Inorganica Chimica Acta 362 (2009) 2015–2019

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

On factors influencing insertion of allylic substrates in Pd–C_{aryl} bonds

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ARTICLE INFO

Article history:
Received 19 June 2008
Received in revised form 5 September 2008
Accepted 14 September 2008
Available online 21 September 2008

Keywords:
Palladium(II) aryl complexes
Allylic substrates
Insertion reactions

ABSTRACT

The main products of reactions between palladium(II) aryl complexes [PdArI(phen)] (**1a**, Ar = C_6H_5–; **2a**, Ar = 4-MeO–C_6H_4–; **3a**, Ar = 4-CF_3–C_6H_4–; phen = 1,10-phenanthroline), [Pd(C_6H_5)Cl(phen)] (**1b**) or [PdAr(phen)(MeCN)]BF_4 (**1**, Ar = C_6H_5–; **3**, Ar = 4-CF_3–C_6H_4–) with allylic substrates CH_2=$CHCH_2$A, where A = OH, OR, OCOR, CN or NMe_3^+ (R = Et or C_6H_5), or 2,5-dihydrofuran were identified. The nature of the products affords information on mechanistic features of arylation of allylic substrates prompted by Pd(II), meanwhile allowing comparison with analogous Pt(II) reactivity. A most noteworthy difference concerns the fate of the early insertion product derived from cationic complexes, containing the moiety $ArCH_2$-$CH(M^{II})CH_2$A. The product can be obtained, in case metal is platinum, only in the absence of a coordinating solvent, and evolves via CAr,H oxidative addition followed by H,A elimination and formation of a stable σ,π-chelated arylallyl moiety, thus avoiding β-elimination. The corresponding palladium species, again in the absence of coordinating species, affords a σ-derivative prone to β-elimination. The choice between the two possible elimination pathways is dictated by the relative stabilities of the end products (both retaining the A function) of the two chains of sequential equilibrium steps.

1. Introduction

The attainment of C–C bonds by metal-induced reaction of an hydrocarbyl group with an unsaturated hydrocarbon is the main achievement of organometal chemistry. Within this area interest assessed by far [1] for arylation of allylic substrates is increased even presently by the effective use of ionic solvents [2,3] or water [4] and by the chance of obtaining new cyclic products [5]. Despite the fact that palladium is the more useful metal in insertion promotion, many mechanistic investigations on allylic substrates, also from our laboratory [6–8], dealt in various grades with platinum chemistry. In fact, the aim of rationalizing the factors of mechanistic relevance gains substantial advantage by the expected minor lability and easier accessibility as isolated compounds of platinum intermediates in comparison with analogous palladium species. However, even recognizing many similarities in the behaviour of the two d^8 ions, extension of results from Pt(II) to Pd(II) has to take into account the possible substantial differences, as at least suggested by the substantial lack of activity of Pt(II) [9] in Heck catalysis. Thus, notwithstanding the expected failure in attempts to isolate intermediates, a direct study of palladium activity in stoichiometric reactions appeared of interest. This work aimed to gain more insight in the insertion of allylic substrates in Pd-aryl moieties and to compare results with platinum chemistry.

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doi:10.1016/j.ica.2008.09.027

2. Experimental

2.1. Materials and methods

All air-sensitive compounds were prepared and handled under a nitrogen atmosphere using standard Schlenk techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under a nitrogen atmosphere. Deuterochloroform (99.8%) and trideuteronitromethane were purchased from Aldrich. ^{1}H NMR spectra were obtained on 200 MHz Varian or 300 MHz Gemini spectrometer. $CDCl_3$ ($CHCl_3$, δ = 7.26 ppm as internal standard), CD_3NO_2 (CHD_2NO_2, δ = 4.33 ppm) and CD_3CN (CHD_2CN, δ = 1.93 ppm) were used as solvents. [Pd(4-R-C_6H_4)I(tmeda)] [10] and [Pd(C_6H_5)Cl(phen)] (**1b**) [11] have been prepared as described.

2.2. Synthesis of 1a–3a

To a stirred solution of [Pd(4-R-C_6H_4)I(tmeda)] (1.36 mmol) in CH_2Cl_2 (30 ml), 1,10-phenantroline (0.425 g, 2.72 mmol) was added. After 36 h stirring at room temperature, the precipitated yellow [Pd(4-R-C_6H_4)I(phen)] was recovered by filtration, washed with CH_2Cl_2 (3 mL) and dried in vacuo. Yield 90%.

Compound **1a**: *Anal.* Calc. for $C_{18}H_{13}IN_2Pd$: C, 44.06; H, 2.67; I, 25.87; N, 5.71; Pd, 21.69. Found: C, 43.97; H, 2.64; I, 25.80; N, 5.68; Pd, 21.73%. ^{1}H NMR in $CDCl_3$: 9.95 (d, 1H, H_2, phen, ^3J = 4.2 Hz); 8.45 (d, 2H, H_4, H_7 phen, ^3J = 4.5 Hz); 8.00–7.43 (m,

3H, H_5, H_6, H_9, phen); 7.75–7.63 (m, 2H, H_3,H_8, phen); 7.58–6.80 (m, 5H, C_6H_5).

Compound **2a**: *Anal.* Calc. for $C_{19}H_{15}IN_2OPd$: C, 43.83; H, 2.90; I, 24.37; N, 5.38; O, 3.07; Pd, 20.44. Found: C, 43.75; H, 2.88; I, 24.42; N, 5.35; O, 3.09; Pd, 20.40%. ^{1}H NMR in $CDCl_3$: 9.85 (d, 1H, H_2, phen, ^3J = 4.2 Hz); 8.47 (d, 2H, H_4, H_7, phen, ^3J = 4.5 Hz); 8.04–7.80 (m, 5H, H_3, H_5, H_6, H_8, H_9, phen); 7.71–6.77 (m, 4H, C_6H_4); 3.80 (s, 3H, OCH_3).

Compound **3a**: *Anal.* Calc. for $C_{19}H_{12}F_3IN_2Pd$: C, 40.85; H, 2.17; F, 10.20; I, 22.72; N, 5.01; Pd, 19.05. Found: C, 40.76; H, 2.16; F, 10.18; I, 22.75; N, 5.98; Pd, 19.07%. ^{1}H NMR in $CDCl_3$: 9.90 (d, 1H, H_2, phen, ^3J = 4.2 Hz); 8.51 (d, 2H, H_4, H_7, phen, ^3J = 4.5 Hz); 8.00–7.60 (m, 5H, H_3, H_5, H_6, H_8, H_9, phen); 7.75–7.20 (m, 4H, C_6H_4).

2.3. Synthesis of [Pd(4-R-C_6H_4)(CH_3CN)(phen)]$^+BF_4^-$ (1, R = −H; 3, R = −CF_3)

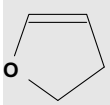
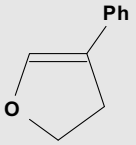
The new trifluoromethyl derivative **3** has been prepared as reported for phenyl compound **1** [6]. Both complexes were stored in nitrogen at −20 °C.

Compound **3**: *Anal.* Calc. for $C_{21}H_{15}BF_7N_3Pd$: C, 45.07; H, 2.70; B, 1.93; F, 23.77; N, 7.51; Pd, 19.02. Found: C, 45.00; H, 2.69; B, 1.93; F, 23.75; N, 7.49; Pd, 19.04%. ^{1}H NMR (CD_3NO_2): δ 9.05 (d, 1H, H_2, phen, ^3J = 3.5 Hz); 8.82 (dd, 2H, H_4, H_7, phen, ^3J = 4.5 Hz, $^3J'$ = 3 Hz); 8.26–8.10 (m, 4H, H_3, H_5, H_6, H_8, phen); 7.82 (app q, 1H, H_9, phen); 7.69–7.43 (m, 5H, C_6H_5); 2.55 (s, 3H, CH_3CN).

2.4. General procedure for the reactions of neutral complexes (1a, 2a, 3a, 1b)

To a stirred suspension of the complex (0.2 mmol) in $CDCl_3$ (1.5 ml), an equimolar amount of the allylic substrate dissolved in $CDCl_3$ (0.20 mg/μl) was added. The mixture was stirred at room temperature with the periodical monitoring of the reaction advancement by the recording of ^{1}H NMR spectra. After reaction completion Pd metal was removed by centrifugation. After filtration on a small bed of Florisil, ^{1}H NMR spectroscopy allowed the identification of 4-R-$C_6H_4CH_2CH_2CHO$ obtained with yields ranging 65–90% (see Table 1).

Table 1
Reaction of allyl substrate with palladium(II) aryl complexes

Allyl substrate	Complex	Organic product	Yield[a]
CH_2=$CHCH_2OH$	**1a**	$C_6H_5(CH_2)_2CHO$	90
	2a	4-MeO–$C_6H_4(CH_2)_2CHO$	85
	3a	4-CF_3–$C_6H_4(CH_2)_2CHO$	75
	1b	$C_6H_5(CH_2)_2CHO$	80
	1	$C_6H_5(CH_2)_2CHO$	60
		$C_6H_5CHMeCHO$	30
	3	4-CF_3–$C_6H_4(CH_2)_2CHO$	60
		4-CF_3–$C_6H_4CHMeCHO$	30
CH_2=$CHCH_2OC_6H_5$	**1**	$C_6H_5(CH_2)_2CH_2O$ C_6H_5	90[b]
	3	4-CF_3–C_6H_4–$(CH_2)_2CH_2O$ C_6H_5	85
CH_2=$CHCH_2OEt$	**1**	$C_6H_5(CH_2)_2CH_2OEt$	90[b]
CH_2=$CHCH_2OCOMe$	**1**	$C_6H_5(CH_2)_2CH_2OCOMe$	90[b]
CH_2=$CHCH_2OCO$ C_6H_5	**1**	$C_6H_5(CH_2)_2CH_2OCO$ C_6H_5	90[b]
CH_2=$CHCH_2CN$	**1**	$C_6H_5(CH_2)_2CH_2CN$	65[c]
CH_2 = $CHCH_2NMe_3^+$	**1**	$C_6H_5(CH_2)_2CH_2NMe_3^+$	65[c]
	**1**		80[c]

[a] ^{1}H NMR yield based on the amount of allyl substrate used.
[b] Based on Pd-derivatives.
[c] Based on isolated product.

2.5. General procedure for the reactions of cationic complexes (1), (3)

To a stirred solution of the complex (0.2 mmol) in CD_3NO_2 (1.5 ml), an equimolar amount of the allylic substrate dissolved in $CDCl_3$ (0.20 mg/μl) was added. The mixture was stirred at room temperature with the periodical monitoring of the reaction advancement by ^{1}H NMR spectra. After reaction completion part of the mixture was filtered on a small bed of Florisil. ^{1}H NMR spectroscopy of isolated fractions allowed the identification of products. Hydrogenolysis of another part with excess $NaBH_4$ and filtration as above allowed to identify the organic moieties still bounded to metal. For a better assessment of eventual presence of unsaturated bonds in residual moieties, protonolysis with HCl was made in some case.

Selected ^{1}H NMR signals of types I and II species from the reaction of **1 and 3** with CH_2=CH–CH_2O–C_6H_5:

From **1**:

I, (CD_3NO_2): δ *7.50–7.00* (m, 5H, C_6H_5); 7.20–6.90 (m, 5H, O–C_6H_5); 4.56 (t, 1H, C_6H_5–CH, ^3J = 6.9 Hz); 4.25 (dt, 2H, CH_2O, ^3J = 4.4); 2.37 (app q, 2H, –CH_2–, ^3J = 6.9 Hz, $^3J'$ = 4.4 Hz).

II, (CD_3CN): δ *7.40–7.10* (m, 5H, C_6H_5); 7.20–6.90 (m, 5H, O–C_6H_5); 5.20 (dd, 1H, C_6H_5–O–CH, ^3J = 4.1); 3.10 (m, 2H, C_6H_5-CH_2); 2.40 (m, 2H, –CH_2–).

From **3**:

I, (CD_3CN): δ *7.80–7.20* (m, 4H, CF_3–C_6H_4); 7.00–6.80 (m, 5H, O–C_6H_5); 4.90 (t, 1H, CF_3–C_6H_4–CH, ^3J = 6.9 Hz); 4.30 (dt, 2H, CH_2O, ^3J = 4.4); 2.37 (app q, 2H, –CH_2–, ^3J = 6.9 Hz, $^3J'$ = 4.4 Hz)

II, (CD_3NO_2): δ *7.80–7.20* (m, 4H, CF_3–C_6H_4); 7.00–6.80 (m, 5H, O–C_6H_5); 5.22 (dd, 1H, C_6H_5–O–CH, ^3J = 4.1); 3.20 (m, 2H, CF_3–C_6H_4–CH_2); 2.49 (m, 2H, –CH_2–).

3. Results and discussion

3.1. Reagents and general reaction procedures

The unsaturated substrates were of the type CH_2=$CHCH_2A$, where A = OH, OR, OCOR, CN or NMe_3^+ (R = ethyl or phenyl). Also a cyclic allylic system, i.e., 2,5-dihydrofuran, was used.

The choice of the complexes was dictated by the aim of homogeneous comparison between the wanted results and the previous findings on platinum complexes [6,7] with the same coordinative environment.

Three neutral complexes of general formula PdArI(phen) (**1a**, Ar = C_6H_5–; **1b**, Ar = 4-MeO–C_6H_4–; **1c**, Ar = 4-CF_3–C_6H_4–; phen = 1,10-phenanthroline) were used. The simple phenyl derivative has been quoted before [6], but no synthetic detail or product characterization was given. The three complexes were obtained as suggested by previous results [9] according to Eq. (1)

$$[PdArI(Me_2NCH_2)_2] + phen = [PdArI(phen)] + (Me_2NCH_2)_2 \qquad (1)$$

The tetramethylethylenediamine precursors were obtained as previously reported [9] also in the case of the new trifluoromethyl complex. The complex [Pd(C_6H_5)Cl(phen)] and the corresponding cationic species **1** were previously obtained in our laboratory [8].

The synthesis of cationic complexes of general formula [PdAr(phen)(MeCN)]BF_4 was attempted by the standard reaction of the suited iodo neutral complex with Ag^+ in the presence of acetonitrile. While compounds **1** and **3** could be isolated, respectively, from **1a** and **3a**, halide abstraction from **2a** afforded decomposition with the release of C_6H_5OMe and (4-MeO–C_6H_4–)$_2$ [12].

The ^{1}H NMR spectra of all complexes show that the two halves of the chelated phen are not equivalent, showing also that in the cationic species the exchange between the nitrogen atoms of the chelate is slow on the NMR time scale.

The general procedure here adopted for the reactions involved a 1.35 M solution of the complex in the suited deuterated solvent

and an equimolar amount of the allylic substrate (dissolved in a minimum volume of the same deuterated solvent) at room temperature. Solubility of complexes required the use of a different solvent for neutral (chloroform) and cationic (nitromethane) species. Although the ^{1}H NMR spectra of the reaction mixture appeared too complicated for sound identification of the products in some case, at least monitoring of a suited reagent signal allowed to assess the reaction completion. Part of the reaction mixture was analyzed by chromatography in order to isolate and identify the directly released organic compounds. Another part was treated with $NaBH_4$ to recover organic fragments not eliminated from the metal. In some case, also protonolysis with HCl was made with the same purpose. Identification of organic products was obtained by the comparison of ^{1}H NMR and mass spectra with those of authentic samples or the literature data.

As a general observation on the results, it is to be noted that neutral complexes were efficient promoters of the reaction only in case the unsaturated substrate was allyl alcohol. Otherwise only the cationic species afforded the products in sufficiently short time to prevent unwanted secondary transformation of the early insertion products.

3.2. Reactions of allyl alcohol with neutral complexes

During the reaction of equimolar amounts of a neutral complex (**1a**–**3a**) and the alcohol in $CDCl_3$, slow separation of palladium metal was observed. The time required for the completion of the reaction was significantly influenced by the nature of the complex. In fact ca.12 h was required for 1a, ca. 24 h for **1b**, while for the trifluoromethyl derivative about 10 days were needed, with conversion less than 10% after 24 h.

In all cases, the analysis of the mixture as such indicated that the process has the pattern depicted by Eq. (2)

$$[PdXAr(phen)] + CH_2{=}CHCH_2OH = ArCH_2CH_2CHO + phen + HX + Pd \quad (2)$$

Very little trace of propanal was also observed.

The mechanism claimed to be operated in this type of processes is well known and involves steps: (i) substitution of halide by the unsaturated species $CH_2{=}CHCH_2A$; (ii) insertion to afford the fragment $CH(CH_2Ar)CH_2A$; (iii) hydrogen shift to yield a metal hydride with π-coordinate $ArCH_2CH{=}CHA$; (iv) release of the arylated product; (v) tautomerization to give the final product.

Our results prompt three comments. First, the reactivity trend of the complexes correlates with the inductive effect of the 4-substituent on the ability of the metal to release (i) the anionic X.

It is also to be noted that the presence of the halide in the starting complex is expected to prompt an easy removal of the reactive hydride through the elimination of HX. This appears as the rationale for the high chemoselectivity, as well as for the very scarce production of propanal (prompted by the hydride). Finally, it is to be noted that the observed chemoselectivity could in principle be ascribed to the stereoselectivity of both insertion (ii) and β-elimination (iii) steps.

In fact, the C=C bond polarization by the OH group prompts an easier formation of the Pd–C σ-bond involving the central allyl carbon in (ii). On the other hand, the substantially irreversible conclusive tautomerization of $ArCH_2$–CH=CHOH is the step that definitively removes the organic product. The alternative pathway affording $ArCH{=}CHCH_2OH$ is not observed, owing to the known reversibility of the β-elimination process in palladium chemistry, and eventually feeds the irreversible selective formation of the linear arylpropanal.

3.3. Reaction of cationic complexes with allyl alcohol

Monitoring by ^{1}H NMR, the reaction between equimolar amounts of the complex (**1** or **3**) and allyl alcohol in CD_3NO_2 indicated that the reaction was complete in ca. 30 min. No appreciable precipitation of metal was observed. Analysis of the reaction mixture disclosed the presence of the linear aldheyde $Ar(CH_2)_2CHO$ and of the isomer ArCHMeCHO (Ar = C_6H_5 or 4-CF_3–C_6H_4–) in ca. 3:1 ratio [13]. Minor presence of propanal was also detected. The presence of the latter product seems to find a rationale in the absence of the halide, allowing a longer life to the reactive hydride. The higher durability of it is in keeping with the production of propanal by isomerization of the alcohol, and with the addition of other steps (ii–iv, Scheme 1), affording the branched product, to those (previous section) affording the linear aldheyde.

The additional sequential equilibria are similar to the ones invoked for the attainment of $C_6H_5CHMeCH_2CHO$ in palladium-catalyzed phenylation of 3-butenol [14].

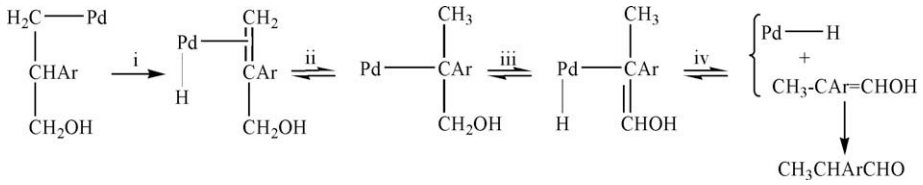
However, decrease in chemoselectivity with respect to the performance of neutral complexes needs explanation, since the early reactive species should be in both cases $[PdAr(CH_2{=}CHCH_2OH)(phen)]^+$. The finding seems to be correlated to the difference in dielectric constant of the two solvents and to the presence of the halide. For a neutral complex, the low dielectric constant of chloroform, together with the presence of the good σ-donor X^-, is expected to favor the presence of ion pairs of type $[\{PdAr(CH_2{=}CHCH_2OH)(phen)\}^+X^-]$ apt to influence the insertion regiochemistry [15]. In nitromethane and in the absence of a good σ-donor the alternative path for insertion reasonably involves the intramolecular assistance of OH via a 5-terms ring [16] and σ-bonding of the allylic terminal carbon to the metal.

The substantial absence of palladium metal in the final mixture points to a fair "stability" of the metal hydride. In fact, the use of excess allyl alcohol in the reaction or addition of more alcohol after reaction completion affords substantial amounts of propanal, thus confirming the presence of hydride with isomerising ability. Final loss of this ability is attained by the formation of the stable $[Pd(phen)(\eta^3\text{-}CH_2CHCH_2)]^+$, identified by ^{1}H NMR spectroscopy and reasonably produced by water elimination from the hydride/allyl alcohol complex.

3.4. Reaction of cationic complexes with $CH_2{=}CHCH_2A$ (A = OEt, OC_6H_5, OCOMe, $OCOC_6H_5$)

The reactions of cationic complexes 1 have been performed in CD_3NO_2 following the general procedure. Within 30 min substantial disappearing of the organic reagent was observed, in the absence of metal precipitation. Treatment of the reaction mixture with $NaBH_4$ afforded $C_6H_5(CH_2)_3A$ as in the schematic Eq. (3) in yields exceeding 80%.

$$[PdC_6H_5(phen)(MeCN)]^+ + CH_2{=}CHCH_2A \longrightarrow \text{Pd-derivatives} \xrightarrow{NaBH_4} Pd + C_6H_5(CH_2)_3A + phen + MeCN \quad (3)$$



Scheme 1.

Attempts to isolate the original palladium species containing the organic moiety failed. Anyway, fair grounds for structure assignment to the major intermediate were given by ^{1}H NMR spectra of the reaction mixture. Particularly, in case A = OC_6H_5, spectra indicated the presence of the moiety Pd–CH(C_6H_5)$CH_2CH_2OC_6H_5$. In detail, signals at δ 4.56 (1H, t, C_6H_5CH), 4.25 (2H, dt, CH_2O part. overlap with CHD_2NO_2), and 2.37 (2H, app.q, CH_2) were observed. Phenyl signals occurred as well-resolved groups at 6.9 and 7.2 δ (5H, OC_6H_5), while a broad group (5H) detected in the 7–7.5 range could be ascribed to C–C_6H_5. Further information derived from addition to the final mixture, again in case A = OC_6H_5, of an equal volume of deuteroacetonitrile. Slow transformation of the early product in a complex displaying ^{1}H NMR signals was observed supporting the sequence Pd–CH(OC_6H_5)$(CH_2)_2C_6H_5$: δ 5.2 (1H, dd, C_6H_5OCH), 3.1 (2H, m, $CH_2C_6H_5$), 2.4 (2H, m, CH_2). Moreover, the addition of excess allylphenyl ether to the mixture prompted the fast release of $C_6H_5CH{=}CHCH_2OC_6H_5$, while the added allylphenyl ether gradually isomerized to $MeCH{=}CHOC_6H_5$.

On the ground of above results, the reaction mechanism depicted in Scheme 2 appears quite plausible.

According to the scheme, the fate of the early product of the reversible hydride insertion/deinsertion would mainly depend on the stabilization of the final complex. In pure nitromethane (steps i–iv), the β-elimination from methylene adjacent to the unsubstituted phenyl is suited to afford a stable type I intermediate that on treatment with $NaBH_4$ produces $C_6H_5(CH_2)_3OC_6H_5$, while in the presence of free $CH_2{=}CHCH_2OC_6H_5$ affords $C_6H_5CH{=}CHCH_2OC_6H_5$. In this latter case, the excess of ether is isomerized to $CH_3CH{=}CHOC_6H_5$.

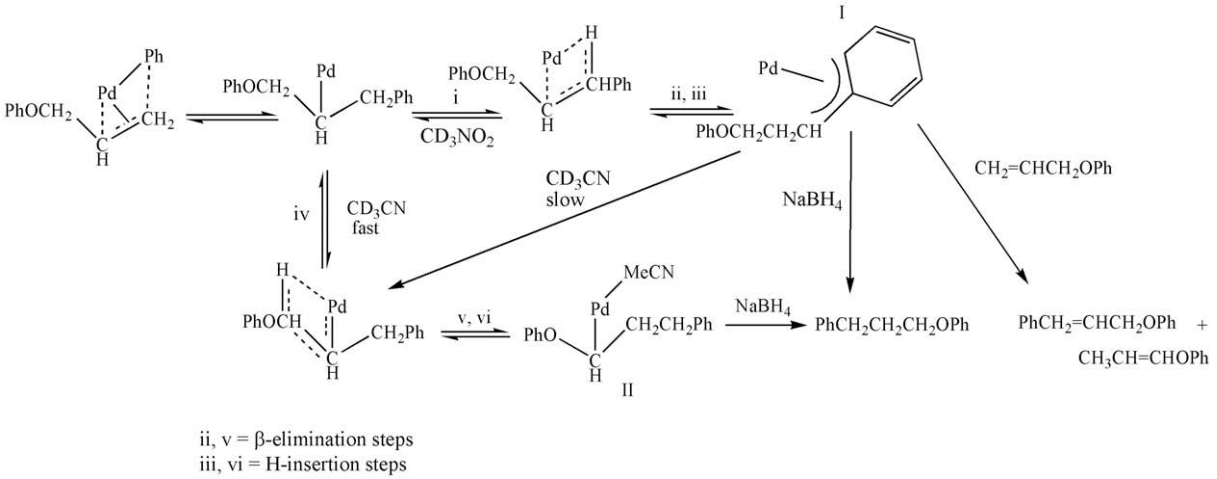
As for structure attribution to I, we recall that analogous assignments in palladium [7] or nichel chemistry [16] had been suggested previously. In fact, ^{1}H NMR spectra do not allow to rule out the alternative assignment of an oxopalladacycle structure [17]. However, this hypothesis finds less convincing ground in the behaviour of **3** (below).

On the other hand, in the presence of a solvent apt to fill the coordinative unsaturation subsequent to the insertion step, it is expected (steps v–vii in the scheme) that the preferred β-elimination involves the methylene near the OC_6H_5 group, affording double bond shift from the allylic to the vinylic position [18]. Accordingly, reinsertion of hydride affords a type II, instead of I, stable end product.

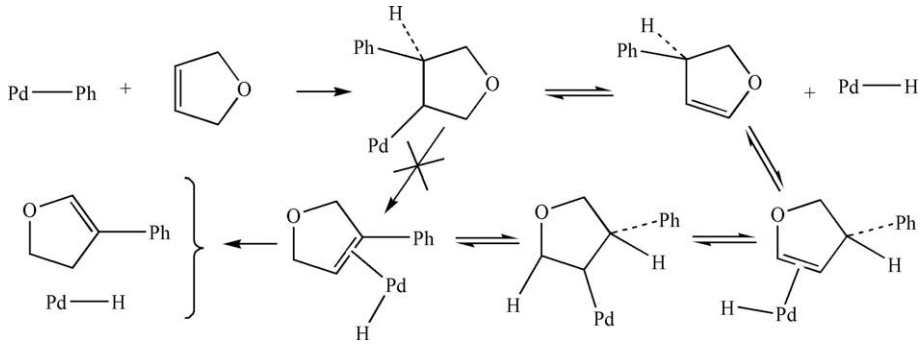
The use of **3** in reaction with allylphenyl ether in nitromethane, carried as for **1**, affords directly a type II species, as indicated by the ^{1}H NMR spectra of the reaction mixture. Treatment with $NaBH_4$ afforded 4-CF_3–C_6H_4–$(CH_2)_3OC_6H_5$ in 75% yield. This finding is of further support to the attribution of the η^3 bonding in I. In fact, it is reasonable that the presence of the electron-withdrawing CF_3 and $CHPd^+$ on the benzene ring is a more significant drawback for η^3-coordination than for oxopalladacyclus formation, enhancing importance of path to II even in the presence of only one equimolar amount of MeCN. In this case, type I species has been obtained in a separate experiment by generating in situ "[(1,10-phen)Pd–$C_6H_4CF_3$]$^+$" through the reaction of **3a** with $AgBF_4$ followed by the addition of $CH_2{=}CHCH_2OC_6H_5$. As expected, subsequent addition of CD_3CN afforded the type II compound.

3.5. Reactions of cationic complex 1 with $CH_2{=}CHCH_2A$ ($A = CN, NMe_3^+$)

In the same general conditions as in the previous section, in nitromethane, the allylic substrate disappeared in about 30 min. No isolated palladium compounds could be obtained, but spectroscopic ^{1}H NMR spectra pointed to a type I structure. Addition of $NaBH_4$ to the reaction mixture allowed to isolate, respectively, $C_6H_5(CH_2)_3CN$ and $[C_6H_5(CH_2)_3NMe_3]Cl$ in ca. 60% yield. As far as we know, no synthetic use of palladium-prompted allyl phenylation had been previously reported to obtain the aryl derivatives $Ar(CH_2)_3A$ reported here.



Scheme 2.



Scheme 3.

3.6. Reaction of 1 with 2,5 dihydrofuran

The reaction of 1 with the cyclic allylic system 2,5-dihydrofuran in deuteronitromethane was accompanied by the fast release of palladium metal. The reaction mixture contained 4-phenyl-2,3-dihydrofuran in ca. 70% yield. We recall that the Heck catalytic phenylation of 2,5-dihydrofuran instead affords 3-phenyl-2,3-dihydrofuran [19] through insertion of the double bond in Pd–C_{ar} and β-elimination on the oxygen side. Our unexpected result can find a rationale according to Scheme 3.

In fact, only in case β-elimination could occur on the phenyl side, the pathway affording the observed product could be activated. However, this type of elimination has to involve also in our case the early formation of 3-phenyl-2,3-dihydrofuran, otherwise the anti position of the H in the putative 4-phenyl-2,3-dihydrofuran palladium hydride derivative would forbid elimination. Thus, dissociation/re-association equilibria with configurational inversion at the coordinated double bond appear to be a needful feature of the mechanism.

As far as we know, no synthetic use of palladium-prompted allyl phenylation to produce 4-phenyl-2,3-dihydrofuran has been reported.

4. Conclusion

The main difference in reactivity of Pd^{II} and Pt^{II} emerging by the above results, beside the expected higher reactivity of palladium complexes (that in contrast with platinum can eventually react also as neutral species), concerns the fate of the early insertion product including the sequence $ArCH_2CH(M^{II})CH_2A$. As for platinum, even the attainment of the coordination of the allylic substrate requires the absence of a coordinating solvent. In this case, the C–H_{Ar} bond is activated, thus prompting *ortho*-metallation of the aryl ring, followed by HA elimination and formation of a σ,π-chelated arylallyl moiety depleted of the A function. Also in the absence of coordinating species, the early insertion of palladium product, through reversible deinsertion/reinsertion steps, affords a stable derivative, possibly a π-allyl species, where the organic moiety retains the A function. If a coordinating solvent is present, the more stable end product of the sequential equilibrium steps is instead a σ-derivative, also retaining the A function.

It is to be noted that the linear organic products are obtained in all cases, but for the reaction of allyl alcohol with cationic complexes, with very high regioselectivity. It is also noteworthy that the product deriving from the reaction of 2,5-dihydrofurane is 4-phenyl-2,3-dihydrofuran, while Heck catalytic phenylation produces 3-phenyl-2,3-dihydrofuran.

Acknowledgments

This work was financially supported by the Ministero dell'Universita' e della Ricerca Scientifica e Tecnologica (PRIN 2004). The authors thank the Centro Interdipartimentale di Metodologie Chimico-Fisiche (C.I.M.C.F.) of the University of Napoli "Federico II" for NMR facilities.

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