Chelate Effect on the Structure and Reactivity of Electron-Rich Palladium Complexes and Its Relevance to Catalysis

Moshe Portnoy and David Milstein*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel

Received September 18, 1992

In order to clarify the origin of the "chelate effect" in catalysis by palladium, complexes of $^{i}Pr_2P(CH_2)_n{}^{i}Pr_2P$ (n = 2, dippe; n = 3, dippp; n = 4, dippb), $Ph_2P(CH_2)_3PPh_2$ (dppp), and $P^{i}Pr_2{}^{n}Bu$ were prepared and their structures, dynamic properties, and reactivities were compared. Pd(dippe)$_2$ **1d** is a coordinatively saturated complex, both in solution and in the solid state. X-ray characterization exhibits a distorted tetrahedral geometry. The dippe bite angle is 87.05°. The compound crystallizes in the orthorhombic space group *Pnna* with a = 16.713(3) Å, b = 17.561(3) Å, c = 11.116(2) Å, V = 3277(1) Å^3, Z = 4. Pd(dippp)$_2$ (**1a**) and Pd(dippb)$_2$ (**1e**) are coordinatively unsaturated, trigonal complexes and are in equilibrium with the binuclear complexes LPd(η^2-L)PdL, **1b** and **1f**, respectively. Whereas **1d** does not exhibit dynamic behavior, **1a** and **1e** undergo fast, intramolecular phosphine exchange, a process which is not observed with **1b** and **1f**. The trigonal complexes (dippp)Pd$P^{i}Pr_2Bu$ (**1c**) and $(P^{i}Pr_2{}^{n}Bu)_3Pd$ were also prepared for comparison. The dippp complexes **1a**–**1c** react with aryl chlorides to produce *cis*-(dippp)Pd(C_6H_4X)Cl as the major product and *trans*-(η^1-dippp)$_2$Pd(C_6H_4X)Cl as the minor one (X = 4-OMe, 4-Me, H, 3-OMe, 4-COMe, 4-CHO, 4-NO_2). In contrast, the dippb complex **1e** oxidatively adds chlorobenzene to yield only the trans complex (η^1-dippb)$_2$Pd(Ph)Cl. Reaction monitoring reveals that the cis and trans complexes are formed in parallel pathways. Cis/trans equilibrium is on the cis side for dippp and on the trans side for dippb. Reactivity toward chlorobenzene follows the trend Pd(dippp)$_2$ > Pd($P^{i}Pr_2{}^{n}Bu$)$_3$ ≫ Pd(dippe)$_2$ ≫ Pd(dppp)$_2$. These results are interpreted in terms of chelate stability, ligand basicity, concentration of the active 14e species and effect of the P–Pd–P angle on its reactivity. The dippp ligand is unique in that it is the only one of those studied which results in Pd(0) complexes which (a) exhibit high reactivity in oxidative addition and (b) form cis complexes preferentially.

Introduction

Chelating phosphine ligands sometimes impart dramatic effects on transition metal homogeneously catalyzed reactions in general and on palladium catalyzed reactions in particular.[1] Tentative explanations have been given, although definite answers for this important effect are generally not available. For example, we have observed that the complex Pd(dippp)$_2$ [dippp = 1,3-bis(diisopropylphosphino)propane] is an excellent catalyst for carbonylation,[2a] formylation,[2b] and reduction[2c] of aryl chlorides (eqs 1–3), whereas complexes of monodentate phosphines are much less reactive under similar conditions.[2-4] Moreover, the chelate ring size has a dramatic effect on reactivity. Thus, reducing or increasing the size of the chelating ligand by one carbon, i.e. utilizing

$$\mathrm{Ar{-}Cl + CO + NuH + base} \xrightarrow{\mathrm{Pd(dippp)_2}} \mathrm{ArC(O){-}Nu + base{\cdot}HCl} \quad (1)$$

$$\mathrm{NuH = H_2O, ROH, RNH_2}$$

$$\mathrm{Ar{-}Cl + CO + HCO_2Na} \xrightarrow{\mathrm{Pd(dippp)_2}} \mathrm{ArC(O){-}H + NaCl + CO_2} \quad (2)$$

$$\mathrm{Ar{-}Cl + HCO_2Na} \xrightarrow{\mathrm{Pd(dippp)_2}} \mathrm{Ar{-}H + NaCl + CO_2} \quad (3)$$

the complexes Pd(dippe)$_2$ and Pd(dippb)$_2$ [dippe = 1,2-bis(diisopropylphosphino)ethane; dippb = 1,4-bis(diisopropylphosphino)butane], results in a substantial reduction of catalytic activity.[2] Also, complexes of chelating phosphines of the same chelate size as dippp but of lower basicity are much less reactive.

In order to clarify the reason for this substantial chelate effect and find out what makes the dippp ligand "special", we prepared Pd(0) complexes of various chelate ring sizes and basicity and compared their structure, dynamic behavior, and reactivity toward aryl chlorides. The dippp ligand was found to present an excellent compromise between the seemingly conflicting needs for a reasonably efficient chelating ligand and for vacant coordination sites.

(1) For example: (a) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984,** *106,* 158. (b) Dolle, R. E.; Schmidt, S. J.; Kruse, L. I. *J. Chem. Soc., Chem. Commun.* **1987,** 904. (c) Pisano, C.; Mezzett, A.; Consiglio, G. *Organometallics* **1992,** *11,* 20. (d) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991,** *417,* 235. (e) Alper, H.; Saldana-Maldonado, M.; Lin, I. J. B. *J. Mol. Catal.* **1988,** *49,* L27.

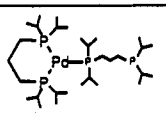
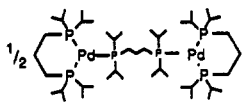
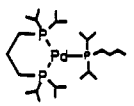
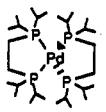
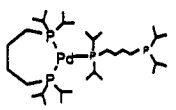
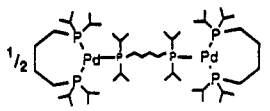
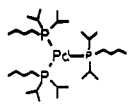
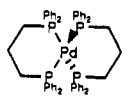
(2) (a) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989,** *111,* 8472. (b) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989,** 1816. (c) Ben-David, Y.; Gozin, M.; Portnoy, M.; Milstein, D. *J. Mol. Catal.* **1992,** *73,* 173.

(3) Complexes of bulky, monodentate phosphines catalyze carbonylation of aryl chlorides at higher temperatures[3a] or under phase transfer conditions.[3b] (a) Huser, M.; Youinou, M.-T.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1386. (b) Grushin, V. V.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1992,** 611.

(4) Heterogeneous Pd catalysis of aryl chloride carbonylation in the presence of an oxidant and absence of phosphines: Dufaud, V.; Thivolle-Cazat, J.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1990,** 426.

0276-7333/93/2312-1655$04.00/0

Table I. Structures of the Pd(0) Complexes 1a–h and the Ligands Used in Their Preparations, According to Eq 4[a]

L	1
2dippp	 **1a**
$^3/_2$dippp	 **1b**
dippp + P^{i}Pr$_2$Bu	 **1c**
2dippe	 **1d**
2dippb	 **1e**
$^3/_2$dippb	 **1f**
3P^{i}Pr$_2$Bu	 **1g**
2dppp	 **1h**

[a] The stoichiometric coefficients *m* and *n* are included.

Results and Discussion

1. Preparation of Pd(0) Complexes. The Pd(0) complexes **1a–h** were prepared by nucleophilic cleavage of an allylpalladium complex (eq 4), where Nu$^\ominus$ is OMe$^\ominus$ or OH$^\ominus$. The ligands L and the complexes **1** are described in Table I.

$$^1/_2[Pd(\eta^3\text{-2-methylallyl})Cl]_2 + Nu^- + mL \rightarrow n\mathbf{1} + Cl^- + CH_2{=}C(Me)CH_2Nu \quad (4)$$

The procedure used is analogous to the one reported for $Pd(PCy_3)_2$.[5] Unlike $Pd(PCy_3)_2$, complexes **1a–d** did not precipitate from the reaction mixture and were isolated by solvent removal and pentane extraction of the residue. Complexes **1a** and **1c** were obtained as yellow oils, which solidified very slowly upon cooling, whereas **1b** was obtained as a yellow solid immediately after pentane evaporation. Complex **1d** crystallized as colorless prismatic crystals during pentane evaporation. A small amount of yellowish, oily impurities was washed out with a little cold pentane. Purification of complex **1g** was carried out similarly to that of **1a–c**, but two pentane extraction–evaporation cycles were needed to get a sufficiently pure compound. During the synthesis of **1e**, precipitation of a very insoluble, probably polymeric yellow solid occurred. Solvent evaporation and several pentane extraction–evaporation cycles yielded a yellow oil, whose ^{31}P NMR in dioxane demonstrated that only ca. 50% of the P-containing species were Pd(0) complexes of dippb (**1e** and **1f**). A small amount of complex **1f** precipitated as yellow needles from the dioxane solution of the mixture upon prolonged standing. Complex **1h** precipitated from the reaction mixture as a lemon-yellow solid, which was washed with cold methanol to yield the pure complex.

2. Solution Structure and Dynamic Behavior of Complexes 1a–1h. The complexes may be divided into a number of groups according to their behavior in solution. Complexes **1d** and **1h** exhibit similar, limited solubility in solvents of different polarity such as pentane, toluene, dioxane, THF, and DMF, which increases significantly upon heating. Slow cooling of hot saturated solutions of **1d** and **1h** yields good crystals of these compounds. $^{31}P\{^1H\}$ NMR of dioxane solutions of these complexes exhibit singlets at 45.5 and 3.7 ppm, respectively, indicating that they are present in solution as 18-electron saturated complexes (Table I). X-ray analysis of **1d** has shown that this is also true in the solid state (see crystallographic section). Complexes **1b**, **1c**, and **1f** have significantly higher solubility, and their solutions have an intense yellow color. $^{31}P\{^1H\}$ NMR of **1b** and **1c** consists of a doublet and a triplet (a small second-order distortion, resulting in a ca. 2-Hz splitting of the central peak of the triplet, is obtained) and **1f** exhibits an A_2B second-order pattern, clearly indicating that these complexes are present in solution in a tricoordinate Y-shaped form (Table I). The large coupling constants (84 Hz for **1b** and **1c** and 95 Hz for **1f**) are probably indicative of such a coordination geometry of Pd(0) complexes.[6] Complexes **1b** and **1f** contain dippp and dippb ligands in both chelating and bridging modes, exhibiting the ambidentate nature of these ligands.

The solution behavior of **1a** is complicated, $^{31}P\{^1H\}$ NMR in toluene exhibiting dynamic behavior (Figure 1). At 213 K, three sharp sets of doublets (in the 21–23 ppm region), triplets (at 44–47 ppm), and singlets (at −1 to +2 ppm) are observed. The coupling constants of the triplets correspond to those of the doublets and are ca. 84 Hz. In addition, three small singlets appear in the region 51–53 ppm. At 253 K slight changes in the chemical shifts occur, but basically the same patterns are observed. Above 273 K, the biggest set of signals (triplet, doublet, and singlet) becomes broader and at 313 K only two (each) sharp triplets, doublets, and singlets are observed. However, at this temperature each group of peaks sits on a "hill"—a residue from the broader signal. At 333 K coalescence of the biggest set of signals is achieved. The three singlets downfield from 50 ppm are almost unaffected by the temperature changes.

The second-in-size doublet and the triplet are identical to the signals of **1b** and are assigned to this complex. The singlet, second in size from the group of singlets near 0 ppm is that of free dippp, and its concentration is approximately equivalent to that of **1b**. The largest set of signals (singlet, doublet, and triplet) is assigned to

(5) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187.

(6) Values in the 80–100-Hz range seem to be characteristic for $^2J_{PMP}$ in trigonal Pd(0) complexes. Although we could not locate an appropriate reference, it fits well between the 15–65 Hz range of the cis-oriented phosphines and the 200–500 Hz range of the trans-oriented phosphines.

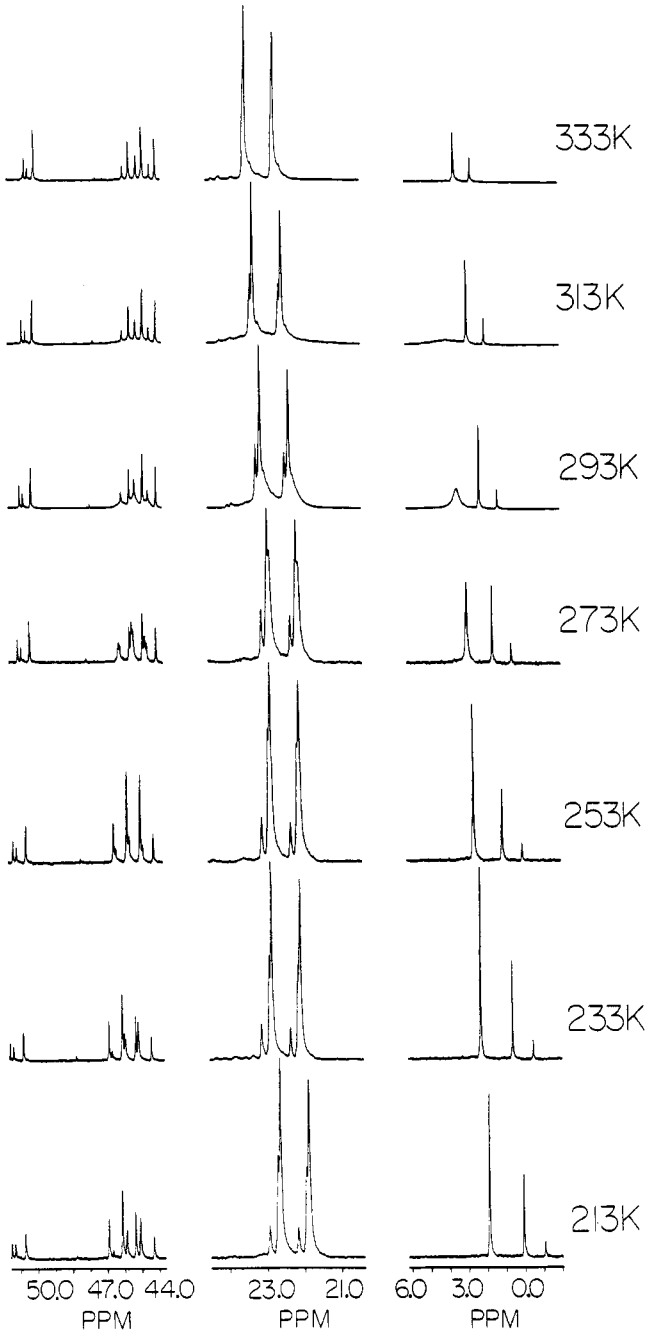
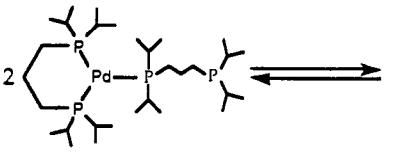


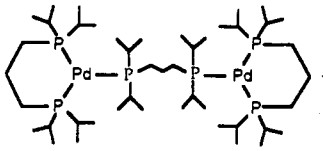
Figure 1. Dynamic behavior of **1a** in a toluene solution.

complex **1a** (Table I). These results indicate that equilibrium 5 is operative.[7] The existence of such an equilibrium is not surprising, since the coordination ability of the free "arm" of **1a** should not differ markedly from that of dippp. The smallest doublet and triplet, as well as one of the three singlets, downfield from 50 ppm, are assignable to the complex (dippp)PdP(^{i}Pr)$_2$.$CH_2CH_2CH_2P(O)^iPr_2$ with the singlet assigned to the oxidized phosphorus moiety. One of the two remaining singlets downfield from 50 ppm is assigned to OP-(^{i}Pr)$_2$$CH_2CH_2CH_2P(O)^iPr_2$, while the last singlet in this region, as well as the smallest signal in the 0 ppm region, are assigned to $^iPr_2P(CH_2)_3P(O)^iPr_2$.

The dynamic behavior of **1a** is interesting, especially in light of the fact that **1b** and **1c** exhibit sharp spectra even



(1a)

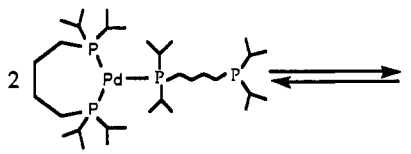


(1b)

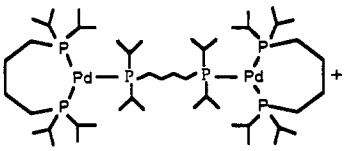
(5)

at elevated temperatures. The major difference in the structures of **1a** and **1b** is the presence of a noncoordinated phosphine moiety in **1a**. The two possible processes that can cause line broadening, spin loss, and at higher temperatures, coalescence of all the signals of **1a** are intramolecular processes, as demonstrated in Scheme I, involving the free phosphine moiety. Intermolecular ligand exchange processes can be excluded as a reason for the spin loss of **1a**, since such processes should take place also with **1b** (Scheme II). In any case, only the intramolecular ligand exchanges described in Scheme I could explain the coalescence of the signals of **1a**. This conclusion does not mean that the intermolecular processes described in Scheme II are not active. The dissociative pathway exists, but it is not fast enough to cause spin loss, as we have shown by the inversion transfer NMR technique[8] for **1c**.[9] (The rate of ligand exchange for a 1:1 mixture of **1c** and $P^iPr_2{}^nBu$ at 60 °C was found to be ca. 8 s^{-1}, which is not fast enough to cause spin loss for the patterns with 84-Hz splitting.) The associative pathway, if it exists, should be even slower than the dissociative one.

The solution behavior of **1e** is expected to be similar to that of **1a**. $^{31}P\{^1H\}$ NMR of the mixture containing the complex exhibits six broad signals at room temperature, one of them close to the chemical shift of free dippb and five others arranged in an A_2B pattern. These patterns support a trigonal planar geometry for **1e** with an open phosphine "arm", similar to that of **1a**. Formation of **1f** from this mixture indicates that equilibrium 6, analogous to equilibrium 5, is operative.



(1e)



(1f)

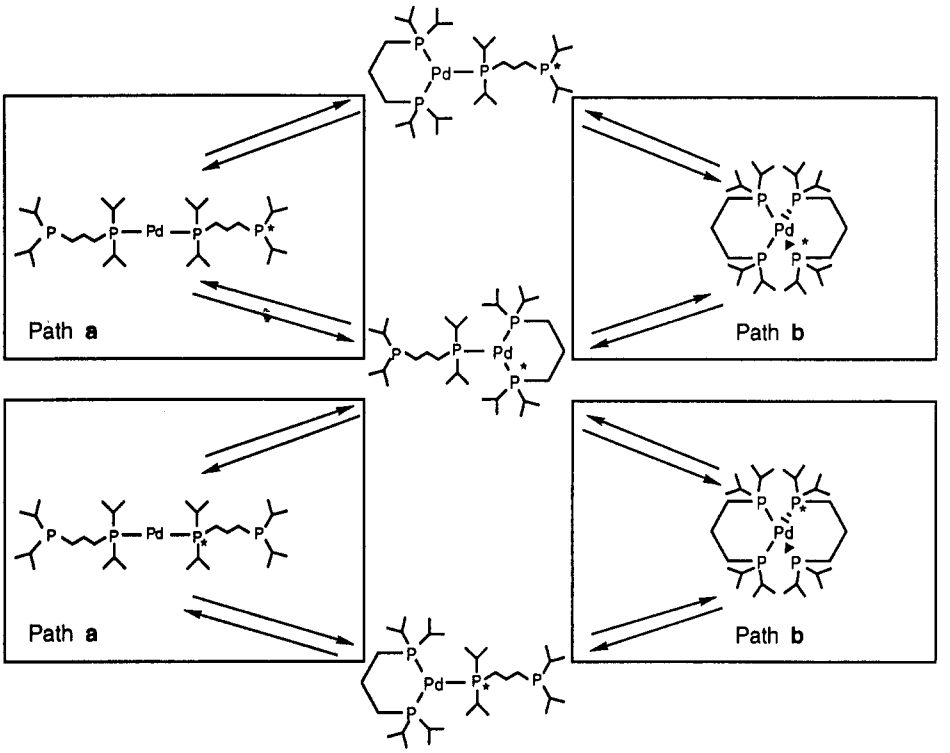
(6)

(7) This equilibrium was also observed by Dr. R. T. Baker, of Du Pont Co., who prepared Pd(0) complexes of dippp independently in parallel to our work.

(8) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy. A Guide for Chemists*; Oxford University Press: New York, 1987; pp 224–229 (see also references therein).

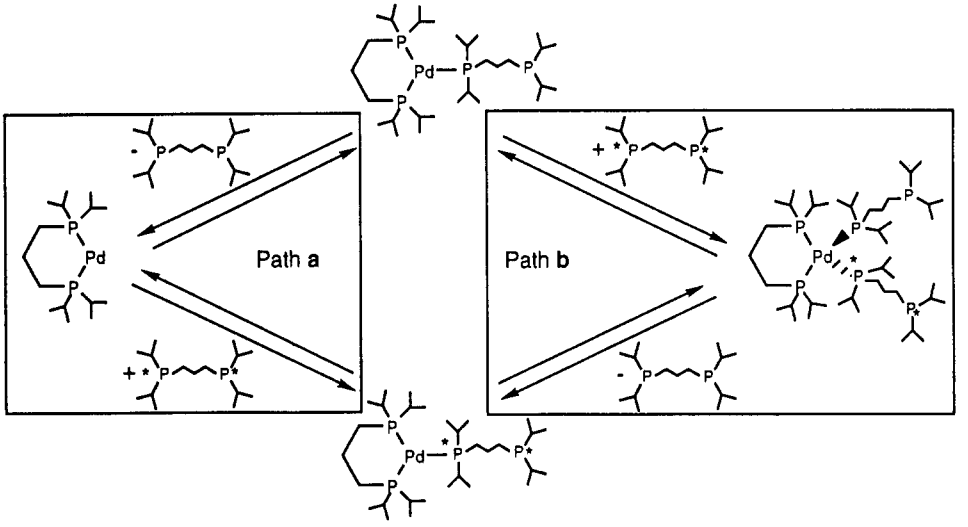
(9) Portnoy, M.; Milstein, D. *Organometallics*, following article in this issue.

Scheme I. Intramolecular Phosphine Exchange Pathways Responsible for Spin Loss and Signal Coalescence in 1a[a]



[a] The star-marked P atom is shown at different sites to emphasize the exchange. Two possible pathways shown are (a) dissociative and (b) associative.

Scheme II[a]



[a] Intermolecular phosphine exchange pathways (a) dissociative and (b) associative are possible, but they are probably masked by the intramolecular process.

Complex **1g**, which was obtained as orange-red crystals at −30 °C, melts at room temperature to form an orange oil, which is very soluble in various solvents (pentane, benzene, dioxane, and THF). $^{31}P\{^1H\}$ NMR of its THF solution exhibits, at room temperature, a very broad hill at ca. 32 ppm, which becomes a sharp singlet at 29.6 ppm upon cooling to 223 K. This compound is frequently accompanied by a small amount of the bis complex $Pd(P^iPr_2{}^nBu)_2$, appearing as a singlet at 35.6 ppm. Addition of $P^iPr_2{}^nBu$ transforms this complex into **1g**. Dissociative equilibria involving palladium[10a] and platinum[10b] complexes of monodentate phosphines have been studied in detail.

3. Crystal Structure of Pd(dippe)$_2$. Colorless prismatic crystals of $Pd(dippe)_2$ (**1d**), suitable for a crystallographic study, were obtained by slow pentane evaporation.

The low temperature molecular structure is shown in Figure 2. We are not aware of other crystallographically characterized P_4Pd^0 complexes (P = phosphine). PdL_2 [L = bis(diphenylphosphino)maleic anhydride] was shown to be a planar, $Pd^{2+}L_2^-$ complex.[11] X-ray structures of

(10) (a) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1673. (b) *Ibid.* **1980**, 776.
(11) Bensman, W.; Fenske, D. *Angew Chem., Int. Ed. Engl.* **1979**, *18*, 677.

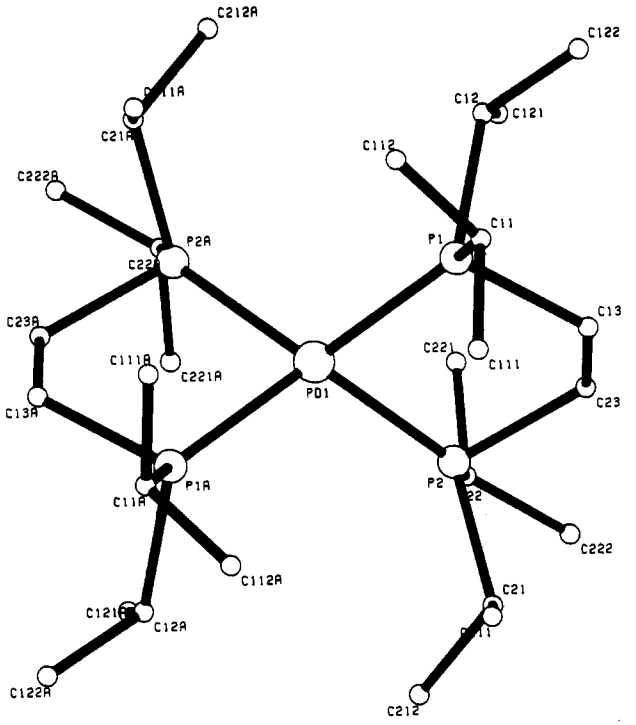


Figure 2. X-ray structure of **1d**.

Table II. Experimental Crystallographic Data for 1d

mol wt	631.108
space group	*Pnna* (orthorhombic)
temp, °C	183
cell constants	
a, Å	16.713(3)
b, Å	17.561(3)
c, Å	11.116(2)
cell vol, Å^3	3277(1)
formula	$C_{28}H_{64}P_4Pd$
D(calc), g cm^{-3}	1.279
μ, cm^{-1}	7.66
diffractometer/scan	Rigaku AFC5R/w-20
source	rotating anode Rigaku RU-300
speed of measmt, deg min^{-1}	8
radiation, graphite monochr	Mo Kα (λ = 0.7114 Å)
max cryst dimens, mm	0.3 × 0.3 × 0.2
transm max/min	0.94/0.79
no. of reflections	
measured	5030
with $I > 1.50$	2968
scan limits, deg	$2.0 \le 2\theta \le 55$
final R, R_w	0.041, 0.038

PdL_2 [L = $P(C_6H_{11})_3$, P^tBu_2Ph] have been reported.[12] Experimental crystallographic data are listed in Table II, and selected bond lengths and angles are listed in Table III.

Complex **1d** crystallizes in the *Pnna* space group. As expected, coordination around the palladium center is distorted tetrahedral. The bite angle of the dippe ligand P(1)-Pd-P(2) is 87.05 (3)°, substantially smaller than the tetrahedral angle (109.5°), whereas the nonchelating P(1)-Pd-P(2a) is 117.52 (3)°. The angle between the planes P(1)-Pd-P(2) and P(1a)-Pd-P(2a) is 82.43(1)°.

4. Reactivity of the Pd(0) Complexes toward Aryl Chlorides. The dippp complexes, **1a-1c** react with aryl chlorides in a similar way, producing the complex *cis*-(dippp)Pd(Ar)Cl (**2**) as a major product and *trans*-(η^1-dippp)$_2$Pd(Ar)Cl (**3**) as a minor one (see Figure 3). The mechanistic details of this oxidative addition reaction are described and discussed in the subsequent paper.[9] The cis complexes were fully characterized by multinuclear NMR measurements (Tables IV-VI). The ring substituent influence on the chemical shift of nuclei of complex **2** are readily observed. Thus, moving along the series of the *cis*-**2** complexes from the 4-methoxy substituent (strong electron donor) to 4-nitro (strong electron acceptor) is accompanied by a strong and consistent downfield shift of the ipso carbon signal (ca. 30 ppm) and by weaker and fairly consistent downfield shifts of the ortho and meta hydrogens and of the phosphorus trans to the phenyl group. The 3-anisyl-substituted complex exhibits significantly broadened lines of the carbons and hydrogens of the aromatic ring and of the two isopropyl groups attached to the phosphorus atom cis to the aromatic ring. This line broadening is probably a result of restricted rotation

(12) (a) Immirz, A.; Musco, A. *J. Chem. Soc., Chem. Commun.* **1974**, 400. (b) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

Table III. Bond Lengths (Å) and Angles (deg) for 1d

Bond Lengths

P(1)-Pd(1)	2.368(3)	P(2)-Pd(1)	2.361(3)
C(11)-P(1)	1.866(6)	C(12)-P(1)	1.883(6)
C(13)-P(1)	1.858(6)	C(111)-C(11)	1.528(8)
C(112)-C(11)	1.531(8)	C(121)-C(12)	1.518(8)
C(122)-C(12)	1.540(8)	C(23)-C(13)	1.536(7)
C(21)-P(2)	1.867(6)	C(22)-P(2)	1.877(6)
C(23)-P(2)	1.863(6)	C(211)-C(21)	1.525(8)
C(212)-C(21)	1.529(8)	C(22)-C(221)	1.529(8)
C(22)-C(222)	1.530(7)		

Bond Angles

P(2)-Pd(1)-P(1)	87.05(3)	C(11)-P(1)-Pd(1)	127.7(2)
C(12)-P(1)-Pd(1)	118.4(2)	C(12)-P(1)-C(11)	99.9(3)
C(13)-P(1)-Pd(1)	106.7(2)	C(13)-P(1)-C(11)	98.5(3)
C(13)-P(1)-C(12)	101.2(3)	C(111)-C(11)-P(1)	111.5(4)
C(112)-C(11)-P(1)	110.6(4)	C(112)-C(11)-C(111)	110.0(4)
C(121)-C(12)-P(1)	109.9(4)	C(122)-C(12)-P(1)	117.2(4)
C(122)-C(12)-C(121)	109.8(4)	C(23)-C(13)-P(1)	113.8(4)
C(21)-P(2)-Pd(1)	121.0(2)	C(22)-P(2)-Pd(1)	124.7(2)
C(22)-P(2)-C(21)	100.6(3)	C(23)-P(2)-Pd(1)	106.5(2)
C(23)-P(2)-C(21)	100.2(3)	C(23)-P(2)-C(22)	99.2(3)
C(211)-C(21)-P(2)	111.3(4)	C(212)-C(21)-P(2)	112.6(4)
C(212)-C(21)-C(211)	110.2(5)	C(221)-C(22)-P(2)	110.5(4)
C(222)-C(22)-P(2)	116.5(4)	C(222)-C(22)-C(221)	108.8(4)
P(2)-C(23)-C(13)	113.9(4)	P(1)-Pd(1)-P(2a)[a]	117.52(3)
P(1)-Pd(1)-P(1a)	128.29(3)	P(2)-Pd(1)-P(2a)	123.85(3)

[a] a = related to designated atom by $x, -y + {}^1/_2, -z + {}^1/_2$.

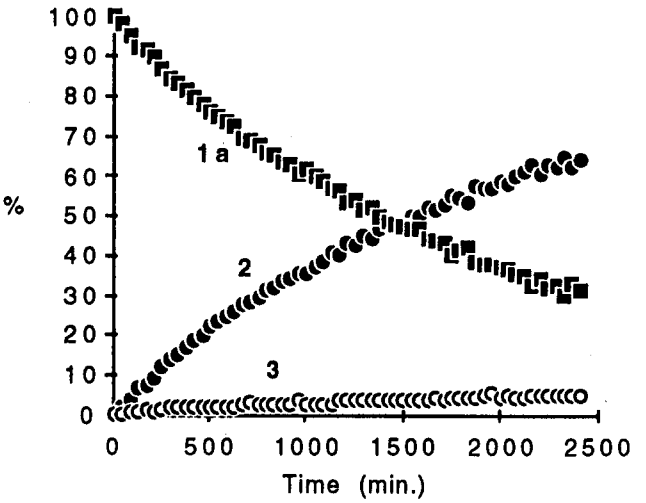
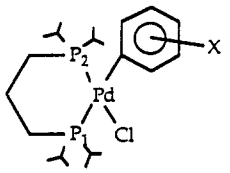


Figure 3. Composition vs time of a typical reaction mixture. A solution of 0.24 mmol of **1a** and a 10-fold excess of PhCl in 2.5 mL of dioxane was monitored by $^{31}P\{^1H\}$ NMR at 50 °C.

Table IV. $^{31}P\{^1H\}$ NMR[a] of



X	P_1 δ, ppm (J, Hz)	P_2 δ, ppm (J, Hz)
4-OMe	11.4 (40.6)	29.5 (40.6)
4-Me	11.1 (41.3)	29.3 (41.3)
4-H	11.2 (41.6)	29.0 (41.6)
3-OMe	11.3 (41.4)	29.2 (41.4)
4-C(O)Me	12.0 (40.6)	29.7 (40.6)
4-C(O)H	12.2 (41.4)	29.2 (41.4)
4-NO_2	12.6 (39.3)	29.6 (39.3)

[a] All resonances are doublets.

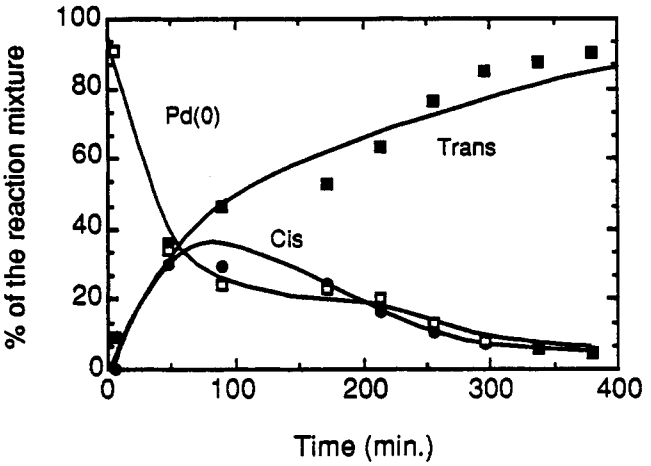
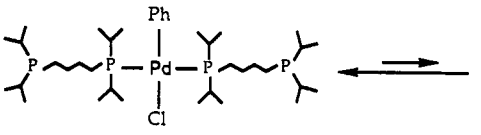


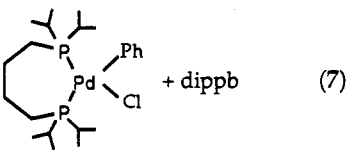
Figure 4. Reaction of **1f** with a large excess of PhCl in dioxane monitored by $^{31}P\{^1H\}$ NMR at 50 °C.

around the Pd–C and P–C bonds, derived from a significant steric repulsion between the anisyl ring and the isopropyl groups.

The chelating ligand size has a dramatic effect on the reactivity patterns of the Pd(0) complexes toward aryl chlorides. Although complex **1f** reacts with PhCl at a rate comparable to that of **1b**, the final products are *trans*-(η^1-dippb)$_2$Pd(Ph)Cl (**4**) and its polynuclear oligomers, *all-trans*-^{i}Pr$_2$P(CH$_2$)$_4$P(^{i}Pr)$_2$[Pd(Ph)(Cl)P(^{i}Pr)$_2$(CH$_2$)$_4$P^{i}Pr$_2$]$_n$, $n \geq 2$ ($^{31}P\{^1H\}$ NMR: several singlets around 24.3 ppm and a small singlet at 3.2 ppm).[13] Complex **4** is analogous to **3**, that was formed as a minor product (ca. 7%) in the reaction of **1b** with chlorobenzene. $^{31}P\{^1H\}$ NMR monitoring of the reaction of **1f** with PhCl reveals that growth of the singlets around 24 ppm (assigned to **4** and its oligomers) is accompanied by formation of two doublets at 20.6 and 43.0 ppm (with a coupling constant of 30 Hz), which grew until ca. 75% of **1f** was converted to Pd(II) products but then started to diminish in intensity until they finally disappeared at the end of the reaction (Figure 4). The doublets are assigned to the complex *cis*-(dippb)Pd(Ph)Cl (**5**). The disappearance of the cis product during the course of the reaction is explained by the fact that equilibrium 7 is completely shifted to the left.[14] An



4



5

analogous equilibrium exists between the dippp complexes **2** and **3**. However, in that case, the equilibrium lies on the extreme right.

Figure 4 demonstrates that even at the beginning of the reaction, there is more of the trans complex **4** and its oligomers than the cis complex **5**. This indicates that **4** is formed directly from the reagents and not only through intermediacy of **5**. Clearly, competition between two thermodynamic factors determines the structure of the chelating phosphine complexes: steric repulsion between the phosphine moieties, which makes the trans configuration preferable, and the chelate stabilization energy, which obviously favors the cis configuration. While the steric repulsion of the phosphine moieties should be similar for the dippp and dippb ligands, the chelate stabilization energy of the six-membered dippp is significantly larger than that of the seven-membered dippb ring.[15] This leads to an opposite thermodynamic preference of equilibrium (7) versus the analogous equilibrium involving dippp and, consequently, to the different trans/cis product distribution in the reaction of **1b** and **1f** with PhCl.

It is noteworthy that the observed rate of formation of the cis dippp complex **2** is significantly higher than that of the trans dippp complex **3**, whereas in the case of dippb, the observed rates are similar. Formation of trans complexes **3** and **4** from their Pd(0) precursors proceeds through an intramolecular chelate opening/closing pre-equilibrium producing a 14e bis(monocoordinated phosphine)palladium intermediate, followed by an oxidative addition of PhCl to this intermediate.[9] Since this oxidative addition step is not likely to be different for dippp and dippb, the different formation rates of **3** and **4** are probably due to the significantly larger concentration of the 14e η^1-dippb intermediate, as compared to that of η^1-dippp, as a result of lower chelate stabilization. Also, the chelated cis 14e complex Pd(dippp) is expected to be more reactive in oxidative addition than the analogous intermediate Pd(dippb) because of the smaller P–Pd–P angle in the former case.[16] In addition, although the rates of direct formation of the cis complexes **2** and **5** are much faster than the rates of their transformation into the trans

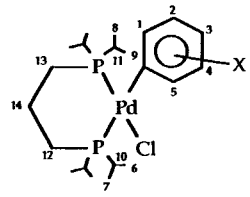
(13) Formation of similar trans oligomers of bis(phosphines) with a four-carbon backbone was reported: (a) de Graaf, W.; Boersma, J.; van Koten, G.; Elsevier, C. J. *J. Organomet. Chem.* **1989**, *378*, 115. (b) Scrivanti, A.; Botteghi, C.; Toniolo, L.; Berton, A. *J. Organomet. Chem.* **1988**, *344*, 261. (c) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1971.

(14) A similar conversion of a cis Pd(II) chelate complex into an oligomeric trans compound was also observed in ref 13a.

(15) (a) Rossotti, F. J. C. In *Modern Coordination Chemistry*; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; p 60. (b) Bao, Q.-B.; Landon, S. J.; Rheingold, A. L.; Haller, T. M.; Brill, T. B. *Inorg. Chem.* **1985**, *24*, 900. (c) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; de la Vega, R. L. *Inorg. Chem.* **1988**, *27*, 81. (d) Reference 13b. (e) Reference 13c.

(16) The influence of the L–M–L angle in ML_2 d^{10} complexes on their propensity to undergo oxidative addition was analyzed by: (a) Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191. (b) Hofmann, P.; Heiss, H.; Mueller, *Z. Naturforsch.* **1987**, *B42*, 395.

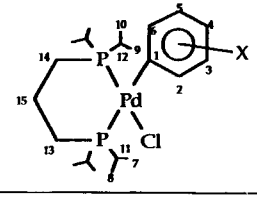
Table V. ^1H NMR[a] of



X	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}	H_{13}	H_{14}	H_{Me} (subst)	H_{CHO} (subst)
4-OMe	7.20 (ddd, 8.4, 7.5, 1.2)	6.62 (dd, 8.5, 1.8)				1.04 (dd, 16.5, 7.3)	1.07 (dd, 14.3, 7.0)	1.12 (dd, 12.7, 7.0)	1.33 (dd, 16.5, 7.2)	2.46 (dhept, 8.5[d], 7.2[h])	2.02 (dhept, 9.3[d], 7.1[h])	1.41 (m)	1.49 (m)	1.92 (bm)	3.64 (s)	
4-Me	7.19 (bdt, 8.1[t], 1.2[d])	6.77 (bd, 5.9)				1.05 (dd, 16.3, 7.4)	1.06 (dd, 14.3, 7.0)	1.11 (dd, 12.7, 7.0)	1.33 (dd, 16.5, 7.2)	2.45 (dhept, 8.3[d], 7.2[h])	2.02 (dhept, 9.1[d], 7.2[h])	1.40 (m)	1.48 (m)	1.91 (bm)	2.11 (s)	
4-H	7.38 (t, 7.7)	6.98 (dt, 7.5[t], 1.2[d])	6.84 (dt, 7.3[t], 0.7[d])			1.07 (dd, 16.5, 7.3)	1.11 (dd, 14.3, 7.0)	1.16 (dd, 12.7, 7.1)	1.38 (dd, 16.5, 7.3)	2.50 (octet, 7.3)	2.07 (dhept, 9.1[d], 7.2[h])	1.45 (m)	1.53 (m)	1.95 (bm)		
3-OMe	6.89 (bd, 8.4)		6.34 (bd, 7.9)	6.83 (bdt, 7.7[t], 2.7[d])	7.08 (bt, 8.1)	0.96 (dd, 14.0, 7.3)	1.03 (dd, 14.4, 7.0)	1.08 (dd, 12.7, 7.0)	1.30 (dd, 16.5, 7.2)	2.43 (octet, 7.2)	2.01 (boctet, 7.2)	1.38 (m)	1.46 (m)	1.87 (bm)	3.63 (s)	
4-C(O)Me	7.57 (m)	7.57 (m)				1.10 (dd, 16.9, 7.2)	1.12 (dd, 14.3, 6.9)	1.18 (dd, 12.8, 7.0)	1.39 (dd, 16.6, 7.2)	2.53 (octet, 7.2)	2.03 (octet, 7.2)	1.47 (m)	1.55 (m)	1.98 (bm)	2.48 (s)	
4-C(O)H	7.63 (t, 7.3)	7.43 (d, 7.1)				1.05 (dd, 16.7, 7.3)	1.09 (dd, 14.6, 6.9)	1.15 (dd, 12.9, 7.0)	1.35 (dd, 16.7, 7.2)	2.49 (octet, 7.3)	1.99 (octet, 7.3)	1.45 (m)	1.53 (m)	1.94 (bm)		9.77 (s)
4-NO_2	7.63 (dd, 7.8, 7.1)	7.81 (dd, 7.8, 1.7)				1.09 (dd, 16.6, 7.2)	1.12 (dd, 14.5, 7.1)	1.17 (dd, 13.0, 7.1)	1.37 (dd, 16.8, 7.2)	2.52 (dheptet, 8.7[d], 7.2[h])	2.00 (dhept, 8.8[d], 7.2[h])	1.48 (m)	1.56 (m)	1.95 (bm)		

[a] Chemical shifts in ppm, coupling constants in Hz.

Table VI. $^{13}C\{^1H\}$ NMR[a] of

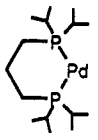


X	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{Me} (subst)	C_{CO} (subst)
4-OMe	146.3 (dd, 129.0, 2.6)	136.3 (t, 2.8)	113.2 (d, 9.2)	156.3 (d, 1.3)			20.5 (d, 5.9)	18.0 (d, 1.4)	17.7 (d, 1.8)	20.0 (d, 2.7)	24.7 (d, 19.8)	25.9 (d, 29.6)	16.8 (dd, 13.0, 2.3)	19.1 (dd, 23.0, 12.0)	22.1 (d, 6.9)	54.8 (s)	
4-H	157.9 (d, 127.2)	136.4 (s)	127.0 (d, 8.6)	122.9 (s)			20.5 (d, 5.4)	18.0 (s)	17.6 (s)	19.9 (s)	24.6 (d, 19.7)	25.8 (d, 29.6)	16.9 (dd, 15.0, <3)	19.2 (dd, 23.2, 11.2)	22.1 (d, 7.0)		
4-Me	153.2 (dd, 127.1, 2.0)	135.9 (t, 2.3)	128.0 (d, 8.8)	131.7 (s)			20.5 (d, 5.9)	18.0 (d,1.2)	17.6 (d, 1.9)	20.0 (d, 2.7)	24.6 (d, 19.6)	25.8 (d, 29.4)	16.8 (dd, 12.8, 2.1)	19.0 (dd, 23.0, 11.9)	22.0 (d, 6.7)	20.8 (s)	
3-OMe	159.3 (d, 127.4)	129.1 (t, 1.7)	157.6 (d, 10.5)	108.1 (s)	126.7 (d, 10.0)	121.5 (t, 2.8)	20.4 (d, 5.8)	17.9 (d, 1.4)	17.5 (bs)	19.8 (bs)	24.5 (d, 19.9)	25.7 (bs, 26.8)	16.6 (dd, 13.1, 2.2)	18.9 (dd, 23.3, 11.8)	21.9 (d, 6.7)	54.6 (s)	
4-C(O)Me	170.8 (dd, 127.6, 3.7)	136.4 (s)	126.0 (d, 7.8)	132.6 (s)			20.5 (d, 5.7)	18.0 (s)	17.6 (s)	20.0 (s)	24.7 (d, 20.1)	25.9 (d, 29.8)	16.6 (d, 6.3)	18.7 (dd, 23.6, 11.6)	22.0 (d, 6.5)	26.1 (s)	199.0 (s)
4-C(O)H	174.4 (dd, 127.5, 2.7)	137.0 (s)	127.1 (d, 8.2)	132.2 (s)			20.5 (d, 5.3)	18.0 (s)	17.6 (s)	19.9 (s)	24.7 (d, 20.5)	25.9 (d, 28.9)	16.5 (d, 14.3)	18.7 (dd, 24.1, 11.5)	21.9 (d, 5.8)		193.0 (s)
4-NO_2	175.7 (d, 129.0)	136.7 (s)	120.3 (d, 8.6)	144.8 (s)			20.5 (d, 5.3)	18.0 (s)	17.6 (s)	20.0 (s)	24.8 (d, 21.0)	26.0 (d, 29.5)	16.3 (dd, 14.4, 2.8)	18.5 (dd, 24.3, 11.5)	21.9 (d, 5.6)		

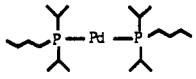
[a] Chemical shifts in ppm, coupling constants in Hz.

complexes (see Figure 4 regarding dippb and the subsequent paper regarding dippp complexes), the same is not necessarily true for the trans to cis transformation, a fact that may also play a role in the observed relative cis/trans rates of formation.

Reaction of complex **1g** with PhCl results in clean formation of *trans*-($P^iPr_2{}^nBu$)$_2$Pd(Ph)Cl (**6**). $^{31}P\{^1H\}$ NMR of the complex is a singlet at 24.6 ppm (very close to the signals of **3** and **4**). There are no traces of any cis product at any stage of the reaction. Obviously, the main driving force for formation of the cis products **2** and **5** is the chelate effect. The reaction of a 1:1 mixture of **1g** and $P^iPr_2{}^nBu$ with PhCl is slightly slower than the reaction of **1a** with PhCl under the same conditions (10-fold excess of PhCl, dioxane, 80 °C, 1.5 h), resulting in 24% conversion as compared with 35% for **1a**. Since the oxidative addition rate to PdP_2 complexes should increase with a decrease in the P–Pd–P angle,[16] oxidative addition of PhCl to the cis 14e intermediate **7** proposed for the major pathway in



7



8

the reaction of **1a**,[9] is expected to be faster than PhCl addition to the 14e moiety **8**, which is likely to be an intermediate in the formation of **6**. However, the larger concentration of **8** (which can be observed spectroscopically, as mentioned above) in the reaction mixture of **1g**, as compared to the concentration of **7** in the reaction mixture of **1a**, probably compensates for the difference in the oxidative addition rates and results in similar overall rates of both reactions.

Changing the diphosphine size from dippp (six-membered chelate ring) to dippe (five-membered chelate ring) causes major changes in both their Pd(0) complex structure and reactivity. As already mentioned, complex **1d** is a tetracoordinated saturated complex, while complexes **1a** and **1b** are tricoordinated unsaturated species. This difference is a result of the extra stabilization of the five-membered chelate ring over the six-membered one.[15a,c,17] The behavior of **1d** toward PhCl is consistent with its saturated nature. For example, whereas the conversion of **1a** into the Pd(II) products **2** and **3** at 60 °C with a 10-fold excess of PhCl is quite facile, complex **1d** remains totally unreacted after 8 h under the same conditions. Reaction of **1d** is observed above 80 °C, leading to *cis*-(dippe)Pd(Ph)Cl (**9**) as the only Pd(II) product. The dippe chelate is so stable that the theoretically possible cis/trans equilibrium analogous to (**7**) is completely shifted to the cis Pd(II) complex.

In order to clarify the influence of basicity on the reactivity of Pd(0) toward aryl chlorides, the reactivity of **1h** toward PhCl was compared with that of **1a** and **1d**. Whereas complex **1h** remains unreactive toward a 10-fold excess of PhCl even at 100 °C, the reaction of complex **1a** is already observable at 40 °C and is quite facile at 60 °C under the same conditions, and the reaction of **1d** is observable at 80 °C and facile at 100 °C. Only at 150 °C was some reaction observed in the case of **1h**. Since generation of coordinative unsaturation by opening up of one of the chelates is expected to be more difficult for **1d** than for **1h**, the low reactivity of **1h** toward PhCl cannot be explained only by its saturated nature and must be attributed to its lower basicity.[18] Thus, the high basicity of the chelating trialkylphosphine ligands is essential for successful activation of aryl chlorides.

Conclusions

The chelate ring size has a major effect on the course of the reaction of Pd(0) complexes of chelating phosphines with chloroarenes. Specifically, while very stable chelates, such as dippe, form saturated complexes with diminished reactivity, the chelating ability of dippb is weak, and as a result trans Pd(II) products are formed exclusively. The dippp ligand is a fortunate compromise: its chelate is strong enough to preferably form cis Pd(II) products with chloroarenes, but it is not too strong to form a saturated Pd(0) complex of low reactivity. We believe that, in the chloroarene functionalization reactions reported by us,[2] the cis configuration of the oxidative addition products, as well as the higher reactivity of Pd(0) catalysts toward aryl chlorides, is crucial. Therefore, the conclusion that we have reached regarding the influence of the chelate ring size on the course of the oxidative addition explains (at least partially) the superiority of **1a** as a catalyst over **1d** and **1e** in the described catalytic processes. The necessity of highly basic phosphine ligands for successful oxidative addition of aryl chlorides to Pd(0) is also exemplified in our work, explaining why the chelating trialkylphosphine complexes are superior to arylphosphine ligands in the catalytic processes mentioned above.

Experimental Section

1. General Information. All procedures with air and moisture-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres, equipped with an MO-40 purification system) or on a high-vacuum line using Schlenk techniques. All solvents were reagent grade or better. Toluene (Frutarom), pentane (Merck), and dioxane (Frutarom), which was predried over KOH pellets, were distilled over sodium/benzophenone ketyl. Methanol (Biolab) was distilled over magnesium. All solvents were degassed and stored under high-purity nitrogen after distillation. All deuterated solvents were purchased from Aldrich and dried over 3-Å molecular sieves. Chloroarenes were purchased from Merck, Sigma, or Fluka in the highest available purity and were used as received, except for *p*-chlorobenzaldehyde, which was purified by distillation in vacuum and stored under nitrogen. 1,3-Bis(diphenylphosphino)-propane was purchased analytically pure from Alfa and used as received. Dippe,[19] dippp, dippb, and $^iPr_2PCl$[20] were prepared according to literature methods. Bis(2-methylallyl)bis(μ-chloro)dipalladium(II) was synthesized by a method reported by Wilkinson.[21] All Pd(0) complexes were synthesized by a procedure similar to the one reported by Musco[5] for $Pd(PCy_3)_2$.

(17) (a) Minahan, D. M. A.; Hill, W. E.; McAuliffe, C. A. *Coord. Chem. Rev.* **1984**, *55*, 31. (b) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265. (c) Brown, M. L.; Cramer, J. L.; Ferguson, J. A.; Meyer, T. J.; Winterton, N. *J. Am. Chem. Soc.* **1972**, *84*, 8707. (d) Hancock, R. D.; Martel, A. E. *Chem. Rev.* **1989**, *89*, 1875.

(18) The basicity order of **1h** vs complexes **1a**,**d** should correspond to the basicities of their ligands. The basicity of diarylalkylphosphines vs trialkylphosphines is exemplified in: (a) Berners-Price, S. J.; Norman, R. E.; Sadler, P. J. *J. Inorg. Biochem.* **1987**, *31*, 197. (b) Sowa, J. R., Jr.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3534.

(19) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B. *Organometallics* **1984**, *3*, 185.

(20) Tani, K.; Tanigawa, E.; Tatsubo, Y.; Otsuka, S. *J. Organomet. Chem.* **1985**, *279*, 87.

(21) Dent, W. T.; Long, R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.

^1H and ^{13}C NMR measurements were recorded at 500 and 125 MHz, respectively, using a Bruker AM500 spectrometer, or at 400 and 100 MHz, respectively, using a Bruker AMX400 spectrometer. ^{31}P NMR measurements were recorded at 109 MHz on a Bruker WH270 spectrometer. ^1H and ^{13}C chemical shifts are reported in ppm downfield from $SiMe_4$ and referenced to the residual solvent-h_1, and all-deuterated-solvent peaks, respectively. ^{31}P NMR chemical shifts are reported in ppm downfield from phosphoric acid and were referenced to external 85% H_3PO_4.

2. Synthesis. Synthesis of $P^iPr_2{}^nBu$. A 25-mL aliquot of a 1.6 M solution of ^{n}BuLi in hexane was added dropwise under nitrogen to a solution of 5.05 g of $^iPr_2PCl$ in 50 mL of ether at −25 °C in a three-necked, round-bottomed flask equipped with magnetic stirrer, dropping funnel, and dry ice condenser. The rate of the addition was slow enough to keep the temperature constant. After the addition was complete, the mixture was brought to room temperature and was then refluxed for 2 h. Excess ^{n}BuLi was neutralized with a saturated NH_4Cl aqueous solution. The organic layer was separated, and the water layer was washed with ether. The ether solutions were combined and dried over anhydrous $MgSO_4$. The ether was removed in vacuo, and the pale yellow residue was distilled at ca. 3 mmHg to yield 4.56 g of pure $P^iPr_2{}^nBu$ (79% yield). $^{31}P\{^1H\}$ NMR: δ 3.5 (s).

Synthesis of (dippp)Pd(η^1-dippp) (1a). A solution of 55 mg of NaOH in 1.5 mL of methanol was added dropwise to a stirred suspension of 197 mg of [(2-methylallyl)PdCl]$_2$ in 6 mL of MeOH in a 50-mL round-bottomed flask under nitrogen. The suspension turned into a pale yellow solution immediately. Then 13 mL of methanol was added, followed by a solution of 522 mg of the phosphine ligand in 7 mL of toluene. The solution was stirred overnight at room temperature. The solvents were removed under vacuum and the yellow-brown solid residue was extracted with several 5-mL pentane portions, until they became colorless. The combined pentane solutions were evaporated on a vacuum line to give a bright yellow oil, which solidified upon cooling to −30 °C for 2 weeks, to give 632 mg of complex **1a** as a yellow solid (96% yield). $^{31}P\{^1H\}$ NMR was discussed in the Results and Discussion. Anal. Calcd: C, 54.66; H, 10.40. Found: C, 54.90; H, 10.34.

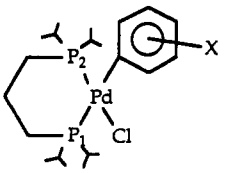
Synthesis of (dippp)Pd(μ-dippp)Pd(dippp) (1b). The procedure described above for the preparation of **1a** was followed, using 1.5 equiv of dippp relative to Pd. Evaporation of the combined pentane extracts gave complex **1b** as a yellow solid (95% yield). $^{31}P\{^1H\}$ NMR (toluene): δ 21.9 (d, $^2J_{PP}$ = 83.8 Hz, 2P), 43.7 (t, $^2J_{PP}$ = 83.8 Hz, 1P).

Synthesis of (dippp)Pd($P^iPr_2{}^nBu$) (1c). A solution of 276 mg of dippp in 3.5 mL of toluene was added to a suspension of 197 mg of [(2-methylallyl)PdCl]$_2$ in 6 mL of methanol under nitrogen, giving a yellow solution. A solution of 55 mg of NaOH in 1.5 mL of methanol was added, followed by 14 mL of methanol and by a solution of 174 mg of butyldiisopropylphosphine in 3.5 mL of toluene. After the pale yellow solution was stirred overnight, the solvents were removed under vacuum. Extraction with pentane and pentane evaporation under vacuum gave complex **1c** as a dark yellow oil. $^{31}P\{^1H\}$ NMR (toluene): δ 21.9 (d, $^2J_{PP}$ = 83.6 Hz, 2P), 44.8 (t, $^2J_{PP}$ = 83.6 Hz, 1P).

Synthesis of Pd(dippe)$_2$ (1d). A procedure similar to that used for the preparation of **1a** was employed. Removal of the methanol and toluene solvents yielded a white residue. Extraction with 10 mL of pentane, followed by pentane evaporation and rapid washing of the solid with 1 mL of cold pentane, gave complex **1d** as colorless crystals (94% yield). $^{31}P\{^1H\}$ NMR (THF): δ 45.5 (s).

Synthesis of Pd($P^iPr_2{}^nBu$)$_3$ (1g). The procedure described above for the preparation of **1a** was followed, using 3 equiv of the monophosphine relative to Pd. Gentle evaporation of the combined pentane extracts gave an orange-yellow oil that crystallized upon cooling to −30 °C but melted at room temperature. $^{31}P\{^1H\}$ NMR (toluene, −50 °C): δ 29.6 (s). Upon prolonged exposure to high vacuum, substantial amounts of Pd($P^iP_2{}^nBu$)$_2$ are formed. $^{31}P\{^1H\}$ NMR (toluene, −50 °C): δ 35.6 (s).

Table VII. Elemental Analysis of



	%C		%H		%Cl		%N	
X	calcd	found	calcd	found	calcd	found	calcd	found
H	50.92	51.19	7.94	7.98	7.16	6.82		
4-Me	51.87	51.73	8.11	7.93				
3-OMe	50.30	50.49	7.87	7.75	6.75	7.04		
4-C(O)Me	51.41	51.74	7.69	7.61	6.60	6.94		
4-NO_2	46.68	46.86	7.09	6.95	6.56	6.90	2.59	2.56

Reaction of [(2-methylallyl)PdCl]$_2$ with dippb. Identification of (dippb)Pd(η^1-dippb) (1e) and (dippb)Pd(μ-dippb)Pd(dippb) (1f). A solution of 29.2 mg of dippb in 3.5 mL of toluene was added to a suspension of 197 mg of [(2-methylallyl)PdCl]$_2$ in 6 mL of methanol under nitrogen, giving a yellow solution. A solution of 55 mg of NaOH in 1.5 mL of MeOH was immediately added, followed by 13.5 mL of methanol and a solution of 292 mg of dippb in 3.5 mL toluene. The resulting pale yellow solution was stirred overnight. A yellow solid started to precipitate after approximately 2 h. All solvents were removed, and the residue was extracted with pentane, giving a yellow solution. Evaporation of the pentane gave a yellow solid. The solid was only partially soluble in dioxane, and attempts to dissolve the insoluble residue in several other solvents failed. The dioxane solution contained complexes (dippb)Pd(η^1-dippb) and (dippb)Pd(μ-dippb)Pd(dippb), as well as several other unidentified complexes according to $^{31}P\{^1H\}$ NMR. Yellow needles of (dippb)Pd(μ-dippb)Pd(dippb) (**1f**) crystallized from the dioxane solution upon very slow evaporation under ambient conditions. The $^{31}P\{^1H\}$ NMR exhibits an A_2B pattern: (A_2 part) δ 29.0 ($^2J_{PP}$ = 94.6 Hz, 2P), (B part) δ 37.6 ($^2J_{PP}$ = 94.6 Hz, 1P).

Synthesis of Pd(dppp)$_2$ (1h). A procedure analogous to that used for the preparation of **1a** was employed. A yellow solid, precipitated during overnight stirring, was separated and washed with cold methanol (79% yield). $^{31}P\{^1H\}$ NMR (THF): δ 3.7 (s). Anal. Calcd: C, 69.64; H, 5.63. Found: C, 69.92; H, 5.56.

Synthesis of *cis*-(dippp)Pd(Ar)Cl (2). Synthesis of 2 (Ar = Ph, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-MeC_6H_4). A 10-mL glass pressure bottle was charged with a solution of 120 mg of complex **1a** and a 10-fold excess of the appropriate chloroarene in 2.5 mL of dioxane. The solution was stirred at 90–100 °C until almost complete color disappearance took place (1–4 h). Then the solvent and excess chloroarene were removed under vacuum, leaving a white to pale yellow solid. The solid was washed with several portions of pentane, and the resulting white powder was usually sufficiently pure. Diffusion of pentane into toluene solutions of the complexes precipitated colorless crystals of high purity.

Synthesis of 2 (Ar = 4-$HC(O)C_6H_4$, 4-$MeC(O)C_6H_4$). A similar procedure was applied, but heating at 60 °C for 2 h was sufficient for completion of the reaction. The solution was allowed to sit for a few days while slow evaporation of the solvent caused precipitation of colorless crystals, which were separated and washed with pentane, yielding the pure complexes.

2 (Ar = 4-$NO_2C_6H_4$) was synthesized by addition of 10 equiv of *p*-nitrochlorobenzene to a solution of 120 mg of **1a** in 2.5 mL of dioxane. The addition was followed by a color change from yellow to brown. After a few minutes, precipitation of brownish crystals started and was complete after ca. 2 h. The crystals were separated and washed with pentane, giving an almost colorless compound.

The complexes were characterized by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR (see Tables IV–VI) and by elemental (Table VII). The yields at the end of the reactions (determined by ^{31}P NMR) varied

from 80–95%, while the yields of the purified complexes were 65–75%. Compounds **2** with Ar = C_6H_5, Ar = 4-MeC_6H_4, and Ar = 4-$NO_2C_6H_4$ melt with decomposition at 167–170, 158–164, and 194–203 °C, respectively, while **2** with Ar = 4-$HC(O)C_6H_4$ decomposes before melting at 194 °C.

Synthesis of (dippe)Pd(Ph)Cl. A 10-mL pressure bottle was charged with a suspension containing 228 mg of $Pd(dippe)_2$ and 400 mg (10 equiv) of chlorobenzene in 5 mL of dioxane. Everything was dissolved upon heating. The solution was stirred at 100 °C overnight, filtered, cooled, and allowed to sit at room temperature for a few days, while slow evaporation of dioxane and precipitation of colorless crystals occurred. The crystals of **8** were washed with cold pentane and characterized by NMR. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 70.7 (d, $^2J_{PP}$ = 18.1 Hz, 1P), 78.1 (d, $^2J_{PP}$ = 18.1 Hz, 1P). ^1H NMR ($CDCl_3$): δ 0.94 (dd, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3), 1.16 (dd, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, CH_3), 1.23 (dd, $^3J_{PH}$ = 13.3 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, CH_3), 1.37 (dd, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, CH_3), 2.22 (dhept, $^3J_{PH}$ = 9.7 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, CH), 2.35 (dhept, $^3J_{PH}$ = 9.3 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, CH), 1.73 (apparent ddt, $^3J_{PH}$ = 21.2 Hz, $^2J_{PP} \approx {}^3J_{HH} \approx$ 8.0 Hz, 2H, CH_2), 2.02 (apparent ddt, $^3J_{PH}$ = 22.5 Hz, $^2J_{PH} \approx {}^3J_{HH} \approx$ 8.2 Hz, 2H, CH_2), 6.88 (t, $^3J_{HH}$ = 7.0 Hz, 1H, H_{para}), 6.99 (t, $^3J_{HH}$ = 6.3 Hz, 2H, H_{meta}), 7.37 (apparent t, $^3J_{PH} \approx {}^3J_{HH} \approx$ 7.2 Hz, 2H, H_{ortho}), $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.7 (s, CH_3), 18.4 (s, CH_3), 18.8 (s, CH_3), 19.7 (d, $^2J_{PC}$ = 5.0 Hz, CH_3), 18.2 (d, $^1J_{PC}$ = 10.7 Hz, CH_2), 24.5 (dd, $^1J_{PC}$ = 23.8 Hz, $^2J_{PC}$ < 2.5 Hz, CH_2), 24.3 (d, $^1J_{PC}$ = 16.2 Hz, CH), 25.0 (d, $^1J_{PC}$ = 27.2 Hz, CH), 123.0 (s, C_{para}), 127.0 (d, $^3J_{PC}$ = 8.8 Hz, C_{meta}), 136.8 (s, C_{ortho}), 158.4 (dd, $^2J_{PC_{trans}}$ = 130.8 Hz, $^2J_{PC_{cis}}$ = 3.2 Hz, C_{ipso}). Anal. Calcd: C, 49.91; H, 7.75. Found: C, 49.82; H, 7.60.

Reaction of 1f with PhCl. A solution of ca. 30 mg of **1f** and 202 mg of PhCl (a large excess) in 2.5 mL of THF was placed in a 10-mm NMR tube and monitored by $^{31}P\{^1H\}$ NMR[22] while being heated at 50 °C. The reaction was complete in 10 h. The final mixture contained mostly the oligomeric products *all-trans*-$^iPr_2PCH_2CH_2CH_2CH_2P(^iPr)_2[Pd(Ph)(Cl)P(^iPr)_2CH_2CH_2CH_2CH_2P^iPr_2]_n$, $n \geq 1$ (see Results and Discussion).

Acknowledgment. We thank Dr. Felix Frolow of the Chemical Services Department for performing the X-ray structural analyses. Thanks are also due to Dr. R. T. Baker for communicating his results to us prior to publication. We are grateful to the Hoechst, AG, Co., Frankfurt, Germany, for their generous gift of chemicals. This work was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities.

Supplementary Material Available: Text describing the data collection, refinement, and crystal data and tables of atom coordinates, antisotropic temperature factors, hydrogen atom coordinates, bond lengths and bond angles (4 pages). Ordering information is given on any current masthead page.

OM920572V

(22) The monitoring technique is described in ref 9.