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PALLADIUM-PROMOTED ADDITION OF AMINES TO ISOLATED DOUBLE BONDS*

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Summary

Palladium(II) complexes have been found to promote amination of terminal olefins, to give, after reduction, high yields of amines. Internal olefins may also be aminated, but the yields are moderate to low. Cyclohexene and cyclooctene react very sluggishly. In order to avoid formation of bis(amine)-palladium complexes, which is a major side reaction, the temperature has to be kept low. Preliminary mechanistic studies show that three moles of amine are required per mole of palladium to ensure good yields.

Introduction

A number of different nucleophiles have been added to simple olefins in reactions promoted by palladium and platinum salts [1]. The palladium-promoted reactions are of particular interest, since some of these, such as the Wacker process [2], are now used industrially. In the Wacker process ethene is converted into acetaldehyde by the nucleophilic addition of water to the double bond [3] (Fig. 1). The reaction is general, and gives a mixture of ketones and aldehydes with higher 1-olefins [2—4].

Acetate [5, 6], alcohols and chloride ion [7] have been added to olefins in the same type of reaction.

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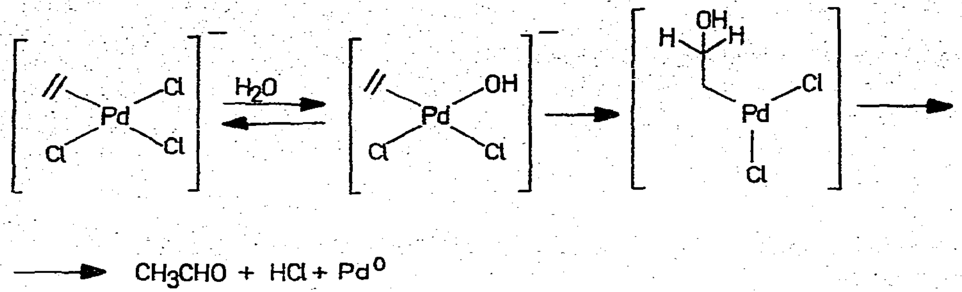

Stronger nucleophiles such as cyanide [8], alkyls [9—11], aryls [9—11] and amines [12, 13] have also been used successfully, although somewhat lower yields were obtained. The addition of cyanide, alkyls and aryls probably proceeds via Pd—X complexes (X = CN, alkyl, aryl) which add across the reacting double bond. In these reactions, therefore, the addition should be regarded as cyclic rather than nucleophilic. The addition of amines proceeds smoothly with dienes [6, 12—14] but gives low yields with mono-olefins [6, 12, 13].

Direct amination of olefins, particularly with long alkyl chains, is of considerable industrial interest, since it might compete favourably with current procedures for the synthesis of fatty amines. A new investigation of palladium-promoted amination therefore appeared desirable. In this paper we present results which show that the amination may indeed be performed in high yield (Table 1).

Results

In the optimized procedure, bis(benzonitrile)palladium chloride was stirred with an excess of appropriate olefin in tetrahydrofuran (THF) at 0°. π-Olefin complexes, e.g. I, are probably formed, but were generally not isolated prior to the addition of the amine. 1-Olefins and *trans*-2-olefins were isomerized to a small extent (2%) during the preparation of the complexes (cf. ref. [17]). The temperature was then lowered to —50°, where isomerisation was negligible, and amine was added. Alkyl—palladium complexes were formed as indicated by preliminary data*. Cleavage of the carbon—metal bonds of the complexes with molecular hydrogen, sodium tetrahydridoborate or hydrochloric acid yielded the amines. When unsymmetric olefins were used, a mixture of the two possible amines was obtained (e.g., VI and VII). The relative ratio of the two products varied greatly with the steric requirements of amine used (Table 2).

The yield of the amination was strongly temperature dependent. Amination of 1-decene with dimethylamine gave a maximum yield of 90% at about —50°. As the temperature was raised, there was a steady decrease in the yield of amination product. At 20° the yield was 7% (Table 1). With 1-butene and 2-octene a similar temperature effect was observed. With ethene, the yield was 100% even at 0° but then rapidly decreased to 60% at 25°. The major side reaction was olefin displacement as indicated by NMR of the crude reaction products. A

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* Due to their thermal lability, none of the crude σ-complexes obtained from amination reactions has been sufficiently characterized. Further work with this aim is in progress.

TABLE 1

PRODUCT YIELDS FROM THE ADDITION OF DIMETHYLAMINE TO OLEFINS AT VARIOUS TEMPERATURES

Olefin	Temp. (°C)	Yield [a,b] (%)	Isomer distribution [c,d] (1/2 or 2/3)
1-Butene	−60	90	1/7
	−50	90	
	−30	72	
	−20	40	
	0	20	
	20	16	
1-Decene	−65	92	1/4.5
	−50	89	
	−30	70	
	−20	59	
	0	20	
	20	7	
trans-2-Butene	−50	44	
cis-2-Butene	−50	15	
trans-2-Octene	−50	66	1/1.5
	−20	48	
	0	33	
	25	12	
cis-2-Octene	−50	24	1/1.8
	−20	12	
	0	4	
	25	2	
Ethene [e]	0	100	
	25	60	
Cyclopentene	−50	62	
Cyclohexene	−50	Trace	
Cyclooctene	−50	0	
3,3-Dimethyl-1-butene	−50	0	

[a] Based upon amount of palladium used. [b] By GLC. [c] Deviation 10%. No variation with temperature observed. [d] 2/3 refers to the 2-octenes. [e] Diethylamine added in place of dimethylamine.

TABLE 2

EFFECT OF THE AMINES ON THE AMINATION REACTION USING $(PhCN)_2PdCl_2$ AT −50°

Olefin	Amine	Yield (%)			Isomer distribution mono (1/2)
		mono-	di-	tri-adduct	
1-Butene	Dimethylamine	90			1/7
	Diethylamine	88			1/1.5
	Diisopropylamine	3			>20/1
	Methylamine	40	0		1/4
	Ammonia	4	0	0	1/3
1-Decene	Dimethylamine	90			1/4.5
	Diethylamine	70			1/1.3
	Diisopropylamine	6			>20/1
	Methylamine	40			[a]
	Ammonia	5			[a]

[a] Not determined.

separate experiment with trimethylamine and preformed butene—palladium chloride complex (I, R = R' = CH_3) at 0° gave 92% of bis(trimethylamine)-palladium dichloride. Contrary to expectations [15], competition from π-allyl formation was negligible at temperatures below 0°.

The effect of the structure of the olefin is noteworthy. Amination of ethene, 1-butene and 1-decene all gave yields greater than 90%, *trans*-2-octene gave 66%, *cis*-2-octene only 24% and cyclohexene less than 1% yield. No amination was detected from the bulky 1-olefin, 3,3-dimethyl-1-butene. The structure of the amine also has a strong influence on the yield. The effect is partially steric as indicated by the observation that diisopropylamine gave very low yields of product with both 1-butene and 1-decene (Table 2). Other factors are also important as shown by the low yields obtained with ammonia and methylamine. Contrary to the results obtained in the platinum-promoted amination of simple olefins [16], no products derived from the addition of more than one molecule of olefin to ammonia or methylamine were detected (Table 2).

A number of palladium complexes other than bis(benzonitrile)palladium dichloride were investigated, e.g. disodium tetrachloropalladate, bis(benzonitrile)palladium dibromide, palladium acetate, and the palladium dichloride—THF complex. All of these gave yields of amine lower than bis(benzonitrile)palladium dichloride (Table 3).

In order to get some information on the stoichiometry of the amination reaction, a complex was prepared from 1-butene and palladium chloride and

TABLE 3

EFFECT OF ADDED LIGANDS AND DIFFERENT COMPLEXES IN THE AMINATION REACTION AT −50°

Olefin	Complex added	Amine	Yield (%)	Isomer distribution (1/2)
1-Decene	$(PhCN)_2PdCl_2$	Dimethylamine	90	1/4.5
	$(PhCN)_2PdBr_2$		63	1/4.5
	$Pd(OAc)_2$		0	
	$(PhCN)_2PdCl_2$/DMFA		70	1/4.0
	$(PhCN)_2PdCl_2$/DMSO		0	
	$[(CH_3)_2NH]_2PdCl_2$		0	
	Na_2PdCl_4		74	1/4.5
	Na_2PdCl_4; −30°		63	
	Na_2PdCl_4; 0°		34	
	$Na_2PdCl_4 + Ph_3P$		8	
	$Na_2PdCl_4 + Bu_3P$		38	
	$Pd(NO_3)_2$		60	
	$(PhCN)_2PdCl_2$	Diethylamine	70	1/1.3
	$(C_{10}H_{20})$-$Pd(Bu_3P)Cl_2$		40	1/1.5
	$(C_{10}H_{20})$-$Pd(CO)Cl_2$		10	1/2.3
	$HgCl_2$ [a]		30	1/20
trans-2-Butene	$(PhCN)_2PdCl_2$	Diethylamine	73	
cis-2-Butene	$(PhCN)_2PdCl_2$		48	
trans-2-Butene	$HgCl_2$ [a]		< 0.5	
cis-2-Butene	$HgCl_2$ [a]		6.9	

[a] Reaction at 25°.

was treated with varied relative amounts of dimethylamine and 1-butene. The attempts to study the effect of added olefins were inconclusive due to the rapid isomerisation of the complexed olefin. For instance, when the presumed 1-butene complex was left at room temperature for 1 h and then treated with cyclooctadiene, a mixture of 1-butene, *trans*-2-butene and *cis*-2-butene in a ratio of 1/1/8 was obtained (cf. ref. 17). When the freshly prepared complex was treated with a ten-fold excess of 1-butene at room temperature, *trans*-2-butene appeared in the solution after about 10 min and *cis*-2-butene after about 30 min. When the freshly prepared complex was rapidly mixed with a ten-fold excess of 1-butene in THF and cooled to —40°, only about 2% of 2-butenes were detected after addition of cyclooctadiene to set free the complexed butenes. At —40° isomerisation was negligible. Amination of the preformed butene complex in the presence of an excess of 1-butene at —40° or below gave the same product pattern as the standard procedure for amination of 1-butene. Amination and olefin exchange are thus rapid relative to isomerisation under the conditions generally used.

The addition of different relative amounts of amine were more informative. When the preformed butene—palladium complex was treated with one or two equivalents of dimethylamine only small amounts of amination product were formed ($\leqslant$ 5%, Table 4). On addition of a third equivalent of amine, the yield was increased to 75%, which was not further increased upon addition of more amine. As the third equivalent might serve to remove hydrogen chloride from a σ-complex III, excess potassium carbonate or one equivalent of other, presumably less nucleophilic, amines like diisopropylamine, tributylamine and 4-(dimethylamino)pyridine was added in place of the third equivalent of dimethylamine. With diisopropylamine 40% yield of product was obtained, but with the other bases only a slight increase was observed (Table 4).

Since added ligands apparently influence the yield of the amination, one equivalent of tributylphosphine, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and carbon monoxide was added per palladium. The yields

TABLE 4

REACTIONS BETWEEN BIS(1-BUTENE)DIPALLADIUM TETRACHLORIDE AND DIMETHYLAMINE

Butene complex (equiv.)	Added 1-butene (equiv.)	Dimethylamine (equiv.)	Yield (%)
1		1	Trace
1		10	28
1	25	1	1
1	10	2	5 ± 2 [a]
1	10	2.5	20 ± 5 [a]
1	10	3	75 ± 5 [a]
1	10	5	71
1	10	10	75 ± 5 [a]
1 [b]	10	2	3
1 [c]	10	2	15
1 [d]	10	2	38
1 [e]	10	2	8
1 [f]	10	2	12

[a] Average of 4 experiments. [b] Reaction time 6 h. [c] Excess potassium carbonate added. [d] 1 equiv. of diisopropylamine added. [e] 1 equiv. of tributylamine added. [f] 1 equiv. of *p*-(dimethylamine)pyridine added.

were low to moderate (Table 3), probably due to olefin displacement. With DMSO, which is known to displace olefins rapidly and essentially irreversibly [18], no amine was detected.

Discussion

A reasonable mechanism for the amination reaction is outlined in Scheme 1. In the first step, the added palladium complex, e.g. (benzonitrile)palladium dichloride, is converted into a bridged complex I, which in some cases can be isolated and aminated separately. Since the first equivalent of amine does not effect amination, it is reasonable to assume that it serves to convert the bridged complex into a mononuclear amine complex II (L = amine). This is quite analogous to results obtained in the platinum series by Panunzi et al. [19]. In the next step a second equivalent of amine is added either to the olefinic double bond to form a σ-complex e.g. III or IV or to the palladium atom with displacement of the olefin to form a bis(amine) complex V*. The relative formation of the bis(amine) complex V, which is irreversible under the amination conditions, is increased with increasing temperature and appears to be main cause of the low yields of amination products at higher temperatures. Attempts to decrease the importance of olefin displacement by addition of donor ligands such as DMSO and phosphines have met with little success. An increase in the optimum temperature from −50° to −30° was observed when triphenylphosphine was added, but the yields were low at both temperatures.

The necessity of adding a third equivalent of amine to assure a good yield in the amination may reflect the need for a base in order to drive the amination towards an uncharged σ-complex IV or an equivalent mononuclear species**. An unexpected feature of the amination is the sluggish reaction of *cis*-olefins and some cyclic olefins such as cyclohexene. Although these olefins form stronger palladium complexes than the corresponding *trans* and terminal olefins [17], the latter give far higher yields of amination products. These results initially led us to believe that the amination of olefins might be a cyclic reaction. We have later been able to show that the amine and palladium add *trans* to the olefinic double bond in the case of *cis* and *trans*-2-butene [20]. The amination and the displacement reaction may therefore probably be regarded as two competing nucleophilic additions. However, the reason for the reactivity order obtained (1-olefin > *trans*-2-olefin > cyclopentene > *cis*-2-olefin ≫ cyclohexene) remains obscure.***

The product distribution, that is the ratio between isomeric amines VII and VI, gives some information on the electron distribution in the complexed olefins. Dimethylamine, methylamine, and ammonia all added preferentially to the most substituted carbon of the reacting terminal olefins. Diethylamine, which is slightly more bulky, gave about equal amounts of the two possible

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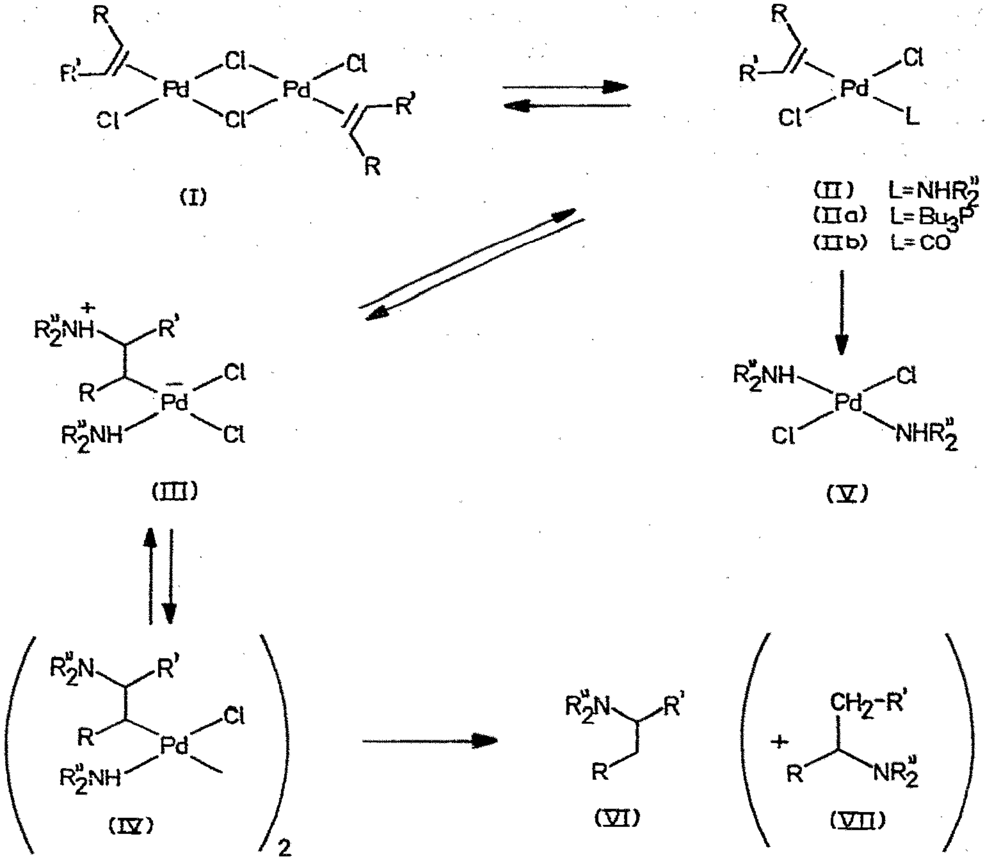
[*] See footnote p. 128.

[**] We have as yet no definite proof that the amination is reversible. However, experiments with the preformed σ-complex show that some added nucleophiles e.g. phenylthiolate, completely reverse the amination reaction (K. Zetterberg, to be published).

[***] Competitive animation of 1-butene, and *trans*-2-butene show that the reactive rates parallel the yields. J.E. Bäckvall, unpublished.

SCHEME 1



addition products while diisopropylamine gave exclusive addition to the terminal position (Table 2). Even the chain length of terminal olefins is important as shown by the greater relative yield of 1-addition for 1-decene than for 1-butene (Table 2). The preference for 2-addition in the unhindered cases is in accordance with the current picture of the palladium(II)—olefin bond: Electron donation to palladium is to some extent compensated by back donation, but the net result is a positive charge on the olefin. This may be compared with the mercury-promoted amination. Here back donation from mercury is presumably unimportant, and the preference for attack at the more substituted position is much more pronounced than in the palladium-promoted addition (Table 3).

Experimental

Instrumentation

IR, NMR, and mass spectra were recorded on a Perkin—Elmer 421, Varian A 60 or HA 100, and LKB 9000 spectrometer respectively.

Gas chromatographic separation of volatile products was done mainly on

the following columns: (1), 1.8 m × 3 mm, 15% carbowax 20 M on Chromosorb WDMCS-AW 60/80 mesh; (2), 2.1 m × 2 mm, stainless steel, 20% apiezon L, 10% KOH on Chromosorb WDMCS-AW 60/80 mesh; (3), 4 m × 2 mm, stainless steel, 12% carbowax 20 M, 4% on Chromosorb 80/100 mesh.
Nitrogen was used as carrier gas.

1-Butylamine, 2-butylamine, di-1-butylamine, tri-1-butylamine, 1-decylamine, 1-decyldimethylamine and cyclohexyldimethylamine were commercial samples (BDH, Schuchardt, KemaNord).

1-Butylmethylamine [22] was prepared by reduction of *N*-methylbutyramide with lithium tetrahydridoaluminate. 2-Butylmethylamine was prepared from 2-butanon and methylamine [23]. The following compounds were made by reacting methylamine, dimethylamine, diethylamine or diisopropylamine with the appropriate alkylbromide in aqueous ethanol (90% by volume):

1-Butyldimethylamine [24], 2-butyldimethylamine [25], 1-butyldiethylamine [26], 2-butyldiethylamine [27], 1-decylmethylamine [29], 1-decyldiethylamine [30], 2-decyldiethylamine [31], 1-butyldiisopropylamine (b.p. 167—168°/760 mm). (Found: C, 76.4; H, 14.3; N, 9.2. $C_{10}H_{23}N$ calcd.: C, 76.4; H, 14.7; N, 8.9%). Cyclooctyldimethylamine [32], 1-octyldimethylamine [24], 2-octyldimethylamine [33], 3-octyldimethylamine (b.p. 186—187°/760 mm). (Found: C, 76.4; H, 14.7; N, 8.9. $C_{10}H_{23}N$ calcd.: C, 76.4; H, 14.7; N, 8.9%.). 1-decyldiisopropylamine (Found: C, 79.3; H, 14.5. Mol. wt. (mass spectroscopy), 241. $C_{16}H_{35}N$ calcd.: C, 79.6; H, 14.6%. Mol. wt. 241.) 2-decyldimethylamine (Found: C, 78.0; H, 14.3; N, 7.7. $C_{12}H_{17}N$ calcd.: C, 77.8; H, 14.7; N, 7.6%.) and cyclopentyldimethylamine [34]. 2-Butyldiisopropylamine was prepared from 1-cyano-1-diisopropylaminoethane and ethylmagnesium bromide according to the method described by Kuffner [28]. The same method was used to synthesize 2-diisopropyldecylamine (Found: C, 79.1; H, 14.7. Mol. wt. (mass spectroscopy), 241. $C_{16}H_{35}N$ calcd.: C, 79.6; H, 14.6%. Mol. wt., 241.)

Bis(1-methyl-π-allyl)dipalladium dichloride was prepared according to the method of Hüttel [14a].

Bis(benzonitrile)palladium dichloride was prepared as described by Kharasch [35].

Bis(dimethylamino)palladium dichloride [36] was prepared by stirring a suspension of palladium dichloride for 12 h in a THF solution containing dimethylamine.

Bis(ethene)dipalladium tetrachloride [(I), $R = R^1 = H$] was prepared as described by Kharasch et al. [35].

Bis(butene)dipalladium tetrachloride (I, $R = R' = CH_3$) [37]. Bis(benzonitrile)palladium dichloride (5.0 g, 13.0 mmol) was suspended at —30° under dry nitrogen atmosphere in 30 ml 1-butene and 5 ml THF in a Fisher and Porter glass autoclave equipped with a magnetic stirrer. The cooling was removed and stirring was continued for 12 h at room temperature. After renewed cooling to about —20° the mixture was filtered under butene atmosphere to yield essentially pure bis(butene)dipalladium tetrachloride (2.5 g, 82%). After 30 min at room temperature, part of the complex was treated with cyclooctadiene to give 1-butene, *trans*-2-butene, and *cis*-2-butene in a ratio of 1/1/8.

General procedure for the amination of olefins

The palladium complex (1.57 mmol) was suspended in a solution of the proper olefin (1 ml) in dry tetrahydrofuran (THF 10 ml) under nitrogen atmosphere. The mixture was stirred for 15 min at 0°, then cooled or heated to the desired reaction temperature (Table 1). A solution of the appropriate amine (1 ml) in THF (5 ml) was added dropwise over a period of 30 min. The reaction temperature was maintained for 1 h. The system was then flushed with hydrogen, and the mixture was allowed to reach room temperature under hydrogen atmosphere. After 1—5 h the reduction was generally complete. The black precipitate, probably a mixture of palladium hydrides and palladium, was removed by filtration and washed with 15 ml THF. Internal standard was added to the combined filtrates, and the mixture was diluted with THF to 25 ml. The yields were then determined by GLC. In some control cases, the yields were also determined by isolation of the amines. The yields obtained in this way were about 5% lower than those obtained by GLC.

The product amines could also be set free from the palladium—σ-alkyl complexes by reduction with sodium tetrahydridoborate or hydrolysis with concentrated hydrochloric acid. Surprisingly, attempts to separate 1-butyldimethylamine and 2-butyldimethylamine by GLC were unsuccessful. The relative yields of 1-butyldimethylamine and 2-butyldimethylamine were therefore determined by mass spectroscopy (peaks at *m/e* 58 and 72, respectively. A standard curve was made with different relative concentrations).

Due to interference with the solvent (THF), the yields of the butylamines and the butylmethylamine were difficult to determine by GLC. These compounds were therefore acetylated prior to the GLC determination.

Amination of ethene. The palladium chloride—benzonitrile complex (0.6 g, 1.57 mmol) was suspended in dry tetrahydrofuran (THF, 10 ml) under nitrogen. An overpressure of ethylene (3 atm) was introduced and the mixture kept for 30 min under stirring at 0°. A solution of diethylamine (1 ml) in THF (5 ml) was added dropwise during 5 min. During addition of the amines the pressure was reduced to 1.2 atm. After the addition the ethylene pressure was again raised and kept for 1 h. Hydrogen was introduced and allowed to react for 5 h. Triethylamine was obtained in 100% yield as determined by GLC.

Amination of cyclohexene. Cyclohexene and bis(benzonitrile)palladium dichloride were reacted in the usual way. Partial precipitation of bis(cyclohexene)dipalladium tetrachloride occurred. The temperature was lowered to —50°, and dimethylamine was added. A palladium complex started to precipitate at once. After 5 h the precipitate was isolated and identified as bis(dimethylamino)-palladium dichloride (60% yield). Treatment of the residual solution with hydrogen or sodium tetrahydridoborate gave only traces of cyclohexyldimethylamine.

Amination of butenedipalladium tetrachloride (I) $R = R' = CH_3$. Butenedipalladium tetrachloride [(I), $R = R' = CH_3$] (0.59 g, 1.1 mmol) was suspended in dry tetrahydrofuran at —50°. The appropriate excess of 1-butene was then added, followed by dimethylamine or a mixture of dimethylamine and added base (Table 4). The reaction was left at —50° for 1 h, hydrogen was introduced, and the external cooling was removed. After 5 h the mixture was filtered through a short silica column, and the yield was determined by GLC (Table 4). In one experiment, the reaction mixture was left at —50° for 6 h before introduction of hydrogen. No increase in the yield was observed (Table 4).

Attempted formation of π-allyl complexes from trimethylamine and bis(1-butene) dipalladium tetrachloride (I), $R = C_2H_5$

Bis(1-butene)dipalladium tetrachloride (I) (0.3 g, 1.29 mmol palladium) was suspended in 10 ml THF containing 1 ml (11 mmol) 1-butene. Trimethylamine (1 ml, 11.4 mmol) was added during 0.5 h at 0°. Evaporation at 0° gave essentially pure bis(trimethylamine)palladium dichloride (0.35 g, 92%). No π-allyl complex could be detected by NMR of the crude product.

The same product was obtained when the reaction was carried out at —50°.

Attempted isolation of an intermediate palladium—σ-alkyl complex

Bis(ethene)dipalladium tetrachloride was aminated in the usual way with dimethylamine at —45°. The solvent and excess dimethylamine were removed in vacuo at —70°. It has not yet been possible to purify sufficiently the crude σ-complex obtained in this way since it is thermally labile and contains dimethylaminehydrochloride which is not readily separated from the σ-alkyl complex. On hydrogenation of the crude σ-complex ethyldimethylamine was formed. The NMR spectrum consists of a broad multiplet at 2.4—2.95 which appears to be partly hidden by the signals from dimethylaminehydrochloride. No olefin is present in the crude σ-complex. Further studies are required to determine the structure of the σ-complex.

Amination of the decene—tributylphosphine complex of palladium dichloride (IIa)

An excess of decene was reacted with bis(benzonitrile)palladium chloride (0.60 g, 1.57 mmol) in 7 ml THF at 0°. The solution was cooled to —50°, and tributylphosphine (0.317 g, 1.57 mmol) in THF (5 ml) was added dropwise, causing the yellow-brown solution to become pale, clear orange. Addition of amine at —25° or below produced a yellow solution. After reduction the amines were obtained in about 40% yield (Table 3).

All attempts to prepare a decene complex from bis(tributylphosphine)-palladium dichloride failed.

Amination of the decene—carbon monoxide complex of palladium chloride (IIb)

The decene—palladium chloride complex, prepared in situ as described above, was exposed to carbon monoxide at —50°. After about 0.25 h, when one equivalent had been absorbed, the carbon monoxide uptake ceased. A tan-coloured solid precipitated. Addition of amine produced a clear brown solution. After reduction with sodium tetrahydridoborate the product amines were obtained in about 10% yields (Table 3).

Mercury-promoted aminations

Mercuric chloride (2.72 g, 10 mmol) was dissolved in dry THF (20 ml) under nitrogen atmosphere. Decene (4 ml) was added during 5 min. The mixture was stirred for 15 min, and a solution of 3 ml diethylamine in 10 ml THF was added during 30 min. The reaction mixture was stirred for 72 h at 25°. Sodium tetrahydridoborate (0.4 g) was adeed. The solution immediately became dark. The mixture was stirred for 1 h. Sodium hydroxide (2 *M*, 30 ml) and ether (30 ml) were added, and the organic phase was extracted with acid. The water phase was washed with ether, made alkaline and extracted with ether. The amination product (0.64 g, 30%) was identified as 2-decyl-diethylamine [31]. No 1-isomer could be detected by GLC.

Contrary to what has been observed for other similar systems [21a], a reduction with lithium tetrahydridoaluminate produced the same results as the hydridoborate reduction.

Cis- and *trans*-2-butene were also aminated in the same way, but the yields were very low (6.9 and < 0.5%, respectively, Table 3).

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