Journal of Organometallic Chemistry, 52 (1973) C58–C60

Preliminary communication

A new synthesis of oxo-π-allyl- and π-allylpalladium complexes via diazoketones and vinyldiazomethanes

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(Received January 18th, 1973)

A considerable amount of information concerning carbene complexes[1–4] and carbene transfer reagents[5–6] has been accumulated recently. However, only few examples are currently available concerning insertion of carbenes to metal–hydrogen[7] and metal–halogen[8–10] bonds of transition metal complexes.

We wish to report insertion of ketocarbenes and vinylcarbenes into palladium–chlorine bonds to give oxo-π-allyl- and π-allylpalladium complexes in high yield, respectively. The former complexes are of interest since an π-oxapropenylmanganese complex[11] is the only such complex hitherto isolated, although oxo-π-allyl-metal complexes have been suggested as intermediates[12–14].

A solution of diazoacetophenone (2 mmol) in CH_2Cl_2 was added with stirring to a solution of dichlorobis(benzonitrile)palladium (I) (2 mmol) in CH_2Cl_2 at –60° under nitrogen. The temperature of the reaction mixture was raised to 0° for 2 h. Hexane was added to precipitate brown crystals which were filtered off. Recrystallization from CH_2Cl_2–hexane gave the air-stable palladium complex (II) in 96 % yield. Analytical data and spectral data of IR and NMR were summarized in Table 1. Hydrogenation of a solution of II in THF over Pd led to α-chloroacetophenone. Furthermore, reaction of II with CO under ambient pressure in methanol gave rise to methyl benzoylacetate in 58 % yield. Therefore, the structure of II was assigned as di-μ-chlorobis(2-phenyl-3-chloro-π-oxapropenyl)dipalladium★, derived from insertion of the ketocarbene into the Pd–Cl bond of I as shown in Eq. 1. The alternative structure (IV) is unlikely, since the characteristic band due to the carbonyl group was not detected in the IR spectrum of the complex II. The strong band at 331 cm^{-1}, which is the only band observed in the 200–350 cm^{-1} region, would be assigned as the palladium–chlorine (bridge) stretching band, although this is rather higher than the usual palladium–chlorine (bridge) stretching

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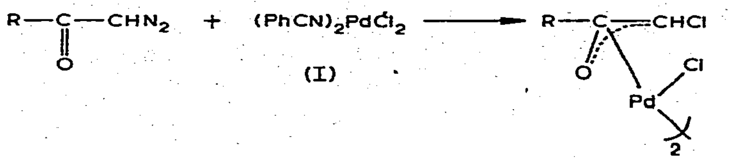
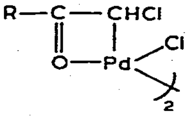
★Satisfactory elemental analyses and molecular weights (osmotic pressure) were obtained for all compounds.



(1)

(II) R = Ph
(III) R = CH_3



(IV)

(310–300 cm^{-1})[15]. The X-ray study of the complex II is in progress. A similar reaction of complex I with diazoacetone afforded the π-oxopropenylpalladium complex (III) in 95 % yield. The complex III was converted to α-chloroacetone on hydrogenation over palladium.

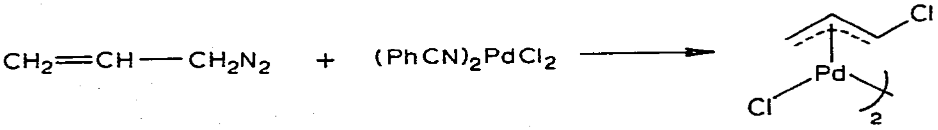
TABLE 1

THE IR, NMR SPECTRAL DATA AND ANALYTICAL DATA OF OXO-π-ALLYLPALLADIUM COMPLEXES

Complex	*m.p. (°C) (dec.)*	*IR[a] (Pd–Cl) (cm^{-1})*	*NMR Proton[b] (δ ppm)*	*Analysis Found (calcd.) (%)*	
				C	*H*
II	161–162	331	7.17–8.00 (m, 6H)	32.35 (32.54)	2.16 (2.06)
III	104–105	340	1.15 (s, 3H) 7.30 (s, 1H)	15.18 (15.45)	1.73 (1.73)

[a] Nujoll mull. [b] CD_2Cl_2 solvent; TMS as internal standard.

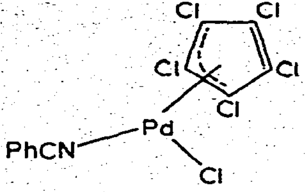
Reaction of allyldiazo compounds with the complex I provided a convenient method to synthesize a π-allylpalladium complex. Thus, treatment of vinyldiazomethane with I in CH_2Cl_2 at −20 to −10° gave the α-chloro-π-allylpalladium complex (V), m.p. 179° (dec.), in 95 % yield. The structure of V was confirmed by comparison of the spectral data with



(V)

those of an authentic sample[16]. Further, reaction of tetrachlorodiazocyclopentadiene with (I) afforded the monomeric π-allylpalladium complex (VI), m.p. 125° (dec.), in 98 % yield, IR, 2270 cm^{-1} (C≡N), 339, 325, 283, 254 cm^{-1} (Pd–Cl). Treatment of VI with chlorine afforded hexachlorocyclopentadiene in 85 % yield.

We are currently exploring other reactions of oxo-π-allylpalladium complexes.



(VI)

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