Journal of Organometallic Chemistry, 182 (1979) 117—119
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CARBON DIOXIDE INSERTION INTO π-ALLYLPALLADIUM COMPLEXES: SYNTHESIS OF 3-METHYLBUTENOIC ACIDS AND THEIR 2-METHYLALLYLIC ESTERS

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(Received May 29th, 1979)

Summary

Carbon dioxide insertion into π-allylpalladium complexes is described. Esters or acids are obtained in moderate to good yields.

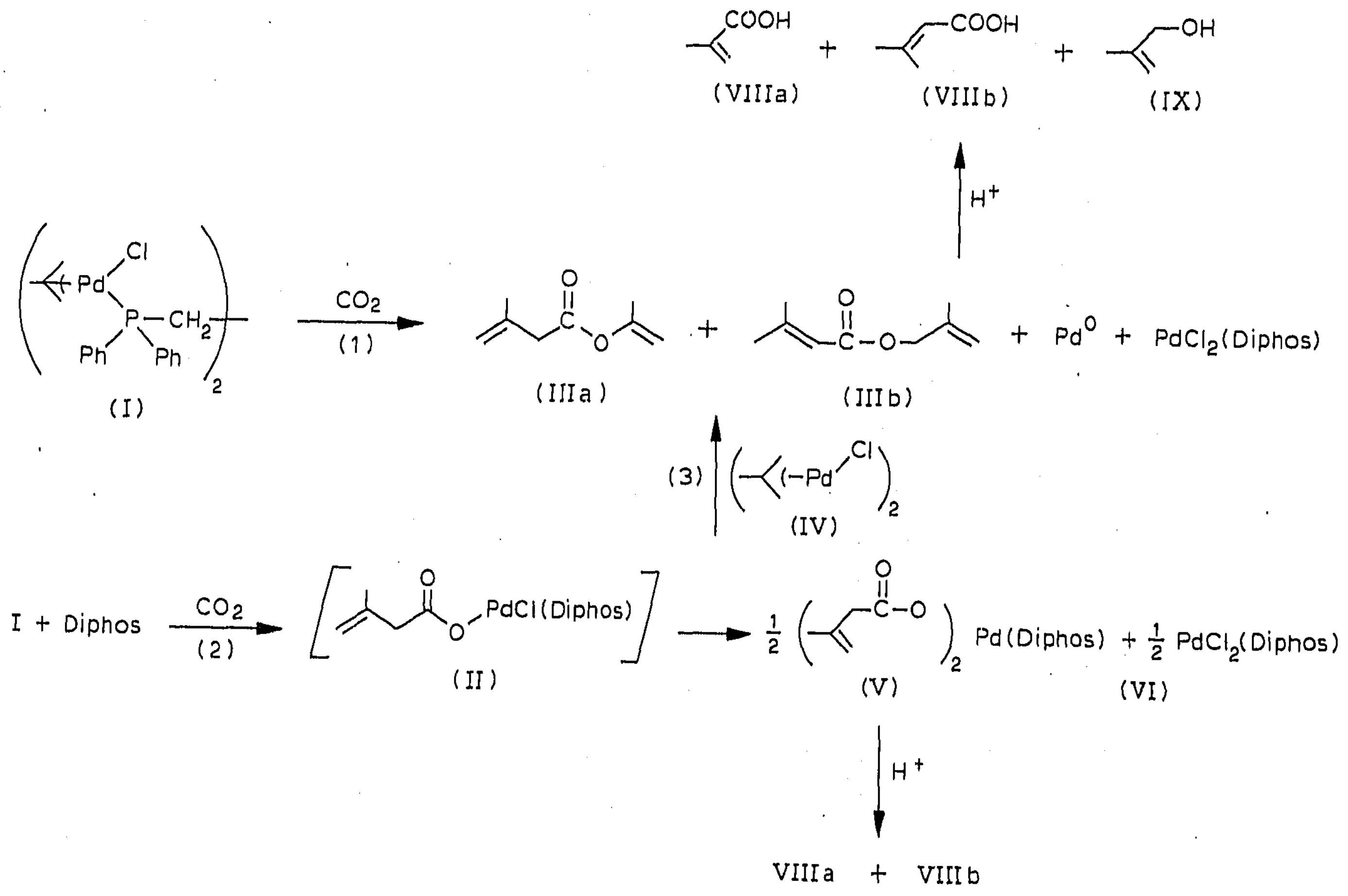
In recent years considerable attention has been paid to carbon dioxide activation by transition metal complexes [1,2]. For example, phosphinepalladium complexes have been shown to catalyse carbon dioxide addition to butadiene [3—5]. We now report the insertion of carbon dioxide into π-allylpalladium complexes, which are probable intermediates in the above mentioned reaction [3]. Such reactions between π-allylpalladium complexes and CO_2 have not, to our knowledge, been described previously [6].

Dichlorobis(2-methylallyl)bis(diphenylphosphinoethane)dipalladium (I) [7] reacts in acetonitrile with carbon dioxide to yield 2-methyl-2-propenyl-3-methyl-3-butenoate (IIIa) and 2-methyl-2-propenyl-3-methyl-2-butenoate (IIIb) in 30 and 15% yields, respectively (yields based on hydrolysed esters) (see reaction 1 of Scheme 1). Under the same conditions, but in the presence of an equimolar amount of 1,2-bis(diphenylphosphino)ethane (Diphos), palladium carboxylates are formed in 60% yield (yield refers to isolated free acids) (reaction 2 of Scheme 1).

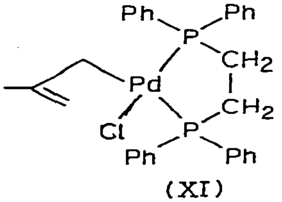
The NMR and IR spectra and the chemical behaviour of the crude reaction mixture suggests that II is the intermediate in reaction 2. Moreover, we found that addition of π-(2-methylallyl)palladium chloride (IV) at the end of reaction 2 (Scheme 1) leads, as expected, to the formation of esters IIIa and IIIb. This suggests that II and IV are probably intermediates in reaction 1 (Scheme 1).

Under similar experimental conditions, no insertion of carbon dioxide was observed in the case of the π-(2-methylallyl)palladium complexes of general formula: π-$C_4H_7Pd(X)L_n(X)$ [7—9] where X = Cl, PF_6; L = PEt_3, PCy_3, Ph_3P; $n = 0, 1, 2$; L = Diphos and X = PF_6 [10].

SCHEME 1


COOH
(VIIIa)
COOH
(VIIIb)
OH
(IX)
H+
Cl
Pd
P
CH2
Ph
Ph
(I)
2
CO2
(1)
O
C
O
(IIIa)
O
C
O
(IIIb)
Pd0
PdCl2(Diphos)
(3)
Pd
Cl
(IV)
2
I + Diphos
CO2
(2)
O
O
PdCl(Diphos)
(II)
1/2
O
C
O
(V)
2
Pd(Diphos)
1/2 PdCl2(Diphos)
(VI)
H+
VIIIa + VIIIb

The fact that CO_2 insertion occurs in the Diphos complexes as opposed to type X complexes suggests that the σ-alkylpalladium complex (XI) containing phosphorus atoms in the *cis* positions is the intermediate. Moreover, we observed that CO_2 is inserted into 1,2-bis(diphenylphosphino)ethanechloromethylpalladium [11] having phosphorus atoms in mutually *cis* positions [12] and not into *trans*-bis(triphenylphosphine)iodomethylpalladium [13]. These findings support our proposal that XI is the key intermediate in these insertions.



(XI)

Experimental

Reaction 1. I (6.4 mmol) is treated at 80°C in acetonitrile (50 ml) with carbon dioxide (50 atm). After 4 h the mixture is filtered. The solid contains 0.3 g of metallic palladium and 1.8 g (3.1 mmol) of VI. The acetonitrile distilled from the filtrate to yield an oil, which was purified by chromatography on a silica gel column using hexane/ethyl acetate as eluent (95% v/v) to give IIIa (0.29 g, 30%) and IIIb (0.15 g, 15%), (IIIa): IR 1735s, 1655m, 1180m, 890s cm^{-1}. IIIb: IR 1720s, 1180m, 810 cm^{-1}. IIIa and IIIb after hydrolysis give VIIIa, IX and VIIIb, IX respectively. These were identified by comparison with authentic samples.

Reaction 2. 1,2-Bis(diphenylphosphino)ethane (6.5 mmol) is added to I (6.4 mmol) in acetonitrile (50 ml). The solution is treated at 80°C with carbon dioxide (50 atm). On standing a solid (VI) slowly separates and this is completely precipitated by adding diethyl ether. VI (3.65 g) is filtered off. The filtrate is evaporated to yield V (2.89 g). IR 1605s, 1180m, 730s, 690s cm^{-1}. (Found: C, 61.73; H, 5.68; P, 9.03; Pd, 15.3. $C_{36}H_{38}O_4P_2Pd$ calcd.: C, 61.53; H, 5.41; P, 8.83; Pd, 15.1%.)

Complexes VIIa and VIIIb are obtained in 60% yield by hydrolysis of V with methanolic sodium hydroxide.

Reaction 3. IV (6.4 mmol) was added to the solution from reaction 2 and the mixture was heated at 80°C under carbon dioxide (50 atm) for a further 4 h. Work-up gave IIIa (0.25 g) and IIIb (0.12 g).

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