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Fluxional Behaviour of Allylpalladium(II) Derivatives of N,N'-Diarylformamidines and 1,3-Diaryltriazenes

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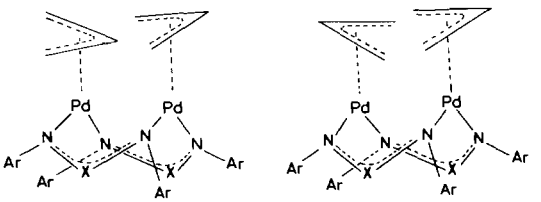
Reactions of allylpalladiumchloride dimer with neutral ligands (L = RN=CH–NHR, R = $C_6H_5CH_2$, p-$CH_3C_6H_4$, p-ClC_6H_4; L = RN=N–NHR, R = p-$CH_3C_6H_4$, p-ClC_6H_4) afford bridge splitting products of the type PdClL(1,3-η-C_3H_5). Variable temperature ^1H and ^{13}C NMR spectra show two dynamic processes in solution. The first one, operating at room temperature, involves the dissociation of the neutral ligand L; the second one, which has a lower activation energy, is concentration dependent and involves chloride–L exchange, probably via *a pentacoordinated chloro bridged species. The influence of the basicity of the ligands on the activation energies of the processes is discussed.*

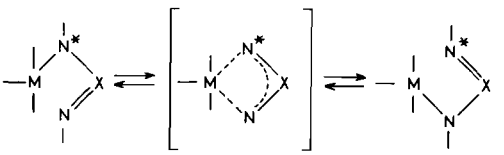
Introduction

In the course of our research on the chemical and coordinative behaviour of the isoelectronic 1,3-diaryltriazenes and N,N'-diarylformamidines and their anions [1–9], we have recently reported some dimeric allylpalladium complexes containing bridging triazenido [2, 5] and formamidido [4] ligands. Both complexes are obtained as mixtures of non-interconverting isomers



I (X = N, CH)

Structure I has been confirmed by X-ray studies [5]. Monomeric complexes [1,3,6–10] of the type ML_2-XY (M = Pd or Pt; L = PPh_3; X = Cl or H; Y = 1,3-di-*p*-tolyltriazenido or N,N'-di-*p*-tolylformamidido) show the following fluxional behaviour, which has been interpreted on the basis of variable temperature ^1H NMR experiments and of X-ray results on several complexes [6–10] as occurring *via* a pentacoordinated intermediate with both nitrogen atoms interacting with the metal through two electron lone pairs.



We now report the synthesis and the temperature dependent dynamic processes of a new class of compounds of the type PdClL(1,3-η-C_3H_5) (L = RN=CH–NHR, R = $C_6H_5CH_2$, *p*-$CH_3C_6H_4$, *p*-ClC_6H_4; L = RN=N–NHR, R = *p*-$CH_3C_6H_4$, *p*-ClC_6H_4).

Experimental

^1H NMR spectra were recorded with a Varian NV-14 (CW mode) and a Bruker WP-60 (FT mode) with TMS as internal standard, and ^{13}C NMR spectra with a Bruker WP-60 spectrometer in the FT mode and using a deuterium lock (spectrum width 3750 Hz, 4096 points).

Diaryltriazenes [11] and diarylformamidines [12] were prepared following literature methods.

Allylpalladium chloride dimer was synthesized from Na_2PdCl_4 and allyl alcohol by the method of Moiseev *et al.* [13].

TABLE I. ^{1}H NMR Spectra of PdClL(1,3-η-C_3H_5).[a]

L		T °C	δ(H_1, H_3) (ppm)	Allyl δ(H_2, H_4) (ppm)	L δ(H_5) (ppm)	L δ(=CH) (ppm)	L δ(others) (ppm)
IIa	$C_6H_5CH_2N$=CH–$NHCH_2C_6H_5$	35	2.70(d)[b,f]	3.72(d)	5.3(m)	~7.5	4.60(s) (CH_2)
		−40	2.30(d), 2.77(d)	3.32(d), 3.87(d)	5.3(m)	~7.5	4.53(d)[c], 4.70(s)
IIb	*p*-$CH_3C_6H_4N$=CH–$NHC_6H_4CH_3$-*p*	35	3.00(d)	3.76(d)	5.5(m)	8.06(s)	2.37(s) (CH_3)
		−40	d			8.2(d)[e]	2.36(s), 2.39(s)
							10.2(d)[e] (N–H)
IIc	*p*-ClC_6H_4N=CH–NHC_6H_4Cl-*p*	35	3.03(d)	3.78(d)	5.5(m)	8.02(s)	
		−40	d			8.02(d)[e]	
IId	*p*-$CH_3C_6H_4N$=N–$HNC_6H_4CH_3$-*p*	35	3.22(d)[d]	4.05(d)	5.6(m)	–	2.36(s)[d] (CH_3)
IIe	*p*-ClC_6H_4N=N–NHC_6H_4Cl-*p*	35	3.32(d)[d]	4.10(d)	5.7(m)	–	d

[a]In $CDCl_3$, TMS as internal standard; s = singlet, d = doublet, m = multiplet. [b]For all complexes: $^3J(H_1–H_5)$ = 12.5 Hz, $^3J(H_2–H_5)$ = 6.8 Hz. [c] $^3J(H_2C–NH)$ = 10.2 Hz. [d]Exchange unblocked at −65 °C. [e] $^3J(HC–NH)$ = 12 Hz. [f]The difference in chemical shift observed at 35° and −40 °C is probably due in part to ligand dissociation at the higher temperatures.

TABLE II. ^{13}C NMR Spectra of PdClL(1,3-η-C_3H_5).[a]

	IIa δ(ppm) +30 °C	IIa δ(ppm) −40 °C	IIa ^1J(CH) (Hz)	IIb δ(ppm) +30 °C	IIb δ(ppm) −40 °C	IIb ^1J(CH) (Hz)
C_1, C_3[b]	61.1(t)	61.4(t), 62.8(t)	160	63.1(t)	[c]	161
C_2	113.1(d)	113.2(d)	160	114.2(d)	[c]	159
=C–H		158.7(d)	174	154.6(d)	153.2(d)	177
C_a, C_a'	140.0(s)	139.3(s), 140.5(s)	–	broad	136.6(s), 148.8(s)	–
C_b, C_b'	128.2(d)	127.8(d), 128.2(d)		130.6(d)	129.7(d), 130.3(d)	157
C_c, C_c'	129.4(d)	127.3(d), 127.5(d)	159	120.4(d)	117.3(d), 122.7(d)	159
C_d, C_d'		128.7(d), 129.1(d)		135.1(s)	133.8(s), 135.1(s)	–
CH_2(α, α')	broad	48.9(t), 59.9(t)	145	–	–	–
CH_3	–	–	–	21.2(q)	20.9(q)	127

[a]In CD_2Cl_2, TMS as internal standard. [b]The numbering scheme is indicated in Figure 1. [c]Exchange unblocked.

Chloro(1,3-η-allyl)(1,3-di-p-tolyltriazene)palladium(II)

Allylpalladiumchloride dimer dissolved in CH_2Cl_2 (180 mg, 5 ml) is treated with 225 mg of the triazene. On adding *n*-hexane to the resulting solution, yellow crystals of the complex precipitated after a few minutes. *Anal.* Found: C, 50.46; H, 4.76; N, 10.67; $C_{17}H_{20}ClN_3Pd$: Calcd.: C, 50.01; H, 4.94; N, 10.29%; m.p. 130–131 °C (dec.); molecular weight: 330 in 1,2-dichloroethane at 37 °C (Calcd. 383). Similarly prepared is the formamidine analog. *Anal.* Found: C, 52.87; H, 5.02; N, 6.56; $C_{18}H_{21}ClN_2Pd$: Calcd.: C, 53.09; H, 5.20; N, 6.88%; m.p. 117–119 °C (dec.).

Results and Discussion

The reaction of allylpalladium chloride dimer with N,N'-diarylformamidines or 1,3-diaryltriazenes (L) in CH_2Cl_2 or $CHCl_3$ solution splits the chloride bridge giving pale yellow complexes of the type II:

$$[PdCl(1,3\text{-}\eta\text{-}C_3H_5)]_2 + 2L \rightleftharpoons 2PdCl(L)(1,3\text{-}\eta\text{-}C_3H_5) \quad (II)$$

L = $C_6H_5CH_2N$=CH–$NHCH_2C_6H_5$ (IIa); *p*-$CH_3C_6H_4$-N=CH–$NHC_6H_4CH_3$-*p* (IIb); *p*-ClC_6H_4N=CH–NHC_6-H_4Cl-*p* (IIc); *p*-$CH_3C_6H_4N$=N–$NHC_6H_4CH_3$-*p* (IId); *p*-ClC_6H_4N=N–NHC_6H_4Cl-*p* (IIe).

The ^{1}H NMR spectra of isolated IIb and IId and those obtained on mixing the starting materials in the stoichiometric ratio show the same pattern. Thus, for the scope of this work complexes IIa, IIc and IIe were prepared *in situ* in the NMR tubes. In the solid state, complexes IIa–IIe have probably a structure with a π-allylic bond analogous to that found for $PdCl(PPh_3)(1,3\text{-}\eta\text{-}(2\text{-}CH_3)\text{-}C_3H_4)$) which

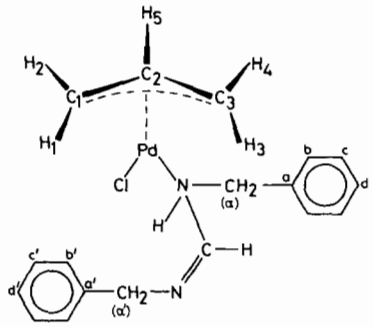
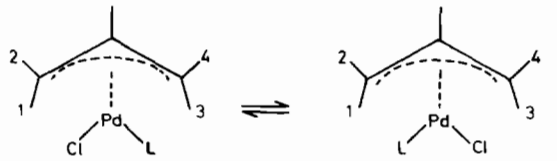


Fig. 1. Numbering scheme.

has no plane of symmetry [14]. In our case, it is likely that the coordination of L occurs through the more basic aminic nitrogen. However, the variable temperature ^1H and ^{13}C NMR spectra of IIa–IIe (Tables I and II) are not consistent with the above rigid configuration as they show changes both in the allyl and ligand L patterns. They present, at room temperature, one allylic A_2B_2 pattern suggesting the occurrence of a process resulting in the equivalence of the *syn* (2 ⇄ 4) and of the *anti* (1 ⇄ 3) protons. This fact is due to a rapid interconversion of L with Cl as observed when L = amine [15–19].



Moreover, the formyl proton in IIb and IIc appears as a broad singlet (not well detectable in IIa because of the closeness to the phenyl peak) and the CH_2-(benzyl) protons in IIa as a broad singlet, which sharpens upon raising the temperature. These last facts indicate the occurence of a second dynamic process which results in the equivalence of the two nitrogen atoms.

We will discuss here in detail the fluxional behaviour of IIa which is the only complex for which we can block the exchange processes before the freezing point of CD_2Cl_2 (the complexes are not soluble in $CHFCl_2$). At −40 °C (no further change is noticeable at −65 °C), the ^1H and ^{13}C NMR spectra of IIa in CD_2Cl_2 are consistent with the frozen geometry reported in Figure 1. The *syn–syn* and *anti–anti* protons equivalences have disappeared and four doublets are observed. The ^{13}C NMR spectrum in the same solvent at −40 °C shows two triplets for the CH_2(allylic) carbon atoms. The methylene resonance of the benzylic substituent gives two ^1H signals (one doublet and one singlet) and two ^{13}C signals (two triplets). Although, in principle, it cannot be excluded that the observed ^1H doublet may rise from an AB pattern of which only the inner components were observed, this hypothesis must be ruled out because the ^{13}C NMR spectrum shows for the CH_2NH carbon a triplet instead of the expected doublet of doublets. Moreover, the ^{13}C NMR spectrum shows that the two benzyl moieties are not equivalent. ^1H NMR spectra recorded in CD_2Cl_2 at lower concentrations as well as in $CDCl_3$ and d_6-acetone show a similar pattern. On raising the temperature, two main features are observable with regard to i) the ligand L and ii) the allyl group.

i) At +20 °C, the CH_2(α and α′) signals broaden and then collapse into a sharp signal at ~40 °C, indicating that the two nitrogen atoms become equivalent.

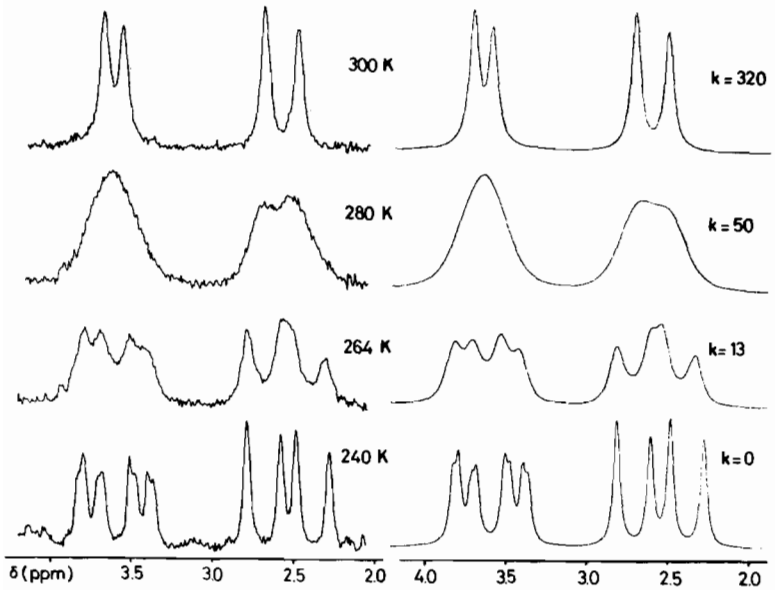


Fig. 2. Allyl exchange process in IIa (left: experimental spectra in CD_2Cl_2, [IIa] = 2.5×10^{-2} *M*; right: calculated spectra, k in s^{-1}).

TABLE III. Allyl Exchange Process in IIa[a].

Solvent	[IIa] *M*	k (s^{-1})[b]	$\Delta G^{\ddagger}$ (kcal/mol)[b,c]
CD_2Cl_2	2.5×10^{-2}	30 ± 2	14.0
CD_2Cl_2	2.5×10^{-1}	91 ± 3	13.5
$CDCl_3$	1.1×10^{-1}	120 ± 10	13.3
d_6-acetone	2.5×10^{-1}	70 ± 3	13.7

[a]The kinetic data refer to the low energy pathway responsible for the 1–3 and 2–4 exchange at lower temperatures (T < 280 K). [b]Measured at 273 K. [c]Calculated from $\Delta G^{\ddagger} = [\ln(k_B/h) - \ln(k/T)]RT$. Alignment coefficients of ln(k/T) *vs.* 1/T range between 0.993 and 0.999. However, the temperature range is too small to report meaningful $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

ii) The four doublets due to H_2, H_4, H_1 and H_3 broaden and then collapse into two broad peaks at ~0 °C. At ~35 °C, two doublets corresponding to the *syn* (H_2 and H_4) and *anti* (H_1 and H_3) protons, are observed. This indicates that the *syn* protons become equivalent, as well as the *anti* ones.

The results of the line shape simulation of the allylic protons exchange (Figure 2, the program of Jesson *et al.* [23] was used to calculate the simulated spectra) are reported in Table III.

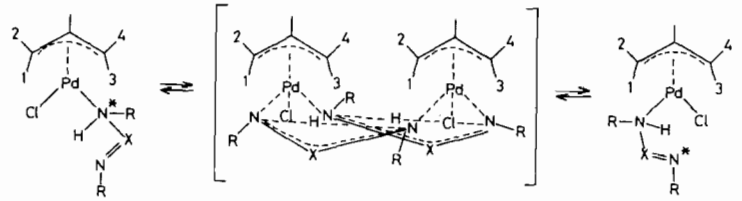
The process depends on the concentration of the complex and seems to be independent of the polarity of the solvent.

One more information is contained in the ^1H NMR spectra: the averaging process of the benzyl moiety is not synchronous with that of the allyl group. Indeed, the two signals of the CH_2 (α and α') protons are still present at temperatures at which the allylic protons are already exchanging. The independence at low temperature of the two processes is more evident in the case of IIb (Tables I, II). At −40 °C, its ^1H NMR spectrum shows that the allyl protons exchange is still unblocked (A_2B_2 pattern) while the two *p*-tolyl substituents of L are not equivalent. The formyl proton is coupled with the N–H proton (this coupling is not observed in the free ligand even at −80 °C) and the methyl protons appear as two singlets. These results are confirmed by the ^{13}C NMR spectrum showing two sets of phenylic carbon atoms and only one signal for the allylic CH_2 carbon atoms.

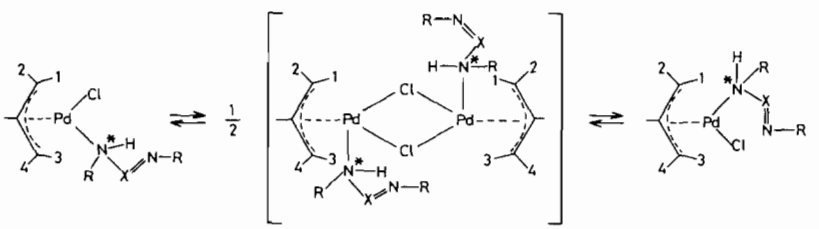
Upon raising the temperature, the coupling between the formyl and aminic protons is lost and the two methyl protons become equivalent; the ^{13}C NMR spectra indicate that the positions of the phenylic carbon atoms are averaged. The loss of the coupling (=CH, NH) is due to the fast exchange between free and coordinated L as found in analogous allylpalladium complexes with substituted pyridines [18, 19]; molecular weight measurements indicate that extensive dissociation of the complex occurs at room temperature.

The behaviour of IIc is similar; however, the coupling (=CH, NH) is lost at lower temperature than for IIb.

The results show that two distinct dynamic processes take place in solution. The first one, responsible for the nitrogen atoms equivalence, involves dissociation of the ligand L; this process is thought to be responsible for the chloride–L exchange in allylpalladium complexes with aromatic amines [18, 19]. The second process, having a lower activation energy, is solely responsible for the allyl exchange at lower temperature. The activation parameters reported in Table III suggest a bimolecular mechanism with an uncharged transition state. Bridging of L between two palladium atoms (Scheme I) is unlikely as it implies an averaging process of the two nitrogen atoms synchronous to that of the allyl moiety. We propose the mechanism reported in Scheme II which fulfills all the experimental results.



Scheme I



Scheme II

Such a mechanism has been proposed for the *syn–syn* and *anti–anti* interchange of $PdCl(PPh_3)(1,3\text{-}\eta\text{-}(2\text{-}CH_3)\text{-}C_3H_4)$ in the presence of PPh_3 [20–22]. The observed trends in the NMR spectra with different L suggest that the basicity of the ligand plays

an important role in both processes. Less basic L will dissociate more easily as observed in the decreasing collapse temperature of the L pattern with the sequence $C_6H_5CH_2$ > p-$CH_3C_6H_4$ > p-ClC_6H_4. Concerning Scheme II, it is likely that less basic ligands will stabilize the pentacoordinated transition state; indeed, the allyl protons exchange is not blocked for p-$CH_3C_6H_4$ or p-ClC_6H_4 even at –65 °C, whereas for $C_6H_5CH_2$ the process is blocked at –40 °C. With the even less basic triazene ligands, neither the ligand nor the allyl exchange processes are blocked at –65 °C.

Acknowledgements

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