) $\mathrm{[Ir(CO)_3L_2]ClO_4}$ (1.05 g, 1.11 mmol) was treated with allyl alcohol (30 ml) containing KOH (1 g) with stirring for 45 min at room temperature. The suspension was concentrated in vacuo, washed with water, ethanol and finally, hexane, (9.8 g, 90% yield).
(b) From $\mathrm{[Ir(CO)_2L_3]ClO_4}$ by the same method as in (a).
(c) $\mathrm{Ir(CO)L_2Cl}$ (7.21 g; 9.15 mmol) was treated with allyl alcohol (100 ml) containing KOH (2 g) with stirring at room temperature in a CO stream for 3 h. The yellow suspension turned white. The suspension was taken to dryness in vacuo at

room temperature and redissolved in benzene and then re-precipitated with hexane, (6.9 g, 91% yield).

(d) From $Ir(CO)_2L_2$ I as described $Ir(CO)L_2Cl$ in (c).

Ia. This was obtained by recrystallisation of I from benzene and hexane.

Ib. This was obtained by recrystallisation of I from chloroform or dichloromethane and hexane.

II. This was obtained by stirring I (2.1 g, 2.5 mmol) in allyl alcohol (100 ml) under a current of CO for 20 h (1.7 g, 78% yield).

III. This was obtained by stirring I (3.25 g, 3.9 mmol) in methanol (30 ml) with CO for 90 min. The solution was finally taken to dryness in vacuo (3.2 g, 93% yield).

IV. This was made as described for I, but starting from cinnamicyl alcohol.

V. This was prepared as described for III, but with use of propyl alcohol.

References

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