C. R. Chimie 5 (2002) 289–296

S1631074802013747/FLA

Effect of chloride ions on allylic diphosphine palladium (II) complexes: NMR characteristics and chemical reactivity

Grégory Malaisé[a], Laurent Barloy[a], John A. Osborn[a]* †, Nathalie Kyritsakas[b]

[a] *Laboratoire de chimie des métaux de transition et de catalyse, UMR 7513 CNRS, institut Le Bel, université Louis-Pasteur, 4, rue Blaise-Pascal, 67070 Strasbourg cedex, France*
[b] *Service commun des rayons X, faculté de chimie, institut Le Bel, université Louis-Pasteur, 4, rue Blaise-Pascal, 67070 Strasbourg cedex, France*

Received 31 January 2002; accepted 19 April 2002

This article is dedicated to the memory of John Osborn by his co-authors with deep respect and great affection.

Abstract – A systematic study of the effect of chloride ions on the NMR characteristics of several cationic diphosphine η^3-allyl palladium complexes has revealed in some instances a deshielding of the protons. Chloride ions also enhance the reactivity of the complexes. Thus [(Me-Duphos)(1,3-diphenylallyl)palladium]chloride leads mostly to [(Me-Duphos)dichloropalladium] and to chalcone at room temperature, whereas at low temperature a pair of cationic and anionic allyl palladium complexes is obtained. ***To cite this article: G. Malaisé et al., C. R. Chimie 5 (2002) 289–296*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

allyl palladium complex / chloride anions / NMR / reactivity / X-ray structure

Résumé – Effet des ions chlorure sur des complexes diphosphines allyliques du palladium : caractéristiques RMN et réactivité chimique. Une étude systématique de l'effet des ions chlorure sur les caractéristiques RMN de plusieurs complexes η^3-allyliques de palladium portant des ligands diphosphines a révélé que les protons étaient déblindés dans certains cas. Les ions chlorures réagissent également sur ces complexes. Ainsi, le chlorure de [(Me-Duphos)(1,3-diphenylallyl)palladium] se transforme essentiellement en complexe [(Me-Duphos)dichloropalladium] et en chalcone à température ambiante, tandis qu'à basse température, ce sont des complexes allyliques de palladium cationique et anionique qui sont obtenus. ***Pour citer cet article : G. Malaisé et al., C. R. Chimie 5 (2002) 289–296*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

complexes allyliques de palladium / anions chlorure / RMN / réactivité / structures radiocristallographiques

1. Introduction

$[Pd(C_3H_5)Cl]_2$ is often used as the palladium source in catalytic allylic substitution reactions, assuming that, in the presence of a bidentate ligand L_2, the cationic active species $Pd(C_3H_5)(L_2)^+$ is readily formed with Cl^- as a simple non-coordinating anion [1]. However, it has been reported that halide ions, and particularly Cl^-, can have an influence on the reactivity or the selectivity of Pd-catalysed [2–7] allylic substitution reactions. In some cases, it has been proposed that this influence is originated from the well-known increase of the isomerisation rate of the Pd η^3-allyl intermediates through η^3–η^1–η^3 interconversion [6–8]. The working models of the key catalytic intermediate are mostly cationic palladium

* *Correspondence and reprints.*
E-mail address: barloy@chimie.u-strasbg.fr (L. Barloy).
† Deceased 23 April 2000.

η^3-allyl complexes with a non-coordinating anion, e.g. triflate. The study of these models has proven to be particularly useful in asymmetric allylic alkylation with chelating chiral ligands [1]. If the anion is Cl^-, which is the case after the reaction of [Pd(η^3-allyl)Cl]$_2$ with 4 equiv monodentate ligand or 2 equiv bidentate ligand, the complex generally remains η^3-allyl: a cationic tetracoordinate complex with a non-coordinating chloride anion, both being present either as separate ions or as tight ion pairs, or a neutral pentacoordinate chloro complex [8–13]. However, neutral tetracoordinate palladium η^1-allyl chloro complexes have also been reported [14, 15].

We have been interested recently in phospholane-derived ligands and their use in palladium-catalysed allylic alkylation [16, 17]. We report hereafter our observations concerning the effect of chloride ions on the NMR characteristics and the chemical reactivity of some palladium(II) allyl complexes bearing the bis-phospholane ligands (*R*,*R*)-Me-Duxantphospholane or (*R*,*R*)-Me-Duphos, or the bis-phosphine ligand (*S*)-Binap.

2. Results and discussion

The palladium complexes we have studied by NMR spectroscopy are listed in Fig. 1. Adding a source of chloride ions (viz. 1 equiv tetraphenylphosphonium chloride) to a solution of [**1**]SbF_6 in deuterated chloroform induces a significant alteration of the allylic signals on the ^{1}H NMR spectrum (Fig. 2). At room temperature, the central allylic proton (H_c) of [**1**]SbF_6 appears as a pseudo-triplet at 6.73 ppm, with an expected value of 13 Hz for $^3J_{HH}$; the signals of the terminal allylic protons (H_t and H_t') are degenerate at 5.20 ppm, with coupling constants with the phosphorus in *trans* position ($^3J_{HP}$) of ca 13 Hz (Fig. 2a). Upon addition of Cl^-, the signals of the terminal allylic protons are strongly shifted to higher frequency at 5.46 and 6.04 ppm, whereas the chemical shift of the H_c signal is almost unchanged. However, the multiplicity and the coupling constants are globally unchanged; incidentally the value of $^3J_{HP}$ with the phosphorus *cis* (3.4 Hz) can be determined for the signal at 6.04 ppm. This shows that the allyl ligand remains η^3-coordinated and Me-Duphos η^2-coordinated on the palladium centre. In addition, both phosphorus atoms of Me-Duphos lie in the equatorial plane, by contrast with the nitrogens of neocuproine in the palladium chloro allyl complex described by Åkermark, Vitagliano et al. [8].

The chemical shifts of some other ^{1}H signals of [**1**]SbF_6 are also modified (although to a lower extent) in the presence of Cl^-, without any change of the coupling constants. The values of $\Delta\delta$ for the methyl

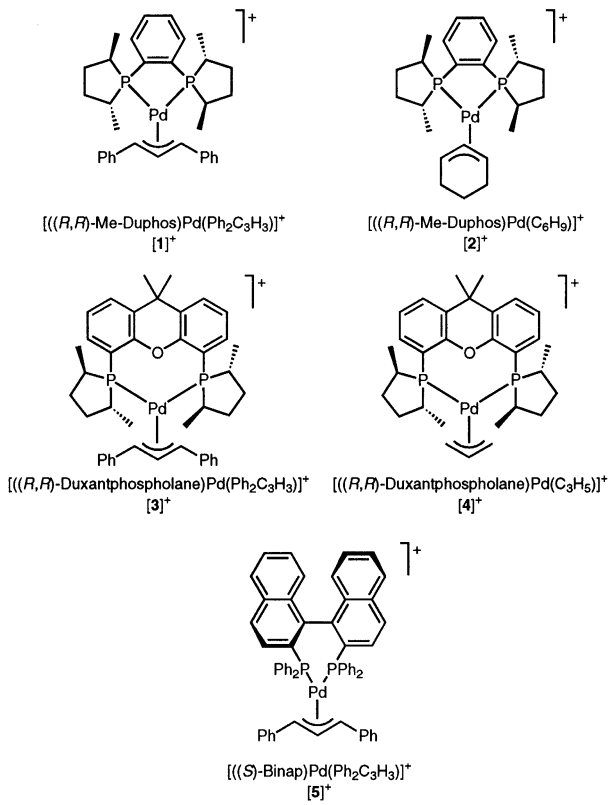

Fig. 1. Studied allylic diphosphine palladium (II) complexes.

signals of Me-Duphos are given in Fig. 3. One salient feature of the 'chloride effect' is that the nuclei located under the coordination plane are deshielded ($+0.12 \leq \Delta\delta \leq +0.84$ ppm), while those located above

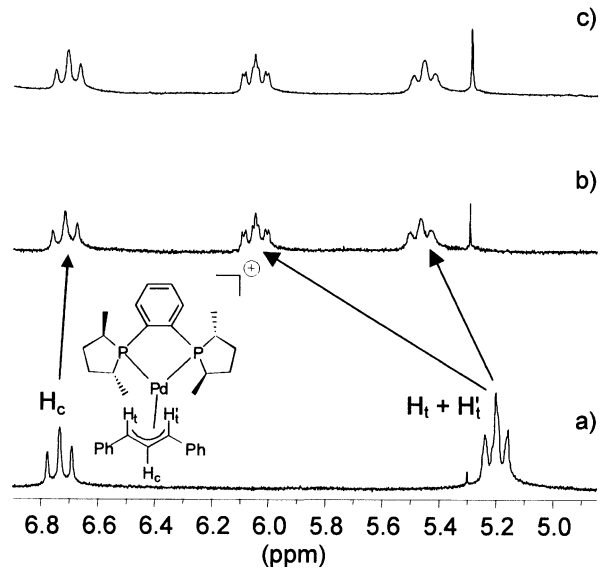

Fig. 2. Section of ^{1}H NMR spectra ($CDCl_3$, 298 K, 300 MHz) of (**a**) complex [**1**]SbF_6; (**b**) complex [**1**]SbF_6 + 1 equiv PPh_4Cl; (**c**) complex [**1**]Cl obtained from the reaction of 1 equiv [Pd(η^3-$Ph_2C_3H_3$)Cl]$_2$ with 2 equiv (*R*,*R*)-Me-Duphos.

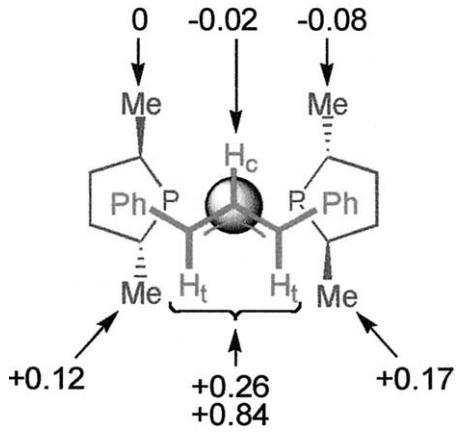

Fig. 3. Values of the chemical shift variations ($\Delta\delta$, ppm) of different proton signals of complex [**1**]SbF_6 upon addition of Cl^- in $CDCl_3$ at 298 K. The metallic centre is represented by the sphere.

are unchanged or little shielded ($-0.08 \leq \Delta\delta \leq 0$ ppm). In parallel, slight modifications of the $^{31}P\{^1H\}$ NMR spectrum of [**1**]SbF_6 in $CDCl_3$ are observed when 1 equiv Cl^- is added. The doublets of the AB system move from 65.5 and 69.0 ppm to 65.9 and 68.3 ppm, and the P–P coupling constant increases from 49 to 53 Hz. We observe that the NMR features of [**1**]Cl, obtained by reacting 1 equiv $[Pd(\eta^3\text{-}Ph_2C_3H_3)Cl]_2$ with 2 equiv (*R*,*R*)-Me-Duphos, are exactly identical to those of the addition product of PPh_4Cl with [**1**]SbF_6 (see for instance Fig. 2b and c). This suggests that SbF_6^- effectively behaves as an inert ion, whereas Cl^- displays a specific interaction with the cationic palladium complex.

In other solvents like CD_2Cl_2 or CD_3CN, similar changes on the ^1H NMR spectrum of [**1**]SbF_6 are induced by chloride ions, but to a lower extent (Table 1, entries 1–5). The terminal allylic signals move from 0.02 to 0.15 ppm when 1 equiv Cl^- is added, whereas the signals of H_c and of the protons of Me-Duphos are unchanged. In CD_2Cl_2, the H_t signals are shifted back to 5.10 ppm when the temperature is lowered from 298 to 233 K (entries 2–3).

We tested the effect of Cl^- on other palladium allyl complexes, changing either the substituents of the allyl ligand (complex [**2**]$^+$), the diphosphine ligand (complexes [**3**]$^+$ and [**5**]$^+$) or both (complex [**4**]$^+$) (Table 1, entries 6–15). Incidentally, the spectra of [**3**]SbF_6 were recorded at 193 K in order to visualise the signals of the frozen *exo* and *endo* isomers [16,

Table 1. Effect of chloride ions on the ^1H NMR allylic signals of palladium allyl complexes.

Entry	Complex	Solvent	*T* (K)	equiv PPh_4Cl added	H_t	H_c
1	[**1**]SbF_6	CD_2Cl_2	298	0	5.04 (13) 5.11 (13)	6.80 (12.9)
2	[**1**]SbF_6	CD_2Cl_2	298	1	5.18 (12) 5.26 (13)	6.80 (12.8)
3[a]	[**1**]SbF_6	CD_2Cl_2	233	1	5.10[c]	6.77 (12.8)
4	[**1**]SbF_6	CD_3CN	298	0	5.14[c]	6.90 (12.9)
5	[**1**]Cl[d]	CD_3CN	298	0	5.16 (10) 5.27 (11)	6.91 (12.9)
6	[**2**]BF_4	$CDCl_3$	298	0	5.94 6.00	5.42 (7.2)
7	[**2**]BF_4	$CDCl_3$	298	1	5.91 5.99	5.40 (7.1)
8[b]	[*exo*-**3**]SbF_6	CD_2Cl_2	193	0	4.68 (10.8) 5.38 (13.7, 9.4)	6.36 (13.8, 10.3, 2.4)
9[b]	[*exo*-**3**]SbF_6	CD_2Cl_2	193	1	4.68 (11.1) 5.38 (13.7, 9.4)	6.35 (13.7, 10.3, 2.3)
10[b]	[*endo*-**3**]SbF_6	CD_2Cl_2	193	0	4.89 (11.1) 5.01 (13.0, 9.2)	5.18 (12.5)
11[b]	[*endo*-**3**]SbF_6	CD_2Cl_2	193	1	4.92 (11.2) 5.05 (12.8, 9.7)	5.18 (12.5)
12	[**4**]SbF_6	CD_2Cl_2	263	0	2.44 (11), 2.61 (11)[e] 4.48, 4.60[f]	5.17
13[b]	[**4**]SbF_6	CD_2Cl_2	263	1	2.49, 2.67[e] 4.49, 4.62[f]	5.18
14	[**5**]BF_4	$CDCl_3$	298	0	4.55 (11.5)[g]	[h]
15	[**5**]BF_4	$CDCl_3$	298	1	4.95 (11.6)[g]	[h]

[a] Chemical shift data (ppm) of spectra recorded on a 300 MHz spectrometer unless otherwise stated. Numbers in parentheses are coupling constants *J* (Hz). The signals are multiplets or large signals (no value of *J* indicated), pseudo-triplets (one value of *J*), doublets of doublets (two values of *J*), or doublets of doublets of doublets (three values of *J*). H_t = terminal allylic protons; H_c = central allylic proton. The data provided for complexes [**1**]$^+$, [**3**]$^+$ and [**5**]$^+$ correspond to overwhelmingly major *syn–syn* isomers; two isomers *exo* and *endo* are observed for [**3**]$^+$ [16–19]. [b] Spectrum recorded at 500 MHz. [c] Two superimposed signals. [d] Obtained from the reaction of 1 equiv. $[Pd(\eta^3\text{-}Ph_2C_3H_3)Cl]_2$ with 2 equiv. (*R*,*R*)-Me-Duphos. [e] H_{anti}. [f] H_{syn}. [g] Only one signal visible [19]. [h] Not visible .

17]. Likewise, the spectra of [**4**]SbF_6 were recorded at 263 K, so that the classical chloride-induced *syn–anti* exchange of Pd-allyl complexes [13] would be frozen. By contrast with complex [**1**]$^+$, the ^{1}H NMR signals of the other complexes are not much affected by Cl^-, the chemical shift variation reaching at the most 0.06 ppm. One exception is complex [**5**]$^+$, the H_t signal of which is deshielded from 4.55 to 4.95 ppm. In summary, the deshielding effect of chloride ions is essentially observed on 1,3-diphenylallyl complexes.

In close analogy with our results, Godleski et al. have studied the ^{1}H NMR spectrum in $CDCl_3$ of a cationic palladium allyl bis(triphenylphosphine) complex with different counteranions [10]. They found that the allylic proton resonances were about the same with PF_6^- at room temperature and with Cl^- at 208 K, but were comparatively deshielded with Cl^- at room temperature. They suggested that the two first cases would correspond to a free ion pair, whereas in the last one Cl^- would be tightly bound to the cation (contact ion pair) or coordinated to Pd (pentavalent species). This interpretation may fit as well with our own observations; all the more, the hypothesis of tight ions pairs between Cl^- and Pd-allyl complexes has also been formulated by others [8, 9, 11, 13].

We focused on the analysis of complex [**1**]Cl, for which the NMR effect was strongest, in order to gather more information concerning its exact nature. Conductivity has proven to be a useful method to study palladium allyl complexes [10]. The value of the molar conductivity of [**1**]Cl in acetonitrile is 104 Ω^{-1} cm^2 mol^{-1} at a 2×10^{-3} M concentration, which falls within the expected range (92–199 Ω^{-1} cm^2 mol^{-1}) for a 1:1 electrolyte in this solvent [20]. By contrast, the complex is non-conducting in chloroform, which is consistent with a close ion pair or a neutral species. We tried to detect a possible Pd–Cl bond by means of FAB–MS analysis or FT–IR spectroscopy. The FAB–MS spectrum of a 1:1 mixture of [**1**]SbF_6 and PPh_4Cl in $CDCl_3$ does not exhibit any peak corresponding to a neutral chloride-coordinated species; the highest peak at $m/z = 605.3$ corresponds to the molecular peak of the [**1**]$^+$ cation. No Pd–Cl stretching band is either observed on the IR spectrum of [**1**]Cl in KBr in the 200–400 cm^{-1} region [21]. Therefore, no evidence of a pentacoordinate complex is provided by those analytical methods. Interestingly, whether Cl^- is bound or not to Pd, the $\Delta\delta$ distribution shown in Fig. 3 may suggest that the anion is preferentially localised on one side of the coordination plane.

In general, cationic palladium diphosphine allyl complexes listed in Fig. 1 are far less stable in solution with chloride as anion than with a non-coordinating anion; palladium black deposition and emergence of unknown signals on NMR spectra are observed. For example, complex [**1**]$^+$ is stable for days in chloroform with SbF_6^- as counteranion, whereas with Cl^- it is reactive (see below).

We endeavoured to isolate the compound [**1**]Cl in a crystalline form by slow vapour-phase diffusion of pentane at room temperature into a mixture of Me-Duphos and the dimeric complex [Pd(η^3-$Ph_2C_3H_3$)Cl]$_2$ (molar ratio 2:1) dissolved in CH_2Cl_2. This led to yellow single crystals suitable for an X-ray diffraction study, whereas the supernatant appeared as a cloudy palladium metal suspension. Unexpectedly, their X-ray analysis revealed that the crystallised molecule was the neutral palladium complex [(*R*,*R*)-Me-Duphos)$PdCl_2$] **6**; one molecule of CH_2Cl_2 co-crystallises with the complex. The preparation of this complex by another route has been reported very recently [22]. The solid-state structure is depicted in Fig. 4, and the selected bond distances and angles are given in Table 2. The palladium atom is coordinated by the two chlorides and the two phosphorus atoms of Duphos in a classical square-planar geometry. The long Pd–Cl bond distances (2.3706(9) and 2.3790(9) Å) are characteristic of complexes bearing ligands with a strong *trans* influence [23], viz. the phospholanes. The weaker *trans* influence of a chloro ligand compared to an allyl ligand explains that the Pd–P bonds are smaller (2.218 7(9) and 2.220 5(9) Å) than in the related complex [(*R*,*R*)-Me-Duphos)Pd(η^3-

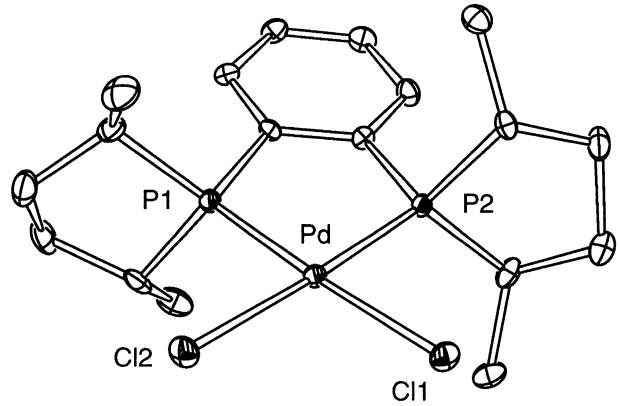

Fig. 4. ORTEP drawing of complex **6** showing 30% probability thermal ellipsoids and the atom-numbering scheme; hydrogen atoms and CH_2Cl_2 are omitted for clarity.

Table 2. Selected bond distances [Å] and bond angles [°] for **6**.

Pd–P1	2.2187(9)	Pd–Cl1	2.3706(9)
Pd–P2	2.2205(9)	Pd–Cl2	2.3790(9)
P1–Pd–P2	86.51(3)	Cl1–Pd–Cl2	95.46(3)
P1–Pd–Cl2	89.37(3)	P1–Pd–Cl1	175.06(3)
P2–Pd–Cl1	88.64(3)	P2–Pd–Cl2	175.85(3)

$Ph_2C_3H_3$)](CF_3SO_3) [18]. The other characteristics of the palladacycle (e.g. the P1–Pd–P2 angle, 86.51(3) Å) and of the Duphos ligand are comparable to those of references [18, 22]. The palladium centre and the four donor atoms are almost coplanar, with the palladium lying only 0.016 1(2) Å away from the plane defined by P1, P2, Cl1 and Cl2. This is probably related to the absence of steric interaction between the chloride atoms and the methyl groups borne by Duphos.

The crystalline complex **6** was isolated in 46% yield and completely characterised. Its NMR features confirm the presence of a C_2 symmetry axis, with two methyle and two methyne signals on the ^1H and ^{13}C NMR spectra, and one singlet at 95.9 ppm on the $^{31}P\{^1H\}$ NMR spectrum. On the ^{13}C NMR spectrum, the methyne carbons appear as two second-order signals at 39.1 and 43.8 ppm. From the interpretation proposed for similar signals in complex [(*R*,*R*)-Me-Duphos)Pd(η^3-$Ph_2C_3H_3$)](CF_3SO_3) [18], we can estimate the values of $|^1J_{CP} + {}^3J_{CP}|$ as 30 and 31 Hz.

In order to understand what was the fate of the allyl ligand, we checked the spontaneous evolution of [**1**]Cl in different solvents at room temperature. For that purpose, 2 equiv Me-Duphos and 1 equiv [Pd(η^3-$Ph_2C_3H_3$)Cl]$_2$ were mixed in $CDCl_3$ or CD_3CN and the solution periodically analysed by ^1H and ^{31}P NMR. The evolution was the same in both solvents, but at a different rate, as the reaction was complete within 2 days in $CDCl_3$ and 10 days in CD_3CN. With time, palladium metal deposited in the tube and the ^1H and ^{31}P signals of **6** appeared, whereas those of [**1**]Cl decreased in intensity. In the final mixture, the allyl ligand has been converted into chalcone (89%), the coupling product 1,3,4,6-tetraphenylhexa-1,5-diene (9%) and diphenylpropene (2%) (Fig. 5). Thus the largest part of the allyl ligand has been oxidised, probably by some dioxygen present in solution. The *trans*/*cis* ratio of chalcone depends on the solvent ($CDCl_3$, 67:33; CD_3CN, 57:43); we note that the proportion of the thermodynamically less stable *cis* isomer is unexpectedly high. It is surprising that the allylic moiety could be oxidised in such soft conditions, insofar as the oxidation of a palladium allyl complex to a ketone generally requires a strong oxidant [24]. In connection with our observations, examples of palladium-catalysed coupling of allylic acetates [25, 26] or carbonates [27], or of coupling of allyl ligands from palladium complexes [28, 29], have been reported.

Another kind of transformation of [**1**]Cl was observed when the crystallisation took place in acetonitrile at low temperature. Crystals suitable for an X-ray analysis were obtained from the slow cooling to 250 K of a solution of [**1**]Cl in CD_3CN. At this temperature, the crystallised species was the ion pair [**1**][$PdCl_2$(η^3-$Ph_2C_3H_3$)] (Figs. 6 and 7, Table 3). A similar transformation upon attempted precipitation of a cationic palladium allyl complex with Cl^- as counteranion has been reported by Crociani et al. [11]. Separate ((*R*,*R*)-Me-Duphos)(η^3-diphenylallyl)palla-

Table 3. Selected bond distances [Å] and bond angles [°] for [**1**][$PdCl_2$(η^3-$Ph_2C_3H_3$)].

Pd1–P1	2.292(2)	Pd2–Cl1	2.380(2)
Pd1–P2	2.270(2)	Pd2–Cl2	2.357(2)
Pd1–C25	2.234(6)	Pd2–C40	2.156(7)
Pd1–C26	2.211(6)	Pd2–C41	2.109(7)
Pd1–C27	2.245(7)	Pd2–C42	2.161(8)
C25–C26	1.402(9)	C40–C41	1.42(1)
C26–C27	1.37(1)	C41–C42	1.41(1)
P1–Pd1–P2	86.51(6)	Cl1–Pd2–Cl2	99.90(7)
P1–Pd1–C27	103.0(2)	Cl1–Pd2–C40	96.8(2)
P2–Pd1–C25	104.6(2)	Cl2–Pd2–C42	95.2(2)
C25–Pd1–C27	65.5(3)	C40–Pd2–C42	68.2(3)
C25–C26–C27	121.9(6)	C40–C41–C42	117.8(7)

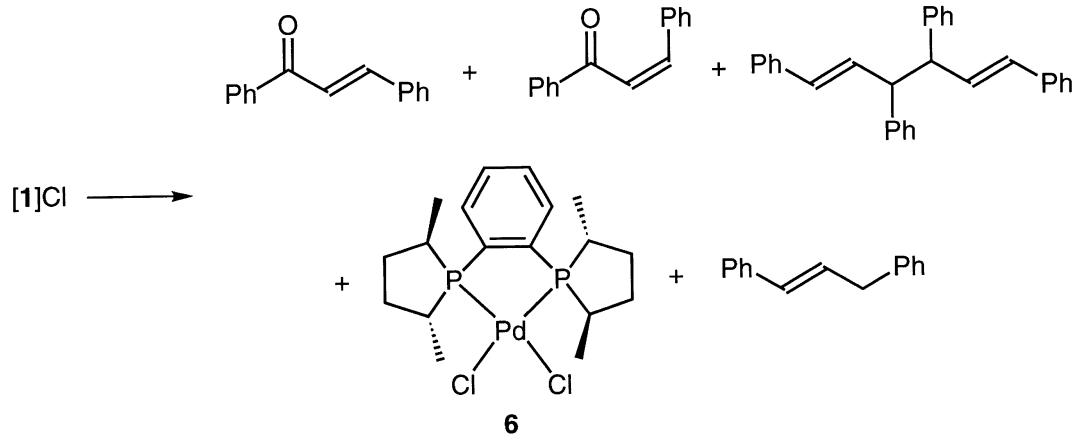

Fig. 5. Spontaneous transformation of complex [**1**]Cl at RT in $CDCl_3$ or CD_3CN.

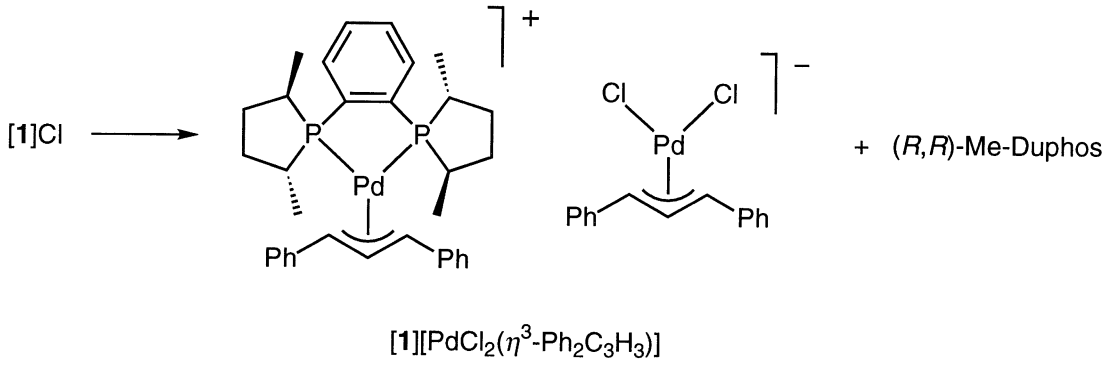

Fig. 6. Spontaneous transformation of complex [**1**]Cl at 250 K in CD_3CN.

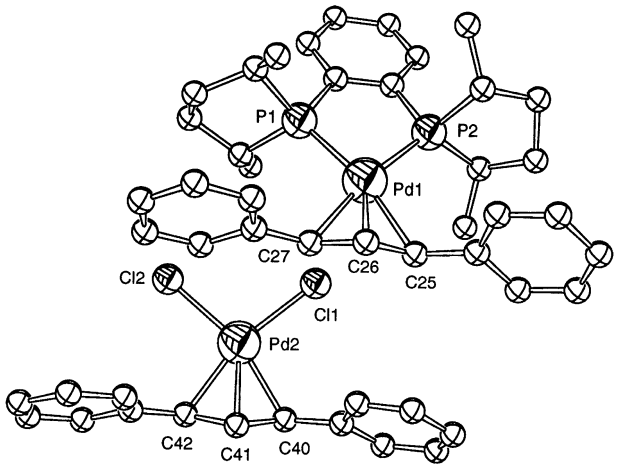

Fig. 7. ORTEP drawing of compound [**1**][$PdCl_2(\eta^3$-$Ph_2C_3H_3$)] showing 30% probability thermal ellipsoids and the atom-numbering scheme; hydrogen atoms are omitted for clarity.

dium (II) cations and dichloro(η^3-diphenylallyl) palladium (II) anions are present in the unit cell. The cation exhibits no significant structural difference with [**1**]CF_3SO_3 [18]. The bond distances and angles of the anionic complex are globally similar to those of the reported X-ray structures of [$PdCl_2(\eta^3$-$C_3H_5)]^-$ [9, 23], except the Cl1–Pd2–Cl2 angle, which is slightly larger (99.90(7)° instead of 95.8(1)° or 97.9(2)°). In a similar crystallographic structure reported by Tresoldi et al. [9], one chloro ligand of the anion weakly coordinates the palladium of the cation with a 3.07 Å distance. It is not the case here, the closest chloro (Cl1) lying 3.517 Å away from Pd1.

3. Conclusion

The first conclusion we can draw from our study is that the structure of the coordination sphere of diphosphine Pd allyl complexes is not strongly altered by chloride ions. However, and in accordance with previously reported observations on other Pd allyl complexes [10], the protons of the complexes are sometimes deshielded. Yet in our case this deshielding effect of Cl^- is not systematic: for instance, with Me-Duphos as the diphosphine, it is strong on the 1,3-diphenylallyl complex $[\mathbf{1}]^+$, but non-existent on the cyclohexenyl complex $[\mathbf{2}]^+$. From a thorough analysis of compound [**1**]Cl, we conclude that this compound is present as separate ions in acetonitrile, whereas it is under the form of a tight ion pair or a neutral pentavalent complex in chloroform.

The presence of chloride ions makes the Pd allyl complexes reactive in solution; this instability may be connected with the fact that Cl^- can improve the performance of allylic alkylation Pd catalysts [2, 17]. Investigations on the nature of the transformation products at room temperature in the case of compound [**1**]Cl reveal that Cl^- pushes the allyl ligand away from the coordination sphere. This leads to the formation of palladium black and of complex **6**, whereas most of the diphenylallyl ligand is oxidised into chalcone. On the reverse, crystals of [**1**][$PdCl_2(\eta^3$-$Ph_2C_3H_3)$] form upon cooling a solution of [**1**]Cl in acetonitrile.

4. Experimental

The NMR spectra were obtained at room temperature (unless otherwise indicated) on Bruker spectrometers. ^1H NMR spectra were recorded at 300.16 MHz (AC-300 instrument) or 500.13 MHz (ARX-500) and referenced to $SiMe_4$. $^{13}C\{^1H\}$ NMR spectra (broadband decoupled) were recorded at 50.32 MHz (AC-200) and referenced to $SiMe_4$; the assignments were supported by DEPT-135°. $^{31}P\{^1H\}$ NMR spectra (broadband decoupled) were recorded at 121.51 MHz (AC-300) and referenced to 85% aqueous H_3PO_4. The NMR tubes were prepared at a concentration ca 15–25 mM under a nitrogen atmosphere using a Vacuum Atmospheres glovebox equipped with Dri-Train HE-493 inert gas purifier; the solutions were

Table 4. Crystal and refinement data for complexes **6** and [**1**][$PdCl_2(\eta^3$-$Ph_2C_3H_3)$].

Compound	**6**·CH_2Cl_2	[**1**][$PdCl_2(\eta^3$-$Ph_2C_3H_3)$]
Formula	$C_{18}H_{28}Cl_2P_2Pd·CH_2Cl_2$	$C_{15}H_{13}Cl_2Pd·C_{33}H_{41}P_2Pd$
Molecular weight	568.61	976.62
Color	Yellow	Yellow
Crystalline system	Orthorhombic	Monoclinic
a (Å)	9.7387(3)	31.979(1)
b (Å)	13.4181(3)	12.2296(3)
c (Å)	18.0813(5)	11.6346(4)
β (deg)		107.668(5)
V (Å^3)	2362.8(2)	4335.6(5)
Z	4	4
D_{calc} (g cm^{-3})	1.60	1.50
*F*000	1152	1992
Wavelength (Å)	0.71073	0.71073
μ (mm^{-1})	1.376	1.059
Space group	$P2_12_12_1$	*C*121
Diffractometer	KappaCCD	KappaCCD
Crystalline dimensions (mm)	0.20 × 0.18 × 0.16	0.20 × 0.16 × 0.12
Temperature (K)	173	173
Radiation	Mo *K*α graphite monochromated	Mo *K*α graphite monochromated
Scan mode	'phi scans'	'phi scans'
hkl limits	–12,12/–17,17/–23,23	–41,41/–15,12/–15,15
θ limits (°)	2.5/27.48	2.5/27.48
No. of data measurements	5417	8879
No. of data with $I > 3\,\sigma(I)$	2650	4506
No. of variables	235	486
R	0.025	0.031
R_w	0.028	0.048
Largest peak in final difference (e Å^{-3})	0.699	1.243
GOF	1.081	1.017

stored in the air after the recording of the spectra. The FT–IR spectra were recorded on a Perkin-Elmer 1600 Series spectrometer on KBr pellets. The FAB–MS spectra (NBA matrix) and elemental analyses were carried out by the corresponding facilities at the 'Fédération de recherche de chimie, université Louis-Pasteur', Strasbourg, France. The ligands (*R*,*R*)-Me-Duphos and (*S*)-Binap were purchased from Strem and used as received. The complex [Pd(η^3-$Ph_2C_3H_3$)Cl]$_2$ was prepared following a reported procedure [30]. The complexes [**1**]SbF_6, [**2**]BF_4, [**3**]SbF_6, [**4**]SbF_6 and [**5**]BF_4 were prepared following reported procedures [16–19]. The ^{1}H NMR signals of [**1**]SbF_6 have been assigned from NOE effects observed on a ^{1}H–^{1}H ROESY spectrum.

4.1. Preparation and transformations of [1]Cl at room temperature

To a suspension of 10 mg (0.015 mmol) [Pd(η^3-$Ph_2C_3H_3$)Cl]$_2$ in 1 ml $CDCl_3$ (or CD_3CN) was added a solution of 10 mg (0.032 mmol) (*R*,*R*)-Me-Duphos in 1 ml $CDCl_3$ (CD_3CN). The mixture was stirred for 10 min at room temperature until a clear yellow solution was obtained. After several days, the different products were identified by ^{1}H and ^{31}P NMR, by comparison with an authentic sample (*cis*- and *trans*-chalcone), with literature data (1,3,4,6-tetraphenylhexa-1,5-diene, 1,3-diphenylpropene) [31] or with NMR data given in § 4.2 (**6**).

4.2. Complex [((*R*,*R*)-Me-Duphos)$PdCl_2$] (6)

A solution of [**1**]Cl was prepared as described above using CH_2Cl_2 as solvent. The volume was reduced under reduced pressure to 0.5 ml, and pentane was slowly added to the solution. Yellow crystals formed after one week, together with a palladium black suspension. The crystals were washed with diethyl ether and dried under vacuum (7 mg, 0.014 mmol, 46%).

^{1}H NMR (CD_3CN, 300 MHz, 298 K): δ (ppm) 0.90 (dd, 6H, $^3J_{HP}$ = 16.8 Hz, $^3J_{HH}$ = 7.3 Hz, CH_3); 1.52 (dd, 6H, $^3J_{HP}$ = 19.5 Hz, $^3J_{HH}$ = 6.8 Hz, CH_3); 1.63–2.50 (m, 8H, CH_2); 2.77 (m, 2H, CH); 3.49 (m, 2H, CH); 7.65–7.90 (m, 4H, H_{ar}).

^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 298 K): δ (ppm) 14.8 (s, CH_3); 17.9 (virtual t, $|^2J_{CP} + {}^4J_{CP}|$ = 6 Hz, CH_3); 36.6 (s, CH_2); 37.9 (s, CH_2); 39.1 and 43.8 (second-order signals, CH); 133.3 (virtual t, $|^2J_{CP} + {}^3J_{CP}|$ = 20 Hz, CH_{ar}); 133.6 (s, CH_{ar}); 142.1 (virtual t, $|^1J_{CP} + {}^2J_{CP}|$ = 74 Hz, C_{ar}).

^{31}P{^{1}H} NMR (CD_3CN, 121.5 MHz, 298 K) : δ (ppm) 95.9 (s, 2P).

Elemental analysis calcd for $C_{18}H_{28}Cl_2P_2Pd$: C, 44.70; H, 5.84; P, 12.81; found C, 44.61; H, 6.02; P, 13.06.

4.3. Reactivity of [1]Cl at low temperature

A solution of [**1**]Cl in CD_3CN was prepared as described above and slowly cooled to 250 K. After 2 days, yellow crystals suitable for X-ray analysis were obtained.

4.4. X-ray crystallography

Details of data collection parameters and refinements results are listed in Table 4. The structures were solved using direct methods. After refinement of the non-hydrogen atoms, difference-Fourier maps revealed maximums of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were introduced as fixed contributors at calculated positions (C–H = 0.95 Å, B(H) = 1.3 Beqv). Final difference maps revealed no significant maximums. All calculations were done using the Nonius OpenMoleN package [32]. Neutral atom scattering factor coefficients and anomalous dispersion coefficients were taken from a standard source [33].

. Supplementary material

The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk] as supplementary material CCDC 177889 / CCDC 177943, and can be obtained by contacting the CCDC.

Acknowledgements. We thank Shailesh Ramdeehul for helpful discussions at the beginning of this work. Financial support from the French 'Centre national de la recherche scientifique' is gratefully acknowledged. GM is indebted to the French 'Ministère de l'Éducation nationale, de l'Enseignement supérieur et de la Technologie' for a grant.

References

[1] B.M. Trost, D.L. Vranken Van, Chem. Rev. 96 (1996) 395.
[2] G.C. Lloyd-Jones, S.C. Stephen, Chem. Commun. (1998) 2321.
[3] M. Bovens, A. Togni, L.M. Venanzi, J. Organomet. Chem. 451 (1993) C28.
[4] M. Kawatsura, Y. Uozumi, T. Hayashi, Chem. Commun. (1998) 217.
[5] A.M. Porte, J. Reibenspies, K. Burgess, J. Am. Chem. Soc. 120 (1998) 9180.
[6] R.J. Haaren van, C.J.M. Druijven, G.P.F. Strijdonck van, H. Oevering, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. Leeuwen van, J. Chem. Soc., Dalton Trans. (2000) 1549.
[7] U. Burckhardt, M. Baumann, A. Togni, Tetrahedron: Asymmetry 8 (1997) 155.
[8] S. Hansson, P.O. Norrby, M.P.T. Sjögren, B. Åkermark, M.E. Cucciolito, F. Giordano, A. Vitagliano, Organometallics 12 (1993) 4940.
[9] G. Munno De, G. Bruno, E. Rotondo, G. Giordano, S. Lo Schiavo, P. Piraino, G. Tresoldi, Inorg. Chim. Acta 208 (1993) 67.
[10] S.A. Godleski, K.B. Gundlach, H.Y. Ho, E. Keinan, F. Frolow, Organometallics 3 (1984) 21.
[11] B. Crociani, F. Di Bianca, A. Giovenco, T. Boschi, Inorg. Chim. Acta 127 (1987) 169.
[12] J. Powell, B.L. Shaw, J. Chem. Soc. A (1968) 774.
[13] M. Oslinger, J. Powell, Can. J. Chem. 51 (1973) 274.
[14] J. Powell, B.L. Shaw, J. Chem. Soc. A (1967) 1839.
[15] P. Braunstein, F. Naud, A. Dedieu, M.M. Rohmer, A. Cian De, S.J. Rettig, Organometallics 20 (2001) 2966.
[16] P. Dierkes, S. Ramdeehul, L. Barloy, A. Cian De, J. Fischer, P.C.J. Kamer, P.W.N.M. Leeuwen van, J.A. Osborn, Angew. Chem. Int. Ed. Engl. 37 (1998) 3116.
[17] G. Malaisé, L. Barloy, S. Ramdeehul, J.A. Osborn, N. Kyritsakas, Titre à venir (in preparation).
[18] D. Drago, P.S. Pregosin, J. Chem. Soc., Dalton Trans. (2000) 3191.
[19] M. Yamaguchi, M. Yabuki, T. Yamagishi, K. Sarai, T. Tsubomura, Chem. Lett. (1996) 241.
[20] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
[21] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th edition, John Wiley & Sons, New York, 1986, pp. 324.
[22] D. Drago, P.S. Pregosin, Organometallics 21 (2002) 1208.
[23] L.S. Hegedus, B. Åkermark, D.J. Olsen, O.P. Anderson, K. Zetterberg, J. Am. Chem. Soc. 104 (1982) 697.
[24] J.A. Davies, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 9, Pergamon, 1995, pp. 355.
[25] S. Sasaoka, T. Yamamoto, H. Kinoshita, K. Inomata, H. Kotake, Chem. Lett. (1985) 315.
[26] H.J. Gais, H. Eichelmann, N. Spalthoff, F. Gerhards, M. Frank, G. Raabe, Tetrahedron: Asymmetry 9 (1998) 235.
[27] C. Goux, P. Lhoste, D. Sinou, A. Masdeu, J. Organomet. Chem. 511 (1996) 139.
[28] G. Carturan, M. Biasiolo, S. Daniele, G.A. Mazzocchin, P. Ugo, Inorg. Chim. Acta 119 (1986) 19.
[29] J. Tsuji, Adv. Organomet. Chem. 17 (1979) 141.
[30] N. Baltzer, L. Macko, S. Schaffner, M. Zehnder, Helv. Chim. Acta 79 (1996) 803.
[31] Y. Masuyama, K. Maekawa, T. Kurihara, Y. Kurusu, Bull. Chem. Soc. Jpn 64 (1991) 2311.
[32] OpenMoleN, Interactive Structure Solution, Nonius B.V., Delft, The Netherlands, 1997.
[33] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. IV, The Kynoch Press, Birmingham, 1974.