

## Photoreactivity of $\eta^3$ -Allylpalladium Complexes Studied by CIDNP

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The photoreaction of  $\eta^3$ -allylpalladium complexes was studied by means of chemically induced dynamic nuclear polarization (CIDNP). Strong polarizations for the protons of 1,5-dienes were observed during photolysis; the addition of organic halides and triphenylphosphine to the reaction mixture led to the formation of polarized alkylated olefins. The origin of these polarizations is discussed and reaction schemes are proposed.

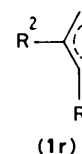
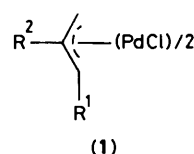
The photochemical transformations of organometallic complexes (other than metal carbonyl complexes) have been studied seriously only in the past decade.<sup>1</sup> One of our two laboratories is particularly interested in the photoreactivity of  $\eta^3$ -allylpalladium complexes. Such a complex, when irradiated at 366 nm in degassed acetonitrile, afforded a 1,5-diene as a result of coupling of the allyl ligands.<sup>2,3</sup> When acetonitrile was replaced by another solvent with co-ordinating properties, the same reaction was observed. However, in a neutral solvent (methylene dichloride), the addition of triphenylphosphine was necessary to promote the photochemical formation of a 1,5-diene.<sup>4,5</sup> In this last case, the irradiated species was a monomeric complex, obtained from the co-ordination of triphenylphosphine to palladium.<sup>6</sup> In the presence of an organic halide (RX) as well as triphenylphosphine, similar irradiation led to exchange of halogen bridging as well as to C-C bond formation between the allyl ligand and the group R.<sup>5</sup> In the absence of triphenylphosphine, *syn/anti*-photoisomerization of  $\eta^3$ -allylpalladium complexes was also observed;<sup>3</sup> furthermore, irradiation of an equimolar mixture of two  $\eta^3$ -allylpalladium complexes yielded the two expected dienes and the dissymmetric 1,5-diene resulting from the coupling of two different allyl ligands.<sup>7</sup> Similar irradiations in the presence of methyl acrylate, acrylonitrile, or styrene led to the polymerization of these additives.<sup>7</sup> All these reactions can be interpreted in terms of the formation of intermediate allyl radicals; these have been trapped with nitrosodurene, and e.s.r. spectra have confirmed their existence.<sup>8</sup>

A CIDNP study was necessary to ascertain whether the observed C-C bond formation was really related to the existence of transient allyl radicals. The importance of this tool in the study of organometallic reactions has been clearly demonstrated by Benn.<sup>9</sup> As a model for these studies, we chose the  $\eta^3$ -allylpalladium complexes (1a-d), which were irradiated in CD<sub>3</sub>CN and C<sub>6</sub>D<sub>6</sub> either in the presence or in the absence of organic halides and triphenylphosphine.

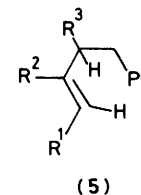
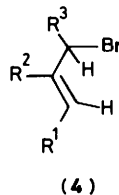
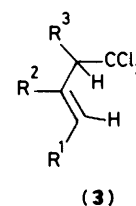
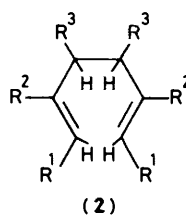
### Results and Discussion

**Irradiation of the Complex (1a) in [2H<sub>3</sub>]Acetonitrile.**—When the various complexes were irradiated in CD<sub>3</sub>CN, palladium was rapidly deposited on the walls of the n.m.r. tube, decreasing the spectral resolution and preventing prolonged irradiation. CIDNP spectra obtained under these conditions are of poor quality and only the results for (1a) are reported here. In this case the only observed polarizations were those due to hexa-1,5-diene (2a); they display multiplet effects (1-H, AE + EA at  $\delta$  5.2; 2-H, AE at  $\delta$  5.75; and 3-H, AE + EA at  $\delta$  2.2) (A = absorption; E = emission).

The same polarizations were observed by Benn during



- a; R<sup>1</sup> = R<sup>2</sup> = H  
 b; R<sup>1</sup> = H, R<sup>2</sup> = Me  
 c; R<sup>1</sup> = Me, R<sup>2</sup> = H  
 d; R<sup>1</sup> = H, R<sup>2</sup> = Ph

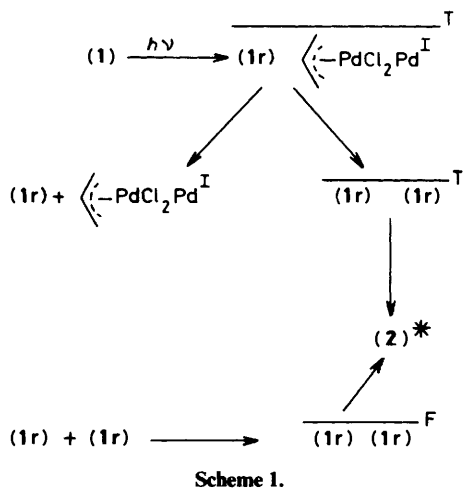


- a; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H  
 b; R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = Me  
 c<sub>1</sub>; R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H  
 c<sub>2</sub>; R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = Me  
 d; R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = Ph

irradiation of other metallic complexes.<sup>9,10</sup> The formation of (2a) results from the recombination of the radicals into a symmetrical radical pair  $(1ra)(1ra)^{T,F}$ . This recombination is consistent with the Kaptein rule<sup>11</sup> relative to the multiplet effect, and the formation of the symmetrical pair can be explained in terms of Scheme 1.

Thus the reaction of (1r) with starting material (1) to give (2) was not observed by CIDNP.

**Irradiation of the Complexes (1a-d) in [2H<sub>6</sub>]Benzene in the Presence of Triphenylphosphine (2 equiv.).**—The most important



**Table 1.** Polarizations of (2a—d) observed during irradiation of (1a—d) in C<sub>6</sub>D<sub>6</sub> in the presence of PPh<sub>3</sub><sup>a</sup>

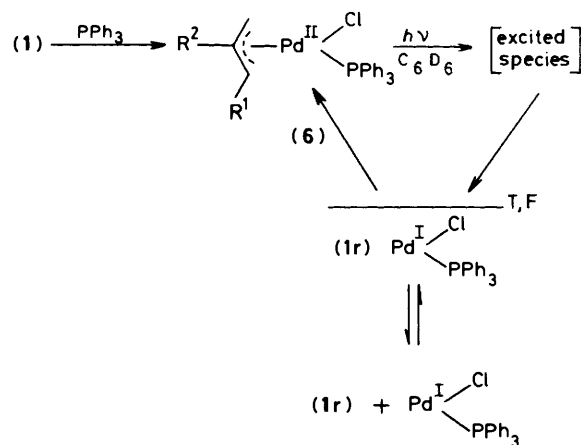
1,5-Dienes	Assignments	δ	Polarization
(2a)	1-H	5.00(p)	A + AE
	2-H	5.75(p)	AE
	3-H	2.00(dd)	A + AE
(2b)	1-H	4.76(p)	A + AE
	2-CH <sub>3</sub>	1.62(d)	E(w) + AE
(2c <sub>1</sub> )	3-H	2.09(s)	A
	1-CH <sub>3</sub>	1.50(p)	E
(2c <sub>2</sub> )	1-H	4.70(q)	A + AE
	2-H	5.45(p)	A + AE
	3-H	2.00(p)	A + AE?
	3-CH <sub>3</sub>	0.95(dd)	E + AE
(2d)	1-H	4.98(d)	A + EA
	1'-H	5.25(d)	A + EA
	3-H	2.63(s)	A

<sup>a</sup> A, enhanced absorption; E, emission; AE or EA multiplet effect (absorption-emission or emission-absorption); w, weak; ?, tentatively assigned; dd, doublet of doublets; p, pattern; q, quartet; s, singlet; δ, chemical shift in p.p.m. relative to Me<sub>4</sub>Si.

polarizations in these experiments originated from the 1,5-dienes (2a—d) (Table 1) produced by photoreaction of the monomeric complexes (6a—d) formed when the dimeric complexes\* (1a—d) and triphenylphosphine are mixed in a 1:2 molar ratio.<sup>6</sup> The absence of a metallic deposit under these conditions enhanced the quality of the CIDNP spectra (Figure 1). In addition to the polarizations mentioned above, we observed polarizations of (6a—d): absorption (A) or line broadening for 1-H and 3-H and emission (E) for R<sup>1</sup> = Me. Under irradiation, this new entity led to the principal pair (1r) Pd<sup>I</sup>Cl<sup>I</sup>.<sup>F</sup> Following the Kaptein rules, we propose a reaction scheme consistent with the observed polarizations (Scheme 2).

First, let us consider the 1,5-dienes which exhibit multiplet and net effect simultaneously (Table 1). The multiplet effects are explained completely by the recombination of two

\* No polarization was observed when irradiations were performed in C<sub>6</sub>D<sub>6</sub> in the absence of PPh<sub>3</sub>.



- (a)  $2(1r) \longrightarrow (1r)(1r)^F \longrightarrow (2)^*$  (multiplet effect)
- (b)  $(1r) + (6) \longrightarrow \text{Pd}^I \begin{matrix} \text{Cl} \\ \text{PPh}_3 \end{matrix} + (2)^*$  (net effect)
- (c)  $(1r) + (6) \longrightarrow (6)^* + (1r)$

**Table 2.** Polarizations observed during irradiation of (1a—d) in C<sub>6</sub>D<sub>6</sub> in the presence of PPh<sub>3</sub> and CCl<sub>4</sub>

Compound	Assignments of observed polarizations (compound, proton, δ, polarization)			
(1a)	(2a)	1-H, 4.90(p), AE + E	(3a)	1-H, 5.10(p), A
	2-H, 5.60(p), AE + E	2-H, 5.80(p), E	3-H, 3.10(dd), A	
	3-H, 2.00(dd), E	3-H, 4.91(p), A	2-CH <sub>3</sub> , 1.68(d), A	
(1b)	(2b)	1-H, 4.73(p), E	(3b)	1-H, 4.91(p), A
	2-CH <sub>3</sub> , 1.63(d), AE + E	2-CH <sub>3</sub> , 1.68(d), A	3-H, 3.09(s), A	
	3-H, 2.10(s), E	3-H, 3.05(s), A	1-CH <sub>3</sub> , 1.40(d), E	
(1c)	(2c <sub>1</sub> )	1-CH <sub>3</sub> , 1.50(p), A + AE	(3c <sub>1</sub> )	1-CH <sub>3</sub> , 1.40(d), E
	1-H, 4.70(q), A?	1-H, 4.70(p), A	2-H, 5.75(p), E(w)	
	2-H, 5.45(p), A?	2-H, 5.75(p), E	3-H, 3.05(d), A	
	3-H, 2.00(p), E	3-H, 3.05(d), A	1-H, 5.00(p), A	
(1d)	(2c <sub>2</sub> )	1-H, 5.00(p), AE?	(3c <sub>2</sub> )	1-H, 5.00(p), A
	2-H, 5.45(p), A?	2-H, 5.75(p), E(w)	2-H, 5.75(p), E	
	3-H, 2.00(p), E	3-H, 2.80(q), A	3-CH <sub>3</sub> , 1.20(d), E	
	3-CH <sub>3</sub> , 0.95(dd), A + AE	3-CH <sub>3</sub> , 1.20(d), E	1-H, 4.97(d), A + EA	
(1d)	(2d)	1-H, 4.97(d), A + EA	(3d)	1-H, 5.39(d), A
	1'-H, 5.24(d), A + EA	1'-H, 5.39(d), A	3-H, 3.61(d), A	
	3-H, 2.62, 0	3-H, 3.61(d), A		

**Table 3.** Polarizations of (4a—d) during irradiations of (1a—d) in C<sub>6</sub>D<sub>6</sub> in the presence of PPh<sub>3</sub> and CCl<sub>3</sub>Br

Compound	Assignments and polarizations		
(4a)	1-H, 4.67 → 4.82(p), AE + E		
	2-H, 5.40 → 5.65(p), EA?		
	3-H, 3.41(d), E		
(4b)	1-H, 4.65 → 4.80(p), E		
	3-H, 3.53(s), E		
(4c <sub>1</sub> )	1-CH <sub>3</sub> , 1.36(p), A		
	1-H, 5.40(p), E		
	2-H, 3.50(d), E		
(4c <sub>2</sub> )	1-H, 5.70(p), E(w)?		
	2-H, 4.70(p), E		
	3-CH <sub>3</sub> , 1.45(d), A		
(4d)	1-H, 5.10 → 5.20(p), E		
	3-H, 3.96(s), E		

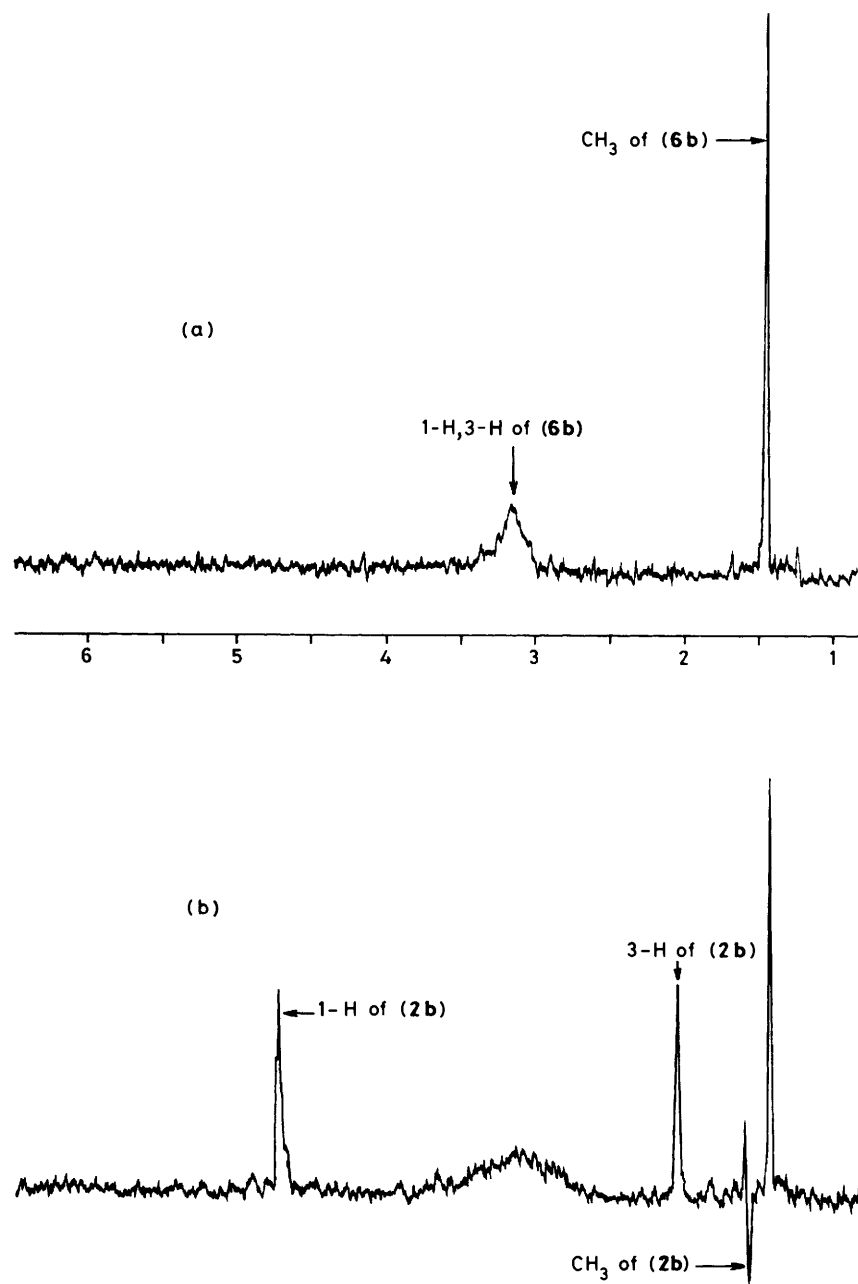


Figure 1.  $^1\text{H}$  N.m.r. spectra of (1b) in  $\text{C}_6\text{D}_6$  in the presence of  $\text{PPh}_3$ : (a) before, (b) during irradiation

identical radicals ( $1r$ ) from a symmetrical pair  $\overline{(1r)(1r)^F}$  (see before). However, the net effect cannot account for such a pair. Thus this effect [A for 1-H and 3-H and E for Me of ( $2c_1$ ) and ( $2c_2$ )] indicates another reaction pathway. If we assume that allyl radical ( $1ra$ )  $g$ -factor (2.00254)<sup>12</sup> has a higher value than that of  $\text{Pd}^{\text{I}}\text{ClL}$ , the net effects on ( $2a$ – $d$ ) arise from the radical ( $1r$ ), which diffuses freely from the principal pair and reacts with a monomeric complex ( $6$ ) [Scheme 2, reaction (b)].

In the same manner, the net effect observed for the monomeric complex may originate from reaction (c) (Scheme 2).

*Irradiation of the Complexes (1a–d) in  $[\text{}^2\text{H}_6]\text{Benzene}^\dagger$  in the Presence of  $\text{PPh}_3$  (2 equiv.) and an Excess of  $\text{CCl}_3\text{X}$  (X = Cl or*

*Br).*—Table 2 summarizes the polarizations observed during irradiation in the presence of both  $\text{PPh}_3$  and  $\text{CCl}_4$ . They proceed first from the various 1,5-dienes ( $2a$ – $d$ ) (the net polarizations of which are the reverse of the preceding case) and then from the trichloromethyl adducts ( $3a$ – $d$ ). No more polarizations were observed for ( $6a$ – $d$ ) but in all cases [except ( $1d$ )] emission was observed for chloroform.

In the presence of  $\text{CCl}_3\text{Br}$ , in addition to the polarizations obtained with  $\text{CCl}_4$ , we observed those arising from the various allyl bromides ( $4a$ – $d$ ) (Table 3). The CIDNP spectra presented

<sup>†</sup> Similar spectra were obtained when  $\text{CD}_3\text{CN}$  was used as solvent; however, the presence of small quantities of  $\text{CH}_3\text{CN}$  may cause overlap of some polarizations and we have preferred to use  $\text{C}_6\text{D}_6$  in this work.

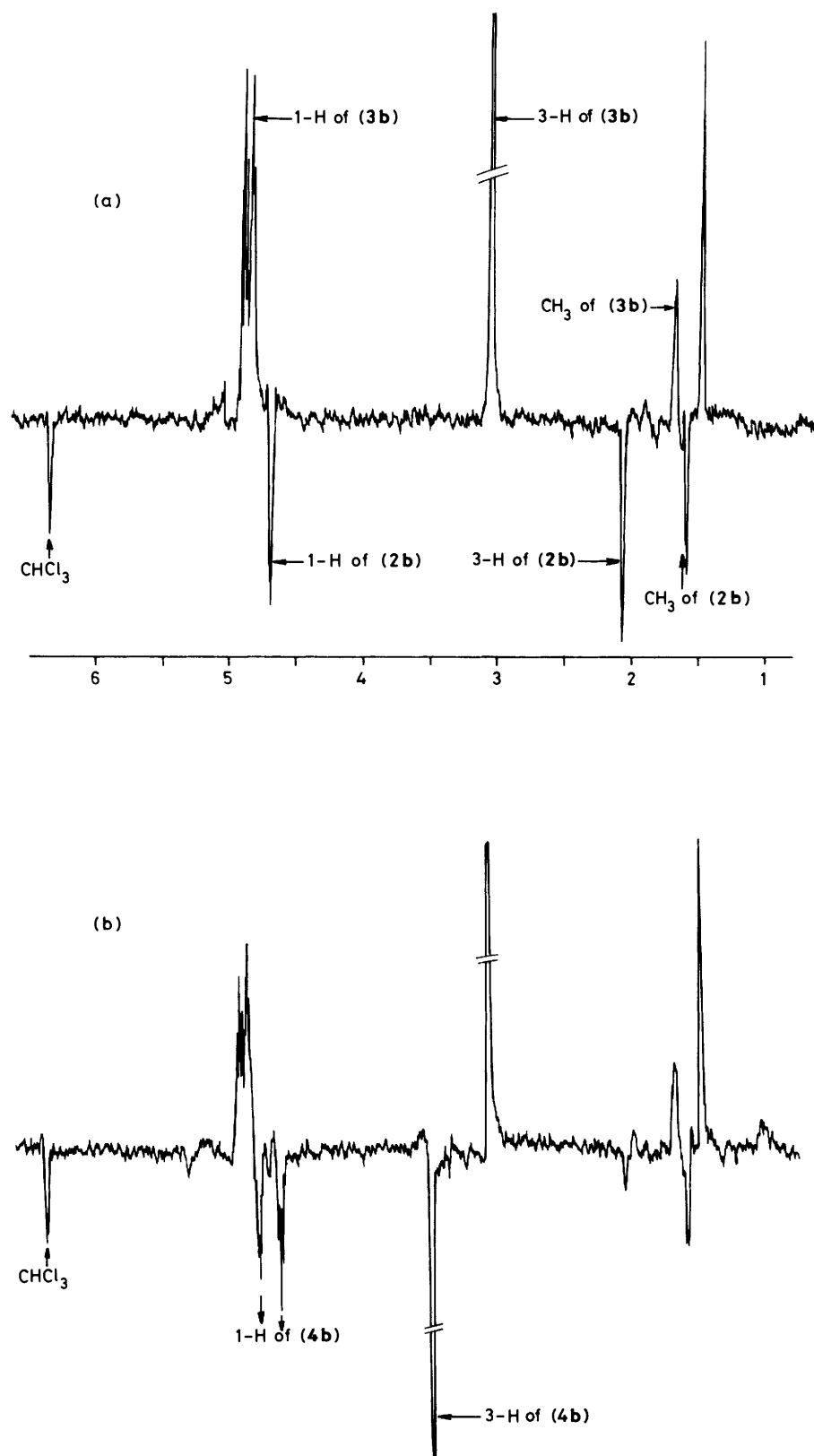
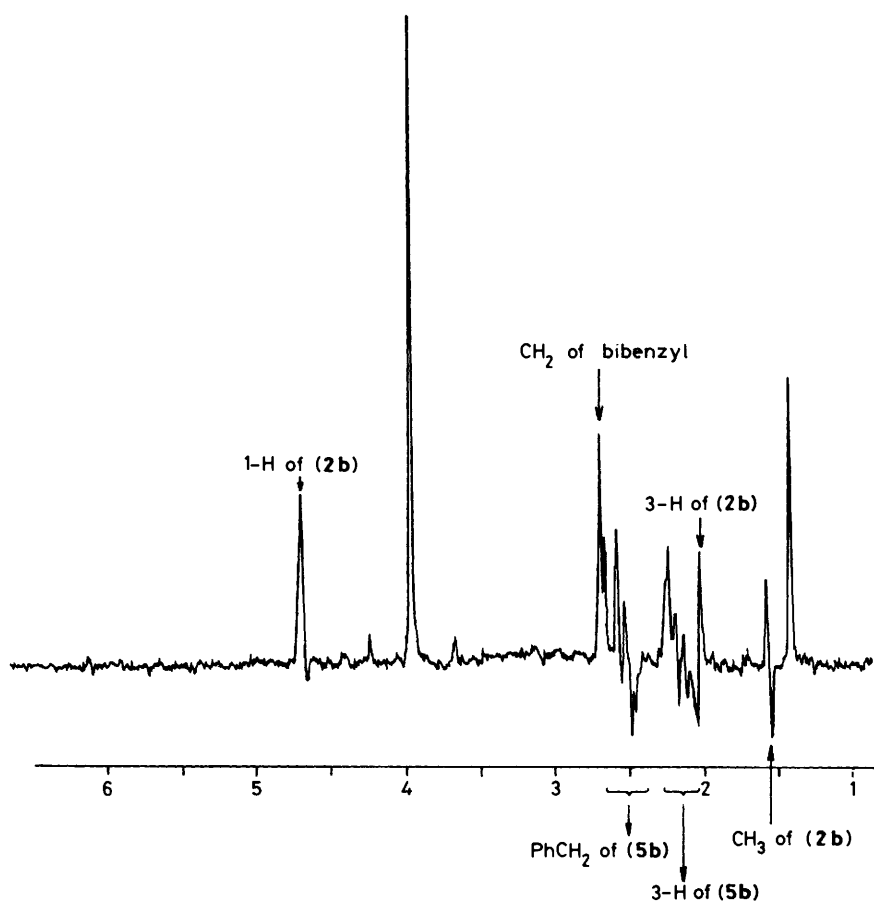
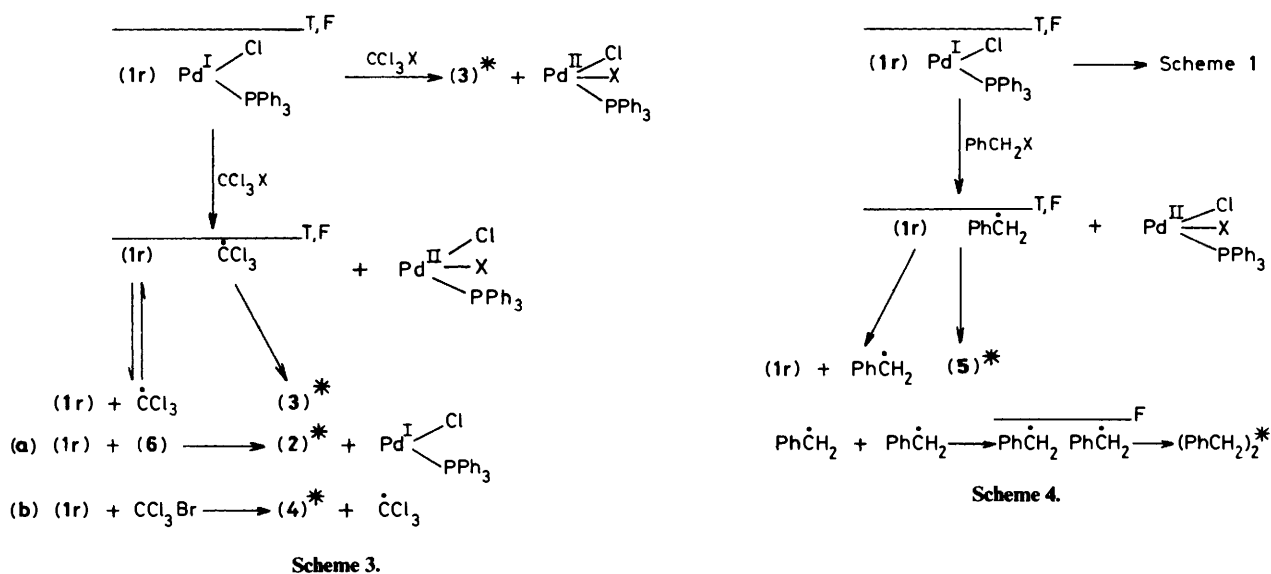


Figure 2.  $^1\text{H}$  CIDNP spectra obtained during irradiation of **1b** in  $\text{C}_6\text{D}_6$  in the presence of  $\text{PPh}_3$  and (a)  $\text{CCl}_4$ , (b)  $\text{CCl}_3\text{Br}$



**Figure 3.** <sup>1</sup>H CIDNP spectrum obtained during irradiation of (1b) in C<sub>6</sub>D<sub>6</sub> in the presence of PPh<sub>3</sub> and PhCH<sub>2</sub>Br

in Figure 2 were recorded during irradiation of (1b) in the presence of  $\text{CCl}_4$  and  $\text{CCl}_3\text{Br}$ .

The trichloromethyl derivatives (3a—d) were formed by recombination of allyl radicals (1ra—d) with the trichloromethyl radical. The polarizations [A for 1-H and 3-H, E for 2-H, as well as the reverse polarizations for the methyl groups, E for Me in (1) or (3) and A for Me in (2)] are explained by the direct recombination of the radicals into the radical pair  $(\text{1r})^{\cdot}\text{CCl}_3^{\cdot}$  (Scheme 3). This pair can be obtained by two different ways: a random encounter between two diffusing radicals or a substitution within the principal pair  $(\text{1r})\text{Pd}^{\text{I}}\text{Cil}^{\text{T,F}}$ .

The scavenging of the allyl radicals (1r) diffusing from the principal pair by  $\text{CCl}_3$  can lead to the same results. The multiplet effects are masked by the magnitude of the net effects due to the great difference in the  $g$  values in the pair  $(\text{1r})^{\cdot}\text{CCl}_3$ , [ $g(\text{allyl}) < g(\text{CCl}_3) = 2.0091$  (ref. 13)].

Another pathway should be considered for the 1,5-dienes (2) since in their case the net effects are reversed. However, the multiplet effects remain the same, but are considerably distorted by the magnitude of the net effects (E for 1-H and 3-H). This observation implies that the symmetrical radical pair recombination  $(\text{1r})(\text{1r})$  is always effective. But another pathway has to be considered in order to account for the net effects. In particular the strong emission for 3-H reflects an important difference in  $g$  values. It proceeds via an escape process from the pair  $(\text{1r})^{\cdot}\text{CCl}_3$  and scavenging by (6) [Scheme 3, reaction (a)].

However, we can see in Table 2 that the signal corresponding to 3-H of (2d) is of zero intensity. The expected emission exactly cancels the enhanced absorption previously observed.

In the presence of  $\text{CCl}_3\text{Br}$ , new polarizations are observed. They are attributed to type (4) products (allyl bromides) and are explained in terms of scavenging of the diffusing radicals (1r) by  $\text{CCl}_3\text{Br}$  [Scheme 3, reaction (b)].

*Irradiation of the Complexes (1a—d) in  $[\text{}^2\text{H}_6]\text{Benzene}$  in the Presence of  $\text{PPh}_3$  (2 equiv.) and an Excess of Benzyl Halide ( $\text{PhCH}_2\text{X}$ ; X = Cl or Br).*—We will only discuss the polarizations observed with benzyl bromide because they are the most intense. Nevertheless CIDNP spectra which are quite similar were observed with  $\text{PhCH}_2\text{Cl}$ . An example is given in Figure 3. The 1,5-dienes (2) were polarized in the same way as in the absence of  $\text{PhCH}_2\text{X}$  (see Table 1). Furthermore we observed polarizations arising from (5a—d) which result from the recombination of benzyl and allyl radicals (Table 4). In all cases, the methylene group of bibenzyl showed enhanced absorption at  $\delta$  2.76, which corresponds to the recombination of two benzyl radicals (co-operative effect)<sup>14</sup> and excludes a reaction between a benzyl radical and a benzyl halide molecule.

The mechanism for the formation of (2a—d) is analogous to that reported in Scheme 2 since the polarizations are the same as those in Table 1. The polarizations of compounds (5a—d) arise from the  $(\text{1r})^{\cdot}\text{CH}_2\text{Ph}^{\cdot}$  pair formed by the reaction of  $\text{PhCH}_2\text{X}$  with the principal pair. As the difference in  $g$  values is very small for this pair [ $g(\text{1r}) = 2.00254$  (ref. 12);  $g(\text{CH}_2\text{Ph}) = 2.0025$  (ref. 15)], we observed a strong multiplet effect for the  $\text{CH}_2\text{CH}_2$  group. However, on recording CIDNP spectra with a flip angle of  $90^\circ$ ,<sup>16</sup> we were able to determine the net effect of each pattern (Table 4). These results and the application of the Kaptein rules are consistent with Scheme 4.

In conclusion, the CIDNP technique has enabled us to confirm and to define the reaction pathway proposed in a preceding paper.<sup>5</sup> Carbon-carbon bonds are formed from coupling of radicals and from reaction of a radical with RX or a monomeric complex; this last reaction could also lead to an exchange between allyl ligands.

From monomeric complexes Scheme 2 always arises; Schemes 3 and 4 have to be added in the presence of organo halides.

**Table 4.** Polarizations of (5a—d) during irradiations of (1a—d) in  $\text{C}_6\text{D}_6$  in the presence of  $\text{PPh}_3$  and  $\text{PhCH}_2\text{Br}$

Compound	Assignments and polarizations
(5a)	PhCH <sub>2</sub> , 2.52(p), A + AE 3-H, 2.20(p), E + AE
(5b)	PhCH <sub>2</sub> , 2.60(p), A + AE 3-H, 2.20(p), E + AE
(5c <sub>1</sub> )	PhCH <sub>2</sub> , 2.60(p), A + AE 3-H, 2.20(p), E? + AE
(5c <sub>2</sub> )	PhCH <sub>2</sub> , 2.60(p), A + AE 3-CH <sub>3</sub> , 0.90(d), A
(5d)	PhCH <sub>2</sub> , 2.70(s), A 3-H, 2.70(s), A

However, in the case of  $\text{CCl}_3\text{X}$ , the magnitude of the  $g$ -factor difference in the radical pairs  $(\text{1r})^{\cdot}\text{CCl}_3$  alters drastically the aspect of the CIDNP spectra.

### Experimental

<sup>1</sup>H CIDNP spectra were run with a Bruker WP 80 SY spectrometer. The CIDNP probe is commercially available from Bruker. A silica light-pipe (length 500 mm; diam. 8 mm) leads the full emission spectrum of a high-pressure Xe-Hg short arc lamp (1 000 W; Oriol) to the level of the detection coil of the n.m.r. probe. We used Pyrex sample tubes to cut off wavelengths under 290 nm. The concentration of organometallic complexes in solution was  $2 \times 10^{-2}\text{M}$ .

The CIDNP spectra were usually recorded using a flip angle value of  $20^\circ$ ,<sup>16</sup> occasionally, for the determination of the net polarization, we used a flip angle of  $90^\circ$ .

Published procedures were used to prepare the complexes (1a), (1b), (1c),<sup>17</sup> and (1d).<sup>18</sup>

### Acknowledgements

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