Journal of Organometallic Chemistry, 174 (1979) 227—235

REACTIONS OF π-ALLYLPALLADIUM COMPLEXES WITH AN OLEFIN METATHESIS CATALYST

HARRY A BOCKMEULEN * and ADRIAN W. PARKINS *

Department of Chemistry, Queen Elizabeth College, Campden Hill Road, London, W8 7AH (Great Britain)

(Received February 27th, 1979)

Summary

Some π-allylpalladium complexes containing a free double bond were treated with the $WCl_6/EtOH/EtAlCl_2$ olefin metathesis catalyst. The principal reaction observed was alkylation of the aromatic solvent by the olefin, although carbon—carbon sigma bond cleavage in the reactant was also noted.

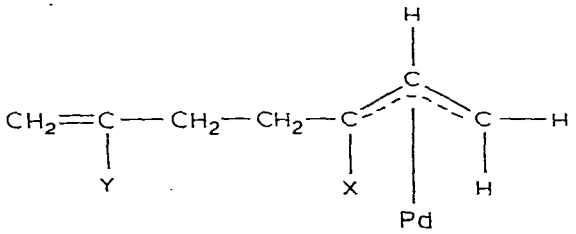
Introduction

The olefin metathesis reaction has been extensively investigated using a large variety of free olefins as substrate [1]. Some recent reports [2] have discussed the olefin metathesis reaction of olefins with functional groups, but very little is known about the reaction between organometallic π-complexes with an uncomplexed double bond and olefin metathesis catalysts [3]. π-Allylpalladium complexes of the type I—III are readily available from the insertion reaction of butadiene or isoprene [4,5] with π-allylpalladium chloride. We investigated the reactions of the acetylacetonato derivatives, Ia—IIIa, with the known [6] $WCl_6/EtOH/EtAlCl_2$ catalyst mixture.

Results and discussion

Reactions of the π-allylmetal complexes were carried out using the acetylacetonato derivatives Ia, IIa and IIIa, as it was felt that these might be less constrained in the reaction than the dimeric chloro complexes I—III. Reaction of Ia with the $WCl_6/EtOH/EtAlCl_2$ catalyst in benzene gave a mixture of

* Present address: INTEVEP, Apartado 76343, Caracas 107 (Venezuela).



(Z)

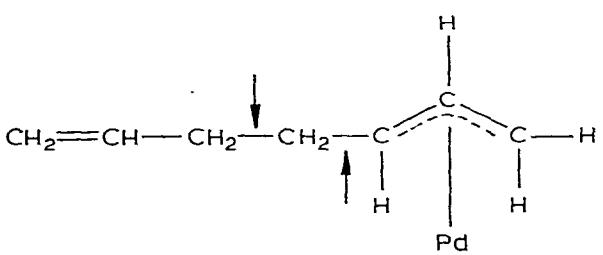
Complex	X	Y	Z	Configuration of side-chain
I	H	H	Cl (dimeric)	*syn*
II	H	CH_3	Cl (dimeric)	*syn*
III	CH_3	H	Cl (dimeric)	*syn*/*anti* mixture
Ia	H	H	acac	*syn*
IIa	H	CH_3	acac	*syn*
IIIa	CH_3	H	acac	*syn*/*anti* mixture

π-allylpalladium complexes in the chloride-bridged form.

$$\pi\text{-}C_7H_{11}Pdacac \xrightarrow[C_6H_6,\ 17\ h,\ 25^\circ C]{WCl_6/EtOH/EtAlCl_2}$$

$$(\pi\text{-}C_7H_{11}PdCl)_2 + (\pi\text{-}C_3H_5PdCl)_2 + (\pi\text{-}C_4H_7PdCl)_2 + \text{organic products}$$

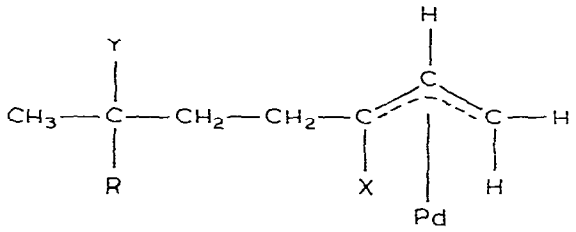
The conversion of the acetylacetonatopalladium complexes to the chloride derivatives is undoubtedly the result of formation of hydrogen chloride from interaction of the catalyst components [7]. Preparative thin-layer chromatography of the mixture showed that one of the components was the chloride form (I) of the starting material (Ia) The other faster moving fraction was identified as an inseparable mixture of the π-allyl- and π-1-methylallyl-palladium chloride complexes. This was determined by 220 MHz ^1H NMR and ^{13}C NMR studies of the mixture and authentic samples. These appear to be the result of C—C bond cleavage in two possible sites in the reactant complex.



(Z)

However, with complex IIIa, the principal products of reaction (under identical conditions), were not the expected π-1-methallyl- and π-1,1-dimethylallyl-palla-

dium complexes, but was a compound of composition $C_{14}H_{19}PdCl$ (IIIb), the result of electrophilic substitution of the solvent (benzene) by the olefinic side-chain. When the reaction was performed in toluene or mesitylene similar results were obtained. The electrophilic substitution or alkylation of aromatic solvents in olefin metathesis reactions has been reported previously [8].



(Z)

Complex	X	Y	R	Z	Configuration of side-chain
III b	CH_3	H	phenyl	Cl	*syn/anti* mixture
III c	CH_3	H	tolyl	Cl	*syn/anti* mixture
III d	CH_3	H	mesityl	Cl	*syn/anti* mixture
I c	H	H	tolyl	Cl	*syn*
II b	H	CH_3	phenyl	Cl	*syn*

Similarly, complex IIa reacted in benzene to give the electrophilic substitution product IIb. With complex Ia it was not possible to alkylate the benzene solvent, but the alkylation reaction did proceed in toluene to give complex Ic. In benzene, complex Ia reacted to give the π-allyl and π-1-methallyl-palladium chloride products. In mesitylene, complex Ia did not react to give the alkylation product, but a higher substrate/catalyst ratio was employed, and the cleavage reaction was observed.

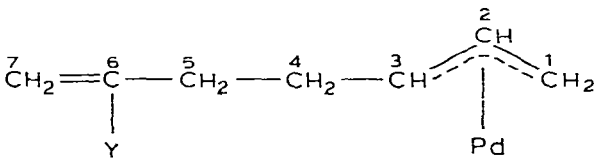
The tolyl complexes IIIc and Ic showed infrared absorptions in the 900—600 cm^{-1} region attributable to products with all three possible orientations of substitution in the aromatic ring. The phenyl and mesityl substitution products can only have one position of attachment to the arene. The structures were identified by ^{13}C (Table 1) and ^1H NMR (Table 2). In the NMR spectra of the substitution products, there is increasing broadening of the resonance signals correlating with the increase in the size of the aromatic group. This phenomenon may arise from possible inter- or intra-molecular interactions between the palladium atom and the aromatic system [9].

The products IIIb—IIId showed the presence of the *syn* and *anti* isomers with predominance of the *anti*-methyl isomer, i.e., *syn* configuration for substituted side-chain. Measurement of the coupling constants of the hydrogen atoms of the π-allylic system of the other products, Ic and IIb indicated a *syn* configuration for the side-chain. Thus, comparison of the spectra of the starting materials [4] and the products (Table 2) shows no change in configuration at the carbon atom attached to the side-chain, during and after reaction with the catalyst.

TABLE 1

^{13}C NMR DATA FOR COMPLEXES

Spectra measured in $CDCl_3$; chemical shifts (ppm) are downfield from, and relative to TMS as internal standard. Spectra were measured using 4132 Hz spectral width with 8k data points, 5 μs pulse width with 2 s interval between pulses.



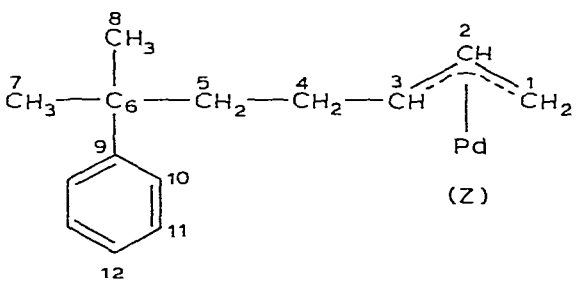
(Z)

Z = Cl

II , Y = CH_3

C(1), 59.01	C(4), 30.04	C(7), 110.12
C(2), 109.92	C(5), 36.79	C(Y), 22.28
C(3), 85.77	C(6), 144.10	

IIb



(Z)

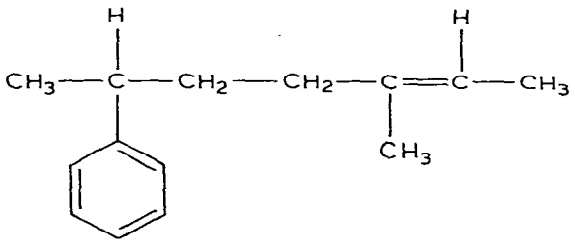
Z = Cl

C(1), 58.40	C(5), 43.08	C(9), 148.58
C(2), 109.18	C(6), 37.46	C(10), 125.64
C(3), 86.57	C(7), 28.43[a]	C(11), 128.05
C(4), 27.30	C(8), 28.90[a]	C(12), 125[b]

[a] Assignment may be interchanged. [b] Signal obscured by C(10) absorption.

Reductive elimination of complex IIIb with sodium borohydride [10] gave the expected olefin IV, $C_{14}H_{20}$, as identified from its spectroscopic properties and GC/MS.

In addition to the electrophilic substitution and cleavage reactions, a side-reaction observed was solvent—solvent coupling, presumably catalysed by the

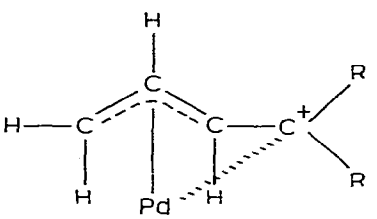


(IV)

palladium components present [11]. These products were obtained as oily hydrocarbon residues after chromatography of the reaction mixture. These side-reactions were suppressed when mesitylene was used as solvent.

Conclusions

Our results are broadly comparable with those of Hocks et al. [12] from their study of the competitive character of metathesis and alkylation reactions catalysed by $WCl_6/EtAlCl_2$ We similarly find the increased ease of alkylation, with change of solvent from benzene, to toluene, to mesitylene. We have not carried out a systematic study of the effect of varying the olefin-to-catalyst ratios on the alkylation/metathesis competition, or possible alkylation/carbon–carbon bond cleavage competition. In the latter case, it is possible that an alkylcarbonium ion (V) of the type proposed by Robinson and Shaw [13] in some alkoxy exchange reactions in ethanolic hydrochloric acid may be involved.



(V)

The lack of metathesis reaction of our starting materials may be caused by the tendency of tungsten-based catalysts to cause non-productive metathesis of terminal olefins as proposed by Muetterties et al. [14]. Reactions of the above palladium complexes with the $Mo(NO)_2Cl_2(Ph_3P)_2/EtAlCl_2$ catalyst are under investigation.

Experimental

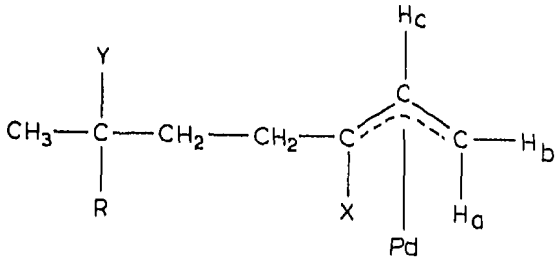
π-Allyl complexes

π-Allyl-, π-1-methallyl-, and π-2-methallyl-palladium complexes were prepared by the method of Dent et al. [15].

TABLE 2

^{1}H NMR DATA FOR ELECTROPHILIC SUBSTITUTION PRODUCTS

Chemical shifts (τ, ppm) are relative to TMS as internal standard, the spectra being measured at 60 MHz in $CDCl_3$. Coupling constants (*J*) in Hz [a]



(Z)

	X	Y	R
IIIb	CH_3	H	phenyl
IIIc	CH_3	H	tolyl
IIId	CH_3	H	mesityl
Ic	H	H	tolyl
IIb	H	CH_3	phenyl

Z = Cl

Complex	H_a	H_b	H_c	H_d	H_e	H_f	H_y	H_X	(H) H_R	(CH_3) H_R	*J*
IIIb	6.9 (d)	6.2 (m)	4.92 (m)	8.25 (mb)	8.04 (m)	8.7 (d)	7.28 (m)	8.62 *syn* (s) 8.82 *anti* (s) 8.63 *syn*	2.65 (m)	—	
IIIc	6.9 (d)	6.24 (m)	4.93 (m)	8.25 (m)	7.95 (m)	8.73 (d)	7.3 (mb)	(s) 8.82 *anti* (s) 8.61 *syn*	2.86 (m)	7.7 (s) 7.7	
IIId	6.89 (d)	6.17 (m)	4.92 (m)	8.27 (mb)	8.0 (m)	8.72 (d)	7.1 (m)	(s) 8.81 *anti* (s)	2.57	(d) 7.78 (s)	
Ic	7.22 (d)	6.12 (d)	4.73 (m)	8.3 (mb)	8.3 (mb)	8.78 (d)	8.3 [b] (m)	6.12 [c] (m)	2.76 (m)	7.7 (s)	$J_{a,c}$ 12.1 $J_{X,c}$ 11.6 $J_{b,c}$ 5.2
IIb	7.29 (d)	6.22 (d)	4.85 (m)	8.44 (mb)	8.08 (m)	8.7 (s)	8.7 (s)	6.25 [c] (m)	2.66 (s)	—	$J_{a,c}$ 12.1 $J_{X,c}$ 11.8 $J_{b,c}$ 5.1

[a] Error ±0.4 Hz. [b] H_y is obscured by H_d and H_e. [c] H_X is obscured by H_b. d = doublet, m = multiplet, mb = broad multiplet, s = singlet.

Although the preparation of the starting materials I—III has been described previously [4,5], in our hands it has been possible to obtain I and II as crystalline solids, and accordingly our procedure is described.

Preparation of (π-$C_7H_{11}PdCl)_2$ (I). Butadiene was passed through a benzene solution (70 ml) of π-allyl-palladium acetylacetonate (3.2 g, 12.9 mol) for 15 min with stirring, followed by hydrogen chloride gas for 5 min. After evaporation of the solvent under reduced pressure, the residue was dissolved in carbon tetrachloride and chromatographed on a 25 × 3 cm column prepared with silica (Merck 7734) and carbon tetrachloride. On elution with chloroform a small first fraction of π-allylpalladium chloride was collected. The product, I, was collected as the second and major fraction and crystallised from diethyl ether/petr. ether 30—40 (1/1) on standing overnight at 2°C. Alternatively, very rapid evaporation of an ethereal solution under moderate vacuum will yield crystalline product. Yield, 1.86 g, 61%. M.p. 72.5—73.5°C.

Preparation of (π-$C_8H_{13}PdCl)_2$ (II). Butadiene (49.6 g, 0.92 mmol) was condensed (dry ice/methanol) into a cooled solution of π-2-methallylpalladium chloride (1.8 g, 4.6 mmol) in benzene (60 ml) in a 250 ml pressure bottle equipped with a pressure release tap. After sealing, the mixture was shaken on a Parr rocker for 18 h at 50°C. After evaporation of excess butadiene, the solvent was removed under reduced pressure, the residue disolved in carbon tetrachloride and transferred onto a 25 × 3 cm column. On elution with chloroform a small first fraction of π-2-methallylpalladium chloride was collected. II was collected as the second and major fraction. After prolonged standing (1—2 days) at room temperature, treatment with a small amount of diethyl ether gave crystalline II, m.p. 67—69°C. Yield, 1.82 g, 79%.

(π-$C_8H_{13}PdCl)_2$ (III) was prepared by the method of Medema and Van Helden [4].

Acetylacetonato-π-allyl complexes

Complexes Ia—IIIa were prepared from their respective chloride-bridged analogues I—III by stirring with 5% molar excess thallous acetylacetonate in the aromatic reaction solvent for 2 h at room temperature.

Reaction of π-C_7H_{11}Pdacac (Ia), π-C_8H_{13}Pdacac (IIa), or π-C_8H_{13}Pdacac (IIIa) with WCl_6/EtOH/$EtAlCl_2$ catalyst. Operations involving preparation and use of catalyst components were carried out in an inert atmosphere of nitrogen. Stock solutions of ethylaluminium dichloride (0.2 *M*) and tungsten hexachloride (0.05 *M*) were prepared in each reactant solvent.

General procedure: Ethanol (0.1 ml, 1.7 mmol) was added to a solution of tungsten hexachloride (35 ml, 1.75 mmol) stirring in a Schlenk tube, followed by addition of ethylaluminium dichloride (35 ml, 7.0 mmol). A solution of the freshly prepared acetylacetonatopalladium complex was added immediately, and the mixture left stirring for 18 h at room temperature stoppered under nitrogen. After filtration the reaction mixture was chromatographed on a cooled (10°C) 45 × 2.5 cm column made up in petr. ether 30—40. The aromatic solvent fraction was eluted with petr. ether 30—40 and the palladium compounds subsequently eluted with diethyl ether. After this point it was possible to handle the products in air. After determination of the best solvent system (chloroform/carbon tetrachloride mixture), the products were separated by preparative

TABLE 3

ANALYTICAL AND MELTING POINT DATA FOR ELECTROPHILIC SUBSTITUTION PRODUCTS

Compound	Formula	Analysis: Found (calc.) (%)			Melting point (°C)
		C	H	Cl	
Ic	$C_{14}H_{19}PdCl$	50.14 (51.09)	5.8 (5.82)		Oil
IIb	$C_{14}H_{19}PdCl$	51.17 (51.09)	5.88 (5.82)	10.72 (10.77)	107—109
IIIb	$C_{14}H_{19}PdCl$	51.68 (51.09)	6.28 (5.82)		Oil
IIIc	$C_{15}H_{21}PdCl$	53.51 (52.5)	6.03 (6.17)		39— 41
IIId	$C_{17}H_{25}PdCl$	55.4 (55.0)	6.66 (6.79)	9.59 (9.55)	48— 50

All compounds have a yellow colour.

thin-layer chromatography. Products, where necessary, were further purified by the same method. Complexes IIb, IIIc and IIId were crystallized by rapid evaporation of an ethereal solution under vacuum, or by treatment with diethyl ether after allowing to stand (2—3 days). Products Ic and IIIb could be precipitated from diethyl ether/petr. ether 30—40 at —20°C, but melted on warming to room temperature. For the ^{1}H NMR and analytical data of these products, see Tables 2 and 3.

Reaction of (π-$C_{14}H_{19}PdCl)_2$ (IIIb) with sodium borohydride. IIIb (0.35 g, 0.53 mmol) in diethyl ether (20 ml) was treated with a solution of sodium borohydride (1 g) in water (10 ml) until no further reaction was observed. After separation of metallic palladium, the ether phase was washed repeatedly with water, separated, and dried over magnesium sulphate. After evaporation of the solvent, the residual oil was analysed by GC/MS. Two major *cis* and *trans* olefin components were found in a 1/1 ratio. The parent ion for both was *m/e* 188. ^{1}H NMR spectrum (CCl_4, TMS as internal standard), showed absorptions at τ (ppm) 2.75 (5 H, phenyl protons), 4.82 (m, 1 H, olefinic proton), 7.4 (m, 1 H), and complex overlapping signals between τ 8.0 and 9.3 (13 H), which could not be assigned with certainty. GLC conditions: Sample was analysed on a 5 ft. column containing 5% OV-17 on Diatomite C-AW HMDA (J.J.'s Chromatography), chromatograph fitted with flame ionisation detection system. Sample was dissolved in cyclohexane and run isothermally (140°C) with carrier gas (nitrogen) flow rate of 30 ml/min.

Acknowledgements

H.A.B. wishes to thank Q.E.C and Foninves (Venezuela) for financial support.

References

1 R.J. Haines and G.J. Leigh, Chem. Soc. Rev., 4 (1975) 155; R. Streck, Chem. Ztg., 99 (1975) 397.
2 J.P. Laval, A. Lattes, R. Mutin and J.M. Basset, J. Chem. Soc. Chem. Commun., (1977) 502.

3 H.A. Bockmeulen, R.G. Holloway, A.W. Parkins and B.R. Penfold, J. Chem. Soc. Chem. Commun., (1976) 298.
4 D. Medema and R. van Helden, Rec. Trav. Chim., 90 (1971) 304.
5 Y. Takahashi, S. Sakai and Y. Ishii, J. Organometal. Chem., 16 (1969) 177.
6 N. Calderon, E.A. Ofstead, J.P. Ward, W.A. Judy and K.W. Scott, J. Amer. Chem. Soc., 90 (1968) 4133.
7 N. Calderon, Acc. Chem. Res., 5 (1972) 127.
8 M. Kothari and J.J. Tazuma, J. Org. Chem., 36 (1971) 2951.
9 Y. Takahashi, T. Inagaki, H. Mori, S. Sakai and Y. Ishii, Kogyo Kagaku Zasshi, 73 (1970) 1697.
10 J.K. Stille and R.A. Morgan, J. Amer. Chem. Soc., 88 (1966) 5135.
11 P.M. Henry, Adv. Organometal. Chem., 13 (1975) 363.
12 L. Hocks, A. Noels, A. Hubert and P. Teyssie, J. Org. Chem., 41 (1976) 1631.
13 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1963) 4806.
14 M.T. Mocella, M.A. Busch and E.L. Muetterties, J. Amer. Chem. Soc., 98 (1976) 1283.
15 W.T. Dent, R. Long and A.J. Wilkinson, J. Chem. Soc., (1964) 1585.