Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ALKYLATION REACTIONS WITH ORGANOMETALLIC COMPOUNDS II*. THE REACTION OF DIPHENYLACETYLENE WITH PALLADIUM COMPOUNDS OF THE TYPE L_2PdCl_2 AND CH_3MgBr

N. GARTY AND M. MICHMAN
Department of Organic Chemistry, The Hebrew University, Jerusalem (Israel)

(Received September 7th, 1971)

SUMMARY

α,α'-Dimethylstilbene is obtained in the reaction of diphenylacetylene with CH_3MgBr and L_2PdCl_2 (L = benzonitrile or norbornadiene), in 65% yield based on the alkyne. Stilbene and α-methylstilbene form as side products (~25%). No reaction takes place when phosphines or arsines are present as L in L_2PdCl_2. The addition of strong nucleophiles like Ph_3P, $Ph_2PCH_2CH_2PPh_2$ or $(PhO)_3P$ to a cold mixture (−70°) of $(C_6H_5CN)_2PdCl_2$ and CH_3MgBr yields the corresponding $L_2Pd(CH_3)_2$, indicating the presence of methyl–palladium components in the reaction reagent and offering thereby a convenient synthesis of these compounds.

INTRODUCTION

Salts and complexes of transition metals were shown to play an important part in a number of alkylation reactions of acetylenic[1] and olefinic[2-4] compounds. These alkylation reactions[1] often lead to the formation of a great number of products which is not always desirable. It is therefore of interest to seek and study those systems which display a certain degree of specificity. We report here the reactions of palladium based reagents in which diphenylacetylene is symmetrically dimethylated to give α,α'-dimethylstilbene. The effect of ligands in the palladium compound on its reactivity or inertness has also been studied. This question which has recently been raised in connection with homogeneous hydrogenation[5] is still a matter of much concern.

Palladium compounds[3] are known to take part in several types of alkylation reactions. However, instances of symmetrical alkylations of unsaturated compounds are still rare. Two cases reported lately deal with the formation of stilbene from the reaction of vinyl halides or vinyl acetate with "C_6H_5PdCl" (not isolated)[3] and the formation of substituted butadienes from the reaction of terminal olefins and diphenylacetylene with bis(benzonitrile)palladium dichloride[4].

---

[*] For Part I see ref. 1.

RESULTS AND DISCUSSION

The alkylation of diphenylacetylene

The reactions of palladium compounds of the type L_2PdCl_2 in which L is benzonitrile or norbornadiene (bicyclo[2.2.1]heptadiene) with CH_3Li or with CH_3MgBr result in the formation *in situ* of very reactive alkylating agents. In their reaction with diphenylacetylene the latter is dialkylated to α,α'-dimethylstilbene (2,3-diphenyl-2-butene) (65%). Side products in low yields were stilbene and α-methylstilbene. Condensation products in which hexaphenylbenzene[6] was identified were obtained only in the case of the benzonitrile compound (yield less than 10%).

Generally, a higher percentage of hydrogenation, at the expense of alkylation was observed when CH_3Li was used (Table 1, run 1). The combined yield of addition products was 80% based on the alkyne.

With other ligands in L_2PdCl_2 such as phosphites, triphenylarsine (Table 1, runs 4–6) or triphenylphosphine the yields were very low or practically zero.

TABLE 1

DISTRIBUTION OF ADDITION PRODUCTS (mole%) IN REACTIONS OF DIPHENYLACETYLENE WITH L_2PdCl_2/CH_3Li OR L_2PdCl_2/CH_3MgBr

Run	L in L_2PdCl_2	Alkylating agent	Max temp. (°C)	Dimethylstilbene		Methylstilbene		Stilbene		Yields (%)
				cis	*trans*	*cis*	*trans*	*trans*	*cis*	
1	C_6H_5CN	CH_3Li	25	29.3	10.3	10.2	10.2	10	30	—
2	C_6H_5CN	CH_3MgBr	25	55.2	14.4	4.5	5	4.8	16.3	80
3	C_7H_8[a]	CH_3Li	25	53.0	16.1	17.5	None	None	13.4	80
4	$(C_6H_5O)_3P$	CH_3MgBr	120	32.0	26.1	5.85	13	19.8	3.7	<5
5	$(CH_3O)_3P$	CH_3Li	70	29.2	14.6	13.5		(13.5)[c]	29.2	$\leqslant 5$
6	$(C_6H_5)_3Sb$	CH_3MgBr	50	50.5	13.3	18.0	18.0	None	18.2	Trace
7	$(C_6H_5)_3As$	CH_3Li	70	Trace	Trace	Trace	Trace	Trace	Trace	Trace
8	— $(PdCl_2)$[b]	CH_3MgCl		15.9	(13.6?)	6.8	6.8	9.1	52.4	~16

[a] Norbornadiene. [b] Data from ref. 13. [c] Quantity too small for each to be determined individually.

Isomerisation of the product

As shown in Table 1 the geometry of the product is predominantly *cis*. When samples were kept for longer periods at 0 or 25° the ratio of *cis*- to *trans*-dimethylstilbene increased considerably (Table 2). No such isomerisation was observed in the reaction of rhodium compounds with diphenylacetylene[1] and in the corresponding reaction with chromium catalysts[7] the isomerisation of olefins in the system was in the opposite direction (*cis* to *trans*).

The trapping of methylpalladium compounds in the reagent system

When potential ligands such as triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, triphenyl phosphite and several others were added to the mixture of $(C_6H_5CN)_2PdCl_2$ and CH_3MgBr at -70 or $-60°$ the corresponding dimethylpalladium compound $L_2Pd(CH_3)_2$ could be isolated. It is well known[8] that compounds of this type can be prepared by the reaction of L_2PdCl_2 with CH_3MgBr and

TABLE 2

cis/trans RATIOS OF α,α'-DIMETHYLSTILBENE AT DIFFERENT REACTION TEMPERATURES AND TIMES, IN THE REACTION OF $(PhCN)_2PdCl_2/CH_3MgBr$ WITH DIPHENYLACETYLENE

Run	Hours at			*cis/trans* ratio
	−60°	0°	Total	
1	1		1	1.5
	4		4	1.92
	4	8	12	2.0
	4	68	72	2.25
2	2	2[a]	4	3.8

[a] At 25°.

they probably also form when $L=C_6H_5CN$ or C_7H_8, but dimethylpalladium compounds having these two ligands were too unstable to be isolated. It seems however that ligand displacement took place without cleaving[9] any palladium–methyl bonds which may have formed, unlike several reported cases where such cleavage was observed[10]. As has been done in other cases[11] it may be argued that a compound such as $(C_6H_5CN)_2Pd(CH_3)_2$ did form in the reaction mixture at −70°. Generally, the method seems to offer a convenient synthetic route to dimethylpalladium compounds.

The reactions can be summarized as follows:

$$\begin{tikzcd}
& & L_2Pd(CH_3)_2 + C_6H_5CN \\
\begin{matrix}(C_6H_5CN)_2PdCl_2\\ +\\ CH_3MgBr\end{matrix} \arrow[r, "-60^\circ"] & {[(C_6H_5CN)_2Pd(CH_3)_2]} \arrow[ur, "L"] \arrow[dr, "PhC\equiv CPh"'] & \\
& & PhC(CH_3){=}C(CH_3)Ph + Pd^0 + C_6H_5CN
\end{tikzcd}$$

$L=Ph_3P, (PhO)_3P, Ph_2PCH_2CH_2PPh_2$

The results suggest that coordination of diphenylacetylene is a prerequisite for the reaction and that ligands in the palladium compound compete with the alkyne in this respect. It is expected that cyclisations and condensations of the alkyne would be more affected by this competition than additions since they apparently require the coordination of more than one diphenylacetylene molecule to the metal. Consequently, with loosely bonded ligands such as benzonitrile which are easily displaced by diphenylacetylene[12], cyclisation of the alkyne is not completely hindered, although it is less than with just $PdCl_2$[13] but with the other, better attached ligands it is not observed. With the complexes containing still more strongly attached ligands even addition reactions occur only at high temperatures and with poor yields, if at all. In comparison with the reported result[13], for the similar reaction of $PdCl_2$ (represented in Table 1, run 8), the yield of addition products increases considerably in the reactions of the benzonitrile and norbornadiene complexes. The extent of hydrogenation is also much smaller with these complexes and this probably causes the considerable increase of dialkylation. In other systems studied so far the dominant product of alkylation of diphenylacetylene was α-methylstilbene mainly because reactions of hydrogen transfer competed strongly with alkylation[7] or because the reaction was a two step process of which only the first consisted of alkylation[1]. When the effect of transition metal salts on the reaction of diphenylacetylene with CH_3MgBr was studied[13], it was found that among many salts examined only $CuCl_2$, $CuBr_2$ and $MnCl_2$ yielded *cis*-α,α'-dimethylstilbene as an important product. The present results show that a desired specificity in alkylation can be achieved not only by a proper choice of the metal ion but also by the choice of different compounds of the same metal. However, the connection between the presence of ligands and the repression of hydrogen transfer reactions is not clear at present.

The role of compounds like $(C_6H_5CN)_2Pd(CH_3)_2$ and $C_7H_8Pd(CH_3)_2$ in the alkylation reaction is questionable. Although probably formed initially they both may yield the same transient complex containing Pd–CH_3 groups and coordinated PhC≡CPh as the reactive species. Those dimethylpalladium compounds which could be isolated [L = Ph_3P, $(PhO)_3P$ or $Ph_2PCH_2CH_2PPh_2$] did not react with the alkyne even at temperatures where disintegration of the Pd–CH_3 bond took place, again probably because the alkyne did not coordinate to the palladium atom in these cases. The triphenyl phosphite compound is a limit case where $[(C_6H_5O)_3P]_2PdCl_2/CH_3MgBr$ gave alkylation products in low yields.

Although benzonitrile in other conditions is known to react with CH_3MgBr, to form acetophenone (after hydrolysis), this did not interfere with the reaction between the Grignard reagent and $(C_6H_5CN)_2PdCl_2$ even though excess of the former was present. In runs carried out below −30° no acetophenone was detected among the products. With runs kept for long periods at room temperature some acetophenone was observed when CH_3Li was used, but none in runs of CH_3MgBr.

EXPERIMENTAL

Ether and tetrahydrofuran (THF), were filtered through alumina, refluxed first over sodium then over $LiAlH_4$, on which they were stored. Other solvents were dried by refluxing over sodium. All operations in this work were carried out under an atmosphere of dry argon.

Starting materials

Palladium compounds were prepared by standard procedures: $(PhCN)_2PdCl_2$[14], $C_7H_8PdCl_2$[15], $[(CH_3O)_3P]_2PdCl_2$[16], $(Ph_3Sb)_2PdCl_2$[17], $(Ph_3As)_2PdCl_2$ (prepared by using the procedure in ref. 17), $[Ph_2P(CH_2)_2PPh_2]PdCl_2$[18], $(Ph_3P)_2PdCl_2$[19].

$[(PhO)_3P]_2PdCl_2$. Into a benzene solution (30 ml) of triphenylphosphite (9.3 g, 3 mmole), $PdCl_2$ (1.76 g, 1 mmole) was added. After stirring for 24 h the slurry was warmed to 90°, cooled and the white precipitate filtered and washed in hexane/benzene mixture. The substance is insoluble in CCl_4, hexane, ether or water, very soluble in THF and chloroform. M.p. 168° (decomp.). (Found: C, 56.86; H, 3.92; Cl, 8.62. $C_{36}H_{30}Cl_2O_6P_2Pd$ calcd.: C, 54.3; H, 3.7; Cl, 8.9%.)

Reaction of $(PhCN)_2PdCl_2$ with CH_3MgBr and PhC≡CPh

A suspension of bis(benzonitrile)palladium dichloride (7.3 g, 19.5 mmole) in

150 ml of THF was cooled to −60° and a solution of CH_3MgBr in THF (1.4 N) was added dropwise, until the mixture gave a positive Gilman test (~100 ml). During the addition $(PhCN)_2PdCl_2$ dissolved and a yellow precipitate formed. (This precipitate would turn black if warmed above −20°.) After stirring for 2 h, diphenylacetylene (1.07 g, 6 mmole) in THF (20 ml) was added, and the mixture kept for 2 h at −60°, then warmed up to room temperature. The black slurry was hydrolysed after 12 h with dilute aqueous HCl (100 ml, pH 4.5). The products are shown in Table 1. Reactions of $(PhCN)_2PdCl_2$ with CH_3Li and PhC≡CPh, were carried out similarly.

Products were also analysed at predetermined times at 0° or 25° (Table 2).

Reaction of $C_7H_8PdCl_2$ with CH_3Li or CH_3MgBr and PhC≡CPh

A solution of norbornadienepalladium dichloride (0.7 g, 3 mmole) in THF (50 ml) was cooled to −60°. Methylmagnesium bromide (20 ml, 1.5 N) or methyllithium (10 ml, 1.5 N), were slowly added and a white precipitate was obtained. With these quantities, the Gilman test was positive. Diphenylacetylene (360 mg, 2 mmole) in THF (20 ml) was added and after 30 min of strong stirring the mixture was warmed up, kept for 2 h at room temperature and hydrolysed. The products were analysed by VPC (Table 1).

Reaction of $[(PhO)_3P]_2PdCl_2$ with CH_3Li and PhC≡CPh

Bis(triphenyl phosphite)palladium dichloride (0.8 g, 1 mmole) in 50 ml THF was reacted with a CH_3MgBr solution (20 mmole). Diphenylacetylene (89 mg, 0.5 mmole) was added in 20 ml THF. Reactions were carried out for 3 h at room temperature, at 70° and at 120°, the latter by adding 100 ml *p*-xylene and refluxing. The slurry turned black only at 120°. Samples were worked up by the standard procedures and products analyzed by VPC. Low yields were detected in the second and third runs only.

Attempted reactions of other compounds of the type L_2PdCl_2

Similar procedures were used with the compounds $[(CH_3O)_3P]_2PdCl_2$, (at 70°), $(Ph_3Sb)_2PdCl_2$ (at 50°) and $(Ph_3As)_2PdCl_2$ and $(Ph_3P)_2PdCl_2$ (at 70°). Very small yields of dimethylstilbene ($\leqslant 5\%$) were obtained with the first two compounds and none with the last two.

Attempted reactions of PhC≡CPh with compounds of the type $L_2Pd(CH_3)_2$

Compounds of the type $L_2Pd(CH_3)_2$ [$L = (PhO)_3P, Ph_3P, (Ph_2)PCH_2CH_2P(Ph)_2$] were reacted with equivalent quantities of diphenylacetylene in cold or in boiling THF, and in boiling *p*-xylene. No alkylation products of the alkyne were detected, despite decomposition of the palladium compounds.

Isolation and identification of products

The work-up of hydrolysed mixtures and their VPC analysis was described previously[1,7]. The presence of decomposed palladium compounds and of metallic palladium interfered with gas-chromatographic analysis and careful filtration was necessary before analysis. All products were isolated and compared with authentic samples.

α,α′-Dimethylstilbene. This compound was prepared according to Kharasch and Kleiman[20]. Both *cis* and *trans* isomers were obtained. The first had the lower retention in gas chromatography on SE-30. The NMR spectrum of each showed two single bands in the ratio of 5/3, at δ 7.08 (aromatic H) and 2.18 (methyl group) for the *cis* isomer (m.p. 66°) and at δ 7.3 and 1.92 for the *trans* isomer (m.p. 107°).

[1,2-Bis(diphenylphosphino)ethane]dimethylpalladium. To $(C_6H_5CN)_2PdCl_2$ (0.76 g, 2 mmole) in THF (60 ml) at −70°, CH_3MgCl (15 mmole) in THF (15 ml) were added. After stirring for 2 h, 1,2-bis(diphenylphosphino)ethane (1.4 g, 3 mmole) was added in 50 ml THF and stirring continued for 3 h while the colour of the mixture turned white. The mixture was brought to room temperature and acidified ice water (pH 5–6) added. The product was extracted with ether and the extract dried and evaporated. Upon addition of a few drops of acetone or ethyl methyl ketone to the residue the crystalline product was obtained, m.p. 163° (decompn.), yield 60%. (Found: C, 62.68; H, 6.03. $C_{28}H_{30}P_2Pd$ calcd.: C, 62.9; H, 5.63%.) The infrared spectrum and m.p. conformed with those reported[8]. NMR spectrum in $CDCl_3$ (TMS as standard) showed three multiplets at δ 0.2–1.0, 2.2 and 7.5–7.6 with the respective intensity of 3, 2, 10 attributed respectively to the methyl, methylene and aromatic hydrogen atoms.

Bis(triphenyl phosphite)dimethylpalladium. The same procedure was used except that 6 mmoles of phosphite were added to a solution containing 2 mmoles of palladium complex, and hexane was used to crystallise the product from the evaporated ethereal extract. The compound, long colourless needles, could be kept in and recrystallised out of cold (0°) hexane but decomposed in dioxane, THF and more slowly in methylene chloride. The yield was about 60%, m.p. 96° (decompn.). (Found: C, 59.59; H, 4.92; P, 7.96. $C_{38}H_{36}O_6P_2Pd$ calcd.: C, 60.03; H, 4.76; P, 8.19%.) NMR spectrum in CH_2Cl_2 showed multiplets at δ 0.0 (six methyl H), and δ 7.1 (30 aromatic H).

Bis(triphenylphosphine)dimethylpalladium. The same procedure was used. THF was added to the final ether extract to prevent fast decomposition of the product, which was insoluble in all solvents used (hexane, ether, THF, dioxane, CCl_4, CH_2Cl_2). The yield was about 40%. M.p. 128° (decompn.) (lit.[8] 198°). (Found: C, 67.97; H, 6.13. $C_{38}H_{36}P_2Pd$ calcd.: C, 69.0; H, 5.45%.) IR (cm^{-1}): 1133 (1129), 875, 655, 529 (529) 482 (480), values in parentheses reported by Coates[8]. NMR in $CHCl_3$, multiplets at δ 0–0.4, and 7.4–7.7 with respective intensity of 1/4.6. The spectrum is not very clear and fast decomposition is observed.

Instrumentation

A Wilkens Hi-Fi model 600 was used for gas chromatographic analysis and a Wilkens model A-700 was used for preparative separations. Infrared spectra were obtained with a Perkin–Elmer model 337 spectrophotometer and NMR spectra were obtained with the Varian T-60 and HR-100 instruments.

REFERENCES

1 M. Michman and M. Balog, *J. Organometal. Chem.*, 31 (1971) 395.
2 L. Farády and L. Markó, *J. Organometal. Chem.*, 28 (1971) 159.
3 R. Hüttel, *Synthesis*, (1970) 225.
4 P. Mushak and M. A. Battiste, *J. Chem. Soc. D*, (1969) 1146.
5 R. S. Coffey in R. Ugo (Ed.) *Aspects of Homogeneous Catalysis*, Vol. 1, Manfredi, Milan, 1970, pp. 33, 61.

6 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 25 (1970) 161.
7 M. Michman and H. H. Zeiss, *J. Organometal. Chem.*, 15 (1968) 139.
8 G. Calvin and G. E. Coates, *J. Chem. Soc.*, (1960) 2008.
9 C. R. Kistner, J. H. Hutchinson, J. R. Doyle and J. C. Strolie, *Inorg. Chem.*, 2 (1963) 1255.
10 G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, 7 (1968) 188.
11 G. E. Coates and C. Parkin, *J. Chem. Soc.*, (1963) 421; G. Herrmann and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 5 (1966) 581; B. Bogdanović, H. Bönnemann and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 5 (1966) 582.
12 A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, 84 (1962) 2329.
13 J. R. C. Light and H. H. Zeiss, *J. Organometal. Chem.*, 21 (1970) 517.
14 M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Amer. Chem. Soc.*, 60 (1938) 882.
15 E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.*, (1959) 3178.
16 J. M. Jenkins and J. G. Verkade, *Inorg. Chem.*, 6 (1967) 2250.
17 J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, (1953) 70.
18 A. D. Westland, *J. Chem. Soc.*, (1965) 3060.
19 J. Chatt and F. G. Mann, *J. Chem. Soc.*, (1939) 1622.
20 M. S. Kharasch and M. Kleiman, *J. Amer. Chem. Soc.*, 65 (1943) 11.