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On the formation of Pd(II) complexes of Trost modular ligand involving N–H activation or P,O coordination in Pd-catalyzed allylic alkylations

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Abstract

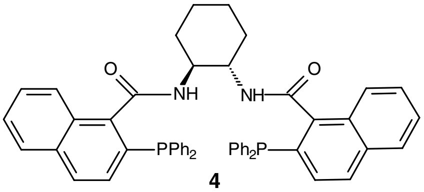
Specific chiral ligands have been designed by Trost et al. to perform enantioselective Pd-catalyzed allylic alkylations. It is shown that the Pd(0) complex formed by addition of the Trost ligand (**4**) to $Pd^0(dba)_2$ is not stable in most solvents (acetone, DMF, CH_2Cl_2). Indeed, Pd^0(dba)(**4**) leads to the formation of a stable Pd^{II} complex **5** (X-ray structure), likely by activation of the two N–H bonds of the ligand by the Pd^0 centre. The formation of the Pd^{II} complex competes with the reaction of Pd^0(**4**) with (*E*)-PhCH=CH–CH(OAc)–Ph, excluding any investigation of the kinetics of the latter reaction. The ionization steps from intermediate (η^2-PhCH=CH–CH(OAc)–Ph)Pd^0(**4**) were found to be very slow. The cationic P,P complex [(η^3-Ph–CH–CH–CH–Ph)Pd(**4**)]$^+$, expected to be generated by addition of 2 equiv. of **4** to the precursor [(η^3-Ph–CH–CH–CH–Ph)Pd(μ-Cl)]$_2$, in the presence of a chloride scavenger, leads to a complex mixture whereas addition of 1 equiv. of **4** affords a stable bis-cationic Pd^{II} complex {[(η^3-Ph–CH–CH–CH–Ph)Pd]$_2$(**4**)]}$^{2+}$, 2(BF_4^-) (X-ray structure) via a P,O complexation of each allyl-Pd moieties. This dissymmetric P,O coordination will favour the enantioselectivity of Pd-catalyzed allylic alkylation of (E)-PhCH=CH–CH(OAc)–Ph by the control of the regioselectivity of the nucleophilic attack onto the allylic ligand which is responsible of the enantioselectivity of the overall catalytic reaction.

Keywords: Palladium; Trost ligand; Oxidative addition; Allylic acetate; Allylic-palladium

1. Introduction

The allylic acetate (*E*)-Ph–CH=CH–CH(Ph)–OAc ((*E*)-1,3-diphenyl-3-acetoxyprop-1-ene) (**1**) has been specifically designed by Trost et al. [1] to test the efficiency of chiral ligands on the enantioselectivity of Pd-catalyzed nucleophilic allylic substitutions [1,2]. We have previously established that the oxidative addition of **1** to the Pd(0) complexes generated from $Pd^0(dba)_2$ and either 2 equiv. of PPh_3 or 1 equiv. of dppb (1,4-bis(diphenylphosphino)butane) was reversible and proceeded by two successive steps as depicted in Scheme 1 [3].

The purpose of the present work was to investigated the same reaction using the chiral bidentate ligand: (1*S*,2*S*)-(−)-1,2-diaminocyclohexane-*N*,*N*′-bis(2-diphenylphosphino-1-naphthoyl) (**4**) [4] designed by Trost et al. [4a] and to characterize the cationic complex [(η^3-Ph–CH–CH–CH–Ph) Pd(**4**)]$^+$ expected to be formed in the reaction of **1** with Pd^0(**4**), as in Scheme 1.



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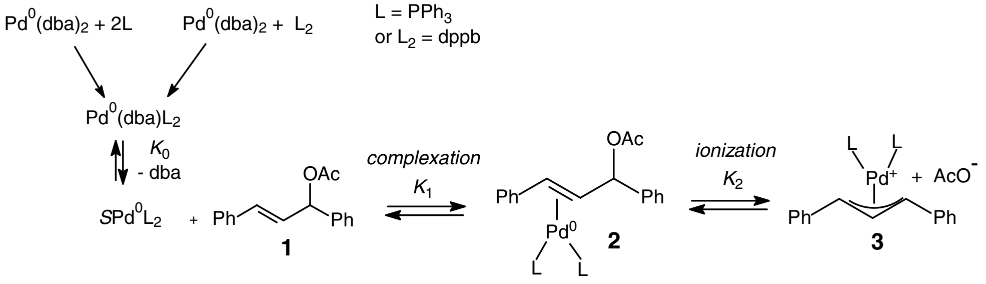


Scheme 1.

We report herein that the expected complex Pd^0(**4**) generated from $Pd^0(dba)_2$ and ligand **4** is not stable and gives rise to a Pd(II) complex, in competition with the oxidative addition of **1**. In addition, in its stabilization of the cationic $[(\eta^3\text{-Ph–CH–CH–CH–Ph})Pd^{II}]^+$ moieties, the ligand **4** behaves as a bis-P,O ligand instead of the expected P,P ligation.

2. Experimental

2.1. General

^{31}P NMR spectra were recorded on a Bruker spectrometer (101 MHz) with H_3PO_4 as an external reference. ^1H NMR spectra were recorded in on a Bruker spectrometer (250 MHz) with TMS as an external reference. Conductivity measurements were performed on a Tacussel CDM210 conductivity meter (cell constant = 1 cm^{-1}). All experiments were performed under Argon atmosphere.

2.2. Chemicals

DMF was distilled from calcium hydride under vacuum and kept under argon. $Pd^0(dba)_2$ [5] and (*E*)-1, 3-diphenyl-3-acetoxyprop-1-ene (**1**) [6] were prepared according to described procedures. $[Pd(\eta^3\text{-Ph–CH–CH–CH–Ph})(\mu\text{-Cl})]_2$ was synthesized according to a reported procedure [7] but from Na_2PdCl_4. The Trost ligand **4** was commercial.

2.3. Complex 5

*Observation of complex **5** by ^{31}P NMR spectroscopy.* 5.8 mg (0.01 mmol) of $Pd^0(dba)_2$ was added into an NMR tube containing 0.5 mL of DMF and 50 μL of acetone-d_6 followed by 7.9 mg (0.01 mmol) of the ligand **4**. The ^{31}P NMR was performed with times. The singlet of **5** at 21.83 ppm was observed on the first recorded spectrum (15 min after mixing). The two broader doublets of Pd^0(dba)(**4**) at 20.10 and 25.43 ppm were also observed (46%). After 1 h, the singlet of **5** was observed as the major signal (73%). Twenty-two hours later, the singlet of **5** was only observed.

*Synthesis of complex **5***. 42 mg (0.053 mmol) of the ligand **4** was added to 3 mL of degassed acetone containing 30.4 mg (0.053 mmol) of $Pd^0(dba)_2$ to give an orange solution under Argon. A yellow precipitate appeared after 2 h at room temperature. The orange acetone solution was transferred under Argon. After evaporation of acetone, the crude was analysed by ^1H NMR as pure dba (comparison with an authentic sample). The yellow solid was crystallized from acetone affording 24.6 mg of complex **5** (52% yield). A monocrystal of the Pd(II) complex **5** was obtained after crystallization from acetone/petroleum ether (see Fig. 1 for the X-ray structure). ^1H NMR (250 MHz,

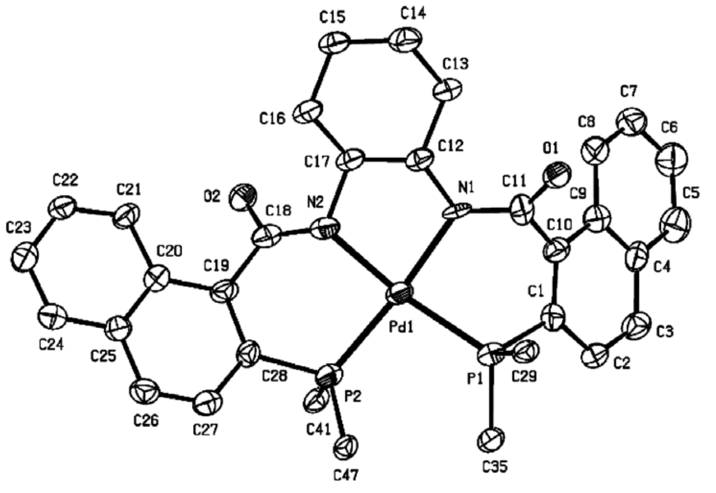


Fig. 1. X-ray structure of complex **5** (for more clarity, the phenyl groups at C29, C35, C41 and C47 have been omitted).

acetone-d_6, TMS): δ 1.0–1.35 (m, 4H), 1.64 (br d, $J = 10$ Hz, 2H), 3.26 (br d, 2H), 3.57 (br d, 2H), 6.46 (t, $J = 9$ Hz, 2H), 6.80 (br t, $J = 7.5$ Hz, 4H), 6.95 (br t, $J = 7$ Hz, 4H), 7.1–7.4 (m, 12H), 7.55–7.8 (m, 8H), 8.42 (br d, 2H); ^{31}P NMR (101.3 MHz, acetone-d_6, H_3PO_4): δ 21.65 (s); ^{31}P NMR (101.3 MHz, DMF + acetone-d_6, H_3PO_4): δ 21.83 (s); ES MS (methanol): $m/z = 917$ $[M+Na]^+$, 895 $[M+H]^+$; *Anal.* Calc. for $C_{52}H_{42}N_2O_2P_2Pd$,$2CH_3COCH_3$: C, 68.87; H, 5.38; N, 2.77. Found: C, 70.40; H, 5.40; N, 2.82%.

2.4. Synthesis of complex $\mathbf{13}^{2+}$, $2(BF_4^-)$

Sixty-nine milligrams (0.088 mmol) of the ligand 4 in 2.5 mL of acetone was added to a solution of 51 mg (0.076 mmol) of $[(\eta^3\text{-Ph–}C_3H_3\text{–Ph})Pd(\mu\text{-Cl})]_2$ in 2 mL of acetone, followed by 611 mg (5.5 mmol) of $NaBF_4$ in 6 mL of water. A yellow precipitate was formed and filtrated. Crystallisation from CH_2Cl_2/pentane give 77 mg (84% yield) of $\mathbf{13}^{2+}$, $2(BF_4^-)$. Monocrystals were formed by diffusion of pentane to a solution of $\mathbf{13}^{2+}$, $2(BF_4^-)$ in CH_2Cl_2 (see Fig. 2 for the X-ray structure).^{1}H NMR (250 MHz, acetone-d_6, TMS): broad signals were observed at 25 °C indicative of fluxionality.^{31}P NMR (101.3 MHz, acetone-d_6, H_3PO_4): δ 22.34 (br. s).

2.5. General procedure for the observation of the oxidative addition of (E)-PhCH=CH–CH(Ph)–OAc, as monitored by ^{31}P NMR spectroscopy

To an NMR tube containing 0.5 mL of DMF and 50 μL of acetone-d_6 was added 5.8 mg (0.01 mmol) of $Pd^0(dba)_2$ followed by 7.9 mg (0.01 mmol) of the ligand **4** and 171 mg (0.68 mmol) of (E)-PhCH=CH–CH(Ph)–OAc. The ^{31}P NMR was performed with time (see text).

3. Results and discussion

3.1. Characterization of the complexes generated from $Pd^0(dba)_2$ and 1 equiv. of the ligand 4 and their reaction with (E)-Ph–CH=CH–CH(Ph)–OAc (1)

The reaction of $Pd^0(dba)_2$ (1 mM) with 1 equiv. of the Trost ligand **4** in DMF or acetone generated $Pd^0(dba)(\mathbf{4})$ upon mixing at room temperature. This complex was characterized by ^{31}P NMR spectroscopy performed in acetone-d_6 by two doublets at 19.72 ($J_{PP} = 14$ Hz) and 25.34 ($J_{PP} = 14$ Hz) (20.10 and 25.43 ppm in DMF, containing 10% acetone-d_6) [8]. However, a second complex was observed on the first recorded spectrum, being characterized as a singlet at 21.65 ppm in acetone (21.83 in DMF, containing 10% acetone-d_6) whose magnitude increased with time at the expense of the two doublets of $Pd^0(dba)(\mathbf{4})$. The formation of the new complex was retarded by excess dba. An X-ray structure of the new complex crystallized from acetone/ether (Fig. 1, Tables 1 and 2) revealed the formation of the Pd^{II} complex **5** ligated to the ligand **4** which has then been formally “deprotonated” (Scheme 2) [9]. The reaction was also followed by cyclic voltammetry performed in acetone containing nBu_4NBF_4 (0.3 M). The

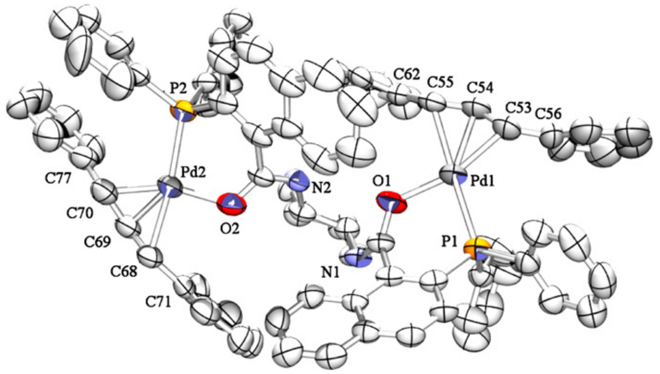


Fig. 2. X-ray structure of complex $\mathbf{13}^{2+}$.

Table 1
X-ray crystallographic data for complex **5**

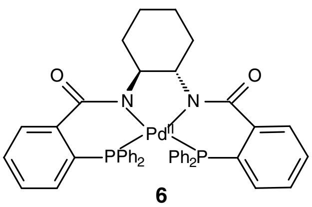
CCDC	626050
Compound	Complex **5**
Molecular formula	$C_{52}H_{42}N_2O_2P_2Pd$, $2(C_3H_6O)$
Molecular weight	1011.37
Crystal habit	Pale yellow needle
Crystal dimensions (mm)	$0.20 \times 0.06 \times 0.03$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	12.2370(10)
b (Å)	13.3510(10)
c (Å)	29.6560(10)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	4845.1(6)
Z	4
d (g cm^{-3})	1.386
F(000)	2096
μ (cm^{-1})	0.499
Absorption corrections	Multi-scan; 0.9067 min, 0.9852 max
Diffractometer	KappaCCD
X-ray source	Mo Kα
λ(Å)	0.71069
Monochromator	Graphite
T (K)	150.0 (1)
Scan mode	Phi and omega scans
Maximum θ	23.82
Ranges	$-13 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 12$, $-33 \leqslant l \leqslant 33$
Reflections measured	12132
Unique data	7237
R_{int}	0.0532
Reflections used	5349
Criterion	$I > 2\sigma I$
Refinement type	Fsqd
Hydrogen atoms	Mixed
Parameters refined	608
Reflections/parameter	8
wR_2	0.0912
R_1	0.0469
Flack's parameter	−0.03(3)
Weights a, b	0.0222; 0.0000
Goodness-of-fit	0.964
Difference peak/hole (e Å^{-3})	0.454(0.076)/−0.881(0.076)

Table 2
Selected bond lengths (Å) and angles (°) for complex **5**

Bond lengths (Å)			
Pd(1)–N(1)	2.062(4)	Pd(1)–N(2)	2.064(5)
Pd(1)–P(2)	2.243(2)	Pd(1)–P(1)	2.273(2)
Bond angles (°)			
N(1)–Pd(1)–N(2)	83.9(2)	N(1)–Pd(1)–P(2)	172.7(1)
N(2)–Pd(1)–P(2)	91.0(1)	N(1)–Pd(1)–P(1)	88.8(1)
N(2)–Pd(1)–P(1)	167.6(1)	P(2)–Pd(1)–P(1)	97.04(6)
C(29)–P(1)–C(1)	105.1(3)	C(29)–P(1)–C(35)	105.5(3)
C(1)–P(1)–C(35)	104.3(3)	C(29)–P(1)–Pd(1)	109.6(2)
C(1)–P(1)–Pd(1)	109.7(2)	C(35)–P(1)–Pd(1)	121.4(2)
C(41)–P(2)–C(47)	109.4(3)	C(28)–P(2)–Pd(1)	112.6(2)
C(41)–P(2)–Pd(1)	111.6(2)	C(47)–P(2)–Pd(1)	116.9(2)
C(11)–N(1)–C(12)	119.9(5)	C(11)–N(1)–Pd(1)	125.9(4)
C(12)–N(1)–Pd(1)	106.9(3)	C(18)–N(2)–C(17)	112.1(4)
C(18)–N(2)–Pd(1)	120.4(4)	C(17)–N(2)–Pd(1)	109.1(3)
N(1)–C(11)–C(10)	118.3(6)	N(1)–C(12)–C(17)	107.7(4)
N(1)–C(12)–C(13)	114.4(5)	C(17)–C(12)–C(13)	107.8(4)
C(12)–C(17)–C(16)	111.2(5)	O(2)–C(18)–N(2)	125.7(5)
O(2)–C(18)–C(19)	117.5(6)	N(2)–C(18)–C(19)	116.1(5)

oxidation peak of the ligand **4** (2 mM) at +1.27 V versus SCE disappeared upon addition of $Pd^0(dba)_2$ (2 mM), leading to an oxidation peak at +0.606 V versus SCE, characterizing Pd^0(dba)(**4**). The orange solution turned progressively to yellow because of the formation of complex **5**. After 6 h, the oxidation peak of Pd^0(dba)(**4**) was no longer observed and two dba (characterized by its reduction peak) were released in solution. The solution did not exhibited any oxidation peak attesting that complex **5** was indeed a Pd(II) complex. This was also confirmed by the fact that no reaction took place between the isolated complex **5** and PhI (50 equiv), as monitored by ^{31}P NMR.

The formation of a similar Pd(II) complex **6** was mentioned by Trost et al. in the reaction of $Pd_2^0(dba)_3$ with the Trost ligand **7** having a phenyl group instead of the naphthyl one [2m,10]. The complex **6** has been characterized by an X-ray structure by Lloyd-Jones et al. [11].



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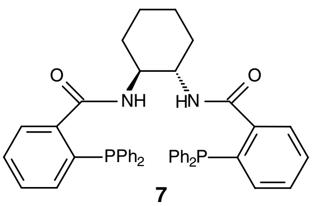

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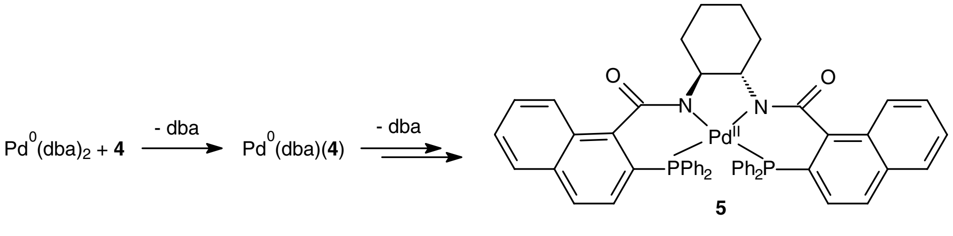
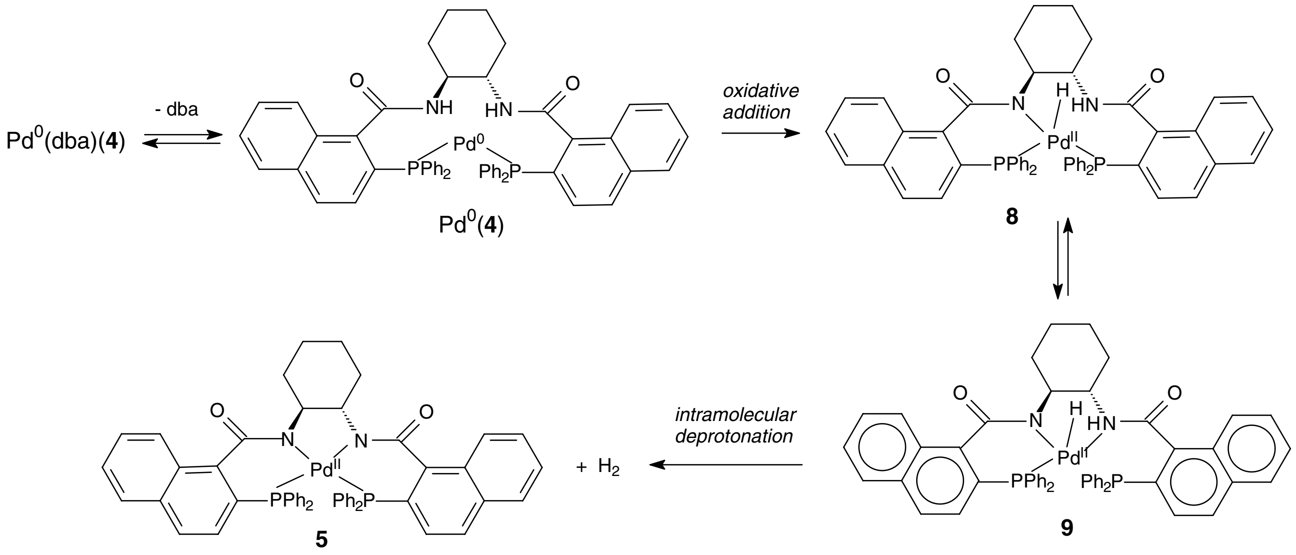
According to Trost et al. the Pd^{II} complex **6** would be generated by oxidation of Pd^0(dba)(**7**) by air [10]. Despite all our efforts to conduct the formation of Pd^0(dba)(**4**) under an atmosphere exempt of dioxygen [12] in degassed solvents, the Pd^{II} complex **5** was always detected in acetone, dichloromethane and DMF, suggesting that an alternative reaction might be at the origin of the formation of the Pd^{II} complex. An intramolecular activation of one N–H bond by the Pd^0 centre might be involved (Scheme 3), leading to a Pd(II) hydride (**8**) [13]. The coordination of the second amino group in complex **9** [14] would generate a proton which is more acidic than that of the free ligand. Intramolecular deprotonation by the hydride would generate complex **5**.

Whatever the mechanism of formation of the Pd(II) complex **5** from Pd^0(dba)(**4**), the formation of this side-product **5** in variable amounts prevented us to get precise kinetic data on the reaction of Pd^0(dba)(**4**) with (*E*)-Ph–CH=CH–CH(Ph)–OAc (**1**). A qualitative study was thus undertaken. When 68 equiv. of **1** were added to a fresh solution of Pd^0(dba)(**4**) generated from $Pd^0(dba)_2$ (18 mM) and **4** (18 mM) in DMF containing 10% acetone-d_6, the two doublets of Pd^0(dba)(**4**) were not observed on the first recorded ^{31}P NMR spectrum. The latter exhibited the singlet of the Pd^{II} complex **5** and two kinds of signals which revealed the formation of two different complexes **10** and **11**. The complex **10** was characterized by two broad singlets of equal magnitude at 32.16 and 26.20 ppm indicative of a P,P bis-ligation of the Pd centre. The second complex **11** was characterized by a singlet at −13.27 ppm close to that of the free ligand (−12.7 ppm), associated with a singlet at 29.98 ppm of same amplitude, which suggests a monoligation of the ligand **4**. Such complexes were neutral. Indeed, the same reaction was monitored by conductivity measurement to follow the formation of the expected cationic complex $[(\eta^3\text{-Ph–}C_3H_3\text{–Ph})Pd(\mathbf{4})]^+$ (**12**) with AcO^- as the counter anion, as done for PPh_3 and dppb ligand [3,15]. No significant increase of the conductivity (1 $\mu S\,cm^{-1}$) was observed after addition of Ph–CH=CH–CH(Ph)–OAc (80 mM) to a solution of $Pd^0(dba)_2$ (1 mM) and **4** (1 mM) in DMF within 2 h [16].

The two neutral complexes **10** and **11** were assigned to intermediate Pd^0 complexes ligated to the C=C bond of **1** [17]. Due to the chirality of the ligand **4**, the reactivity of the two enantiomers of **1** with the chiral Pd^0(**4**) complex would be different and would generate two different



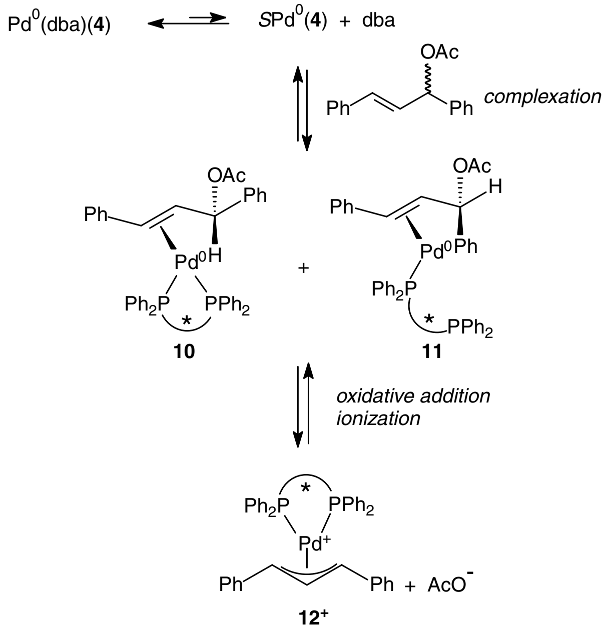
Scheme 2.



Scheme 3. Tentative explanation for the formation of complex **5** from Pd^0(dba) (**4**).

intermediate Pd^0 complexes **10** and **11** in a first complexation step (Scheme 4).

No significant signals that would have characterized the cationic complex **12**$^+$, AcO$^-$ have been detected in the time scale investigated here (6 h). Consequently, the cationic complex **12**$^+$ was not formed in significant amount in the oxidative addition, as also confirmed by conductivity measurement (vide supra) due to sluggish ionization steps from the neutral complexes **10** and **11**. As a comparison, when the reaction of Pd^0(dba)(**4**) with $CH_2{=}CH–CH–OAc$ was performed in acetone-d_6, one singlet was detected in the ^{31}P NMR spectrum at 31.77 ppm and assigned to the cationic complexes [(η^3–CH_2–CH–CH_2)Pd(**4**)]$^+$. It is worthwhile to note that under such experimental conditions, no neutral intermediate complex [(η^2-$CH_2{=}CH–CH_2$-OAc)Pd^0(**4**)] was observed, attesting for its fast ionization. The fact to observe one ^{31}P NMR singlet for [(η^3–CH_2–CH–CH_2)Pd(**4**)]$^+$ instead of two doublets (expected because of the chirality of **4**, [18]) attested for a scrambling due to the reaction of the acetate ion with the cationic complex in a reversible ionization step. Such a situation has already been observed with the chiral ligand diop [19]. Indeed, whereas the cationic complex [(η^3–CH_2–CH–CH_2)Pd^{II}(diop)]$^+$, BF_4^- exhibited two ^{31}P NMR doublets in DMF, one singlet was observed after addition of nBu$_4$-NOAc due to the reversibility of the ionization step [19].



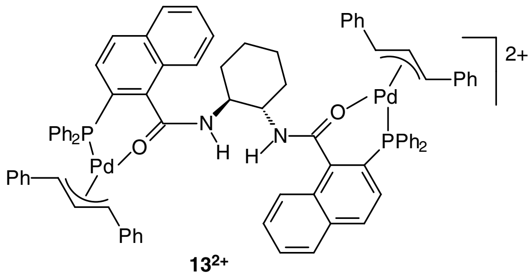
Scheme 4.

Consequently, the complex [(η^3-Ph–CH–CH–CH–Ph)Pd(**4**)]$^+$ expected to be formed in the reaction of Pd^0(**4**) and PhCH=CH–CH(Ph)–OAc has not been observed under our experimental conditions, attesting for a sluggish ionization step from [(η^2-Ph–CH=CH–CH(Ph)–OAc)Pd^0 (**4**)]. We decided thus to synthesize such cationic complex by an independent reaction: addition of the ligand **4** to (η^3-Ph–CH–CH–CH–Ph)palladium(II) precursors, as classically done in Pd-catalyzed allylic alkylations [1,2].

3.2. Characterization of cationic (η^3-Ph–CH–CH–CH–Ph)-palladium(II) complexes ligated by 4

Up to now, the cationic complex [(η^3-Ph–CH–CH–CH–Ph)Pd(**4**)]$^+$, BF_4^- has not been isolated as a stable complex when reacting [(η^3-Ph–CH–CH–CH–Ph)Pd(μ-Cl)]$_2$ with 2 equiv. of ligand **4**, followed by addition of $NaBF_4$ as a chloride scavenger, as also observed by Lloyd-Jones et al. using the Trost ligand **7** in the more simple complex [(η^3–CH_2–CH–CH_2)Pd(**7**)]$^+$, OTf$^-$ [20]. A set of 2 doublets at 21.88 (d, $J_{PP} = 12$ Hz, 1P) and 27.88 (d, $J_{PP} = 12$ Hz, 1P) ppm were observed by ^{31}P NMR performed in $CDCl_3$ which could characterize [(η^3-Ph–CH–CH–CH–Ph)Pd (**4**)]$^+$, BF_4^-. However, the major signal was a broad singlet at 29.43 ppm, which, by comparison with the work reported by Lloyd-Jones et al. for the ligand **7** [18], was assigned to polymeric complexes $\{\text{-}[(\eta^3\text{-Ph–C}_3\text{H}_3\text{–Ph})\text{Pd}]\text{–P–P–}\}_n]^{n+}$, where one ligand **4** (P–P) was ligated to two different $[(\eta^3\text{-Ph–C}_3\text{H}_3\text{–Ph})\text{Pd}]$ moieties via the P atoms. The complex $[(\eta^3\text{-Ph–CH–CH–CH–Ph})\text{Pd}(\mathbf{4})]^+$ was indirectly detected by ES MS by the observation of two peaks centred at $m/z = 1105$ $[\text{M+16}]^+$ and $m/z = 1121$ $[\text{M+32}]^+$ due to an artefact of the ES MS, the ionization may indeed produces some phosphine oxide which coordinates the cationic Pd complex [21]. This is nevertheless an indirect proof for the formation of $[(\eta^3\text{-Ph–CH–CH–CH–Ph})\text{Pd}(\mathbf{4})]^+$.

Orange crystals have been isolated when the ligand **4** (1 equiv.) was added to the dimer $[(\eta^3\text{-Ph–CH–CH–CH–Ph})\text{Pd}(\mu\text{-Cl})]_2$ followed by addition of NaBF_4 as a chloride scavenger. The X-ray structure revealed the formation of complex $\mathbf{13}^{2+}$, $2(\text{BF}_4^-)$ (Fig. 2, Tables 3 and 4). Two cationic $[(\eta^3\text{-Ph–CH–CH–CH–Ph})\text{Pd}]^+$ moieties are connected via the ligand **4** which behaves now as a bis-P,O ligand. A similar structure has been established by Lloyd-Jones et al. when considering the Trost ligand **7** in $\{[(\eta^3\text{–CH}_2\text{–CH–CH}_2)\text{Pd}]_2(\mathbf{7})\}^{2+}$, 2TfO^- [18,20].



$\mathbf{13}^{2+}$

Table 3
X-ray crystallographic data for complex $\mathbf{13}^{2+}$

CCDC	626051
Molecular formula	$\text{C}_{82}\text{H}_{70}\text{N}_2\text{O}_2\text{P}_2\text{Pd}_2$,2($\text{BF}_4$), CH_2Cl_2
Molecular weight	1648.69
Crystal habit	Orange block
Crystal dimensions (mm)	0.20 × 0.18 × 0.18
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	9.9430(10)
b (Å)	20.1020(10)
c (Å)	38.7850(10)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	7752.1(9)
Z	4
d (g cm^{-3})	1.413
F(000)	3352
μ (cm^{-1})	0.641
Absorption corrections	Multi-scan; 0.8825 min, 0.8933 max
Diffractometer	KappaCCD
X-ray source	Mo Kα
λ (Å)	0.71069
Monochromator	Graphite
T (K)	150.0(1)
Scan mode	Phi and omega scans
Maximum θ	23.82
Ranges	$-11 \leqslant h \leqslant 11$; $-22 \leqslant k \leqslant 22$; $-43 \leqslant l \leqslant 44$
Reflections measured	11825
Unique data	11825
Rint	0.0000
Reflections used	9628
Criterion	$I > 2\sigma I$
Refinement type	Fsqd
Hydrogen atoms	Mixed
Parameters refined	901
Reflections/parameter	10
wR_2	0.1529
R_1	0.0515
Flack's parameter	−0.01(3)
Weights a, b	0.1049; 0.0000
Goodness-of-fit	1.056
Difference peak/hole (e Å $^{-3}$)	0.729(0.071)/−0.761(0.071)

Note: A highly disordered CH_2Cl_2 molecule located near 0, 0.5, 0.5 was accounted for using the Platon SQUEEZE function.

Table 4
Selected bond lengths (Å) and angles (°) for complex $\mathbf{13}^{2+}$

Bond lengths (Å)			
Pd(1)–O(1)	2.112(5)	Pd(1)–C(54)	2.124(6)
Pd(1)–C(53)	2.133(7)	Pd(1)–C(55)	2.218(6)
Pd(1)–P(1)	2.292(2)	Pd(2)–O(2)	2.143(6)
Pd(2)–C(69)	2.169(8)	Pd(2)–C(70)	2.181(9)
Pd(2)–C(68)	2.206(6)	Pd(2)–P(2)	2.293(2)
P(1)–C(29)	1.816(7)	P(1)–C(35)	1.820(7)
P(1)–C(3)	1.828(6)	P(2)–C(28)	1.804(9)
P(2)–C(41)	1.827(6)	P(2)–C(47)	1.836(8)
C(53)–C(54)	1.32(1)	C(53)–C(56)	1.44(1)
C(54)–C(55)	1.40(1)	C(55)–C(62)	1.46(1)
C(68)–C(69)	1.40(1)	C(68)–C(71)	1.49(1)
C(69)–C(70)	1.41(1)	C(70)–C(77)	1.48(1)
Bond angles (°)			
O(1)–Pd(1)–C(54)	127.2(3)	O(1)–Pd(1)–C(53)	163.0(3)
C(54)–Pd(1)–C(53)	36.2(3)	O(1)–Pd(1)–C(55)	95.2(2)
C(54)–Pd(1)–C(55)	37.6(3)	C(53)–Pd(1)–C(55)	68.1(3)
O(1)–Pd(1)–P(1)	87.1(1)	C(54)–Pd(1)–P(1)	141.2(3)
C(53)–Pd(1)–P(1)	109.7(2)	C(55)–Pd(1)–P(1)	177.1(2)
O(2)–Pd(2)–C(69)	128.7(2)	O(2)–Pd(2)–C(70)	160.3(2)
C(69)–Pd(2)–C(70)	37.9(3)	O(2)–Pd(2)–C(68)	94.9(3)
C(69)–Pd(2)–C(68)	37.4(3)	C(70)–Pd(2)–C(68)	67.0(3)
O(2)–Pd(2)–P(2)	91.7(1)	C(69)–Pd(2)–P(2)	137.0(2)
C(70)–Pd(2)–P(2)	106.2(2)	C(68)–Pd(2)–P(2)	173.2(2)
C(35)–P(1)–C(3)	105.1(3)	C(29)–P(1)–Pd(1)	111.1(2)
C(35)–P(1)–Pd(1)	120.2(2)	C(3)–P(1)–Pd(1)	106.2(2)
C(41)–P(2)–C(47)	102.3(4)	C(28)–P(2)–Pd(2)	109.9(2)
C(41)–P(2)–Pd(2)	115.9(2)	C(47)–P(2)–Pd(2)	116.7(2)
C(1)–O(1)–Pd(1)	128.4(5)	C(18)–O(2)–Pd(2)	123.0(4)
C(16)–C(17)–C(12)	110.7(5)	O(2)–C(18)–N(2)	120.6(5)
O(2)–C(18)–C(19)	121.8(6)	N(2)–C(18)–C(19)	117.5(5)
C(54)–C(53)–C(56)	129(1)	C(54)–C(53)–Pd(1)	71.6(5)
C(56)–C(53)–Pd(1)	127.9(6)	C(53)–C(54)–C(55)	127(1)
C(53)–C(54)–Pd(1)	72.3(4)	C(55)–C(54)–Pd(1)	74.8(4)
C(54)–C(55)–C(62)	122.6(8)	C(54)–C(55)–Pd(1)	67.5(4)
C(62)–C(55)–Pd(1)	114.9(4)	C(57)–C(56)–C(61)	117(1)
C(57)–C(56)–C(53)	122(1)	C(61)–C(56)–C(53)	121(1)
C(56)–C(57)–C(58)	125(2)	C(69)–C(68)–C(71)	125.6(8)
C(69)–C(68)–Pd(2)	69.9(4)	C(71)–C(68)–Pd(2)	115.1(4)
C(68)–C(69)–C(70)	118.5(8)	C(68)–C(69)–Pd(2)	72.7(4)
C(70)–C(69)–Pd(2)	71.5(5)	C(69)–C(70)–C(77)	122.7(8)
C(69)–C(70)–Pd(2)	70.6(5)	C(77)–C(70)–Pd(2)	123.6(5)

4. Conclusion

It is shown that it is very hard to get a stable Pd^0 complex ligated by the Trost P,P ligand **4** by addition of **4** to $Pd^0(dba)_2$. Indeed, the complex $Pd^0(dba)(\mathbf{4})$ gives rise to the formation of a stable Pd^{II} complex **5** after activation of the two N–H bonds of the ligand. This side reaction was found to be in competition with the reaction of $Pd^0(\mathbf{4})$ complex with (*E*)-PhCH=CH–CH(OAc)–Ph, even used at large concentration. The latter reaction gives the neutral complexes (η^2-PhCH=CH–CH(OAc)–Ph)$Pd^0(\mathbf{4})$ involved in a sluggish ionization step. Independent synthesis of the expected cationic P,P complex $[(\eta^3\text{-Ph–CH–CH–CH–Ph})Pd(\mathbf{4})]^+$ by addition of 2 equiv. of **4** to the precursor $[(\eta^3\text{-Ph–CH–CH–CH–Ph})Pd(\mu\text{-Cl})]_2$ leads to a complex mixture. Addition of 1 equiv. of **4** to $[(\eta^3\text{-Ph–CH–CH–CH–Ph})Pd(\mu\text{-Cl})]_2$ leads to a bis-cationic allylic Pd^{II} complex via a bis-P,O complexation: $\{[(\eta^3\text{-Ph–CH–CH–CH–Ph})Pd]_2(\mathbf{4})\}^{2+}$ ($\mathbf{13}^{2+}$). In Pd-catalyzed allylic alkylation of PhCH=CH–CH(OAc)–Ph, the enantioselectivity of the overall reaction is controlled by the regioselectivity of the nucleophilic attack onto the η^3-Ph–CH–CH–CH–Ph allylic ligand [1,2]. The dissymmetric P,O coordination in complex **13** seems of interest since this may induce a regioselectivity of the attack of the nucleophile and consequently may favour the enantioselectivity of catalytic reactions performed from (*E*)-PhCH=CH–CH(OAc)–Ph. Trost ligands are thus versatile ligands which may display P,P or P,O coordination.

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Appendix A. Supplementary material

CCDC 626050, 626051 contains the supplementary crystallographic data for **5** and $\mathbf{13}^{2+}$. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.039.

References

[1] B.M. Trost, D.J. Murphy, Organometallics 4 (1985) 1143.
[2] (a) P.R. Auburn, P.B. Mackenzie, B. Bosnich, J. Am. Chem. Soc. 107 (1985) 2033;
(b) T. Hayashi, Pure Appl. Chem. 60 (1988) 7;
(c) G. Consiglio, R. Waymouth, Chem. Rev. 89 (1989) 257;
(d) T. Hayashi, T. Yamamoto, Y. Ito, E. Nishioha, H. Miura, K. Yanagi, J. Am. Chem. Soc. 111 (1989) 6301;
(e) S.A. Godleski, in: B.M. Tost, I. Pflemming, M.F. Semmelhack (Eds.), Compr. Org. Synth., Vol. 4, Pergamon, Oxford, 1991;
(f) C.G. Frost, J. Howard, J.M.J. Williams, Tetrahedron Asymmtr. 3 (1992) 1089;
(g) M. Sawamura, Y. Ito, Chem. Rev. 92 (1992) 857;
(h) A. Pfaltz, Acc. Chem. Rev. 26 (1993) 339;
(i) P. Barbaro, P.S. Pregosin, R. Salzman, A. Albinati, R.W. Kunz, Organometallics 14 (1995) 5160;
(j) J. Herrmann, P.S. Pregosin, R. Salzman, A. Albinati, Organometallics 14 (1995) 3311;
(k) J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, 1996, p. 290;
(l) P.S. Pregosin, R. Salzman, Coord. Chem. Rev. 155 (1996) 36;
(m) B.M. Trost, Acc. Chem. Res. 29 (1996) 355;
(n) B.M. Trost, D.L. Van Vranken, Chem. Rev. 96 (1996) 395;
(o) A. Togni, U. Burckhardt, V. Gramlich, P.S. Pregosin, R. Salzman, J. Am. Chem. Soc. 118 (1996) 1031;
(p) N. Baltzer, L. Macko, S. Schaffner, M. Zehnder, Helv. Chim. Acta. 79 (1996) 803;
(q) U. Burckhardt, V. Gramlich, P. Hofmann, R. Nesper, P.S. Pregosin, R. Salzman, A. Togni, Organometallics 15 (1996) 3496;
(r) H. Steinhagen, S. Reggelin, G. Helmchen, Angew. Chem. Int. Ed. Engl. 36 (1997) 2108;
(s) P.S. Pregosin, R. Salzman, Organometallics 18 (1999) 1207;
(t) G. Helmchen, A. Pfaltz, Acc. Chem. Res. 33 (2000) 336;
(u) D.G. Watson, B.M. Trost, Chem. Rev. 103 (2003) 2921;
(v) C. Markert, A. Pfaltz, Angew. Chem. Int. Ed. 43 (2004) 2498;
(w) I.D.G. Watson, A.K.J. Yudin, J. Am. Chem. Soc. 127 (2005) 17516.
[3] C. Amatore, A.A. Bahsoun, A. Jutand, L. Mensah, G. Meyer, L. Ricard, Organometallics 24 (2005) 1569.
[4] For the use of the ligand 4 in Pd-catalyzed reactions, see: (a) Ref [2m];
(b) B.M. Trost, R.C. Bunt, Angew. Chem. Int. Ed. 35 (1996) 99;
(c) B.M. Trost, R.C. Bunt, R.C. Lemoine, T.L. Calkins, J. Am. Chem. Soc. 122 (2000) 5968;
(d) B. Dominguez, N.S. Hodnett, G.C. Lloyd-Jones, Angew. Chem. Int. Ed. 40 (2001) 4289.
[5] Y. Takahashi, Ts. Ito, Y. Ishii, J. Chem. Soc. Chem. Commun. (1970) 1065.
[6] W. Leung, S. Cosway, R.H.V. Jones, H. McCann, M. Wills, J. Chem. Soc. Perkins Trans. 1 (2001) 2288.
[7] T. Hayashi, A. Yamamoto, Y. Ito, E. Nishioha, H. Miura, K. Yanagi, J. Am. Chem. Soc. 111 (1989) 6301.
[8] For Pd^0(dba)(P,P) complexes see: (a) C. Amatore, G. Broeker, A. Jutand, F. Khalil, J. Am. Chem. Soc. 119 (1997) 5176;
(b) C. Amatore, A. Jutand, Coord. Chem. Rev. 178–180 (1998) 511.
[9] L. Mensah, PhD thesis, University Pierre et Marie Curie VI, Paris, October 5, 2005.
[10] (a) B.M. Trost, B. Breit, M.G. Organ, Tetrahedron Lett. 35 (1994) 5187;
(b) B.M. Trost, F.D. Toste, J. Am. Chem. Soc. 121 (1999) 4545.
[11] (a) E. Filali, G.C. Lloyd-Jones, unpublished work;
(b) G.C. Lloyd-Jones, personal communication, E-mail exchange on January 7, 2004.
[12] The phosphine oxide of ligand **4** was often detected at traces concentration in the ^{31}P NMR spectra at 28.79 ppm. Complex **5** was formed when the NMR tube was prepared in an atmosbag filled with Argon.
[13] For oxidative addition of amines with Pd(0) complexes, see: (a) T. Yamamoto, K. Sano, A. Yamamoto, Chem. Lett. (1982) 907;
(b) A.I. Siriwardana, M. Kamada, I. Nakamura, Y. Yamamoto, J. Org. Chem. 70 (2005) 5932.
[14] For the displacement of a phosphine ligand by an amine, see: A. Jutand, S. Negri, A. Principaud, Eur. J. Inorg. Chem. (2005) 631.

[15] For the use of conductivity measurement for the elucidation of the mechanism of Pd-catalyzed reactions, see: A. Jutand, Eur. J. Inorg. Chem. (2003) 2017.

[16] As an example, the conductivity of the complex $[(\eta^3\text{-Ph–C}_3\text{H}_3\text{–Ph})\text{Pd(dppb)}]^+\text{AcO}^-$ formed in the reaction of (E)-Ph–CH=CH–CH(Ph)–OAc (32 mM) with the Pd^0 complex generated from $\text{Pd}^0(\text{dba})_2$ (1 mM) and dppb (1 mM) in DMF increased from 4 to 60 μS cm^{-1} within 4 h 20 at 30 °C [3].

[17] For the formation of relatively stable $(\eta^2\text{-Ph–CH=CH–CH(Ph)–OAc})\text{Pd}^0\text{L}_2$ complexes see ref [3].

[18] I.J.S. Fairlamb, G.C. Lloyd-Jones, Chem. Commun. (2000) 2447.

[19] C. Amatore, S. Gamez, A. Jutand, J. Organomet. Chem. 624 (2001) 217.

[20] (a) C.P. Butts, J. Crosby, G.C. Lloyd-Jones, S.C. Stephen, Chem. Commun. (1999) 1707;
(b) G.C. Lloyd-Jones, Synlett (2001) 161.

[21] (a) M.A. Aramendia, F. Lafont, M. Moreno-Mañas, R. Pleixats, A. Roglans, J. Org. Chem. 64 (1999) 3592;
(b) M. Moreno-Mañas, R. Pleixats, J. Spengler, C. Cherin, B. Estrine, S. Bouquillon, F. Hénin, A. Pla-Quintina, A. Roglans, Eur. J. Org. Chem. (2003) 274.