

Identification of the Effective Palladium(0) Catalytic Species Generated *in Situ* from Mixtures of Pd(dba)₂ and Bidentate Phosphine Ligands. Determination of Their Rates and Mechanism in Oxidative Addition

Christian Amatore,^{*,†} Gregory Broeker,[†] Anny Jutand,^{*,†} and Fouad Khalil[‡]

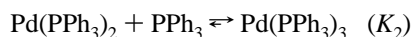
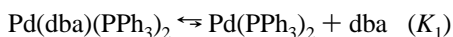
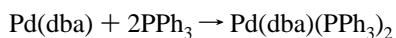
Contribution from the Département de Chimie, Ecole Normale Supérieure, URA CNRS 1679, 24 Rue Lhomond, 75231 Paris Cedex 05, France, and Département de Chimie, Faculté des Sciences et Techniques, Université Sidi Mohammed Ben Abdellah, Fes-Saïss, Morocco

Received October 24, 1996[⊗]

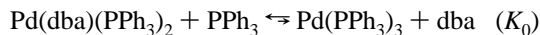
Abstract: Mixtures of Pd(dba)₂ + 2L-L (where L-L is a bidentate ligand such as dppe, dppe, dppp, dppb, dppf, and DIOP) lead to the formation of Pd(L-L)₂ complexes which do not undergo an oxidative addition with phenyl iodide. Mixtures of Pd(dba)₂ + 2 BINAP do not afford Pd(BINAP)₂ but Pd(dba)(BINAP). Mixtures of Pd(dba)₂ + 1L-L (L-L = dppe, dppe, dppp, dppb, dppf, DIOP, and BINAP) lead to Pd(dba)(L-L) complexes *via* the formation, at short time, of the complex Pd(L-L)₂, except for dppf and BINAP where the complex Pd(dba)(L-L) is directly formed. Pd(dba)(L-L) is the main complex in solution but is involved in an endergonic equilibrium with the less ligated complex Pd(L-L) and dba. Pd(L-L) is the more reactive species in the oxidative addition with phenyl iodide. However, Pd(dba)(L-L) also reacts in parallel with phenyl iodide. From the kinetic data concerning the reactivity of these different catalytic systems in the oxidative addition with phenyl iodide, one observes the following order of reactivity: Pd(dba)₂ + 1DIOP > Pd(dba)₂ + 1dppf ≫ Pd(dba)₂ + 1BINAP. All these systems associated to one bidentate ligand are less reactive than Pd(dba)₂ + 2PPh₃.

Introduction

The complex Pd(0)(dba)₂ (dba = *trans,trans*-dibenzylideneacetone) associated with phosphine ligands is commonly used as a source of palladium(0) complexes.^{1–6} One can vary the phosphine ligand at will and thus test the reactivity of the resulting complexes in catalytic reactions. We reported a mechanistic investigation on the system Pd(0)(dba)₂ + nPPh₃ (n ≥ 2). The following mechanism was established on the basis of ³¹P NMR spectroscopy and voltammetry:²



Since Pd(PPh₃)₂ is present only as a transient species in endergonic equilibrium state, it was advisable to consider the overall equilibrium:



* To whom correspondence should be addressed.

† URA CNRS 1679.

‡ Université Sidi Mohammed Ben Abdellah.

⊗ Abstract published in *Advance ACS Abstracts*, May 15, 1997.

(1) For the use of Pd(dba)₂ with monodentate ligands, see ref 11 in ref 2.

(2) Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168.

The value of the equilibrium constant $K_0 = K_1K_2 = 0.14$ was determined in THF.² From this value, we concluded that dba is a better ligand for Pd(PPh₃)₂ than PPh₃, and it was established that dba is not very labile as usually admitted, since the deligation of the second dba ligand requires at least 8 equiv of

(3) (a) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1980**, *21*, 4437. (b) Fiaud, J. C.; Malleron, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 1159. (c) Ahmar, M.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1984**, *25*, 4505. (d) Ahmar, M.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1985**, *26*, 3795. (e) Rajanbabu, T. V. *J. Org. Chem.* **1985**, *50*, 3642. (f) Fiaud, J. C.; Legros, J. Y. *J. Org. Chem.* **1987**, *52*, 1907. (g) Bäckwall, J. E.; Vagberg, J. E.; Zercher, C.; Genêt, J. P.; Denis, A. *J. Org. Chem.* **1987**, *52*, 5430. (h) Genêt, J. P.; Uziel, J.; Jugé, S. *Tetrahedron Lett.* **1988**, *29*, 4559. (i) Fournet, G.; Balme, G.; Barrieux, J. J.; Goré, J. *Tetrahedron* **1988**, *44*, 5821. (j) Lin, I. J. B.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1989**, 248. (k) Susuki, O.; Inoue, S.; Sato, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 239. (l) Fiaud, J. C.; Legros, J. Y. *J. Organomet. Chem.* **1989**, *370*, 383. (m) El Ali, B.; Alper, H. *J. Org. Chem.* **1991**, *56*, 5357.

(4) (a) Fiaud, J. C.; Hibon de Gournay, A.; Larchevêque, M.; Kagan, H. B. *J. Organomet. Chem.* **1978**, *154*, 175. (b) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1981**, *22*, 1399. (c) Fiaud, J. C.; Denner, B.; Malleron, J. L. *J. Organomet. Chem.* **1985**, *291*, 393. (d) Fiaud, J. C.; Arribi-Zouieueche, L. *J. Organomet. Chem.* **1985**, *295*, 383. (e) Genêt, J. P.; Jugé, S.; Ruiz Montés, J.; Gaudin, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 718. (f) Arzoumanian, H.; Buono, G.; Choukrad, M.; Petrigliani, J. F. *Organometallics* **1988**, *7*, 59. (g) Genêt, J. P.; Jugé, S.; Achi, S.; Mallart, S.; Ruiz Montés, J.; Levif, G. *Tetrahedron* **1988**, *44*, 5263. (h) Arzoumanian, H.; Choukrad, M.; Nuel, D. *J. Mol. Catal.* **1993**, *85*, 287.

(5) (a) Genêt, J. P.; Féroud, D.; Jugé, S.; Ruiz Montès, J. *Tetrahedron Lett.* **1986**, *27*, 4573. (b) Fiaud, J. C.; Legros, J. Y. *Tetrahedron Lett.* **1988**, *29*, 2959. (c) Hodgson, M.; Parker, D.; Taylor, R. J.; Ferguson, G. *Organometallics* **1988**, *7*, 1761. (d) Fiaud, J. C.; Legros, J. Y. *J. Org. Chem.* **1990**, *55*, 4840. (e) Gil, R.; Fiaud, J. C. *Bull. Soc. Chim. Fr.* **1994**, *131*, 584. (f) Legros, J. Y.; Toffano, M.; Fiaud, J. C. *Tetrahedron Asymmetry* **1995**, *6*, 1899. (g) Dani, P.; Dupont, J.; Monteiro, A. L. *J. Braz. Chem. Soc.* **1996**, *7*, 15.

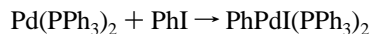
(6) (a) Stolle, A.; Salaun, J.; De Meijere, A. *Synlett.* **1991**, *5*, 327. (b) Stolle, A.; Ollivier, J.; Piras, P. P.; Salaun, J.; De Meijere, A. *J. Am. Chem. Soc.* **1992**, *114*, 4051. (c) McGaffin, G.; Michalski, S.; Stolle, A.; Braese, S.; Salaun, J.; De Meijere, A. *Synlett.* **1992**, *7*, 558. (d) Legros, J. Y.; Fiaud, J. C. *Tetrahedron* **1994**, *50*, 465.

Table 1. ^{31}P NMR Chemical Shifts^a of Palladium(0) Complexes Generated in the Mixture $\text{Pd}(\text{dba})_2 + n\text{L-L}$ ($n = 1$ or 2) and of the Complexes $\text{PhPd}(\text{L-L})$ Resulting from the Oxidative Addition with PhI ($n = 1$), in THF

L-L	L-L	$\text{Pd}(\text{dba})_2 + 2\text{L-L} \rightarrow \text{Pd}(\text{L-L})_2$		$\text{Pd}(\text{dba})_2 + 1\text{L-L} \rightarrow \text{Pd}(\text{dba})(\text{L-L})$		$\text{PhPd}(\text{L-L})$	
	δ_0	δ_1	δ_2	δ_3	δ_4	δ_5	
dppm	-10.12	13.30	19.70	21.28	10.50	13.56	
dppe	-12.61	30.46	34.41	36.63	33.82	49.11	
dppp	-17.41	3.95	8.35	13.44	-9.85	10.82	
dppb	-16.18	27.81	17.46	21.28	14.73	15.46	
dppf	-16.96	25.91	17.95 (d) ($J_{\text{PP}} = 9$ Hz)	19.83 (d) ($J_{\text{PP}} = 9$ Hz)	7.64 (d) ($J_{\text{PP}} = 34$ Hz)	25.65 (d) ($J_{\text{PP}} = 34$ Hz)	
DIOP	-22.39	-0.75	7.25	9.46	-4.94 (d) ($J_{\text{PP}} = 45$ Hz)	11.68 (d) ($J_{\text{PP}} = 45$ Hz)	
BINAP	-15.30	n.o. ^b	25.63 ^c	26.86 ^c	9.08 (d) ($J_{\text{PP}} = 40$ Hz)	22.28 9d) ($J_{\text{PP}} = 40$ Hz)	

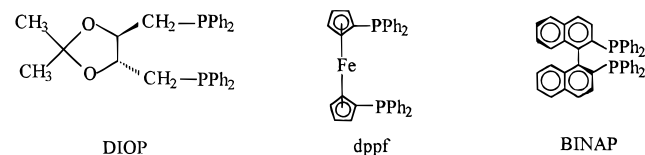
^a Determined *vs* H_3PO_4 at 40 °C. ^b n.o. = not observed. ^c One single broad signal was observed at 27.03 ppm at 80 °C.

PPh_3 .⁷ The reactive species in oxidative addition with PhI was the less ligated 14-electron complex $\text{Pd}(\text{PPh}_3)_2$.



This species is faced to two equilibria, and its concentration is lower than when, *e.g.*, $\text{Pd}(0)(\text{PPh}_3)_4$ is used at the same concentration. This explains why, in contradiction with the common belief, mixtures of $\text{Pd}(\text{dba})_2$ and triphenylphosphine are less reactive *vis à vis* oxidative addition than $\text{Pd}(\text{PPh}_3)_4$.²

The catalytic systems $\text{Pd}(0)(\text{dba})_2 + \text{L-L}$, where L-L is a bidentate phosphine ligand,³⁻⁶ are of great interest because some ligands are chiral chelating diphosphines (DIOP,^{4,5} BINAP,^{5,6} *etc.*) and thus may cause asymmetric induction. In this respect, it is of the utmost importance to know the nature of the zero-valent palladium species which undergoes the oxidative addition. This information might indeed be crucial for the rationalization of the chiral induction when the substrate undergoing oxidative addition is chiral at the center of oxidative addition. We report here the first kinetic results concerning the structure and reactivity in oxidative addition of the palladium(0) complexes generated *in situ* in mixtures of $\text{Pd}(0)(\text{dba})_2$ and bidentate ligands such as DIOP, dppf, and BINAP.⁸ Main attention was given to



chiral chelating diphosphines such as DIOP and BINAP. The oxidative addition of the related palladium(0) complex are investigated with phenyl iodide. Although phenyl iodide does not present any chiral center, the resulting phenylpalladium complex will be chiral and might play a role in enantioselective inductions such as in Heck reactions. Phenyl iodide was chosen as a model molecule because, on the one hand, it will allow the characterization of the different complexes involved in the oxidative addition and, on the other hand, the results could be compared with our previous works on the reactivity of other commonly used palladium(0) complexes in oxidative additions.^{2,9,10} Despite the fact that phenyl iodide is not chiral, it allows (i) the existence of two palladium(0) catalytic centers

(7) In other words, the first dba ligand is easily exchanged by two phosphine ligands, while the second one is hard to remove. We ascribe this result, surprising at first glance, to a conflict between electronic and steric requirements. Thus, in our view, one dba and two phosphine ligands appear to be the best compromise between electronic factors (which would lead to exchange of the second dba by the third phosphine) and steric constraints (which oppose this exchange).

(8) Khalil, F. Ph.D. Thesis, University Paris VI, 1993.

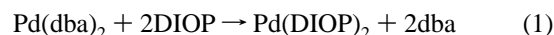
(9) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 1670.

(10) Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818.

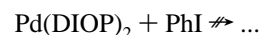
and (ii) their dynamics to be characterized. These features relative to the palladium(0) catalyst are expected to play a similar role with any other organic derivative in particular when the latter is chiral.

Results and Discussion

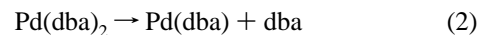
I. Identification of the Palladium(0) Complexes Formed *in situ* by Mixture of $\text{Pd}(\text{dba})_2$ and Bidentate Phosphine Ligands in THF, As Investigated by ^{31}P NMR Spectroscopy and Cyclic Voltammetry. (a) $\text{Pd}(\text{dba})_2 + 2\text{DIOP}$ with (+)-DIOP = (4*S*,5*S*)-(+)-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane. ^{31}P NMR spectroscopy was performed on a solution of $\text{Pd}(\text{dba})_2$ (14 mM) with 2 equiv of DIOP in 3 mL of THF. The ^{31}P NMR spectrum exhibited a single signal at $\delta_1 = -0.75$ ppm characteristic of $\text{Pd}(\text{DIOP})_2$ (Figure 1a, Table 1).¹¹ The free ligand at $\delta_0 = -22.39$ ppm was not detected, and thus, the formation of $\text{Pd}(\text{DIOP})_2$ is a fast and quantitative reaction.



The signal at δ_1 was still observed in the presence of 1000 equiv of phenyl iodide, after 2 h, demonstrating that the oxidative addition to the 18-electron $\text{Pd}(\text{DIOP})_2$ did not take place.



These results were confirmed by cyclic voltammetry. As we already reported,² the cyclic voltammetry of $\text{Pd}(\text{dba})_2$ exhibited one oxidation peak O_0 at $E^p = +1.26$ V (Figure 2a) and three reduction peaks (Figure 2b). The first reversible one at $E^p(\text{R}_0) = -0.93$ V characterizes the reduction of $\text{Pd}(\text{dba})_2$; the two others at $E^p(\text{R}_1) = -1.29$ V (reversible) and $E^p(\text{R}_2) = -2.00$ V (irreversible) characterize the two successive 1-electron reductions of dba, released in reaction 2, as previously estab-



lished.² When 2 equiv of DIOP was added to a solution of $\text{Pd}(\text{dba})_2$, 2 mM in THF, the peak R_0 was no longer observed whereas the two reduction peaks of the ligand dba were present at R_1 and R_2 (Figure 2b).

Both reduction peak currents were doubled with respect to the above experiment in the absence of DIOP. The reaction of $\text{Pd}(\text{dba})_2$ with 2DIOP thus released 2dba in solution according to reaction 1.¹² The oxidative section of the voltammograms showed that the oxidation peak O_0 of $\text{Pd}(\text{dba})_2$ disappeared

(11) For the synthesis and characterization of $\text{Pd}(\text{DIOP})_2$, see: Elmes, P. S.; Jackson, W. R. *Aust. J. Chem.* **1982**, *35*, 2041.

(12) The ratio $i/V^{1/2}$ (i = reduction current of R_1 , V = scan rate) did not vary with the scan rate. This means that the peak current of R_2 exactly corresponds to the concentration of free dba in solution and not to a dynamic concentration due to an eventual equilibrium of dba and a palladium(0) complex as observed for PPh_3 .²

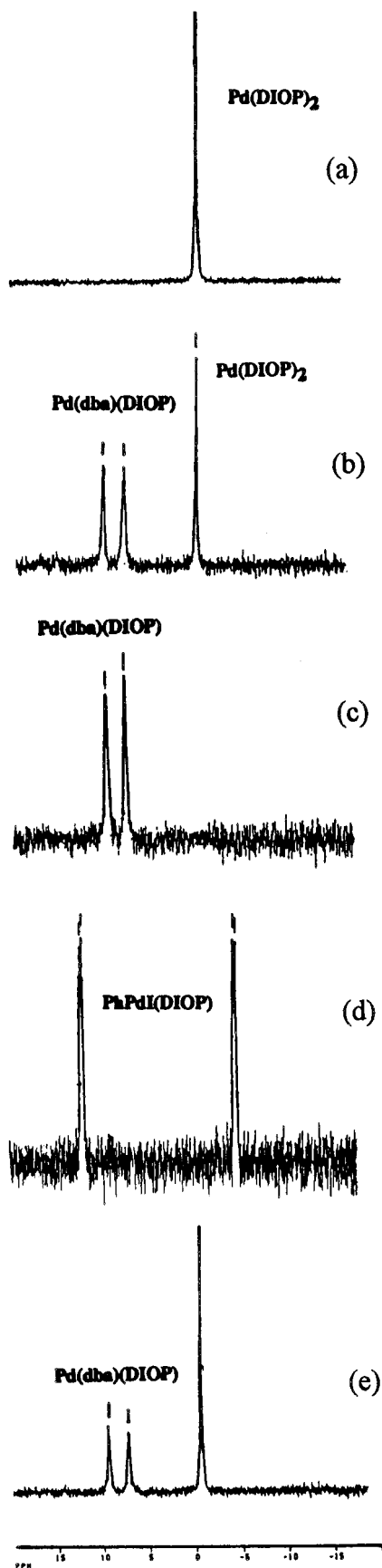


Figure 1. ^{31}P NMR spectrum (162 MHz) performed in 3 mL of THF and 0.2 mL of acetone- d_6 with H_3PO_4 as an external reference: (a) $\text{Pd}(\text{dba})_2$ (14 mM) + 2DIOP, (b) $\text{Pd}(\text{dba})_2$ (14 mM) + 1DIOP after 10 min, (c) $\text{Pd}(\text{dba})_2$ (14 mM) + 1DIOP after 4 h, (d) $\text{PhPdI}(\text{DIOP})$ after addition of 100 equiv of PhI to (c), (e) $\text{Pd}(\text{dba})_2$ (14 mM) + $\text{Pd}(\text{DIOP})_2$ (14 mM) generated *in situ* from a mixture of $\text{Pd}(\text{dba})_2$ (14 mM) + 2DIOP as in (a).

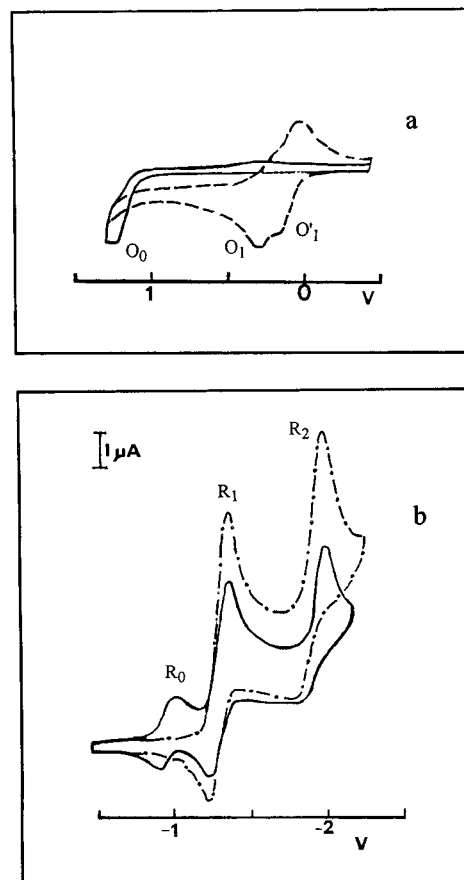


Figure 2. Cyclic voltammetry performed in THF ($n\text{-Bu}_4\text{NBF}_4$, 0.3 M) at a stationary gold disk electrode (0.5 mm diameter) with a scan rate of 0.2 V s^{-1} : (a) (—) oxidation of $\text{Pd}(\text{dba})_2$ (2 mM), (---) oxidation of $\text{Pd}(\text{dba})_2$ (2 mM) + 2 DIOP, (b) (—) reduction of $\text{Pd}(\text{dba})_2$ (2 mM), (- · -) reduction of $\text{Pd}(\text{dba})_2$ (2 mM) + 2 DIOP.

whereas two new oxidation peaks were observed at $E^p(\text{O}_1) = +0.33 \text{ V}$ and $E^p(\text{O}'_1) = +0.19 \text{ V}$ (Figure 2a, Table 2). Addition of more than 2 equiv of DIOP did not modify the voltammograms of the system, neither in oxidation nor in reduction. Therefore, the complex $\text{Pd}(\text{DIOP})_2$ is quantitatively formed *in situ* from a mixture of $\text{Pd}(\text{dba})_2$ with 2 equiv of DIOP. It is characterized by two oxidation peaks, O_1 and O'_1 , whose magnitudes were equal when the voltammetry was performed at a rotating disk electrode. This shows that the oxidation of $\text{Pd}(\text{DIOP})_2$ involves two successive 1-electron transfers. These two oxidation peaks still remained unchanged in the presence of 1000 equiv of PhI, confirming our above observations in ^{31}P NMR spectroscopy, viz., that $\text{Pd}(\text{DIOP})_2$ does not react with phenyl iodide.

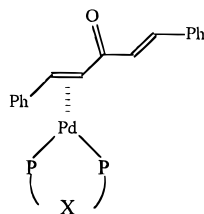
(b) $\text{Pd}(\text{dba})_2$ + 1DIOP. The ^{31}P NMR spectrum of a mixture of $\text{Pd}(\text{dba})_2$ (14 mM) with 1 equiv of DIOP exhibited after 10 min three signals (Figure 1b, Table 1): one single signal at $\delta_1 = -0.75 \text{ ppm}$ which is characteristic of $\text{Pd}(\text{DIOP})_2$, as established above, and two signals of equal magnitude at $\delta_2 = +7.25 \text{ ppm}$ and $\delta_3 = +9.46 \text{ ppm}$ whose structure suggests two doublets. However, the signals were too broad ($\Delta\nu_{1/2} = 60 \text{ Hz}$) to allow the determination of any coupling constant J_{pp} . The system changed as a function of time. After 4 h, the signal of $\text{Pd}(\text{DIOP})_2$ had disappeared. The two signals at δ_2 and δ_3 only remained present (Figure 1c). They disappeared after addition of 100 equiv of PhI, and two new doublets were detected at $\delta_4 = -4.94 \text{ ppm}$ and $\delta_5 = 11.68 \text{ ppm}$ ($J_{\text{pp}} = 45$

Table 2. Oxidation Peak Potentials^a of the Palladium(0) Complexes Generated in the Mixture Pd(dba)₂ + nL-L (n = 1 or 2) in THF

L-L	Pd(dba) ₂ + 2L-L → Pd(L-L) ₂ E ^p _{ox} (O ₁)	Pd(dba) ₂ + 1L-L → Pd(dba)(L-L) E ^p _{ox} (O ₂)	L-L	Pd(dba) ₂ + 2L-L → Pd(L-L) ₂ E ^p _{ox} (O ₁)	Pd(dba) ₂ + 1L-L → Pd(dba)(L-L) E ^p _{ox} (O ₂)
dppe	-0.31	+0.42	DIOP	+0.19, +0.33 ^c	+0.66
dppf	+0.88	+0.68 ^b	BINAP	n.o. ^d	+0.52

^a Oxidation peak potentials are relative to the SCE electrode. They were determined at a gold disk electrode with a scan rate of 0.2 V s⁻¹ at 20 °C. ^b A second reversible oxidation peak was observed at +1.27 V. ^c Two oxidation peaks were detected; see the text. ^d n.o. = not observed.

Hz) characteristic of PhPdI(DIOP) (Figure 1d).¹³ This means that a mixture of Pd(dba)₂ + 1DIOP afforded at short times the complex Pd(DIOP)₂, while at long times, a new complex was formed in which the two phosphorous atoms are not equivalent. This latter reacts with PhI while the former does not. The structure of the reactive complex is compatible with the formula Pd(dba)(DIOP), in which monoligation of dba makes the two phosphorous atoms of DIOP not equivalent:



P-X-P symbolizes the DIOP ligand. The same monoligation of dba was observed for the complex Pd(dba)(PPh₃)₂.²

When Pd(dba)₂ was added to a solution of Pd(DIOP)₂, previously generated *in situ* from the mixture of Pd(dba)₂ and 2DIOP, i.e., in the presence also of free dba (1 equiv per palladium), the two doublets characteristic of Pd(dba)(DIOP) appeared in the ³¹P NMR spectrum (Figure 1e), demonstrating that a reaction occurred between Pd(DIOP)₂ and Pd(dba)₂ to yield Pd(dba)(DIOP). Surprisingly, addition of dba only (i.e., without Pd(dba)₂) to the solution of Pd(DIOP)₂ did not modify its ³¹P NMR spectrum.

To delineate the kinetic evolution of the mixture Pd(dba)₂ + 1DIOP, cyclic voltammetry was performed as a function of time. In the presence of 1 equiv of DIOP per Pd(dba)₂, after 5 min (as required for preparation of the cyclic voltammetry experiment), the oxidation current of Pd(dba) at O₀ was half of its initial value (Figure 3a) and the current magnitudes of the two oxidation peaks O₁ and O'₁, representative of Pd(DIOP)₂, were half of their values measured for Pd(DIOP)₂ formed *in situ* in the mixture Pd(dba)₂ + 2DIOP (compare Figures 2a and 3a). Therefore, a mixture of Pd(dba)₂ + 1DIOP rapidly (*t*_{1/2} < 5 min) afforded (1/2)Pd(DIOP)₂ and (1/2)Pd(dba).

Evolution as a function of time showed that the oxidation peak of Pd(dba) slowly disappeared concomitantly with the disappearance of the oxidation peaks O₁ and O'₁ of Pd(DIOP)₂ (Figure 3a). A new oxidation peak O₂ was detected at E_p(O₂) = +0.66 V and its magnitude increased concomitantly with the disappearance of O₁ and O'₁ (Figure 3a). Peak O₂ was assigned to Pd(dba)(DIOP) on the basis of the ³¹P NMR investigations (see above). After 4 h, the only oxidation peak detected was O₂, featuring the presence of Pd(dba)(DIOP) only (Figure 3a). This oxidation peak disappeared in the presence of 50 equiv of

(13) (a) The ³¹P NMR spectrum of PhPdI(DIOP) was identical to that obtained after substitution of PPh₃ from PhPdI(PPh₃)₂ by 1 equiv of DIOP and to that reported by De Graaf, W.; Boersma, J.; Van Koten, G.; Elsevier, C. J. *J. Organomet. Chem.* **1989**, 378, 115. (b) Although the yield of PhPdI(DIOP) could not be precisely quantified, it was observed in the ³¹P NMR spectrum that the two signals characteristic of Pd(dba)(DIOP) completely disappeared in the presence of phenyl iodide and that the two signals of PhPdI(DIOP) were detected without any other signals that could characterize a byproduct bearing a phosphine ligand. We are thus inclined to conclude that the yield of the oxidative addition is quantitative.

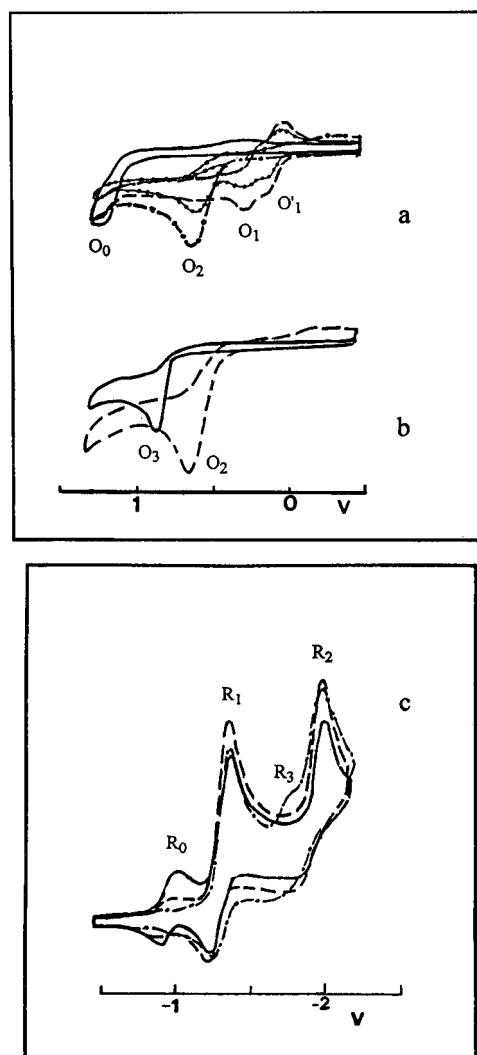


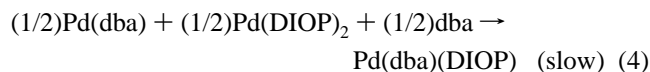
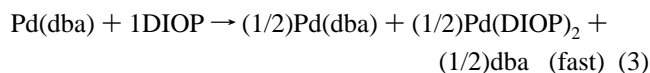
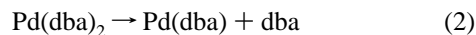
Figure 3. Cyclic voltammetry performed in THF (*n*-Bu₄NBF₄, 0.3 M) at a stationary gold disk electrode (0.5 mm diameter) with a scan rate of 0.2 V s⁻¹: (a) (—) oxidation of Pd(dba)₂ (2 mM), (---) oxidation of Pd(dba)₂ (2 mM) + 1DIOP after 5 min, (- · -) after 2 h, and (- · -) after 4 h, (b) (---) oxidation of Pd(dba)₂ (2 mM) + 1DIOP after 4 h, (—) {Pd(dba)₂ (2 mM) + 1DIOP after 4 h} + 50 PhI, oxidation of PhPdI(DIOP), (c) (—) reduction of Pd(dba)₂ (2 mM), (---) reduction of Pd(dba)₂ (2 mM) + 1DIOP after 10 min and (- · -) after 4 h.

PhI and was replaced by a new oxidation peak, O₃, at +0.90 V, which characterized the complex PhPdI(DIOP) resulting from the oxidative addition (Figure 3b).

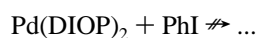
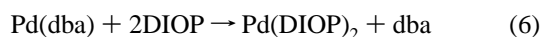
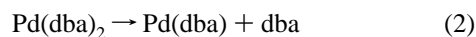
The same overall reactivity was observed through the reductive side of the cyclic voltammogram. Thus, in mixtures of Pd(dba)₂ + 1DIOP, the reduction peak R₀ was still detected after 10 min, yet its magnitude was half of the initial one (Figure 3c). One also observed that the reduction peak currents of the free dba were multiplied by approximately 3/2 when compared to their initial values. Therefore, a mixture of Pd(dba)₂ + 1DIOP rapidly (*t*_{1/2} < 5 min) afforded (1/2)Pd(DIOP)₂ and (3/2)dba. One then observed a decay of the reduction peaks of dba as a function of time, up to a final value corresponding to

1 equiv per palladium (Figure 3c). The reduction peak of Pd(dba)(DIOP) was also observed at R_3 (-1.60 V), corresponding to the reduction of the dba ligand ligated to the palladium(0) center.

On the basis of these observations, the following mechanism is proposed:



Therefore, 1/2 equiv of Pd(DIOP)₂ is rapidly formed (eq 3) which then reacts slowly with 1/2 equiv of Pd(dba)¹⁴ to form Pd(dba)(DIOP) which reacts with PhI. In the mixture Pd(dba)₂ + 2DIOP, the unreactive Pd(DIOP)₂ only is formed.



(c) Pd(dba)₂ + nL-L (n = 1 or 2) with L-L = dppm, dppe, dppp, and dppb. Irrespective to the exact nature of the bidentate ligand (dppm, dppe, dppp, and dppb), reactions similar to those for DIOP were observed by ³¹P NMR spectroscopy and cyclic voltammetry. The complex Pd(L-L)₂ was formed from the mixture Pd(dba)₂ + 2L-L. It did not react with phenyl iodide.¹⁵ The complex Pd(dba)(L-L) was formed at longer times from the mixture of Pd(dba)₂ + 1L-L *via* the complex Pd(L-L)₂ as observed above for DIOP.¹⁶ Pd(dba)(L-L) reacted with PhI to afford PhPd(L-L). The ³¹P NMR signals of the different complexes are gathered in Table 1. Herrmann *et al.*¹⁷ also reported that complexes Pd(dba)(dppe) and Pd(dba)(dppp) have been isolated from mixtures of Pd(dba)₂ and 1dppe or 1dppp. The X-ray structure of Pd(dba)(dppe)^{17a} confirms that the two phosphorous atoms are not equivalent because of a monoligation of dba in Pd(dba)(L-L) as postulated above for Pd(dba)(DIOP).

(d) Pd(dba)₂ + nBINAP (n = 1 or 2) with BINAP = (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl. The ³¹P NMR spectrum of a mixture of Pd(dba)₂ (14 mM) + 1BINAP exhibited at short times (10 min) two signals δ_2 and δ_3

(14) When alone in solution, the complex Pd(dba)₂ is mainly present as Pd(dba) since 1 equiv of the free dba ligand is always detected in ¹H NMR spectroscopy. Since this species is unsaturated (14 electrons), it probably aggregates. The external part of these aggregates should only be accessible for the reaction with DIOP which is therefore always in high concentration relative to the reactive Pd(dba) at the interface. We believe this is the reason why Pd(DIOP)₂, the kinetic product, was mainly produced at the beginning of the reaction. However, investigation of this initial mechanism was impossible because the formation of Pd(DIOP)₂ was complete ($t_{1/2} < 5$ min) before ³¹P NMR spectroscopy or cyclic voltammetry could be performed.

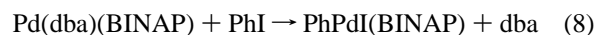
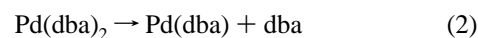
(15) It is already reported that Pd(dppe)₂ does not react with aryl iodides; see: Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

(16) Similar behavior concerning the dppe ligand has been observed: (a) Fiaud, J. C.; Legros, J. Y. Unpublished results, private communication, Paris, 1991. (b) Legros, J. Y. Ph.D. Thesis, University Paris 11, Orsay, 1988.

(17) (a) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Öfele, K.; Priemeier, T.; Scherer, W. *J. Organomet. Chem.* **1993**, *461*, 51. (b) Herrmann, W. A.; Brossmer, C.; Priemeier, T.; Öfele, K. *J. Organomet. Chem.* **1994**, *481*, 97.

characteristic of Pd(dba)(BINAP) together with some free BINAP ligand (Table 1). After 4 h, the free ligand had disappeared and only Pd(dba)(BINAP) was observed which shows that the ligation of Pd(dba) by BINAP is a slow reaction. The two ³¹P NMR signals δ_2 and δ_3 of Pd(dba)(BINAP) were broad ($\Delta\nu_{1/2} = 60$ Hz), and increasing the temperature at 80 °C resulted in a coalescence of the two signals (Table 1), indicating either a deligation of dba or a fast scrambling of dba around the palladium center. Addition of 100 equiv of PhI to the mixture Pd(dba)₂ + 1BINAP (after complete formation of Pd(dba)(BINAP)) resulted in the formation of PhPdI(BINAP) characterized by its ³¹P NMR spectrum (Table 1).¹⁸

The ³¹P NMR spectrum of a mixture of Pd(dba)₂ (14 mM) + 2BINAP exhibited, after 4 h, the two signals characteristic of Pd(dba)(BINAP) (Table 1) and the signal of the free BINAP ligand, at -15.30 ppm. Addition of a large excess of BINAP (10 equiv per palladium) did not modify the signals of Pd(dba)(BINAP), and no singlet was detected that could be characterized as Pd(BINAP)₂^{19a} under our experimental conditions (one night at 40 °C). When the mixture Pd(dba)₂ + nBINAP ($n = 1$ or 2) was investigated by cyclic voltammetry, the oxidative and reductive voltammograms remained identical whatever the value of n . Only one oxidation peak, O₂, characteristic of Pd(dba)(BINAP), was observed (Table 2). The reductive voltammogram exhibited the two reduction peaks of dba. From the value of the reduction peak current of the first reduction peak, we concluded that only 1 equiv of dba per palladium was released in solution even when $n = 2$. The electrochemical investigation thus confirmed that the complex Pd(BINAP)₂ was never formed from a mixture of Pd(dba)₂ and 2BINAP, under our experimental conditions. Thus, the following mechanism was established:



Therefore, mixtures of Pd(dba)₂ + 2BINAP behave differently from those involving the other ligands investigated here, in the sense that the main species is always Pd(dba)(BINAP) and that the complex Pd(BINAP)₂ could not be observed. From this we conclude that dba is a better ligand for the Pd(BINAP) moiety than BINAP, even for a BINAP/dba ratio of 10/1.²⁰

The complex Pd(dba)(BINAP)^{19b} was isolated in 86% yield, as an orange powder, from a mixture of Pd(dba)₂ + 1BINAP in toluene and was characterized by cyclic voltammetry (E^p (O₁) = $+0.51$ V) and ³¹P NMR spectroscopy ($\delta_2 = 25.64$ ppm and $\delta_3 = 26.84$ ppm). Thus, the isolated complex Pd(dba)(BINAP) has the same physical properties as the complex generated *in situ* in the mixture of Pd(dba)₂ + 1BINAP (see Tables 1 and 2).

(e) Pd(dba)₂ + ndppf (n = 1 or 2) with dppf = 1,1'-Bis(diphenylphosphino)ferrocene. The complex Pd(dba)(dppf)

(18) The ¹H NMR spectrum of PhPdI(BINAP) was identical to that obtained after substitution of PPh₃ from PhPdI(PPh₃)₂ by 1 equiv of BINAP.

(19) (a) For the synthesis and characterization of Pd(BINAP)₂, see: Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T. *Nishioka*, E.; Yanagi, K.; Moriguchi, K.-I. *Organometallics* **1993**, *12*, 4188. (b) For the isolation of Pd(dba)(BINAP) as an orange powder, from a mixture of Pd₂(dba)₃ and BINAP, see: Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215.

(20) The first dba ligand is easily exchanged by one bidentate ligand, while the second one is hard to remove. We ascribe this result to a conflict between electronic and steric requirements, as for PPh₃; see ref 7.

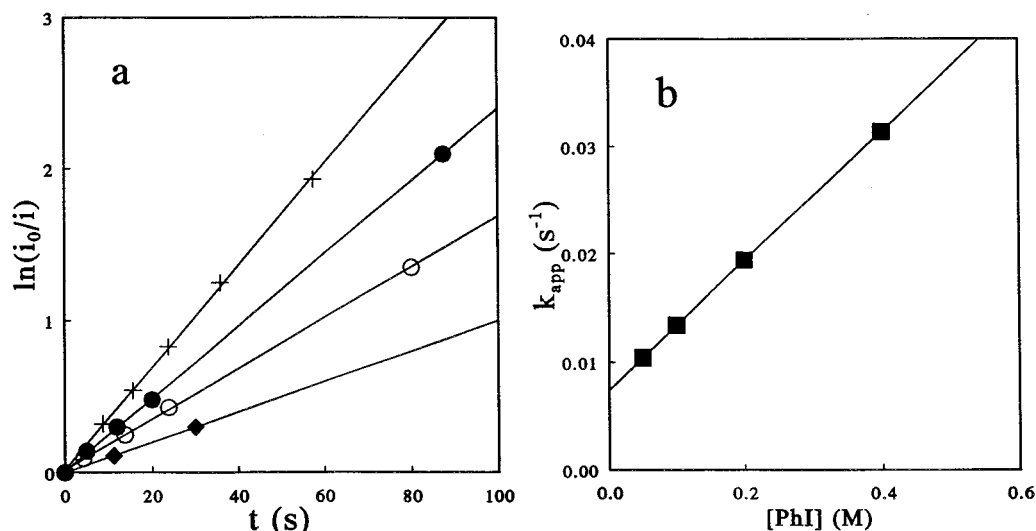
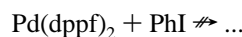
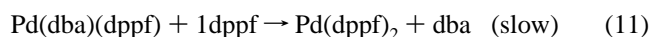
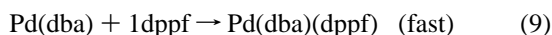
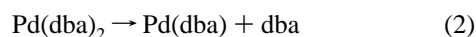


Figure 4. Kinetics of the oxidative addition of PhI with the palladium(0) complex generated *in situ* in the mixture of Pd(dba)₂ (2 mM) + 1DIOP in THF, at 40 °C: (a) variation of $\ln(i_0/i)$ (i = oxidation plateau current at 0.60 V *vs* SCE, at a rotating gold disk electrode (2 mm diameter, ω = 105 rad s⁻¹) as a function of time, in the presence of PhI [(+) 0.4 M, (●) 0.2 M, (○) 0.1 M, (◆) 0.05 M], (b) Variation of k_{app} (slope of the straight lines in Figure 4a) as a function of the concentration of PhI.

was instantly formed in THF from a mixture of Pd(dba)₂ + 1dppf (for its characterization, see Tables 1 and 2). Pd(dba)-(dppf) was isolated as a yellow powder in 96% yield, according to the procedure employed for the synthesis of Pd(dba)(dppe),¹⁷ using toluene as solvent. The isolated complex possesses the same physical properties as the complex generated *in situ* in THF, from the mixture of Pd(dba)₂ + 1dppf. Their ³¹P NMR spectra were identical and their oxidation peaks located at the same potential (Tables 1 and 2). The complex Pd(dppf)₂ was formed from a mixture of Pd(dba)₂ + 2dppf, by a slow reaction (the oxidation peak of Pd(dba)(dppf) completely disappeared after 22 h) while 2 equiv of dba was released into the solution. The complex Pd(dppf)₂ precipitated out of the solution and was isolated. Its physical properties (³¹P NMR data and oxidation potential in Tables 1 and 2) were identical to those of an authentic sample synthesized by reduction of PdCl₂(dppf) in the presence of 1dppf.²¹ Pd(dppf)₂ did not react with PhI.



II. Rate and Mechanism of the Oxidative Addition of PhI with the Palladium(0) Complexes Generated *in Situ* in the Mixture of Pd(dba)₂ + 1 Bidentate Phosphine Ligand, in THF. Since mixtures of Pd(dba)₂ and 2 equiv of L-L afforded the complex Pd(L-L)₂ (except for BINAP), which did not react with phenyl iodide, only the reactivity of the complex Pd(dba)-(L-L) generated *in situ* from the mixture Pd(dba)₂ + 1L-L presents some interest from a synthetic point of view.²² We observed by ³¹P NMR spectroscopy and cyclic voltammetry that

(21) Fang, Z.-G.; Low, M. N.; Ng, S.-C.; Hor, A. J. *Organomet. Chem.* **1994**, 483, 17.

(22) Although complexes Pd(L-L)₂ do not react with PhI, they can activate other organic substrates such as allylic acetates.³ The reaction probably proceeds by substitution of one bidentate ligand L-L by the double bond of the allylic acetate.

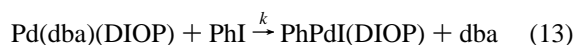
complexes Pd(dba)(L-L) reacted with phenyl iodide to yield PhPdI(L-L). However, this does not establish that Pd(dba)(L-L) itself was the reactive species. Indeed, the oxidative addition could proceed *via* another more reactive palladium(0) complex²³ involved in an endergonic equilibrium with Pd(dba)(L-L) and thus present at such a low concentration that it could not be detected, neither by ³¹P NMR spectroscopy nor by cyclic voltammetry.

(a) Pd(dba)₂ + 1DIOP. The detailed mechanistic investigation for the oxidative addition with PhI is described hereafter in the case of the mixture Pd(dba)₂ (2 mM) + 1DIOP, in THF at 40 °C. After evolution of this mixture to the complete formation of Pd(dba)(DIOP) at 20 °C (monitored by cyclic voltammetry; see section Ib), the single oxidation peak of Pd(dba)(DIOP) was detected at +0.66 V. The kinetics of the oxidative addition was then monitored by amperometry at a rotating disk electrode, at 40 °C. The electrode potential was set at +0.6 V, i.e., near the plateau of the oxidation wave of Pd(dba)(DIOP). The decay of the anodic current i was then monitored as a function of time, after addition of an excess of PhI.

Typical plots of $\ln(i_0/i)$ (i_0 = initial oxidation current, i = oxidation current at t) as a function of time and for different concentrations of PhI are represented in Figure 4a. These plots are linear, showing that the reaction order in palladium(0) is 1. The slope k_{app} of the straight lines was plotted as a function of the concentration of PhI (Figure 4b). The variation is linear, but surprisingly, the regression line does not pass through the origin:

$$k_{app} \text{ (s}^{-1}\text{)} = 0.0075 + 0.06[\text{PhI}] \quad (12)$$

showing that the reaction order in PhI differs from 1. Indeed were Pd(dba)(DIOP) to react with phenyl iodide according to the reaction



the plot of the variation of $\ln(i_0/i)$ as a function of time should

(23) Starting from Pd(0)(PPh₃)₄, it was established that the major species was Pd(0)(PPh₃)₃ involved in an endergonic equilibrium with PPh₃ and the reactive complex Pd(0)(PPh₃)₂. See: Fauvarque, J. F.; Pflüger, F. *Troupel, M. J. Organomet. Chem.* **1981**, 208, 419.

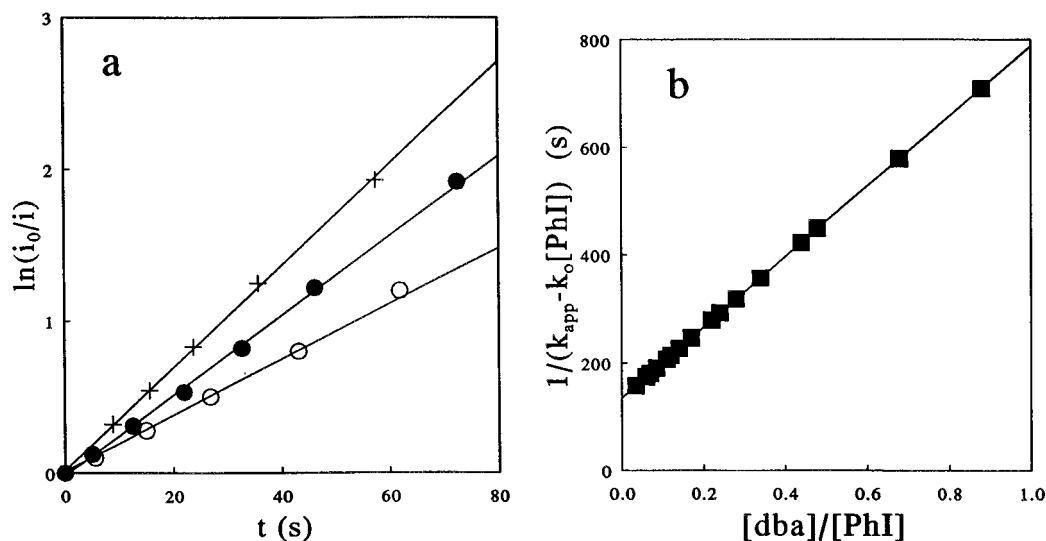


Figure 5. Kinetics of the oxidative addition of PhI with the palladium(0) complex generated *in situ* in the mixture of Pd(dba)₂ (2 mM) + 1DIOP in THF, at 40 °C: (a) variation of $\ln(i_0/i)$ (i = oxidation plateau current at +0.60 V *vs* SCE, at a rotating gold disk electrode (2 mm diameter, ω = 105 rad s⁻¹)) as a function of time, in the presence of PhI (0.4 M) and various concentrations of dba [(+) 0 M, (●) 0.02 M, (○) 0.04 M], (b) variation of $1/(k_{app} - k_0[\text{PhI}])$ as a function of the ratio $[\text{dba}]/[\text{PhI}]$.

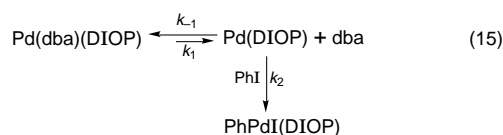
obey the following law:

$$\ln(i_0/i) = k[\text{PhI}]t = k_{app}t \quad \text{with} \quad k_{app} = k[\text{PhI}] \quad (14)$$

The same kinetic investigations were undertaken in the presence of various amounts of dba, added to the solution of Pd(dba)(DIOP). Typical plots of the variations of $\ln(i_0/i)$ as a function of time, for different concentrations in dba, are shown in Figure 5a. Straight lines were again obtained, and their slopes k_{app} were found to be smaller and smaller when the concentration of dba increased. Thus, the presence of extra dba slows the overall rate of the oxidative addition in contradiction with the usual belief. This implies that dba is involved in a fast equilibrium with the effective reactive palladium(0) species.

The most simple and reasonable explanation consisted in considering that the reactive species is the 14-electron complex Pd(DIOP), being in equilibrium with the 16-electron Pd(dba)(DIOP) (eq 15, Scheme 1). Note that Pd(DIOP) is probably

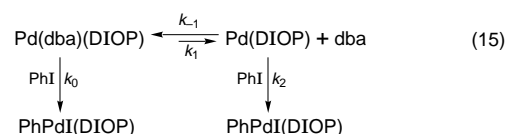
Scheme 1



ligated by the solvent which is omitted in the equation for simplification. In this system Pd(DIOP) is expected to be the more reactive species because of it being the less ligated one. However, were Pd(DIOP) the only reactive species, $1/k_{app}$ should vary linearly with the concentration of dba for a given concentration of PhI (see the Experimental Section). Since this is in contradiction with experimental observations (Figure 5b), we had to consider a more complex sequence, in which both Pd(dba)(DIOP) and Pd(DIOP) may react with PhI (Scheme 2).²⁴

(24) Pd(dba)(DIOP) is stable in solution under argon for at least one night. Its stability has been controlled by performing ³¹P NMR spectroscopy. As one can see in Table 3, the half time of the oxidative addition with phenyl iodide is rather small, and no degradation of Pd(dba)(DIOP) can occur during this short time. Thus, a degradation of Pd(dba)(DIOP) could not be invoked to explain the nonproportionality to PhI (rate law in eq 12 and intercept different from 0, Figure 4b).

Scheme 2



With the framework of Scheme 2, one has (see the Experimental Section)

$$k_{app} = k_0[\text{PhI}] + \frac{k_1 k_2 [\text{PhI}]}{k_{-1}[\text{dba}] + k_2[\text{PhI}]} \quad (16)$$

When the concentration of dba is low, i.e., when no dba in excess is present, one has

$$k_{-1}[\text{dba}] \ll k_2[\text{PhI}]$$

Under these conditions, eq 16 simplifies into $k_{app} = k_1 + k_0[\text{PhI}]$, which is identical to the experimental eq 12. The values of k_0 and k_1 could thus be determined:

$$k_0 = 6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} \quad k_1 = 7.5 \times 10^{-3} \text{ s}^{-1}$$

In a more general case, the expression of k_{app} in eq 16 can be rewritten as eq 17, where k_0 is precisely known from the slope obtained at low dba concentrations (eq 12).

$$\frac{1}{k_{app} - k_0[\text{PhI}]} = \frac{k_{-1}[\text{dba}]}{k_1 k_2 [\text{PhI}]} + \frac{1}{k_1} \quad (17)$$

When the ratio $1/(k_{app} - k_0[\text{PhI}])$ was plotted as a function of the ratio $[\text{dba}]/[\text{PhI}]$, a linear correlation was obtained (Figure 5b). This fact validates our hypothesis concerning the parallel reactivity of the two palladium(0) complexes as postulated in Scheme 2. $k_1 = 7.5 \times 10^{-3} \text{ s}^{-1}$ is obtained from the intercept, and is the same as determined above through an independent method, thereby confirming the mechanism in Scheme 2.

Table 3. Comparative Reactivity of Palladium(0) Complexes with PhI in THF, as a Function of the Ligand and the Precursor

[Pd(0)] = 2 mmol dm ⁻³	T (°C)	[PhI] (mol dm ⁻³)	t _{1/2} (s)	bite angle P–Pd–P, θ (deg)
Pd(PPh ₃) ₄	20	0.01	3.5	
Pd(dba) ₂ + 2PPh ₃	20	0.01	20	
Pd(dba) ₂ + 4PPh ₃	20	0.01	26	
Pd(dba) ₂ + 1DIOP	40	0.2	34	106.4
Pd(dba) ₂ + 1dppf	40	0.2	110	99.07
Pd(dba) ₂ + 1BINAP	40	0.2	16300	92.69
Pd(dba)(BINAP) ^a + 1dba	40	0.2	16000	
Pd(dba)(BINAP) ^a	40	0.2	9700	

^a Isolated complex from the mixture Pd(dba)₂ + 1BINAP.

Table 4. Comparative Reactivity of Palladium(0) Complexes, Generated in the Mixture Pd(dba)₂ + 1L-L, with PhI in THF at 40 °C, According to Scheme 3

[Pd(0)] = 2 mmol dm ⁻³	k ₀ (M ⁻¹ s ⁻¹)	k ₁ (s ⁻¹)	k ₋₁ (M ⁻¹ s ⁻¹)	k ₂ (M ⁻¹ s ⁻¹)	k ₂ /k ₀
Pd(dba) ₂ + 1DIOP	(6.0 ± 0.1) × 10 ⁻²	(7.5 ± 0.1) × 10 ⁻³	>200	>40	>600
Pd(dba) ₂ + 1dppf	(3.0 ± 0.1) × 10 ⁻²	(1.0 ± 0.1) × 10 ⁻³	>30	>30	>1000
Pd(dba) ₂ + 1BINAP	(5.0 ± 0.1) × 10 ⁻³	(1.5 ± 0.1) × 10 ⁻³	>40	>2	>400

From the slope we get

$$\frac{k_{-1}}{k_1 k_2} = 650 \text{ s} \quad \text{and then} \quad \frac{k_{-1}}{k_2} = 4.9$$

$$k_1/k_{-1} = [\text{Pd}(\text{DIOP})]_{\text{eq}}[\text{dba}]_{\text{eq}}/[\text{Pd}(\text{dba})(\text{DIOP})]_{\text{eq}} \quad (18)$$

In the ³¹P NMR spectrum of Pd(dba)(DIOP) generated in mixtures of Pd(dba)₂ + 1DIOP, we only observed the signals of Pd(dba)(DIOP). From this we conclude that equilibrium 15 is considerably shifted to its left-hand side. Under these conditions, the maximum value of the ratio [Pd(DIOP)]_{eq}/[Pd(dba)(DIOP)]_{eq} must be less than 10⁻².

From eq 18, one then obtains k₁/k₋₁ ≪ [dba]_{eq}/100. When dba was not added to the solution, its concentration was 4 mM, showing then that k₁/k₋₁ ≪ 4 × 10⁻⁵ M. Since the value of k₁ is known, a minimum value of k₋₁ can be estimated:

$$k_{-1} \gg 200 \text{ M}^{-1} \text{ s}^{-1}$$

From the ratio k₋₁/k₂, the minimum value of k₂ can be estimated: k₂ ≫ 40 M⁻¹ s⁻¹. Since the value of k₀ has been determined, this showed that k₂/k₀ ≫ 600, from which one sees that Pd(dba)(DIOP) is at least 600 times less reactive than Pd(DIOP).

The values of the rate constants are summarized as follows:

$$k_0 = (6 \pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_1 = (7.5 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$$

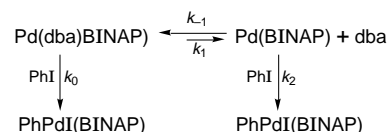
$$k_{-1} \gg 200 \text{ M}^{-1} \text{ s}^{-1}, \quad k_2 \gg 600k_0$$

Therefore, a mixture of Pd(dba)₂ and 1DIOP results in the formation of a major complex, Pd(dba)(DIOP). This species is involved in a fast endergonic equilibrium, yielding a free dba and the less ligated complex Pd(DIOP). This latter species is at least 600 times more reactive in the oxidative addition with PhI than Pd(dba)(DIOP). However, we have established that Pd(dba)(DIOP) also reacts with PhI. Indeed its lower reactivity is easily compensated by its larger availability in the reaction medium, so that its effective rate of oxidative addition is comparable to that of the much more reactive Pd(DIOP) species. This contrasts with monodentate ligands such as PPh₃. Indeed, in this case, we have demonstrated that the only reactive species was Pd(PPh₃)₂ and that Pd(dba)(PPh₃)₂ did not react with PhI, probably due to steric hindrance around the palladium center.²

From the comparison of the values of t_{1/2}, gathered in Table 3, we observe that the catalytic system Pd(dba)₂ + 1DIOP is considerably less reactive than Pd(dba)₂ + 2PPh₃ at identical concentration.

(b) Pd(dba)₂ + 1BINAP. Similar investigations were undertaken to evaluate the reactivity of the palladium(0) complexes generated *in situ* in the mixture Pd(dba)₂ + 1BINAP, with phenyl iodide in THF at 40 °C. Conclusions were essentially the same as for DIOP; *i.e.*, the major complex is Pd(dba)(BINAP) which is involved in an equilibrium with dba and the less ligated complex Pd(BINAP). The latter is the most reactive species, but Pd(dba)(BINAP) also reacts in parallel with PhI, owing to its larger concentration. The values of the corresponding rate constants are collected in Table 4.

Although it is more convenient in a catalytic reaction to start from a mixture of Pd(dba)₂ + 1BINAP, it was of interest to examine the reactivity of the isolated complex Pd(dba)(BINAP) in the oxidative addition with PhI. We thus investigated the reactivity of Pd(dba)(BINAP) alone and in the presence of dba (1 equiv), which should mimic the mixture Pd(dba)₂ + 1BINAP. The values of t_{1/2} for the oxidative additions performed under the same conditions as for the mixture Pd(dba)₂ + 1BINAP are collected in Table 3. We observed that the reactivity of the isolated complex Pd(dba)(BINAP) in the presence of 1dba was the same as that of the mixture Pd(dba)₂ + 1BINAP. As expected, the isolated complex Pd(dba)(BINAP) was more reactive when alone in solution than in the presence of 1 equiv of dba. These results confirm the mechanism established in Scheme 2:



Indeed, the isolated complex Pd(dba)(BINAP) is more reactive alone than in the presence of 1 equiv of dba, because in the former case, the concentration of dba is smaller and thus the equilibrium is more shifted to its right-hand side. Under these conditions, the concentration of the most reactive species Pd(BINAP) increases and the overall reactivity is enhanced. From the value of t_{1/2} (Table 3), we observe that the system Pd(dba)₂ + 1BINAP is considerably less reactive than Pd(dba)₂ + 1DIOP (see further discussion).

(c) Pd(dba)₂ + 1dppf. The major complex Pd(dba)(dppf) was found to be involved in a fast endergonic equilibrium with dba and the most reactive complex Pd(dppf). The kinetic data

are collected in Tables 3 and 4²⁵ and compared to those obtained with BINAP and DIOP (see further discussion).

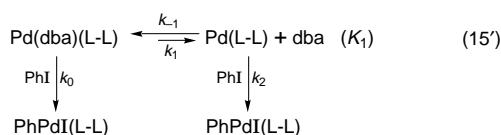
III. Final Discussion and Conclusion. Complementary use of ³¹P NMR spectroscopy and voltammetry proved essential in the investigation of the mechanism of oxidative addition of palladium(0) complexes generated *in situ* from mixtures of Pd(dba)₂ and bidentate ligands. Indeed, voltammetry allowed a fine investigation of the mechanistic features but lacked the structural information which could only be provided by ³¹P NMR spectroscopy. Conversely ³¹P NMR did not allow a fine investigation of the kinetics at hand, which only could be provided by voltammetry.

Mixtures of Pd(dba)₂ + 2L-L afford the complex Pd(L-L)₂, except for BINAP. The rate of formation of Pd(L-L)₂ obeys the order DIOP > dppf ≫ BINAP and thus is higher when the bite angle is higher ($\theta(\text{DIOP})^{5c,26} > \theta(\text{dppf})^{27} > \theta(\text{BINAP})^{18}$), evidence that this factor is not kinetically predominant.

Whatever the bidentate phosphine ligand investigated, mixtures of Pd(dba)₂ + 1L-L always afford the complex Pd(dba)-(L-L) as the major species, directly (with dppf and BINAP) or through the intermediate Pd(L-L)₂ when the latter can be rapidly formed (DIOP, dppm, dppe, dppp). In this later case, it is worth recognizing that since Pd(L-L)₂ does not react with PhI, the reactive species prone to react with PhI are not present at the beginning of the reaction. In this respect, it is important to note that, for example, about 4 h at 20 °C or 2 h at 40 °C is required for quantitative formation of Pd(dba)(DIOP).

Pd(dba)(L-L) is involved in an endergonic equilibrium (eq 15'), releasing dba and the very reactive Pd(L-L) species. Albeit the latter is intrinsically much more reactive than Pd(dba)(L-L), the direct oxidative addition to Pd(dba)(L-L) cannot be overload since the intrinsic reactivities of the two species are partly compensated by their actual available concentrations (Scheme 3).

Scheme 3



From the values of $t_{1/2}$ gathered in Table 3, one observes that whatever the bidentate ligand, the catalytic system Pd(dba)₂ + 1L-L is considerably less reactive than Pd(dba)₂ + 2PPh₃. In all cases, the most reactive species is formed *via* endergonic equilibrium. The pertinent equilibrium constants could not be determined and therefore could not be compared. It is thus impossible to compare the intrinsic reactivity of Pd(L-L) with that of Pd(PPh₃)₂. In other words, one cannot decide whether the lower reactivity of Pd(dba)₂ + 1L-L is due to a lower

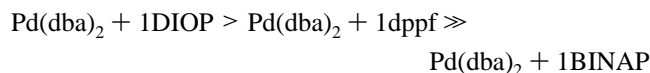
(25) The isolated complex Pd(dba)(dppf) was characterized by UV spectroscopy, in THF ($\lambda_{\text{max}} = 386 \text{ nm}$) and in toluene ($\lambda_{\text{max}} = 393 \text{ nm}$, $\epsilon = 10760 \text{ mol}^{-1} \text{ cm}^2$) at 25 °C. When THF was progressively added to the complex Pd(dba)(dppf) in solution in toluene, one observed a decay of the absorbance of Pd(dba)(dppf) until a constant value obtained after addition of 16% of THF in volume. We do not know whether toluene was able to ligate Pd(dppf) or not, but it seems that THF coordinates the complex Pd(dba)(dppf) to afford Pd(dppf)(THF), resulting in a decay of the initial concentration of Pd(dba)(dppf). From the ϵ value for Pd(dba)(dppf), determined above in toluene, one knows $[\text{Pd(dba)(dppf)}]_{\text{eq}}$ and then $[\text{Pd(dppf)(THF)}]_{\text{eq}}$ by the difference from the initial concentration. Therefore, the value of the following equilibrium constant was determined in toluene: $\text{Pd(dba)(dppf)} + \text{THF} \rightleftharpoons \text{Pd(dppf)(THF)} + \text{dba}$ ($K = 8 \times 10^{-5}$).

(26) The bite angle was determined in the complex $(\text{CH}_2=\text{CH}_2)\text{Pd}(\text{DIOP})$.^{6c} To our knowledge, the bite angle in the complex $\text{Cl}_2\text{Pd}(\text{DIOP})$ is not reported as it is for $\text{Cl}_2\text{Pd}(\text{dppf})^{27}$ and $\text{Cl}_2\text{Pd}(\text{BINAP})$.¹⁸

(27) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

intrinsic reactivity of Pd(L-L) or arises from a concentration effect due to a smaller value of the equilibrium constant which imposes a lower steady state concentration of the reactive species Pd(L-L).

By comparing the three bidentate ligands investigated in this work (Table 3), one sees that their respective reactivity in the oxidative addition with phenyl iodide obeys the following order:



Since the oxidative addition to Pd(L-L) is preceded by an equilibrium (Scheme 3), one has to take into account the influence of the ligand, both on the equilibrium constant K_1 and on the intrinsic rate constants of the oxidative addition to Pd(L-L). For monodentate ligands, it is generally considered and also established^{10,28} that the oxidative addition is favored by basic ligands (electronic effects) and by ligands possessing a small cone angle (steric effects). For bidentate ligands, it is also considered that the oxidative addition is favored by basic ligands and by ligands possessing a small bite angle.

Although to our knowledge no data concerning the basicity of the bidentate ligands are available from the literature, one expects the following order for their basicity:²⁹



From our results (Table 3), we deduce that the rate of the overall reaction follows the order of basicity of the ligands: the more basic the ligand, the faster the overall reaction.

The bite angles follow the order $\theta(\text{DIOP}) > \theta(\text{dppf}) > \theta(\text{BINAP})$. Therefore, the higher the bite angle, the faster the overall reaction. This is an unexpected reverse order. In fact, the rate of the overall reaction is governed by two factors: (i) the value of the intrinsic rate constant k_2 of the oxidative addition (which is expected to increase when the basicity of the ligand increases) and (ii) the concentration of the reactive species Pd(L-L) (which is determined by the value of the equilibrium constant K_1). When the bite angle is high, equilibrium 15' is probably more shifted to its right-hand side because the complex Pd(L-L) is less sterically hindered than Pd(dba)(L-L). Thus, the concentration of the reactive species Pd(L-L) should be higher when the bite angle is larger. Therefore, even if the effect of high bite angles is also to decrease the intrinsic rate of the oxidative addition to Pd(L-L), such a negative effect is certainly more than compensated for by the fact that the concentration of Pd(L-L) is higher for complexes possessing a high bite angle.

Therefore, we observe that whatever the ligand, monodentate (L) or bidentate (L-L), the dba ligand plays a crucial role, in contradiction with the usual belief, since it is always involved in the major and less reactive complex Pd(dba)L₂ or Pd(dba)(L-L). The presence of these stable complexes diminishes the concentration of the more reactive species PdL₂ or Pd(L-L) and consequently controls the apparent rate of the overall reaction. Moreover, in the case of bidentate ligands, we established here that Pd(dba)(L-L) complexes also react with PhI. It is also important to note that an increase of the concentration of dba

(28) Stille, J. K.; Lau, K. S. Y. *Acc. Chem. Res.* **1977**, *10*, 434.

(29) The ligand DIOP is undoubtedly more basic than dppf and BINAP. Concerning the comparative basicity of dppf and BINAP, we have observed by ³¹P NMR spectroscopy that when PhPd(PPh₃)₂ was added to a solution containing 1 equiv of dppf and 1 equiv of BINAP in THF, the resulting complex was PhPd(dppf). A 2 equiv portion of PPh₃ was released in solution, and the BINAP was detected as the free ligand. In another experiment, we observed that the complexation of PdCl₂ by dppf was faster than that by BINAP. Therefore, we conclude that dppf is more basic than BINAP. Note that we are considering here relative kinetic basicities and not thermodynamic basicities.

(which may for example arise from an increase of Pd(dba)₂ concentration in catalytic conditions) results in a shift of equilibrium 15' to the formation of the less reactive species Pd(dba)(L-L). In the case of chiral chelating diphosphines, the spatial environment in Pd(dba)(L-L) is expected to be different from that in Pd(L-L) because of the monoligation of dba in Pd(dba)(L-L). Therefore, starting from a prochiral organic derivative, the potential asymmetric induction could then differ from one complex to another, showing that the overall asymmetric induction might vary with the experimental conditions, particularly with the concentration of Pd(dba)₂ and of course with the relative concentration of the dba and bisphosphine ligands.

Experimental Section

³¹P NMR spectra were recorded on a Bruker spectrometer (162 MHz) using H₃PO₄ as an external reference. All experiments were performed under argon and at controlled temperature. UV spectroscopy was recorded on a Beckman DU 7400 spectrometer.

Chemicals. THF was distilled on sodium–benzophenone. Iodobenzene was from a commercial source (Aldrich) and used after filtration on alumina. Bidentate phosphines, dppm, dppe, dppp, dppb, (+) DIOP, dppf, and (–)-BINAP, were also from a commercial source (Aldrich). Pd(dba)₂ was synthesized according to published procedures.³⁰

Electrochemical Setup and Electrochemical Procedure for Cyclic Voltammetry. Cyclic voltammetry was performed as previously described in ref 2. Typical procedure: investigation by cyclic voltammetry of the mixture of Pd(dba)₂ and 1DIOP in THF. To 15 mL of anhydrous THF containing *n*-Bu₄NBF₄ (0.3 mol dm⁻³) was added 17 mg (0.03 mmol) of Pd(dba)₂ followed by 15 mg (0.03 mmol) of DIOP. The formation of Pd(dba)(DIOP) was monitored by performing cyclic voltammetry as a function of time. When the formation of Pd(dba)(DIOP) was completed as attested by the absence of the reduction peak R₀ of Pd(dba)₂, the rotating gold disk electrode was polarized at +0.06 V on the plateau of the oxidation wave of Pd(dba)(DIOP) and the decay of the oxidation current was recorded as a function of time after addition of 17 μL (0.15 mmol) of phenyl iodide. At the end of the oxidative addition, the value of the residual oxidation current was about 5% of its initial value.

Derivation of the Rate Law Corresponding to Scheme 1. Since Pd(DIOP) could not be observed, it has to obey the steady state

approximation

$$d[\text{Pd}(\text{DIOP})]/dt = k_1[\text{Pd}(\text{dba})(\text{DIOP})] - (k_{-1}[\text{dba}] + k_2[\text{PhI}])[\text{Pd}(\text{DIOP})] = 0$$

from which it follows that

$$[\text{Pd}(\text{DIOP})] = \frac{k[\text{Pd}(\text{dba})(\text{DIOP})]}{k_{-1}[\text{dba}] + k_2[\text{PhI}]}$$

Thus, the overall rate is obtained as follows:

$$v = k_2[\text{PhI}][\text{Pd}(\text{DIOP})] = k_2[\text{PhI}] \frac{k_1[\text{Pd}(\text{dba})(\text{DIOP})]}{k_{-1}[\text{dba}] + k_2[\text{PhI}]} = k_{\text{app}}[\text{Pd}(\text{dba})(\text{DIOP})]$$

with

$$k_{\text{app}} = \frac{k_1 k_2 [\text{PhI}]}{k_{-1} [\text{dba}] + k_2 [\text{PhI}]}$$

Derivation of the Rate Law Corresponding to Scheme 2. The overall rate is now given by

$$v = k_0[\text{PhI}][\text{Pd}(\text{dba})(\text{DIOP})] + k_2[\text{PhI}][\text{Pd}(\text{DIOP})]$$

which, still considering the steady state approximation for Pd(DIOP), affords

$$v = k_0[\text{PhI}][\text{Pd}(\text{dba})(\text{DIOP})] + k_2[\text{PhI}] \frac{k_1[\text{Pd}(\text{dba})(\text{DIOP})]}{k_{-1}[\text{dba}] + k_2[\text{PhI}]} = k_{\text{app}}[\text{Pd}(\text{dba})(\text{DIOP})]$$

with

$$k_{\text{app}} = k_0[\text{PhI}] + \frac{k_1 k_2 [\text{PhI}]}{k_{-1} [\text{dba}] + k_2 [\text{PhI}]}$$

Acknowledgment. This work has been supported in part by the Centre National de la Recherche Scientifique (CNRS, URA 1679, “Processus d’Activation Moléculaire”) and the Ministère de l’Enseignement Supérieur et de la Recherche (Ecole Normale Supérieure). A Chateaubriand, postdoctoral grant from the French Ministère des Affaires Etrangères to G.B. is also greatly acknowledged. This paper is dedicated to Professor H. Schäfer on the occasion of his 60th birthday.

(30) (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc. D* **1970**, 1065. (b) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 134.