Journal of Organometallic Chemistry, 280 (1985) 441–448
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STEREOCHEMISTRY OF THE FORMATION OF π-ALLYLPALLADIUM COMPLEXES FROM DIALKYLCYCLOHEXA-1,3-DIENES

SHIN IMAIZUMI*, TOSHIO MATSUHISA and YASUHISA SENDA

Department of Engineering Science (Chemistry), Faculty of Engineering, Tohoku University, Sendai 980 (Japan)

(Received July 23rd, 1984)

Summary

1,4-Dimethyl-, 1-isopropyl-4-methyl- and 1-t-butyl-4-methylcyclohexa-1,3-diene reacted with a palladium salt to form, in each case, a single isomer of the corresponding π-allylpalladium chloride complexes, while 2-isopropyl-5-methylcyclohexa-1,3-diene gave two stereoisomeric complexes. An excess of diene (diene/Pd = 2.5–3.0) was required to produce a high yield of the complex. The hydrogen atom, which is incorporated onto the terminal carbon of the diene system, is shown (i) to come from the excess diene, which in turn is converted to an aromatic compound, and (ii) to attack the diene, stereo- and regio-selectively, from the same side as the palladium chloride portion.

Introduction

There have been a number of methods for the synthesis of π-allylpalladium complexes from olefins, conjugated dienes and allylic compounds with palladium salts [1]. Robinson and Shaw reported that cyclohexa-1,3-diene (Ia) reacted with sodium chloropalladate in methanol to give the methoxy adduct at −20°C, whereas the cyclohexenyl complex IIa was obtained at 60°C [2]. However, no mechanistic study was carried out on this interesting reaction. Recently, Bäckvall et al. revealed that the attack of methoxide ion on a diene occurs on the face opposite to the coordinated palladium [3].

In this study, 1,4-dimethyl- (Ib), 1-isopropyl-4-methyl (Ic), 1-t-butyl-4-methyl- (Id) and 2-isopropyl-5-methylcyclohexa-1,3-diene (Ie) were employed as the starting materials for the synthesis of π-allylpalladium complexes IIb–IId. The stereo- and regio-chemistry of the reaction as well as the origin of the hydrogen incorporated into the complex were also investigated.

Results and discussion

All reactions of the cyclohexa-1,3-dienes were carried out in methanol at a relatively high temperature by the method of Robinson and Shaw [2]. The reaction

0022-328X/85/$03.30

TABLE 1

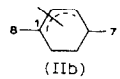
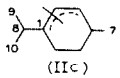
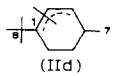
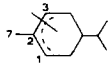
PREPARATION OF COMPLEXES FROM CYCLOHEXA-1,3-DIENES

Diene	Complex	Reaction temperature (°C)	Reaction time (min)	Dec.p. (°C)	Yield (%)
 (Ia)	 (IIa)	60	10	96–100 (80–83) [a]	98 (53) [a]
 (Ib)	 (IIb)	60	10	84–85	45
 (Ic)	 (IIc)	30	5	(oil)	(85) [b]
 (Id)	 (IId)	30	2	94–97	50
 (Ie)	 (IIe)	60	10	(oil)	(90) [b]

[a] Ref. 2. [b] Crude product.

TABLE 2

^{13}C CHEMICAL SHIFTS OF COMPLEXES FROM CYCLOHEXA-1,3-DIENES

Complex	Chemical shift (δ, ppm) [a]									
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)
 (IIa)	78.8	101.7	78.8	28.8	19.5	28.8				
 (IIb)	95.1	100.8	80.3	34.5	28.3	34.3	22.3	25.0		
 (IIc)	106.3	97.9	80.6	34.9	28.7	31.1	(22.1)	35.1	(19.9)	(21.2)
 (IId)	110.1	97.5	80.6	34.9	29.0	30.6	22.1	37.2	28.3	
 (IIe)	78.3 76.9	116.9 114.6	78.3 76.9	31.5 34.1	37.1 42.8	31.5 34.1	22.0 22.6	32.9 31.9	19.9 20.3	19.9 20.3

[a] The values in parentheses may be interchanged.

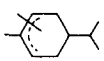
conditions and the ^{13}C and ^{1}H chemical shifts of complexes II are summarized in Tables 1–3, respectively.

The ^{13}C NMR spectrum of the resulting complex from Ib revealed a pure single isomer. This suggests that the stereoselective hydrogen addition occurs from a specific side of the diene molecule. The complexes from the unsymmetrical cyclohexa-1,3-dienes, Ic and Id, also proved to be pure single isomers. No signal was observed at δ 40–50 ppm; usually, the signal of sp^3 carbons with a t-butyl or an isopropyl group should appear in this region [4]. The proton signals of the methyl group at C(4) were split into a doublet with a coupling constant of ca. 7 Hz. This indicates that the hydrogen atom is stereo- and regio-selectively incorporated onto the terminal carbon of the diene which bears less bulky alkyl substituents. Such a trend was also found by Lee and Maitlis in the reaction of an open chain diene with a hydridometal complex [5]. Since the composition of regioisomers is not affected by the reaction temperature, the regioselectivity is thought to be kinetically controlled [5]. On the other hand, the appearance of two sets of signals in the ^{13}C NMR spectrum of the product from Ie indicates that this may be a mixture of two isomers. The observed number of carbon signals and the appearance of only one proton signal (a multiplet which corresponds to two protons) in the region of the π-allylic unit suggest the formation of two stereoisomers of the symmetrical π-allylic complex bis(5-isopropyl-2-methylcyclohexenylpalladium chloride) (IIe).

Green suggested that the hydrogen atom that is incorporated into the π-allylpalladium complex comes from the solvent [6]. Trost believed that excess diene in the system must be the hydrogen source [7]; however, no experimental evidence was given. In order to elucidate the hydrogen source, the following examinations were

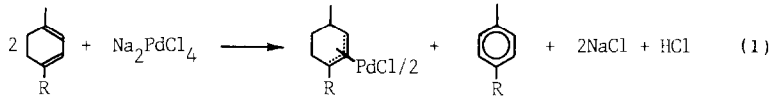
TABLE 3

^{1}H CHEMICAL SHIFTS OF COMPLEXES FROM CYCLOHEXA-1,3-DIENES

Complex	Chemical shift (δ, ppm) [a]				
	π-allylic		methyl		others
	central	terminal	methyl	t-butyl or isopropyl	
 (IIb)	5.35 (d, 6.5)	4.72 (dd, 6.5, 2.0)	1.50(1-Me) 1.05(4-Me)	(s) (d, 6.5)	1.60–2.30
 (IIc)	5.30 (d, 6.5)	4.73 (dd, 6.5, 2.0)	1.04 (d, 6.5)	1.15 (d, 7.0)	1.40–2.50
 (IId)	5.31 (d, 6.0)	4.67 (dd, 6.0, 2.0)	1.04 (d, 7.0)	1.22 (s)	1.50–2.15
 (IIe) [b]		4.75 (bs)	2.05 (s) 1.95 (s)	0.95 (d, 7.0) 0.90 (d, 7.0)	1.20–2.30

[a] The values in parentheses are coupling constants (Hz). [b] Stereoisomeric mixture.

conducted and several informative results were obtained. (i) Complex IIa was prepared at various ratios of Ia to palladium. As seen in Table 4, excess diene (Ia/Pd is more than 2.5–3.0) is required to produce the complex in high yield. On the other hand, when the methoxy group was incorporated onto the diene (Ia/Pd 1.9) at a low temperature, the yield of the product, bis(4-methoxycyclohexenylpalladium chloride), was 69%. (ii) When heated with Ia at 60°C in methanol, the methoxy adduct was not converted to the hydrogen adduct. Stirring Ia with sodium chloropalladate at −20°C in methanol for 20 min followed by warming at 60°C for 1 h produced only the methoxy complex. (iii) The recovered hydrocarbons of the reaction medium, in which 1-t-butyl-4-methylcyclohexenylpalladium complex (IId) was prepared, consisted mainly of t-butyltoluene accompanied by the starting diene and other unsaturated hydrocarbons. On the other hand, no aromatic hydrocarbon was detected in the formation of the methoxy adduct. (iv) When the reaction was performed in methanol-d_4, no deuterium was incorporated into the product. These observations suggest that the hydrogen atom, which is used for the formation of the π-allylpalladium chloride complex, arises from dehydrogenation of a diene. Therefore, the stoichiometry of this reaction can be expressed as eq. 1.



(1)

Formation of the corresponding single stereoisomers from 1,4-disubstituted cyclohexa-1,3-dienes infers stereoselective addition of hydrogen to a diene. The π-allyl complexes IVb and IVd were prepared from *cis*-3,6-dimethylcyclohexene (*cis*-IIIb) and *cis*-3-t-butyl-6-methylcyclohexene (*cis*-IIId), respectively, by the method of Trost et al. [8]. Since Harvie and McQuillin have revealed that the stereospecific loss of hydrogen *syn* to palladium occurs during the formation of a π-allylpalladium complex from an olefin [9], the stereochemistry of IVb and IVd is assumed to be *trans* with respect to the methyl group and the palladium atom. The ^{13}C NMR chemical shifts of IVb and IVd were in fair agreement with those of IIb and IId, respectively. These configurational assignments were further confirmed by comparing the carbon chemical shifts with those of alternative stereoisomers, Vb and Vd, prepared from the s-*trans*-diene, 4-methyl-1-methylene-2-cyclohexene (1b′) [10] and *trans*-3-t-butyl-6-methylcyclohexene (*trans*-IIId). The ^1H and ^{13}C chemical shifts of the π-allylic unit of these complexes are summarized in Table 5.

TABLE 4

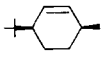
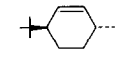
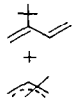
PREPARATION OF IIa IN VARIOUS RATIOS OF DIENE TO PALLADIUM

Diene / Na_2PdCl_4	Reaction temperature (°C)	Reaction time (min)	Yield (%)
1.5 [a]	60	5	0 [b]
2.2	60	7	0 [b]
3.0	60	10	80
7.7	60	11	98
1.9	−20	360	69 [c]

[a] Molar ratio. [b] Pd metal was deposited. [c] Methoxy complex.

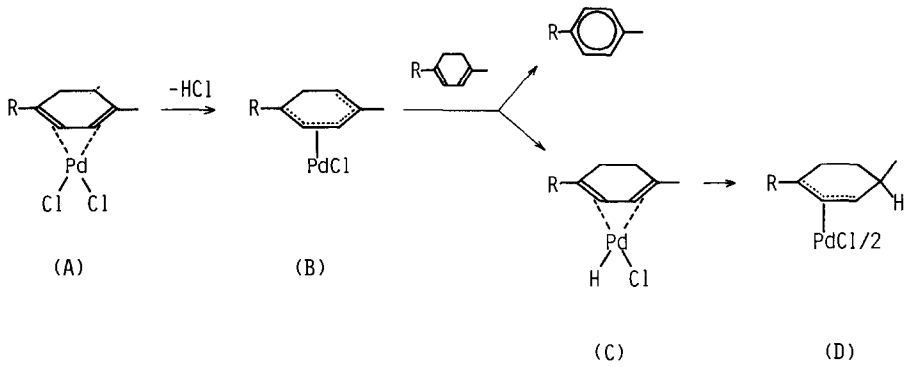
TABLE 5

^{13}C AND ^{1}H CHEMICAL SHIFTS OF COMPLEXES FROM OLEFINS AND s-*trans*-DIENE

Starting material	Complex	Chemical shift (δ, ppm) [a]				
		Carbon			Proton	
		C(1)	C(2)	C(3)	central	terminal
 (*cis*-IIIb)	 (IVb)	95.1	100.8	80.3	5.35 (d, 6.5)	4.72 (dd, 6.5, 2.0)
 (Ib')	 (Vb)	96.7	100.4	81.6	5.35 (d, 6.5)	4.66 (dd, 6.5, 2.0)
 (*cis*-IIId)	 (IVd)	110.1	97.6	80.6	5.31 (d, 6.0)	4.67 (dd, 6.0, 2.0)
 (*trans*-IIId)	 (Vd)	109.9	97.3	82.1	5.31 (d, 6.0)	4.63 (dd, 6.0, 2.0)
		110.0	97.5	80.5		

[a] The values in parentheses are the coupling constants (Hz).

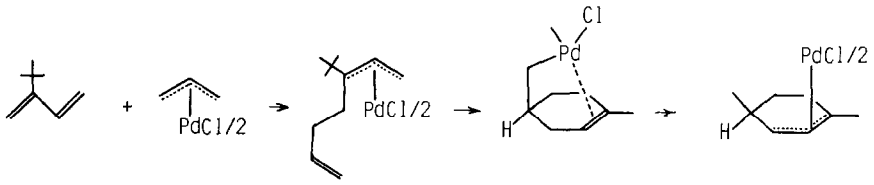
The structural allocation was substantiated by the nature of the olefin obtained by reducing IIb with $LiAlH_4$. The reduction was performed in the presence of excess triphenylphosphine to prevent deposition of metallic palladium which may give rise to the isomerization of the resultant olefin. Since the hydride has been known to cleave the allyl–palladium bond with retention of configuration [11], the fact that the stereochemistry of the reduction product, IIIb, is *cis* reveals the *trans* relation between the methyl at C(4) and the palladium atom.



SCHEME 1

The presumable pathway for the formation of the π-allylpalladium complex is illustrated in Scheme 1. The chloride ligand of diene-palladium complex **A** acts as a proton acceptor, as suggested by Harvie and McQuillin [9]. The intermediate **B** is transformed into the next intermediate **C** by elimination of an aromatic compound and coordination of another diene. Finally, the hydride in **C** attacks the terminal carbon of the conjugated diene bearing the less bulky alkyl group to give II.

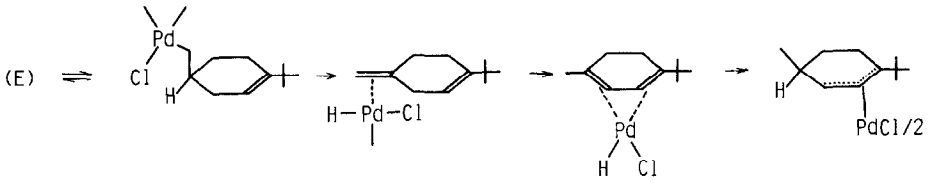
Kiji et al. have prepared 4-t-butylcyclohexenylpalladium chloride complexes by the reaction of π-allylpalladium complexes with 2-t-butyl-1,3-butadiene [12] (Scheme 2). The IR spectrum of the isolated compound E, which is the precursor of the cyclic



(E) (Vd)

SCHEME 2

π-allylpalladium complex, revealed the existence of an intramolecular π-complex. According to their proposed mechanism, the stereochemical correlation between the methyl group at C(4) and the palladium atom should be *cis* in these cyclic π-allylpalladium complexes. However, the ^{13}C NMR spectra of both complexes, arising from this cyclization reaction and from Id with a palladium salt, were identical. This suggests that the proposed mechanism of the cyclization should be revised to that shown in Scheme 3. The cyclization intermediate **E** is in equilibrium



(F) (G) (H) (IVd)

SCHEME 3

with **F**. Elimination of the hydride results in the formation of **G**, whose double bond migrates to produce the conjugated diene complex **H**. Finally, the *trans* complex IVd, which is identical to IId, is obtained.

Experimental

Materials

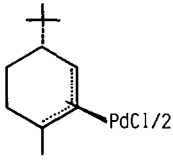
Cyclohexa-1,3-dienes [13] and cyclohexenes (*cis*-IIIb [14] and IIId [15]) have previously been reported. For preparative purposes, *cis*-IIIb and *cis*-IIId were prepared as follows. Partial hydrogenation of Ib or Id was performed over a

Raney-Co catalyst, followed by fractional distillation with a 30 cm spinning band column (*cis*-IIIb) or separation by preparative gas chromatography (*cis*-IIId) [13]. These products were identified by comparison (GLC and NMR) with authentic samples [14,15].

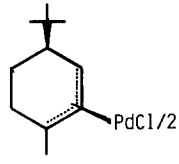
π-Allylpalladium chloride complexes

(i) From cyclohexa-1,3-dienes. 1,4-Disubstituted cyclohexa-1,3-diene (6 mmol) was added to a solution of Na_2PdCl_4 (0.88 g, 2.4 mmol) in methanol under a N_2 atmosphere and the mixture was warmed to 60°C. The solution, which turned greenish yellow, was poured into water and extracted with benzene. The extract was washed with water, saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution, and dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the crude yellow oil was subjected to column chromatography on SiO_2 eluting with hexane in order to remove the recovered hydrocarbons. Subsequent elution with $CHCl_3$ gave a purified yellow oil. Addition of pentane to this oil induced crystallization to give the π-allylpalladium complex (IIb, Found: C, 38.19; H, 5.15. $C_{16}H_{26}Pd_2Cl_2$ calcd.: C, 38.27; H, 5.22%. IId, Found: C, 45.28; H, 6.75. $C_{22}H_{38}Pd_2Cl_2$ calcd.: C, 45.07; H, 6.53%). GLC analysis of hexane used for the purification of IId by column chromatography showed that the recovered hydrocarbons consisted of *p*-t-butyltoluene (80%), Id (17%), IIId (2%) and 4-t-butyl-1-methylcyclohexene (1%). Two other palladium complexes, bis(1-isopropyl-4-methylcyclohexenylpalladium chloride) (IIc) and IIe, obtained as oily products, could not be subjected to elemental analysis. Only ^1H and ^{13}C NMR spectra were examined.

(ii) From olefin. Sodium acetate (1.20 g, 14.6 mmol), NaCl (0.84 g, 14.6 mmol), $CuCl_2$ (1.16 g, 8.63 mmol) and $PdCl_2$ (0.20 g, 1.13 mmol) in 50 ml of acetic acid were stirred for 2 h at 95°C under a N_2 atmosphere. The solution was cooled to 60°C and the olefin (8–10 mmol) was added. Having been kept at 60°C for 20 h, the mixture was cooled to room temperature and filtered. The solution was poured into water and extracted with benzene. The extract was washed with water, saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution, and dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the crude yellow oil was subjected to column chromatography on SiO_2 eluting with hexane in order to remove the recovered hydrocarbons. Subsequent elution with $CHCl_3$ gave a purified yellow oil. Addition of pentane to this oil gave a crystalline π-allylpalladium chloride complex (IVb). IVd and Vd did not crystallize on addition of pentane to the purified yellow oil. The ^{13}C and ^1H NMR spectra of oily IVd and Vd indicated that each of them contained one of the two stereoisomers of bis(4-t-butyl-1-methylcyclohexenylpalladium chloride) (VId from *cis*-IIId and VIId from *trans*-IIId) as minor products. The ratios of these regioisomers were IVd/VId 3/1 and Vd/VIId 5/1. The NMR



(VId)



(VIId)

spectral data for the π-allylic portion of VId and VIId are as follows: VId ^{13}C NMR: δ 94.7 (C(1)), 101.7 (C(2)), 76.3 (C(3)) ppm. ^1H NMR: δ 5.32 (d, 6.5) (central H), 4.93 (bd, 6.5) (terminal H) ppm. VIId ^{13}C NMR: δ 94.1 (C(1)), 101.1 (C(2)), 78.0 (C(3)) ppm. ^1H NMR: δ 5.32 (d, 6.5) (central H), 4.90 (bd, 6.5) (terminal H) ppm.

$LiAlH_4$ reduction of IIb

$LiAlH_4$ (0.3 mmol) in dimethoxyethane (the solution was titrated with I_2/benzene solution prior to use) was added to a solution of IIb (0.074 g, 0.3 mmol) and triphenylphosphine (0.078 g, 0.6 mmol) in dimethoxyethane (6 ml) at 0°C. After 5 min, water was added and the product was extracted with pentane. The dried extract was passed through a short column of SiO_2 and the solution was concentrated. The residue was analyzed by GLC. The reduction product contained *cis*-IIId and 1,4-dimethylcyclohexene in a ratio of 1/1.

NMR spectra

^1H NMR spectra were obtained with JEOL C-60HL and PMX-60 spectrometers, and ^{13}C NMR spectra were recorded with JEOL MH-100 and FX-100 spectrometers in the FT-mode using TMS as the internal standard. $CDCl_3$ was used as the solvent.

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