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A Palladium−Ferrocenyl Tetraphosphine System as Catalyst for Suzuki Cross-Coupling and Heck Vinylation of Aryl Halides: Dynamic Behavior of the Palladium/Phosphine Species

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The system combining the new ferrocenyl tetraphosphine 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene (called $\mathrm{Fc(P)_4{}^tBu}$, **1**) and $[\mathrm{PdCl}(\eta^3\text{-}\mathrm{C_3H_5})]_2$ has been found to be an active catalyst for the cross-coupling of aryl halides with aryl boronic acids (i.e., Suzuki reaction) and for the vinylation of aryl halides with alkenes (Heck reaction). A variety of chlorides reacts in good yield with aryl boronic acids in the presence of 1−0.01% catalyst. The more reactive aryl bromides were reacted with aryl boronic acids or alkenes in the presence of 0.01−0.0001% catalyst. This system compares well with other catalytic systems that have been described for Suzuki or Heck reactions. ^{1}H, ^{13}C, and ^{31}P NMR studies in solution were conducted with the view to obtain a better understanding of the interaction involving the palladium dimeric precursor and the tetraphosphine. The initial formation of kinetic and then different thermodynamic species was evidenced. A dynamic evolution from labile Pd(π-allyl)/tetraphosphine species toward the well-defined, stable, and nonfluxional complexes $[\mathrm{PdCl_2\{Fc(P)_4{}^tBu\}}]$ (**3**) and $[\mathrm{Pd_2Cl_4\{Fc(P)_4{}^tBu\}}]$ (**4**) is observed. This behavior is different from the other known active tetraphosphine Tedicyp [*cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane]. The palladium mononuclear **3** and dinuclear **4** complexes were isolated and fully characterized in the solid state by X-ray diffraction analysis and in solution by multinuclear NMR. The blocked conformation in solution of compounds **1**, **3**, and **4** respectively leads to original AA′BB′, ABMX, and A_2B_2 ^{31}P NMR spin-systems for the four phosphorus atoms.

Introduction

Among the recently discovered catalytic reactions of organic chemistry, the synthesis of biaryl compounds via carbon−carbon bond formation using organoboron reagents with organic halides/triflates has been, lately, one of the most intensively studied.[1−6] Promising research pathways include (i) the search for easier coupling of the widely available and low-cost aryl chlorides,[2] (ii) the search for exponential turnover numbers (TON),[3,4] (iii) the search for ever milder reaction conditions,[2a,b,5] and (iv) the opportunity to substitute the expensive palladium precatalysts for cheaper nickel ones.[6]

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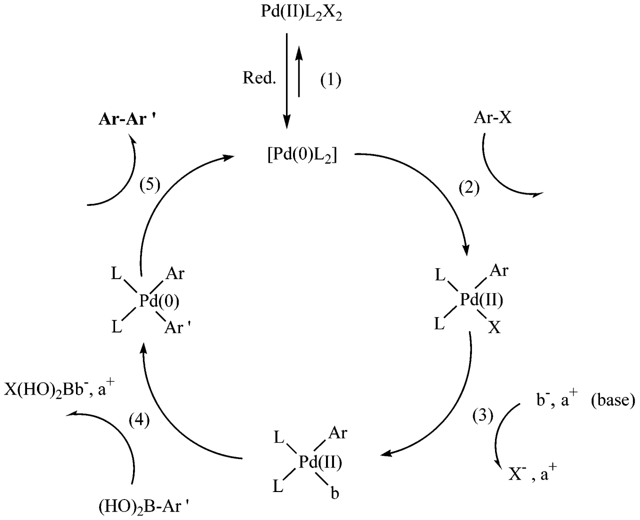
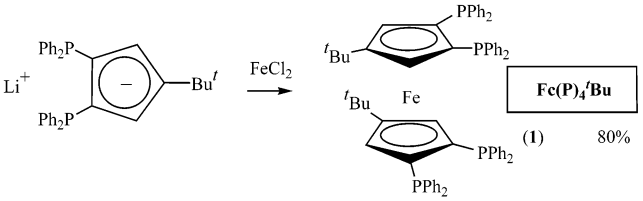
Scheme 1. Catalytic Cycle Rationalizing the Organoboron/Organic Halide Cross-Coupling Reactions



During the past few years significant advances have been reported concerning the palladium-catalyzed cross-coupling of the relatively inert *aryl chlorides* (by comparison to their bromide and iodide analogues). The catalytic mechanism usually postulated in the Suzuki reaction is shown Scheme 1. The low reactivity of aryl chlorides is often ascribed to their reluctance to perform the oxidative addition to palladium (step 2, Scheme 1). The better results obtained with palladium combined with hindered strongly σ-electron-donating ligands support this hypothesis, since tri*alkyl*phosphines [such as $PBu(adamantyl)_2$,[7] $P(^tBu)_3$,[8] and $P(Cy)_3$[2f,8]] or di*alkyl*-arylphosphines [such as $P(Cy)_2$(*o*-biphenyl) and $P(^tBu)_2$(*o*-biphenyl)][2c,d] show an activity generally not observed with the less electron-rich tri*aryl*phosphines. The results reported by Fu et al.,[5b] however, interestingly reveal that good activity can be obtained from a catalytic system combining $Pd_2(dba)_3$ with the ferrocenyl tri*aryl*phosphine $\{PPh_2(Me_3Si)CpFeCp(Me)_5\}$ (coupling of a variety of unactivated aryl chlorides, 70 °C, yields >85%). Comparable results were reported by Richards and Pickett using $Pd_2(dba)_3$ with tris(2-methylferrocenyl)phosphine.[9]

From a different perspective, recent reports by Bedford et al. have argued that the excellent reactivity of their phosphite-containing catalysts is conferred by the π-acidic nature of the aryloxide and salicylate phosphite ligands,[10] which are poor σ-electron-donating ligands. In this case, the spectacular turnover numbers were attributed to the catalyst *longevity*, without any indication that the presumed limiting oxidative addition step is facilitated. This concept of catalyst longevity, and consequently of *stability* of the catalytic species, was also evoked as an explanation for the activity of the tetraphosphine ligand *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane (Tedicyp) in a broad range of palladium-catalyzed reactions, which include the Suzuki cross-coupling of aryl chlorides or bromides.[4,11,12]

Scheme 2. Ferrocenyl Tetraphosphine 1,1′,2,2′-Tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene



Considering these stimulating results, we found of particular interest the catalytic and spectroscopic study of the recently reported ferrocenyl tetraphosphine 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene ($Fc(P)_4{}^tBu$, **1**, Scheme 2) combined with the palladium allylic dimer in the cross-coupling of aryl halides with boronic acid. Indeed, this tetraphosphine combines a priori some essential characteristics of the active catalytic systems reported by the Fu ($\{PPh_2(Me_3Si)CpFeCp(Me)_5\}$, hindered ferrocenyl tri*aryl*phosphine) and Santelli groups (Tedicyp, *tetraphosphine* with specifically orientated $-PPh_2$ groups). Moreover, the importance of the nature of the phosphine ligand on the Suzuki or Heck reactions has been widely proved; nevertheless, while several systems using monodentate or bidentate ligands or palladacycles have been explored,[13,14] the present study is, to the best of our knowledge, only the second one using an active tetradentate phosphine ligand, despite the great number of known polyphosphines.[15]

Preparation and Characteristics of $Fc(P)_4{}^tBu$, 1. The synthesis of 1,2-disubstituted ferrocene derivatives directly from ferrocene has been recently renewed, in particular to yield enantiopure asymmetric species.[16] The general synthetic procedures to obtain symmetri-

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Table 1. Suzuki and Heck Reactions Catalyzed by the Fc(P)$_4{}^t$Bu/Palladium System[a]

entry	aryl halide	aryl boronic acid or alkene	ligand	time (h)	ratio substrate/catalyst	yield, %
1	4-MeOC$_6$H$_4$Cl	PhB(OH)$_2$	dppe	20	100	0
2	4-MeOC$_6$H$_4$Cl	PhB(OH)$_2$	**1**	20	100	20
3	4-MeOC$_6$H$_4$Cl	4-MeOC$_6$H$_4$B(OH)$_2$	**1**	3	100	25
4	4-MeOC$_6$H$_4$Cl	4-MeOC$_6$H$_4$B(OH)$_2$	**1**	20	100	48
5	4-MeCOC$_6$H$_4$Cl	PhB(OH)$_2$	PPh$_3$	20	1000	<2[b]
6	4-MeCOC$_6$H$_4$Cl	PhB(OH)$_2$	dppe	20	1000	22
7	4-MeCOC$_6$H$_4$Cl	PhB(OH)$_2$	**1**	20	1000	50
8	4-MeCOC$_6$H$_4$Cl	4-MeOC$_6$H$_4$B(OH)$_2$	**1**	20	100	98 (88)[c]
9	4-MeCOC$_6$H$_4$Cl	4-MeOC$_6$H$_4$B(OH)$_2$	**1**	20	10 000	74
10	4-NCC$_6$H$_4$Cl	4-MeOC$_6$H$_4$B(OH)$_2$	**1**	20	1000	89 (83)[c]
11	4-NCC$_6$H$_4$Cl	PhB(OH)$_2$	**1**	20	1000	42
12	4-MeOC$_6$H$_4$Br	PhB(OH)$_2$	**1**	20	10 000	100 (92)[c,d]
13	4-MeOC$_6$H$_4$Br	PhB(OH)$_2$	**1**	20	100 000	77[d]
14	4-MeCOC$_6$H$_4$Br	PhB(OH)$_2$	**1**	20	100 000	100 (94)[c]
15	4-NCC$_6$H$_4$Br	PhB(OH)$_2$	**1**	20	100 000	100 (87)[c]
16	4-F$_3$CC$_6$H$_4$Br	PhB(OH)$_2$	**1**	20	1 000 000	15[d]
17	PhI	^{n}BuOCOCH=CH$_2$	**1**	48	1 000 000	100 (85)[c,d]
18	4-MeOC$_6$H$_4$Br	^{n}BuOCOCH=CH$_2$	**1**	48	10 000	100 (88)[c,d]
19	4-MeOC$_6$H$_4$Br	PhCH=CH$_2$	**1**	20	100 000	65[c,d]
20	4-CHOC$_6$H$_4$Br	^{n}BuOCH=CH$_2$	**1**	20	250	100 (83)[c−e]
21	4-CHOC$_6$H$_4$Br	^{n}BuOCH=CH$_2$	**1**	20	1000	41[d,e]

[a] Conditions: catalyst [PdCl(η^3-C$_3$H$_5$)]$_2$/phosphine: 1/2, aryl halide (1 equiv), aryl boronic acid or alkene (2 equiv), K$_2$CO$_3$ (2 equiv), xylene, 130 °C, under argon, GC yields. [b] Ratio [PdCl(η^3-C$_3$H$_5$)]$_2$/PPh$_3$: 1/4. [c] Isolated yields. [d] DMF as solvent. [e] Ratio of the isomers: branched/*Z*/*E*: 16/21/63.

cally 1,1′,2,2′-tetrasubstituted ferrocene derivatives are much less developed.[17] In the search for convenient methodologies, we considered the reaction of the appropriate 1,2-disubstituted cyclopentadienyl salts with FeCl$_2$. The use of tertiobutylcyclopentadienyllithium allowed us to *direct* a 1,2-phosphine disubstitution on the Cp rings, without the need to previously block all the other positions (3, 4, 5).[18a,b] Indeed, on Cp rings without a prior blocking of positions, a 1,3-phosphine disubstitution was invariably obtained upon lithiation and reaction with chlorophosphine.[18c]

The 1,2-phosphino-disubstituted cyclopentadienyl salt yielding Fc(P)$_4{}^t$Bu was prepared from successive lithiations and reactions with ClPPh$_2$ on dimethylfulvene.[19] Fc(P)$_4{}^t$Bu is air-stable and, consequently, very easy to handle in microscale catalytic experiments. A X-ray diffraction structure of **1** has been reported,[19] which shows that two enantiomers are present in the unit cell, resulting in an original conformational chirality (or atropoisomery). An analogous blocked conformation is probably conserved in solution, as was shown by the ^{31}P NMR spectrum, which has revealed the magnetic nonequivalence of the four phosphorus atoms.

Results and Discussion

Carbon−Carbon Coupling Catalysis Results. The first results obtained for the catalyzed Suzuki cross-coupling reaction of aryl boronic acids with aryl halides and for the Heck vinylation of aryl halides using the ferrocenyl tetraphosphine **1** as ligand are presented in the following.

To compare **1** with other more classical ligands, several Suzuki cross-coupling reactions have been performed using identical conditions in the presence of PPh$_3$ or dppe (1,2-bis(diphenylphosphino)ethane). This comparison has been carried out with 4-chloroacetophenone as test substrate (Table 1, Scheme 3a). When 0.1 mol % of [PdCl(η^3-C$_3$H$_5$)]$_2$ was used as catalyst precursor in the presence of PPh$_3$ as ligand, only 2% conversion were observed (entry 5). In the presence of the bidentate dppe a better result was obtained (entry 6, TON 220). With **1** as ligand a TON of 500 has been obtained using similar conditions (entry 7). The species formed by association of **1** and [PdCl(η^3-C$_3$H$_5$)]$_2$ appears to be much more stable than the systems formed with classical monodentate triarylphosphines.

Next, the reactivity of activated and deactivated aryl halides has been compared. A lower TON of 48 was observed in the course of the coupling of 4-chloroanisole with 4-methoxybenzeneboronic acid (entry 4). As expected, higher reaction rates were obtained with aryl bromides. For instance, turnover numbers of 77 000 and 150 000 have been observed for the coupling of 4-bromoanisole and 4-trifluoromethylbromobenzene, respectively, with benzene boronic acid (entries 13 and 16).

Finally, we tested the efficiency of **1** for the Heck reaction of aryl halides with *n*-butyl acrylate, styrene, and *n*-butyl vinyl ether (Table 1, Scheme 3b): with iodobenzene and *n*-butylacrylate a very high TON of 1 000 000 has been obtained (entry 17). With the non-activated bromoanisole in the presence of *n*-butyl acrylate or styrene, reasonable TONs (10 000 and 65 000, entries 18 and 19, respectively) were observed. Even the electron-rich alkene *n*-butyl vinyl ether led to the corresponding adducts in the presence of 0.1% catalyst (entry 21). Moreover, these reactions have been performed *without* addition of tetra-alkylammonium salts, which are often used to avoid precipitation of palladium black.

Spectroscopic Studies. As underlined by Beller et al.,[20] the exact nature of the in situ species that have

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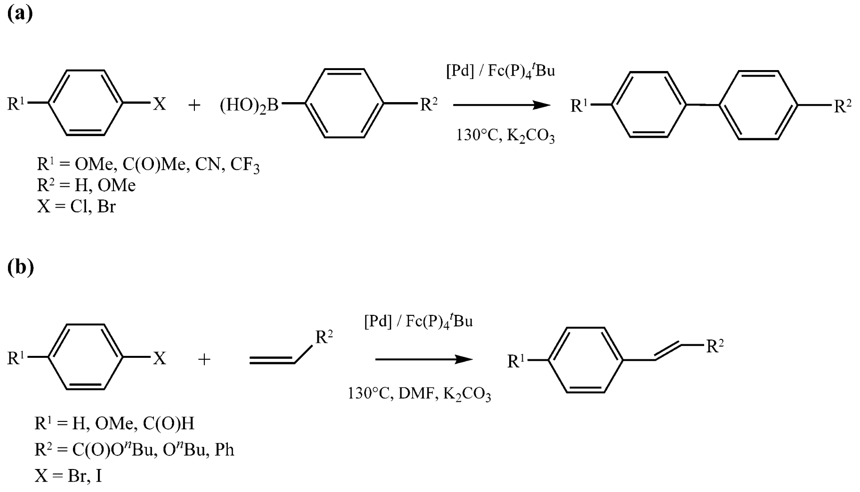
Table 2. Crystal Data, Data Collection, and Structure Refinements for Compounds 3 and 4

	3	4
formula	$C_{66}H_{62}Cl_2P_4FePd$	$C_{66}H_{62}Cl_4P_4FePd_2$, $2CDCl_3$
fw	1212.19	1628.22
temp, K	180(2)	180(2)
cryst color	red	red
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	13.682(5)	14.288(5)
b, Å	21.928(5)	22.874(5)
c, Å	27.427(5)	21.427 (5)
β, deg	97.865(5)	105.951 (5)
volume, Å^3	8151(4)	6733 (3)
Z	4	4
calcd density, mg·m^{-3}	0.988	1.606
abs coeff, mm^{-1}	0.571	1.274
$F(000)$	2496	3280
θ range for data collection	2.18−23.26°	3.30−51.50°
no. of reflns collected/unique	46 915/11 658	27 947/7018
R(int)	0.0683	0.1004
refinement method	full-matrix least-squares on F^2	
goodness-of-fit on F^2	0.947	1.103
final R indices [$I > 2\sigma(I)$]	R1 = 0.0462, wR2 = 0.1029	R1 = 0.0771, wR2 = 0.2050
R indices (all data)	R1 = 0.0641, wR2 = 0.1082	R1 = 0.0957, wR2 = 0.2373
residuals, e Å^{-3}	0.433, −0.421	1.412, −1.281

Scheme 3. (a) Suzuki Cross-Coupling and (b) Heck Vinylation



given good results in cross-coupling reactions is often ignored or at least poorly characterized. This is mainly due to the difficulties in identifying the fluxional species that could appear during the reaction. Following an objective of better characterization, ^{1}H, ^{13}C, and ^{31}P NMR studies in deuterated chloroform have been conducted to clarify the interaction involving the palladium complex and the tetraphosphine Fc(P)$_4{}^t$Bu. Several relevant studies of (π-allyl)palladium chemistry with tertiary mono- or diphosphine ligands have been reported.[21,22] The results presented here give a new account of possible processes occurring in solution upon reaction of polydentate phosphines with palladium.

In similar conditions to the in situ preparation of the catalyst used for the cross-coupling reactions, the mixture of 2 equiv of Fc(P)$_4{}^t$Bu and 1 equiv of [PdCl(η^3-C_3H_5)]$_2$ (ratio 1 Pd:4 P) reacts immediately at room temperature upon dissolution in $CDCl_3$. ^{1}H and ^{31}P NMR (Figure 1a) spectra clearly show, respectively, that within the first 20 min (0.3 h) the dimeric (π-allyl)palladium complex is dissociated[23] and that the typical phosphorus signals of the free Fc(P)$_4{}^t$Bu in solution completely disappear,[24] despite the 1:4 palladium:phosphorus ratio. The two broad signals observed at 8.90 and 3.50 ppm show that, on the NMR time scale, no free phosphorus can be detected. The two peaks suggest, as observed in some cases,[12,25] the existence of several equilibrating species involved in fast coordination−dissociation processes of the four phosphorus of the tetraphosphine. As demonstrated in the following, these species (called **2**) can be best described as "labile palladium-allyl" compounds bearing phosphine ligands.

A time-prolonged ^{31}P NMR scanning at constant room temperature is presented in Figure 1. During the first 100 h (Figure 1a−d), a slow dynamic behavior was observed, where the decrease of the two broad signals

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[23] ^{1}H NMR spectrum available as Supporting Information.

[24] See ref 19 for the AA′BB′ spin system details (doublet of sextuplet, δ = −28.28, −28.44, −28.54, −28.72, −28.81, −28.99 and −31.86, −32.04, −32.13, −32.31, −32.40, −32.58 ppm).

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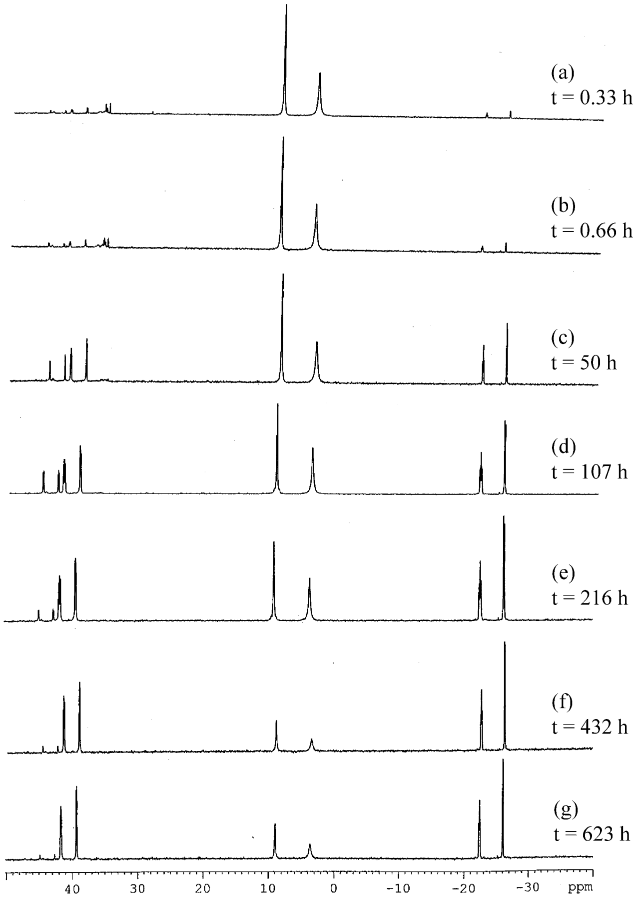


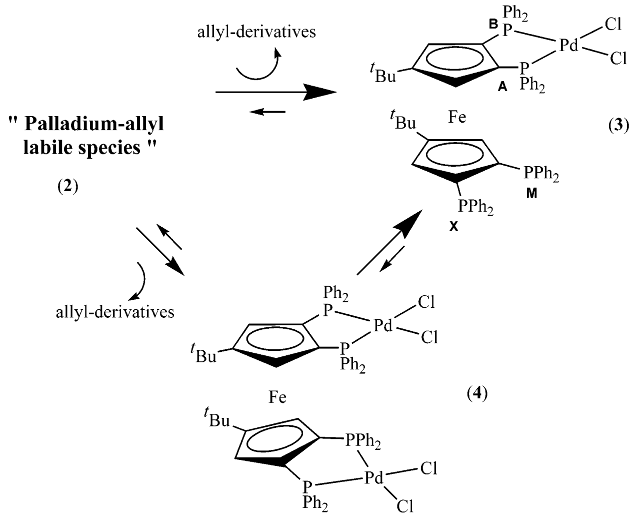
Figure 1. In-time ^{31}P NMR monitoring of the reaction of **1** with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ at ambient temperature (ratio 1 Pd:4 P).

runs parallel to the increase of six well-defined multiplets (respectively centered at $\delta = 44.9$, 42.6, 41.7, 39.2, -22.6, and -26.3 ppm). These products were identified as the palladium chloride mononuclear and the palladium chloride dinuclear complexes $[PdCl_2\{Fc(P)_4{}^tBu\}]$ (**3**) and $[Pd_2Cl_4\{Fc(P)_4{}^tBu\}]$ (**4**), respectively. Complex **4** had been already identified.[19] Complex **3** has been isolated and fully characterized for the first time,[26] since after 100 h a small amount of the mononuclear palladium product slowly crystallized. The ^{31}P NMR monitoring of the reaction (Figure 1) demonstrates that, from this time, the dynamic equilibrium is, as well, displaced from **4** toward **3**. The amount of "labile palladium-allyl" species preferentially formed at the beginning still decreases in favor of the formation of **3**. Scheme 4 is a tentative summary of the intricate equilibrium observed.

After 600 h the mononuclear palladium is the major compound in solution, in agreement with the initial 1:4 ratio of palladium to phosphorus. The chemical equilibrium from **4** toward **3** inevitably involves some "labile palladium-allyl" species, since supplementary ligands should be necessary to coordinate the second palladium of the dissociating dinuclear complex. After more than 600 h no palladium black formation was detectable.

In the following, for clarity and accuracy reasons, the detailed signals of the spectrum are given rather than the average chemical shift of the multiplets. Figure 2 presents an enhancement of the ^{31}P NMR spectrum (121.49 MHz) shown in Figure 1d. The four nonequivalent phosphorus of the mononuclear compound **3** give four multiplets which might be described as a first-order ABMX spin system: δ_A (dd) = 41.84, 41.72, 41.65, 41.53, $J_{AB} = 14.7$ Hz, $J_{AM} = 22.9$ Hz; δ_B (dd) = 39.32, 39.27, 39.20, 39.15, $J_{BM} = 5.8$ Hz; δ_M (ddd) = -22.40, -22.45, -22.53, -22.59, -22.64, -22.72, -22.77, $J_{MX} = 15.3$ Hz; δ_X (d) = -26.28, -26.41 ppm. Due to the J_{AM} value very close to $J_{BM} + J_{MX} \cong 22$ Hz, the signal δ_M appears not as a doubled doublet of doublets, but as a pseudo-heptuplet. This highly unsymmetrical spin system suggests that, in a blocked conformation, one of the noncoordinated phosphorus is closer to one of the two palladium-bonded phosphorus, as evidenced by the strong coupling constant through space, $J_{AM} = 22.9$ Hz compared to the analogue, $J_{BM} = 5.8$ Hz (see Scheme 4). The coupling constant between the phosphorus attached to the same Cp ring are of the same order of magnitude ($J_{AB} = 14.7$ Hz and $J_{MX} = 15.3$ Hz). The dinuclear complex **4** in $CDCl_3$ shows a more simple A_2B_2 type spectrum with two pairs of isochronous phosphorus: δ_1 (d) = 44.93, 44.84 and δ_2 (d) = 42.61, 42.52 ppm, $J_{PP} = 11.0$ Hz. This obvious symmetry gain in the spectrum, thus, indicates the existence of a new symmetry element in **4** compared to **3**. Thus, a blocked conformation with a 2-fold axis located between the Cp rings is proposed for the dinuclear complex.

Scheme 4. Spontaneous Evolution in Time of a Mixture of 1 and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (ratio 1 Pd:4 P)



^1H NMR monitoring of the behavior in solution completes and supports the NMR data obtained for phosphorus. Especially, in the first 20 min (spectrum corresponding to Figure 1a), the proton signals from the ^tBu and the Cp groups of the tetraphosphine ligand are, respectively, shifted from 0.70 (H ^tBu), 4.05, and 4.14 ppm (H Cp) to 0.85, 4.34, and 4.67 ppm.[23] The shift of signals in the area of the protons from the phenyl groups is also noticeable. The existence of only *one* set of shifted signals supports the hypothesis of an average spectrum due to species involved in fast exchanges (at the NMR scale rate). The presence of fluxional allyl ligands is marked by small broad signals appearing at 3.65, 4.55, and 4.80 ppm. Comparable fluxional behavior of (π-allyl)palladium species formed in the presence of an excess of monophosphine has been reported.[22] With the

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(26) ^{31}P NMR spectrum available as Supporting Information.

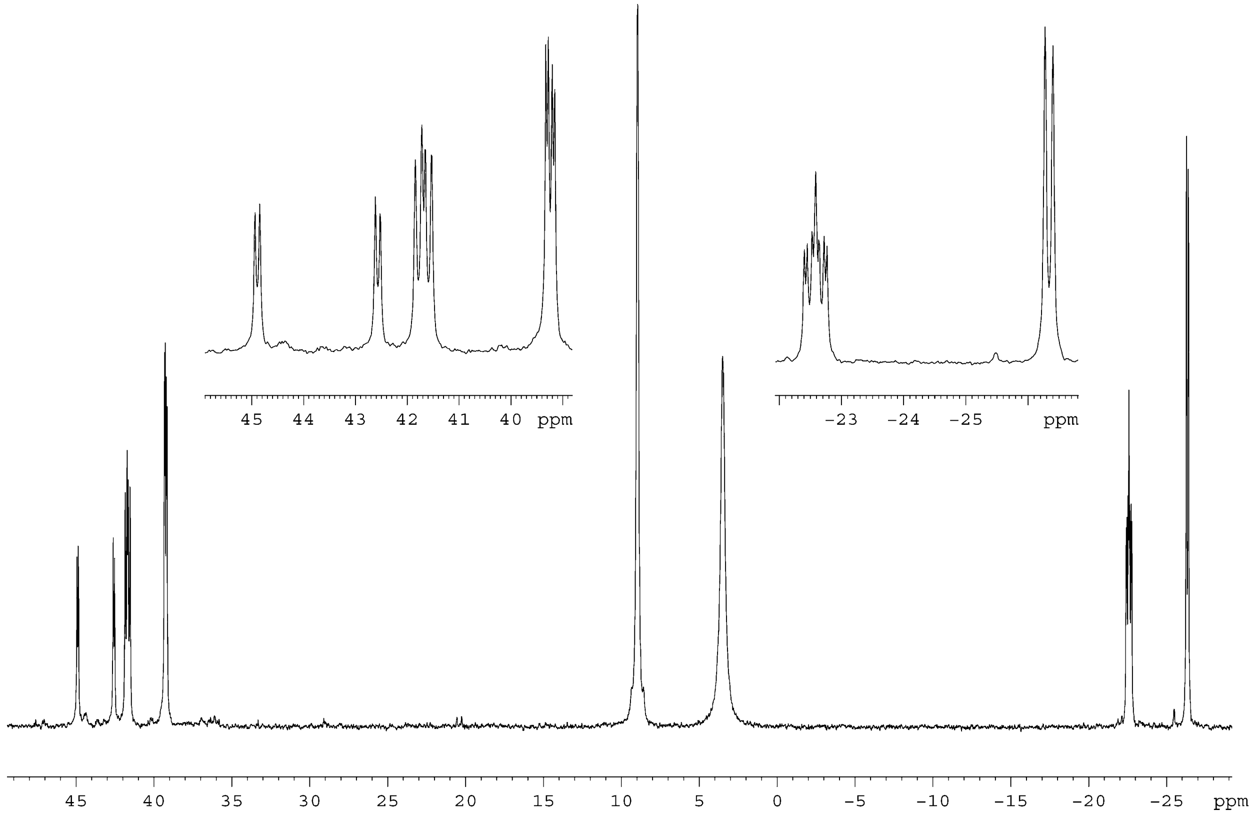

Figure 2. Enhancement of the ^{31}P NMR spectrum presented in Figure 1d.

view to obtain more insight concerning these "labile palladium-allyl" species, **2**, variable-temperature ^{31}P NMR experiments were carried out. As shown in Figure 3, the experiment conducted in $CDCl_3$/toluene (1:3 v/v) with a mixture of 2.2 equiv of Fc(P)$_4{}^t$Bu and 1 equiv of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (ratio about 1 Pd:4 P, with a slight excess of **1**) gives at 300 K the expected mixture of **2**, **3**, and **4** and the signals for the excess of **1**. Upon cooling, **2** exhibits the characteristic behavior of labile compounds, with the two broad signals at 8.90 and 3.50 ppm slowly coalescing to 200 K. At 190 K, four new very broad signals are detected (centered at 34.8, 24.2, −2.7, and −27.0 ppm), which are even more clearly confirmed at 185 K. These peaks might characterize four different phosphorus of an (allyl)palladium compound bearing biligate-phosphorus. However, at 185 K, the solvent limit temperature being reached, it seems difficult to further improve the quality of the obtained data.

The dynamic phenomenon is reversible, since upon increasing the temperature again above the coalescence temperature, the species **2** exhibits again characteristic average broad signals at 8.90 and 3.50 ppm. At high temperature the (allyl)palladium labile species are stable until a temperature of 370 K (97 °C) is attained. After a few minutes at this temperature, **2** is quantitatively replaced by the mononuclear palladium thermodynamically favored compound **3**. No decomposition of **3** was noted after 20 min at 370 K.

First, our efforts to determine the allyl derivative compounds formed (Scheme 4) failed. In ^{1}H and ^{13}C NMR the characteristic signals for allyl chloride[21] or hexadiene[27] compounds were not identified. The GC−MS analysis conducted on the solution remains unclear and allowed us to detect only recombination of products

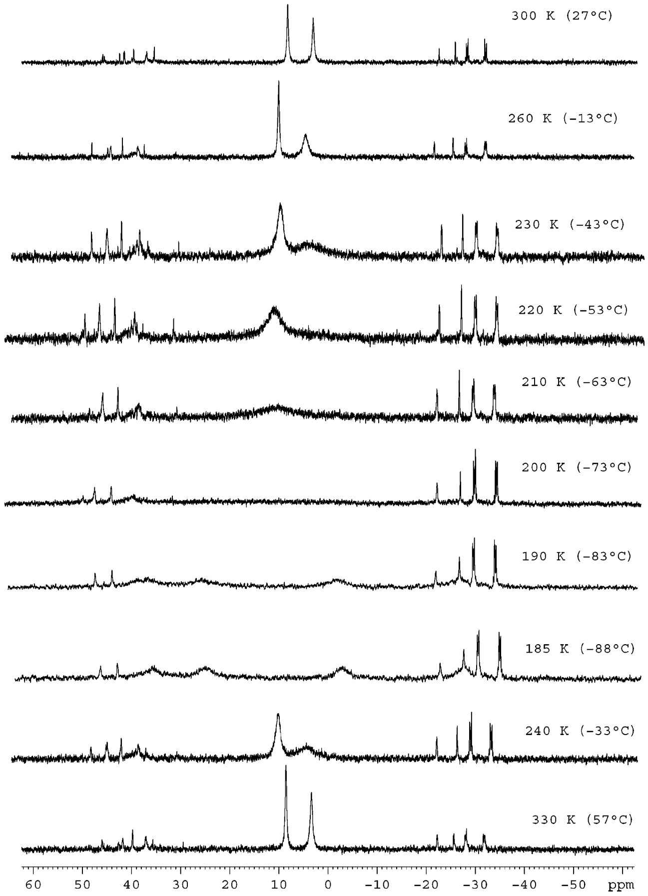

Figure 3. Variable-temperature ^{31}P NMR monitoring of the reaction of **1** with $[PdCl(\eta^3\text{-}C_3H_5)]_2$.

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[27] Krause, J.; Bonrath, W.; Pörschke, K. R. *Organometallics* **1992**, *11*, 1158.

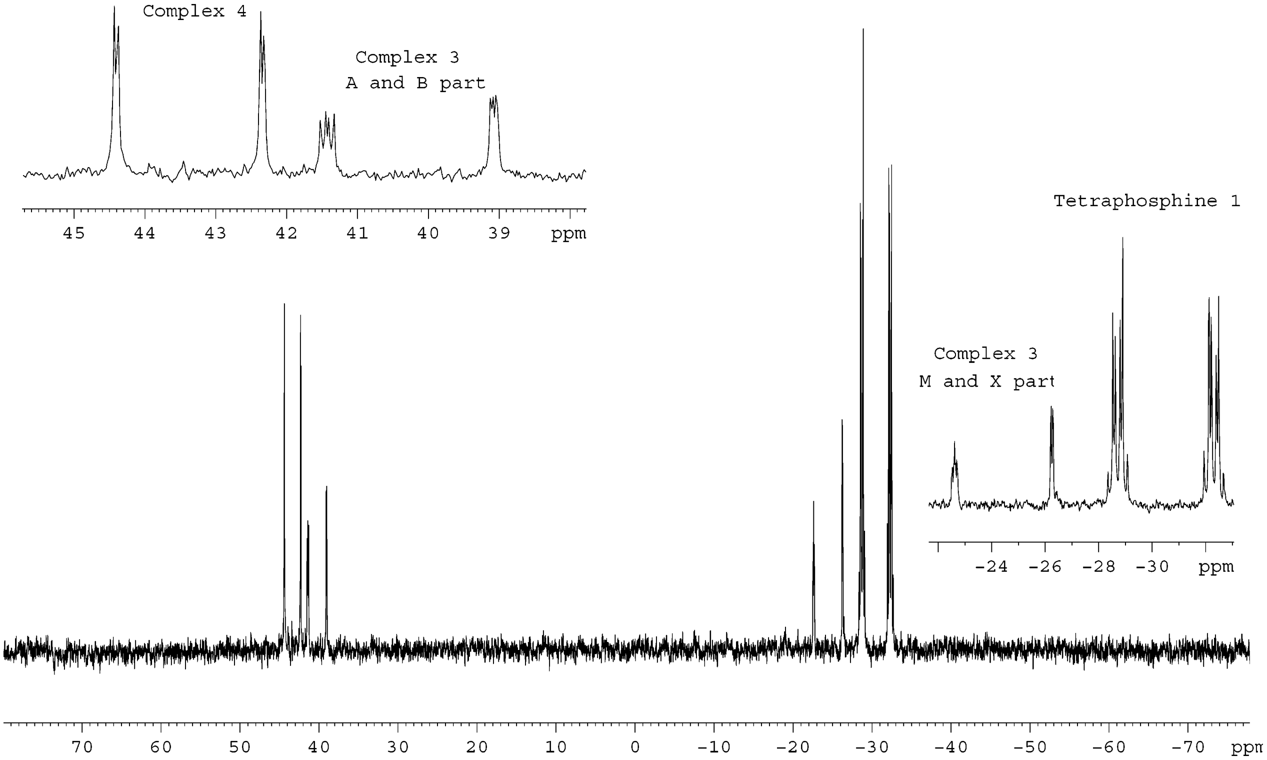

Figure 4. ^{31}P NMR spectrum of the reaction of **1** with $PdCl_2(PhCN)_2$ at ambient temperature (ratio 1 Pd:4 P).

bearing chlorine and phosphorus, arising from the thermal decomposition of the complexes. Then, considering that to finally obtain virtually quantitatively the thermodynamically favored complex **3** *one* supplementary chlorine atom was necessary per molecule of **3**, we figured out the role of the $CDCl_3$ solvent. $CDCl_3$, as the only source of supplementary chlorine atoms, would produce unsaturated $^{\bullet}CDCl_2$ species, which could consequently combine with an allyl moiety $CH_2{=}CH{-}CH_2^{\bullet}$, forming the terminal alkene $CH_2{=}CH{-}CH_2{-}CDCl_2$. This product was, a posteriori, successfully identified as the major allyl derivative formed in solution in each of our NMR studies (both in long-time and variable-temperature experiments).[28] As an unsymmetrical terminal alkene, $CH_2{=}CH{-}CH_2{-}CDCl_2$ displays a rather classical ^1H NMR spectrum with *trans*, *cis*, and *gem* proton coupling constants (see Experimental Section): four multiplets are observed, centered at 2.47 (d) (2H, H_2CCDCl_2), 4.86 and 4.93 (qd) (1H each, $=CH_2$), 5.50 ppm (tdd) (1H, C*H*). That kind of carbon−carbon coupling product, e.g., $CH_2{=}CH{-}CHR{-}CR'Cl_2$ (R = H, Me; R′ = Cl, H), has been identified before by Kurosawa et al.,[29] from the reaction of η^1-allyl complexes of palladium(II) with CCl_4 and $CHCl_3$ under analogous very mild conditions.

To definitely establish that the allyl ligand is at the origin of the entire fluxional behavior observed, the mixture of 1 equiv of $Fc(P)_4{}^tBu$ and 1 equiv of $PdCl_2(PhCN)_2$ (ratio 1 Pd:4 P) was monitored by ^{31}P and ^1H NMR in conditions identical to the ones described above. In the first 20 min, a static equilibrium was obtained, where the characteristic signals of noncoordinated **1**, the mononuclear **3**, and the dinuclear **4** were detected (Figure 4). After 50 h in solution at ambient temperature, no noticeable evolution of the mixture was observed, the ratio 50:30:20 for **1**:**3**:**4** being conserved.[30]

Crystallographic Studies. The X-ray molecular structures obtained for **3** and **4** (see Figures 5 and 6, respectively) are consistent with the NMR spectra observed in solution. For both **3** and **4**, as noticed in the case of the X-ray resolution for $Fc(P)_4{}^tBu$,[19] the conformational chirality leads to distinguishing two enantiomers present in the unit cell. In the palladium mononuclear complex **3**, as expected from the NMR studies, two 1,2-homoannular phosphorus are chelating a palladium(II) center [Pd−P(3) 2.2544(11) Å, Pd−P(4) 2.2447(11) Å], while the two other phosphorus remain noncoordinated. The metal center lies in a slightly distorted square-planar environment completed by two chlorides [Pd−Cl(1) 2.3715(11) Å, Pd−Cl(2) 2.3545(11) Å], the major deviation being observed for the angle P(4)−Pd−P(3) = 84.83(4)°. The highly unsymmetrical conformation observed in the solid state leads, among other things, to very different P−P distances in space (especially considering P(2)−P(3) = 3.8423(7) Å, P(2)−P(4) = 4.4397(9) Å, and P(1)−P(4) = 6.2915(18) Å). Interestingly, this particular conformation, whether it is conserved in solution, might explain the different J_{PP} through space observed in ^{31}P NMR. The phosphorus bonded to palladium exhibit a strong *exo* (outside) deviation from the average plane of the Cp ring: P(3) 0.4581 Å and P(4) 0.2505 Å. For the noncoordinated phosphorus the deviation from the mean plane is insignificant: P(1) 0.0158 Å and P(2) −0.0216 Å (*endo* deviation, thus toward Pd). Compared to the X-ray structure determined for **1**, in the molecular structure of **3** the Cp planes show a larger deviation from an eclipsed conformation (17.1(6)°, while 8.2(4)° was found

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[28] ^1H NMR spectrum available as Supporting Information.

[29] Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002.

[30] Ratio determined from ^1H NMR integration of *H*Cp signals.

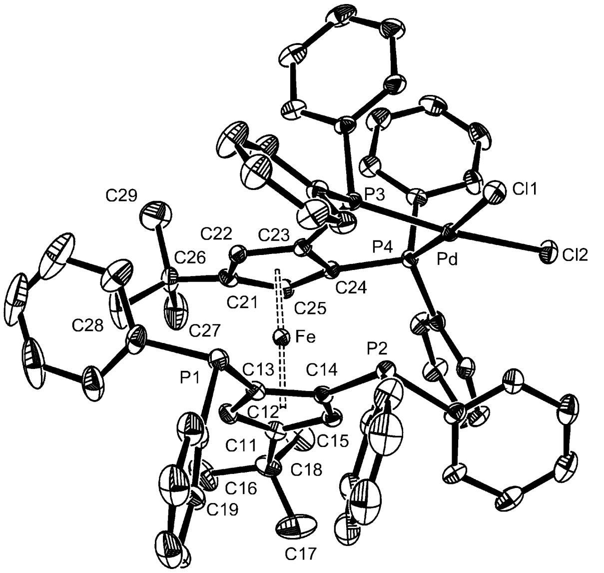

Figure 5. Plot of the molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Fe−CNT(1) 1.681, Fe−CNT(2) 1.691, P(1)−C(13) 1.832(4), P(2)−C(14) 1.836(4), P(3)−C(23) 1.796(4), P(4)−C(24) 1.788(4), Pd−P(3) 2.2544(11), Pd−P(4) 2.2447(11), Pd−Cl(1) 2.3715(11), Pd−Cl(2) 2.3545(11); CNT(1)−Fe−CNT(2) 177.71, P(4)−Pd−P(3) 84.83(4), P(4)−Pd−Cl(2) 89.59(4), P(3)−Pd−Cl(1) 93.14(4), Cl(2)−Pd−Cl(1) 91.74(4). C(14)−C(13)−P(1) 122.7(3), C(13)−C(14)−P(2) 125.9(3), C(24)−C(23)−P(3) 114.7(3), C(23)−C(24)−P(4) 117.8(3). Through-space noticeable distances (Å): P(2)−P(3) 3.8423(7), P(2)−P(4) 4.4397(9), P(1)−P(4) 6.2915(18), P(1)−P(3) 4.6978(17), Pd−P(2) 3.4878.

in **1**),[31] which results in carbons holding the tertiary butyl groups staggered with a closer twist angle of 55°, while 64° was found in **1**.

As a result of poorer crystal quality, the data for the palladium dinuclear complex **4** are somewhat less accurate. The obtained crystals contain two chloroform molecules per ferrocenylphosphine moiety. In the molecule each palladium center is chelated by two 1,2- or 1′,2′-homoannular phosphorus. Similarly to **3** the palladium centers are in a square-planar environment completed by two chlorine atoms. The values of Pd−P and Pd−Cl bond distances are consistent with the ones found for **3**, and the main deviation from ideal square-planar is also observed for the angles P−Pd−P (84.40(10)° and 87.41(10)°). However, the chelation to a palladium center of the phosphorus of the second Cp ring induces changes in the conformation of the ferrocenyl backbone compared to **3**: the Cp planes show a smaller deviation from an eclipse conformation (13.1(3)°, while 17° was found in **3**), and so the carbon atoms holding tertiary butyl groups are staggered with a more open twist angle of 59° (55° in **3**). It is also worth noting that, compared to **3**, the global distances between the phosphorus centers are larger (P(2)−P(3) = 4.9845(43) Å, P(3)−P(4) = 5.3508(40) Å, P(1)−P(2) = 5.3717(46) Å, and P(1)−P(4) = 6.5822(43) Å). The four phosphorus, bonded in pairs to a palladium center, exhibit smaller deviation from the average planes of the Cp rings: P(2), −0.1840 Å, and P(4), −0.0149 Å, show an *endo* deviation, and P(1), 0.0209 Å, and P(3), 0.1869 Å, an *exo* deviation.

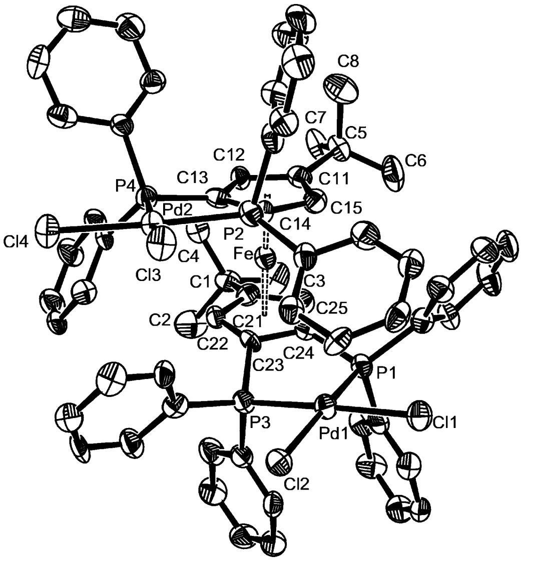

Figure 6. Plot of the molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Fe−CNT(1) 1.697, Fe−CNT(2) 1.715, P(1)−C(24) 1.807(10), P(2)−C(14) 1.812(11), P(3)−C(23) 1.822(10), P(4)−C(13) 1.815(11), Pd(1)−P(1) 2.244(3), Pd(1)−P(3) 2.248(3), Pd(2)−P(2) 2.246(3), Pd(2)−P(4) 2.260(3), Pd(1)−Cl(1) 2.344(3), Pd(1)−Cl(2) 2.336(3), Pd(2)−Cl(3) 2.343(3), Pd(2)−Cl(4) 2.367(3); CNT(1)−Fe−CNT(2) 178.06, P(1)−Pd(1)−P(3) 84.40(10), P(3)−Pd(1)−Cl(2) 89.87(10), P(1)−Pd(1)−Cl(1) 91.48(10), Cl(2)−Pd(1)−Cl(1) 93.70(10), P(2)−Pd(2)−P(4) 87.41(10), P(4)−Pd(2)−Cl(4) 91.00(10), P(2)−Pd(2)−Cl(3) 90.95(11), Cl(3)−Pd(2)−Cl(4) 90.45(11), C(23)−C(24)−P(1) 118.1(7), C(13)−C(14)−P(2) 116.5(7), C(24)−C(23)−P(3) 113.4(7), C(14)−C(13)−P(4) 118.8(8). Through-space noticeable distances (Å): (P(2)−P(3) 4.9845(43), P(3)−P(4) 5.3508(40), P(1)−P(2) 5.3717(46), P(1)−P(4) 6.5822(43).

Conclusions

The catalytic results have shown that the system combining the tetraphosphine **1** and the complex [PdCl(η^3-C$_3$H$_5$)]$_2$ compares well with other catalytic systems that have been described for Suzuki or Heck cross-coupling reactions. The NMR spectroscopic experiments conducted at elevated temperature proved that the mononuclear complex **3** is the palladium(II) predominant species above 100 °C. The better results obtained using Fc(P)$_4{}^t$Bu compared to the monodentate triarylphosphine PPh$_3$ or the bidentate diarylalkylphosphine dppe seem to result from geometric factors more than electronic factors. Thus, comparing the chelating properties of dppe and **1**, it is likely that the ferrocenyl backbone provides greater stability to the active species.

Concerning the Pd/phosphorus interaction in solution, Jutand and Amatore have shown that in THF or DMF solvent PPh$_3$ reduces Pd(II) acetate species to "Pd^0(PPh$_3$)$_n$" species and forms triphenylphosphine oxide.[32] In our present case, the ^{31}P NMR spectra obtained in time or temperature do not reveal any high-field signal of oxidized phosphorus, excluding, thus, the oxidation−reduction process that seems to require the

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(31) Twist angles calculated from the mean value of the dihedral angles C(1i)−CNT(1)−CNT(2)−C(2i), where C(1i) and C(2i) are chemically equivalent atoms of the Cp rings.

(32) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009.

presence of oxygenated ligands.[33] Another report worth mentioning, by Godleski et al.,[22] concerns the preparation of complexes by the addition of varying amounts of PPh_3 to a π-allyl-norbornyl-derivative palladium chloride dimer. For a PPh_3/Pd ratio > 2, *ionic* chloride Pd/allyl species have been identified on cooling at −40 °C, due to the nonfluxional spectrum obtained. In our case, as in the case of Tedicyp,[12] even the lowest temperature (−88 °C) did not block fluxional processes enough to precisely identify **2**.

Finally, the present studies demonstrated the potential of ferrocenyl tetradentate polyphosphines for carbon−carbon coupling catalysis, mostly due to the steric stability provided to the active species. Our current investigations are focused on the feasibility of electronic modification around (tetraphosphine)palladium catalysts, through phosphorus substituents, with the view to increasing their activity.

Experimental Section

General Considerations. All reactions and workup procedures were performed under an inert atmosphere of argon using conventional vacuum-line and glasswork techniques. Toluene and diethyl ether were degassed and distilled by refluxing over sodium benzophenone under argon. $CDCl_3$ and CD_2Cl_2 degassed and stored over molecular sieves under argon were used for NMR studies. Xylene and DMF analytical grade (98%) were not distilled before use. Potassium carbonate (99+) was used without drying. Except for the tetraphosphine ligand and for some of the aryl halides, which were distilled before use, the organic and organometallic products were received from commercial sources and used without further purification. Flash chromatography was performed on silica gel (230−400 mesh). Elemental analyses and ^1H (300.13 and 500.13 MHz), ^{31}P (121.49 and 202.46 MHz), and ^{13}C NMR (75.47 and 125.77 MHz), including low-temperature NMR experiments, were performed in our laboratories (respectively on Bruker 300 and DRX 500). The evolution of catalyzed reactions was followed by GC and NMR for high boiling point substrates and by GC for low boiling point substrates.

NMR Experiments, Ligands, and Complexes. 1,1′,2,2′-Tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene, Fc(P)$_4$^{t}Bu, 1. This tetraphosphine ligand was prepared with only minor modifications of the literature-reported synthesis.[18c,19] $C_{66}H_{62}P_4Fe$ (1035.04): calcd C 76.6, H 6.0; found C 76.3, H 6.0. ^1H NMR ($CDCl_3$): δ 6.40−8.90 (m, 40 H, Ph), 4.14, 4.05 (s, 2 H each, Cp), 0.70 (s, 18 H, ^{t}Bu). $^{31}P\{^1H\}$-($CDCl_3$): δ −28.60, −32.20 (m, J_{PP} = 70, 40, 3 and 2 Hz).$^{13}C\{^1H\}$($CDCl_3$): δ 29.3 (s, 2C, ^{t}BuCCH$_3$), 30.5 (s, 6C, ^{t}BuCH$_3$), 69.6 and 71.1 (s, 2C each, CpCH), 78.3 (m, 2C, CpCP), 86.8 (dd, 2C, $^1J_{CP}$ = 36 Hz, $^2J_{CP}$ = 11 Hz, CpCP), 106.3 (s, 2C, CpC^{t}Bu), 124−137 (m, 40 C, C_6H_5), 136.4, 137.0, 137.5, 137.9 (d, 2C each, 11 < $^1J_{CP}$ < 14 Hz, *ipso*-C_6H_5).

Reaction of the Palladium Allyl Chloride Dimer with *2* equiv of Fc(P)$_4$^{t}Bu in $CDCl_3$. The allyl dimer $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (15 mg, 0.041 mmol) and **1** (84.7 mg, 0.082 mmol) were dissolved in $CDCl_3$ (0.5 mL) under an argon atmosphere at room temperature. The mixture was vigorously shaken and briefly heated (40 °C) to help dissolution. The resulting limpid red solution was immediately monitored by NMR. The tube storing was done at ambient temperature. After 4 days, single crystals of **3** were obtained (yield 5%). In some cases, we observed that a slight amount of the complex **4** first precipitates, then after filtration, the slow crystallization of **3** occurs in the filtrate. With the same ratio of starting products, complex **3** was quantitatively obtained from a solvent mixture of chloroform and toluene (1:3 v/v) heated above 90 °C for a few minutes.

[PdCl$_2${Fc(P)$_4$^{t}Bu}], 3. $C_{66}H_{62}Cl_2P_4FePd$ (1212.28): calcd C 65.4, H 5.2; found C 65.2, H 4.9. ^1H NMR ($CDCl_3$): δ 6.40−8.90 (m, 40 H, Ph), 4.79, 4.55, 4.31, 4.28 (s, 1 H each, Cp), 0.80, 0.71 (d, J_{HP} = 1 Hz, 9 H each, ^{t}Bu). $^{31}P\{^1H\}$($CDCl_3$): δ 41.84, 41.72, 41.65, 41.53 (dd, J_{AB} = 14.7 Hz, J_{AM} = 22.9 Hz), 39.32, 39.27, 39.20, 39.15 (dd, J_{BA} = 14.7 Hz, J_{BM} = 5.8 Hz), −22.40, −22.45, −22.53, −22.59, −22.64, −22.72, −22.77 {pseudo-heptuplet (ddd), J_{MA} = 22.9 Hz, J_{MX} = 15.3 Hz, J_{MB} = 5.8 Hz}, −26.28, −26.41 (d, J_{XM} = 15.3 Hz). $^{13}C\{^1H\}$ ($CDCl_3$): δ 30.8 and 31.6 (s, 1C each, ^{t}BuCCH$_3$), 31.8 and 31.9 (s, 3C each, ^{t}BuCH$_3$), 66.7 and 70.4 (d, 1C each, $^2J_{CP}$ = 15 Hz, CpCH), 66.7 and 70.4 (d, 1C each, $^2J_{CP}$ = 15 Hz, CpCH,), 71.4 (d, 1C, $^2J_{CP}$ = 4.4 Hz, CpCH), 75.6 {pseudo-triplet (dd), 1C, 2 × J_{CP} ≅ 4 Hz, CpCH}, 80.0 (m, 2C, CpCP), 81.4 (dd, 1C, $^1J_{CP}$ = 24 Hz, $^2J_{CP}$ = 9 Hz, CpCP), 91.5 (dd, 1C, $^1J_{CP}$ = 29 Hz, $^2J_{CP}$ = 19 Hz, CpCP), 108.5 (s, 1C, CpC^{t}Bu), 119.5 (m, 1C, CpC^{t}Bu), 127−137 (m, 40 C, C_6H_5), 138−140 (m, 2C each, *ipso*-C_6H_5).

Reaction of the Palladium Allyl Chloride Dimer with *1* equiv of Fc(P)$_4$^{t}Bu in $CDCl_3$. The above-described procedure was used for a degassed mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (15 mg, 0.041 mmol) and **1** (42.3 mg, 0.041 mmol). The dinuclear palladium complex **4** is quite insoluble in $CDCl_3$ and precipitates in high yield (72%) after 48 h at ambient temperature. After filtration and storing the filtrate at −18 °C, single crystals suitable for X-ray diffraction studies were obtained.

[Pd$_2$Cl$_4${Fc(P)$_4$^{t}Bu}], 4. $C_{66}H_{62}Cl_4P_4FePd_2$ (1389.61): calcd C 57.0, H 4.5; found C 56.8, H 4.6. ^1H NMR (CD_2Cl_2): δ 6.95−8.35 (m, 40 H, Ph), 4.68 (s, 2 H, Cp), 4.23 (s, 2 H, Cp), 0.84 (s, 18 H, ^{t}Bu). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 46.83, 46.77 (d, J_{PP} = 11.8 Hz), 44.12, 44.06 (d). ^1H NMR ($CDCl_3$): δ 6.95−8.35 (m, 40 H, Ph), 4.63 (s, 2 H, Cp), 4.31 (s, 2 H, Cp), 0.74 (s, 18 H, ^{t}Bu). $^{31}P\{^1H\}$ ($CDCl_3$): δ 44.93, 44.84 (d, J_{PP} = 11.0 Hz), 42.61, 42.52 (d). $^{13}C\{^1H\}$ ($CDCl_3$): δ 31.3 (s, 6C, ^{t}BuCH$_3$), 31.9 (s, 2C, ^{t}BuCCH$_3$), 66.3 and 70.3 (d, 2C each, CpCH, $^2J_{CP}$ = 13.6 and 15.0 Hz), 120.8 (s, 2C, CpC^{t}Bu), 125.5, 127.4, 128.9, 130.4 (d, 2C each, 50 < $^1J_{CP}$ < 55 Hz, *ipso*-C_6H_5), 128.1, 128.3, 128.7(d), 131.1, 131.2, 132.4(d), 132.7, 133.4(d), 133.8, 134.7(d), 135.8(d) (40 C, for the doublets: 10 < $^2J_{CP}$ < 13 Hz, C_6H_5). Some quaternary carbons cannot unambiguously be detected due to the lack of solubility of **4** even in CD_2Cl_2.

Reaction of Bis(benzonitrile)dichloride Palladium with *1* equiv of 1 in $CDCl_3$. The above-described procedure was used for a degassed mixture of $PdCl_2(PhCN)_2$ (3.5 mg, 0.010 mmol) and **1** (10.5 mg, 0.010 mmol).

Variable-Temperature NMR Experiments. The low- and high-temperature measurements were made using solutions prepared as above-described in $CDCl_3$. Then to a volume of 0.5 mL of the mixture was added 1.5 mL of toluene. With the resulting limpid orange solution, temperatures from −88 to 97 °C were reachable.

^1H NMR of Deuterated 1,1-Dichlorobut-3-ene, $CH_2{=}CH{-}CH_2{-}CDCl_2$. Homodecoupling experiments were carried out to determine the coupling constant values. In $CDCl_3$/toluene-d_8, 1:3 v/v (500.13 MHz), δ_a (br d) = 2.47 (2H, J_{ad} = 7.0 ± 0.5 Hz, long-range coupling constants not resolved), δ_b (qd) = 4.86 (1H, J_{bd}*trans* = 17.0 ± 0.5 Hz, J_{bc}*gem* = 1.5 ± 0.5 Hz, long-range J_{ba} = 1.5 ± 0.5 Hz), δ_c (qd) = 4.93 (1H, J_{cd}*cis* = 10.0 ± 0.5 Hz, J_{cb}*gem* = 1.0 ± 0.5 Hz, long-range J_{ca} = 1.0 ± 0.5 Hz), δ_d (tdd, pseudo-decuplet) = 5.50 ppm (1H, J_{db}*trans* = 17.0 ± 0.5 Hz, J_{dc}*cis* = 10.0 ± 0.5 Hz, J_{da} = 7.0 ± 0.5 Hz).

Preparation of the Pd/Fc(P)$_4$^{t}Bu Catalyst. An oven-dried Schlenk tube equipped with a magnetic stirring bar under argon atmosphere was charged with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.8 mg, 0.005 mmol) and Fc(P)$_4$^{t}Bu, **1** (10.5 mg, 0.010 mmol). Five milliliters of dichloromethane or chloroform was added, then the solution was stirred at room temperature for 20 min. The solvent was removed in vacuo, then the catalyst was dissolved with the appropriate solvent of reaction.

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[33] Amatore, C.; Carré, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818.

Catalytic Reactions. As a typical experiment: the reaction of aryl halide (10 mmol), aryl boronic acid or alkene (20 mmol), and K_2CO_3 (2.76 g, 20 mmol) at 130 °C during 20 h in dry xylene or DMF (10 mL) in the presence of $\{2Fc(P)_4{}^tBu/[PdCl(\eta^3\text{-}C_3H_5)]_2\}$, under argon, affords the corresponding products. Isolated yields were obtained after addition of water, extraction with ether or dichloromethane, separation, drying on $MgSO_4$, evaporation, and chromatography on silica gel.

Crystallographic Data. Single crystals of **3** and **4** were obtained from $CDCl_3$ solution. For the two compounds data were collected at low temperature on a IPDS STOE diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryosystems cryostream cooler device. The final unit cell parameters were obtained by means of a least-squares refinement performed on a set of 8000 well-measured reflections. Crystal decay was monitored, and no significant fluctuations of intensities have been observed during the data collection. Structures were solved by direct methods using SHELX97[34] and refined by means of least-squares procedures on F^2 with the aid of the program SHELXL97, which is included in WinGX version 1.63.[35] The atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[36] All hydrogens atoms were located on a difference Fourier maps and refined by using a riding model. The C−H distances were fixed at 0.93 Å for C sp^2 atoms and 0.96 Å for C sp^3 atoms, with an isotropic parameter 20% higher than the U_{eq} value of C sp^2 atoms to which they were attached and 50% higher for the C sp^3 atoms. Methyl groups were refined using a rigid group, with the torsion angle as a free variable. Concerning the compound **4**, two molecules of chloroform were located and found disordered. However, a suitable model could be found for each molecule, which were refined using any restraints. All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights were calculated from the following formula: $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ with $P = (F_o{}^2 + 2F_c{}^2)/3$. Drawings of the molecules were obtained with the ORTEP32 program,[37] with 50% probability displacement ellipsoids for the non-hydrogen atoms.

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Supporting Information Available: X-ray crystal data and data collection and structure refinement for **3** and **4**, as well as NMR spectra corresponding to refs 23, 26, and 28 are available free of charge via the Internet at http://pubs.acs.org.

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(35) *WINGX-1.63* Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-Ray Diffraction Data. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(36) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(37) *ORTEP3* for Windows. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.