# Reactions of ${}^{t}Bu_{2}P-PLi-P{}^{t}Bu_{2}$ with $[(Et_{3}P)_{2}MCl_{2}]$ (M = Ni, Pd, Pt). Synthesis and Properties of $[(1,2-\eta-{}^{t}Bu_{2}P=P-P{}^{t}Bu_{2})M(PEt_{3})Cl]$ (M=Ni, Pd).

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Dedicated to Professor Hansgeorg Schnöckel on the Occasion of his 65<sup>th</sup> Birthday

Abstract.  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2{}\cdot 2THF$  reacts with  $[cis-(Et_3P)_2MCl_2]$ (M = Ni, Pd) yielding  $[(1,2-\eta-{}^{t}Bu_2P=P-P{}^{t}Bu_2)Ni(PEt_3)Cl]$ and  $[(1,2-\eta-{}^{t}Bu_2P=P-P{}^{t}Bu_2)Pd(PEt_3)Cl]$ , respectively.  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2$  undergoes an oxidation process and the  ${}^{t}Bu_2P-P-P{}^{t}Bu_2$  ligand adopts in the products the structure of a side-on bonded 1,1-di-*tert*-butyl-2-(di-*tert*-butylphosphino)diphos-

# phenium cation with a short P–P bond. Surprisingly, the reaction of ${}^{t}Bu_{2}P-PLi-P{}^{t}Bu_{2}\cdot 2THF$ with [*cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>] does not yield [(1,2-\eta-{}^{t}Bu\_{2}P=P-P{}^{t}Bu\_{2})Pt(PEt\_{3})Cl].

Keywords: P ligands; nickel; palladium; platinum

#### **1** Introduction

The reactivity of lithium derivatives of phosphanes and silvlphosphanes towards metal chlorides of the nickel group has been the subject of thorough studies. It was established that  $LiP(SiMe_3)_2$  reacts with  $[(R_3P)_2NiCl_2]$  finally yielding the stable phosphido bridged dinuclear Ni<sup>I</sup> complexes  $[(R_3P)Ni\{\mu-P(SiMe_3)_2\}_2Ni(PR_3)](Ni-Ni)$  [1, 2] as well as diphosphene complexes and diphosphorus complexes of  $Ni^{0}$  as  $[(R_{3}P)_{2}Ni\{\eta^{2}-(PSiMe_{3})_{2}\}]$  and  $[\{(R_{3}P)_{2}Ni\}_{2}\{P_{2}\}][1,$ 3, 4]. Chelate complexes as  $[(dRpe)NiCl_2]$  (dRpe =  $R_2PCH_2CH_2PR_2$ ) react similarly [5, 6] but the products are more stable [6]. With a C5H5 group instead of Cl it was possible to isolate products with a trigonal surrounded Ni<sup>II</sup> atom [7]. The reaction of  $[(Me_3P)_2NiCl_2]$  with LiP<sup>t</sup>Bu<sub>2</sub> yields  $[(Me_3P)Ni(\mu-P^tBu_2)_2Ni(PMe_3)](Ni-Ni)$  [8]. PhP(SiMe<sub>3</sub>)<sub>2</sub> reacts with NiCl<sub>2</sub> in the presence of PPh<sub>3</sub> vielding cluster compounds [9]. Similar to the related Ni<sup>II</sup> compounds, [(R<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>] reacts with LiP(SiMe<sub>3</sub>)<sub>2</sub> yielding  $[(R_{3}P)Pt{\mu-P(SiMe_{3})_{2}}_{2}Pt(PR_{3})](Pt-Pt),$  $[(R_{3}P)_{2}Pt\{\eta^{2} (PSiMe_3)_{2}$  and  $[{(R_3P)_2Pt}_2(P_2)]$  [10]. Li(Ph)P-P(Ph)Lireacts with [*cis*-L<sub>2</sub>MCl<sub>2</sub>] (M = Pd, Pt and L =  $\frac{1}{2}$ dppe, PPh<sub>3</sub>) yielding the related diphosphene complexes  $[(\eta^2 -$ PhP=PPh)ML<sub>2</sub>] [11].

Continuing our studies on the chemistry of phosphinophosphinidenes as ligands in transition metal complexes [12, 13], we successfully exploited derivatives of lithiated diphosphanes as  $R_2P-P(SiMe_3)Li$  as precursors of  $R_2P-P$  ligands during the past two years. Such, we obtained [ $\mu$ -(1,2:2- $\eta$ -tBu<sub>2</sub>P=P){Zr(Cl)Cp<sub>2</sub>}], the zirconium complex containing both a side-on and a terminally bonded tBu<sub>2</sub>P-P group, and [( $\eta$ <sup>1</sup>-tBu<sub>2</sub>P-P){Zr(PPhMe<sub>2</sub>)Cp<sub>2</sub>}], the first complex in which this ligand is terminally bonded [14].

In a quite different manner  ${}^{t}Bu_{2}P-P(SiMe_{3})Li$  reacts with  $Cp_{2}TiCl_{2}$  yielding  $Ti^{III}$  complexes as  $[Cp_{2}TiCl]_{2}$ ,  $[Cp_{2}Ti(\mu-Cl)_{2}Li\cdot2THF]$  and  $[Cp_{2}TiCl(PMe_{3})]$ , where the phosphorus backbone undergoes dimerisation and rearrangement reactions under splitting of the P-P bond [15].

The splitting of the P–P bond and the formation of  $Ph_2P-P(Li)-PPh_2$  were also observed in the reaction of  $[(Et_3P)_2PtCl_2]$  with  $Ph_2P-P(SiMe_3)Li$  [16].

We have extended our investigations on the new precursors, and in this paper we describe reactions of  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2{}^{\cdot}2THF$  with  $[(Et_3P)_2MCl_2]$  (M = Ni, Pd, Pt). The reactivity of  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2$  towards transition metal compounds was investigated only recently. With  $[Cp_2TiCl_2]$  it forms  $({}^{t}Bu_2P)_2P-P(P{}^{t}Bu_2)_2$ , but it does not react with  $[Cp_2ZrCl_2]$  under ambient conditions [17]. However, we were able to link the  ${}^{t}Bu_2P-P{}^{t}Bu_2$  backbone to the Pt atom. The reactions of  $[Pt(PPh_3)_4]$  or  $[(Ph_3P)_2Pt(\eta^2-C_2H_4)]$  with  ${}^{t}Bu_2P-P{}^{-}P{}^{e}Bu_2$  yield similar  $[(1,2-\eta-{}^{t}Bu_2P{}^{-}P{}^{-}P{}^{t}Bu_2)Pt(PPh_3)Br]$ , formally a d<sup>8</sup> complex of Pt<sup>II</sup> [18].

#### 2 Results and Discussion

#### 2.1 Reactivity

Reactions of  $[(Et_3P)_2NiCl_2]$  and  $[(Et_3P)_2PdCl_2]$ , respectively, with  ${}^tBu_2P-PLi-P{}^tBu_2{}^2THF$  in THF in a molar ratio of

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Scheme 1

1 : 1 yield the Ni complexes (1a, 1b) and the Pd complexes (2a, 2b) in good yield as depicted in scheme 1.

[(Et<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>] reacts with <sup>t</sup>Bu<sub>2</sub>P-PLi-P<sup>t</sup>Bu<sub>2</sub>·2THF giving **1a** and **1b** in comparable amounts (**1a** : **1b** ~ 55 : 45). This process is accompanied by a minor side reaction: splitting of the P-P bond in the backbone of <sup>t</sup>Bu<sub>2</sub>P-P-P<sup>t</sup>Bu<sub>2</sub> which yields a small amount of the planar *iso*-tetraphosphane (<sup>t</sup>Bu<sub>2</sub>P)<sub>3</sub>P [19] together with a small amount of <sup>t</sup>Bu<sub>2</sub>P-PH-P<sup>t</sup>Bu<sub>2</sub>.

[(Et<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>] reacts with <sup>t</sup>Bu<sub>2</sub>P-PLi-P<sup>t</sup>Bu<sub>2</sub>·2THF giving **2a** almost exclusively (**2a** : **2b** ~ 95 : 5). Small amounts of (<sup>t</sup>Bu<sub>2</sub>P)<sub>3</sub>P and of <sup>t</sup>Bu<sub>2</sub>P-PH-P<sup>t</sup>Bu<sub>2</sub> were found in this case, too. After 3 weeks at ambient temperature some amounts of <sup>t</sup>Bu<sub>2</sub>P-P=PEt<sub>3</sub> [20] were found in the mother liquor together with a small amount of an unknown compound with four phosphorus atoms probably in a linear alignment (**2c**) according to a <sup>31</sup>P NMR study.

Quite unexpectedly,  $[cis-(Et_3P)_2PtCl_2]$  does not react with  ${}^tBu_2P-PLi-P{}^tBu_2\cdot 2THF$  under formation of  $[(1,2-\eta-{}^tBu_2P=P-P{}^tBu_2)Pt(PEt_3)Cl]$ . This is surprising because the first known complex of this type was  $[(1,2-\eta-{}^tBu_2P=P-P{}^tBu_2)Pt(PPh_3)Br]$  (**3a**) which proved to be fairly stable [18]. Additionally, similar phosphinophosphinidene complexes  $[(\eta^2-{}^tBu_2P=P)M(PR_3)_2]$  are most stable and were isolated only in the case of M = Pt.

The reaction of  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2{}^{\cdot}2THF$  with [*cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>] in THF (molar ratio 1 : 1) at ambient temperature yields pale yellow crystals the structure of which we were so far unable to resolve. A  ${}^{31}P$  NMR study of the mother liquor reveals the presence of PEt<sub>3</sub>,  ${}^{t}Bu_2P-PH-P{}^{t}Bu_2$ , [*trans*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>] and [*cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>].

The reaction of  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2{}\cdot 2THF$  with  $[(Ph_3P)_2PtCl_2]$  in THF in a molar ratio of 2 : 1 after 5 days at ambient temperature and 2 days at 50 °C yields colourless crystals in form of needles (structure not resolved). A new attempt to crystallize this compound led to its decomposition. A <sup>31</sup>P NMR study of the mother liquor reveals the presence of small amounts of unknown compounds together with 'Bu<sub>2</sub>P-PH-P'Bu<sub>2</sub> and PPh<sub>3</sub>.

#### 2.2 X-Ray Crystallographic Studies and Discussion

The structures of 1a and 2a were determined by X-ray diffraction methods [21, 22]. The crystal data and details of the data collection and refinement are given in table 1. These two compounds are isotypic. Fig. 1 shows the molecular structure with displacement ellipsoids for 1a and Fig. 2 for 2a.

**Table 1** Crystal and Data Collection Parameters for  $[(1,2-\eta^{+}Bu_2P=P-P^{+}Bu_2)Ni(PEt_3)Cl]$  (1a) and  $[(1,2-\eta^{-}Bu_2P=P-P^{+}Bu_2)-Pd(PEt_3)Cl]$  (2a)

|                                   | 1a  | 2a  |
|-----------------------------------|---|---|
| empirical formula                 | C22 H51 Cl Ni P4                          | C22 H51 Cl P4 Pd                          |
| formula weight                    | 533.67                                    | 581.36                                    |
| crystal system                    | monoclinic                                | monoclinic                                |
| space group                       | $P2_1/c$                                  | $P2_1/c$                                  |
| a /Å                              | 20.534(3)                                 | 20.5554(14)                               |
| b /Å                              | 9.5809(5)                                 | 9.6881(4)                                 |
| c /Å                              | 15.2712(12)                               | 15.3679(13)                               |
| β /deg                            | 104.010(12)                               | 104.305(9)                                |
| V /Å <sup>3</sup>                 | 2915.0(4)                                 | 2965.5(3)                                 |
| Z (calculated density)            | 4 (1.216 Mg/m <sup>3</sup> )              | $4 (1.302 \text{ Mg/m}^3)$                |
| cryst. size /mm <sup>3</sup>      | 0.35 x 0.3 x 0.06                         | 0.6 x 0.3 x 0.2                           |
| diffractometer                    | Stoe IPDS                                 | Stoe IPDS                                 |
| wavelength /Å                     | 0.71073 (Mo Kα)                           | 0.71073 (Mo Kα)                           |
| temperature /K                    | 180(2)                                    | 180(2)                                    |
| abs. coeff. $/mm^{-1}$            | 0.984                                     | 0.939                                     |
| $\theta$ range for data collect.  | 2.36-24.95 deg                            | 2.93-25.92 deg                            |
| reflections collected             | 11551                                     | 19281                                     |
| unique reflections                | $4894 [R_{int} = 0.0690]$                 | 5738 [ $\mathbf{R}_{int} = 0.0318$ ]      |
| Completeness to $\theta$          | $\theta = 24.95 \text{ deg}, 95.9 \%$     | $\theta = 25.92 \text{ deg}, 99.3 \%$     |
| Refinement method                 | Full-matrix least-                        | Full-matrix least-                        |
|                                   | squares on F <sup>2</sup>                 | squares on F <sup>2</sup>                 |
| Data/restraints/paramet.          | 4894 / 0 / 254                            | 5738 / 0 / 457                            |
| final R indices                   | R1 = 0.0389                               | R1 = 0.0199                               |
| $[I > 2\sigma(I)]$                | wR2 = 0.0917                              | wR2 = 0.0510                              |
| R indices (all data)              | R1 = 0.0557                               | R1 = 0.0242                               |
|                                   | wR2 = 0.0964                              | wR2 = 0.0521                              |
| Goodness-of-fit on F <sup>2</sup> | 0.914                                     | 1.010                                     |
| Largest diff. peak and            | $0.371, -0.336 \text{ e.}\text{\AA}^{-3}$ | $0.380, -0.590 \text{ e.}\text{\AA}^{-3}$ |





hole

The Ni atom in **1a** and the Pd atom in **2a** are in an almost planar environment defined by  $Et_3P1$ , Cl and the P2=P4 bond. The P2-P4 distances are short: 212.81(10) pm in 1a, 213.68(5) pm in 2a. These values are typical for the double P=P bond of diphosphenes upon  $\eta^2$ -coordination [23]. The P2-P3 distances of 223.46(12) pm for 1a and 222.60(5) pm for 2a are in the range of a single P-P bond [24]. The metal phosphorus bonds show characteristic trends: in 1a: Ni-P4 213.53(8) pm (very short), Ni-P1 221.70(9) pm and Ni-P2 231.98(8) pm (very long). Similar in 2a: Pd-P4 222.86(4) pm, Pd-P1 232.32(5) pm and Pd-P2 244.09(5) pm. The same trend was observed for 3a (scheme 3) [18]; Pt-P4 223.1(1) pm, Pt-P1 229.1(1) pm, Pt-P2 240.5(1) pm. Fig. 1 and 2 clearly show that the geometry around P4 in 1a and 2a deviates significantly from planarity. Torsion angles C7-P2-P4-C11 are 133.81° (1a) and 135.37° (2a). The deviation from planarity of a "genuine" diphosphene upon  $\eta^2$ -coordination to a d<sup>10</sup> ML<sub>2</sub> metal centre is much less significant



Fig. 1 Displacement ellipsoid drawing (50 % probability) of  $[(1,2-\eta-^tBu_2P=P-P^tBu)_2]$ Ni(PEt<sub>3</sub>)Cl] (1a) with selected bond lengths/pm and angles/deg:

Ni-P1 221.70(9), Ni-P2 231.98(8), Ni-P4 213.53(8), Ni-Cl 220.48(8), P2-P4 212.81(10), P2-P3 223.46(12), P1-Ni-P4 111.39(3), P1-Ni-Cl 89.79(3), P2-Ni-P4 56.89(3), P2-Ni-Cl 101.87(3), P3-P2-P4 107.46(4).



Fig. 2 Displacement ellipsoid drawing (50 % probability) of  $[(1,2-\eta-{}^tBu_2P=P-P{}^tBu_2)Pd(PEt_3)Cl]$  (2a) with selected bond lengths/pm and angles/deg:

Pd-P1 232.32(5), Pd-P2 244.09(5), Pd-P4 222.86(4), Pd-Cl 238.58(4), P2-P4 213.68(5), P2-P3 222.60(5), P1-Pd-P4 112.784(15), P1-Pd-Cl 87.239(16), P2-Pd-P4 54.235(13), P2-Pd-Cl 105.599(15), P3-P2-P4 106.96(2).

[11, 23]. In  $[(\eta^{2-t}BuP1=P2SiMe_3)Pt(PPh_3)_2]$  the torsion angle  $(CH_3)_3$ C-P1-P2-Si is of 151.17° [23]. The planar alignment around the metal centre in 1a and 2a may indicate that the  $(Et_3P)MCl$  groups in 1a and 2a exhibit the properties of a d<sup>10</sup> ML<sub>2</sub> metal centre [25] and that this ligand can be viewed as an  $\eta^2$  bonded 1,1-di-*tert*-butyl-2-(di*tert*-butylphosphino)diphosphenium cation, similar to a planar phosphanylphosphenium ion [26]. Thus, this cation may be an 2e oxidation product of the parent



Scheme 3

<sup>t</sup>Bu<sub>2</sub>P-PLi-P<sup>t</sup>Bu<sub>2</sub>·2THF, *cf.* (a) in scheme 2. The geometry of the <sup>t</sup>Bu<sub>2</sub>P-P-P<sup>t</sup>Bu<sub>2</sub> moiety in **1a** and **2a** can be explained according to Lewis structure (b) in scheme 2. **1a**, **2a** and **3a** can be seen as zwitterionic compounds with a negative charge located on the metal. The shortening of the P4-Pt bond vs. P1-Pt in **1a**, **2a** and **3a** may be due to electrostatic attraction.

The NMR studies upon 1a, 2a and 3a in solutions are fully consistent with the X-ray structural data. The <sup>31</sup>P NMR data of **3a** [18], especially the values of <sup>1</sup>J(Pt-P), provide some insight into the electronic properties of the bonding in **3a**. The most striking phenomenon is the very small <sup>1</sup>J(Pt-P2) of 95 Hz vs. <sup>1</sup>J(Pt-P4) of 2740 Hz. This is not consistent with the Lewis structure of 3a (Scheme 3a). In the case of a P=P double bond of a "genuine" diphosphene coordinated side-on to  $Pt(0)L_2$  the <sup>1</sup>J(Pt-P) value should be in the range of 200-300 Hz [11, 23]. According to the interpretation of <sup>1</sup>J(Pt-P) constants in terms of Fermi contact it is evident that the Pt-P4 bond in 3a has a significant scharacter. It has the character of a Pt bond to a "normal" tertiary phosphine. Thus the bonding in 3a may be best described as a mixture of two resonance structures as shown in scheme 3.

The resonance form (b) clearly explains  ${}^{1}J(Pt-P4)$  of **3a**. The planar geometry of P1-Br-P2-P4-Pt is obvious in terms of the planarity of low spin d<sup>8</sup> M<sup>II</sup> complexes (scheme 3b).

Crystal structures and NMR data of some complexes with the phosphanyl phosphenium ion moieties R'(X)P1 =P2R (X = H, Cl, alkyl or aryl) coordinated in an  $\eta^2$ -fashion to metal (M) centres are known [27, 28, 29, 30]. The alignments of these moieties, especially the short P1-P2 distances of 210 ÷ 214.5 pm and the short P1-M distance compared to P2-M show similar features as 'Bu<sub>2</sub>P=P-P'Bu<sub>2</sub> in **1a**, **2a** and **3a**. The <sup>31</sup>P NMR data indicate large absolute values of the couplings constants <sup>1</sup>J(P1-P2) of  $-536 \div -550$  Hz and significant high field shifts of P2 ( $\delta_{P2} \sim -150 \div$ -200 ppm), which are similar to the NMR data of **1a**, **2a** and **3a**, too. For [{ $\eta^2$ -P'Bu=P'Bu(Cl)}WCp(CO)\_2] no data upon <sup>1</sup>J(P-W) were reported however [28].

Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as supplementary publications CCDC 225541 (1a) and CCDC 225542 (2a). Copies of the data can be obtained free of charge on application to the Director CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44) 1223-336-033; e-mail for inquiring: fileserv@ccdc.cam.ac.uk, e-mail for deposition: deposit@ccdc.cam.ac.uk

All manipulations were performed in flame-dried Schlenk type glassware on a vacuum line. THF and toluene were dried over Na/benzophenone and distilled under nitrogen. Pentane was dried over Na/benzophenone/diglyme and distilled under nitrogen. <sup>31</sup>P NMR spectra were recorded on Bruker AC250 and on Bruker AMX300 spectrometers (external standard 85 % H<sub>3</sub>PO<sub>4</sub>) at ambient temperature. The <sup>1</sup>H NMR signals for **1a** and **2a** were established from <sup>31</sup>P-<sup>1</sup>H-correlation spectra. Chemical shifts and coupling constants of **1b** (<sup>31</sup>P{<sup>1</sup>H}) were optimised using Bruker software [31]. <sup>1</sup>Bu<sub>2</sub>P-P(SiMe<sub>3</sub>)-P<sup>1</sup>Bu<sub>2</sub> was prepared in a one-pot reaction [32] and lithiated according to literature procedures [33].

# Synthesis of $[(1,2-\eta^{-t}Bu_2P=P-P^{t}Bu_2)Ni(PEt_3)Cl]$ (1a and 1b).

A solution of  ${}^{1}Bu_{2}P-PLi-P{}^{1}Bu_{2}\cdot 2THF$  (0.112 g, 0.24 mmol) in THF (2 mL) was added at room temperature to a solution of [*cis*-(Et<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>] (0.085 g, 0.23 mmol) in THF (3 mL). The mixture turned immediately deep red. The mixture was stirred for 0.5 h, then evacuated at  $2 \cdot 10^{-3}$  Torr for 1 h. The residue was dissolved in THF (8 mL), filtered and investigated by  ${}^{31}P{}^{1}H{}$  NMR. 1a, 1b,  ${}^{1}Bu_{2}P-PH-P{}^{1}Bu_{2}$  and  $({}^{1}Bu_{2}P)_{3}P$  were found. The volume was reduced to 1 mL and the solution stored for 2 d at -20 °C. A mixture of two sorts of crystals deposited (~0.085 g, 67 %), brown needles (1b) and deep brown plates (1a).

Elemental analysis 1a + 1b,  $C_{22}H_{51}ClP_4Ni$ : C 49.9 (calc. 49.51); H 9.88 (9.63) %.

**1b:** <sup>1</sup>**H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 1.14$  (dt, <sup>3</sup>J<sub>H,P1</sub> = 14.5 Hz, <sup>2</sup>J<sub>H,H</sub> = 7.5 Hz, H<sub>3</sub>CCH<sub>2</sub>P1); 1.646 or 1.648 (quintet, <sup>2</sup>J<sub>H,H</sub> = 7.6 Hz, <sup>2</sup>J<sub>H,P1</sub> ~ 7.6 Hz, H<sub>3</sub>CCH<sub>2</sub>P1); 1.41 (d, <sup>3</sup>J<sub>H,P3</sub> = 10.8 Hz,H<sub>3</sub>CCP3 and probably H<sub>3</sub>CCP4). <sup>13</sup>C{<sup>1</sup>H} **NMR** (62.9 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta = 36-34$  (m, C(CH<sub>3</sub>)<sub>3</sub>); 33.5-32.0 (m, C(CH<sub>3</sub>)<sub>3</sub>); 17.13 (d, <sup>1</sup>J<sub>C,P</sub> = 19.6 Hz, PCH<sub>2</sub>CH<sub>3</sub>); 9.35 (s, PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} **NMR** (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, higher order spectrum)  $\delta = 7.1$  (d, P1); -101.8 (dd, P2); 34.1 (m, P3); 31.3 (m, P4). <sup>2</sup>J<sub>P1,P2</sub> = 2.36 Hz, <sup>3</sup>J<sub>P1,P3</sub> = 2.18 Hz, <sup>2</sup>J<sub>P1,P4</sub> = 194.3 Hz, <sup>1</sup>J<sub>P2,P4</sub> = -518.0 Hz, <sup>2</sup>J<sub>P3,P4</sub> = 27.8 Hz;

 ${}^{t}Bu_{2}P1-P2H-P1{}^{t}Bu_{2} \,\, {}^{31}P\{{}^{1}H\}$  NMR (101.3 MHz, THF, C<sub>6</sub>D<sub>6</sub>, 25 °C,)  $\delta=27.0$  (d,  ${}^{1}J_{P1,P2}=-227.8$  Hz, P1); -135.2 (t, P2) [33].

('Bu<sub>2</sub>P1)<sub>3</sub>P2 <sup>31</sup>P{<sup>1</sup>H} NMR (101.3 MHz, THF, C<sub>6</sub>D<sub>6</sub>, 25 °C,)  $\delta = 87.3$  (d, <sup>1</sup>J<sub>P1,P2</sub> = -649.8 Hz, P1); -143.5 (quartet, P2) [19]. The resonances of P2 were very weak.

# Synthesis of $[(1,2-\eta^{-t}Bu_2P=P-P^{t}Bu_2)Pd(PEt_3)Cl]$ (2a).

A solution of  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2{}^{\cdot}2THF$  (0.164 g, 0.37 mmol) in THF (3 mL) was added in 5 min at room temperature to a solution of [*cis*-(Et<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>] (0.127 g, 0.36 mmol) in THF (7 mL). The yellow solution turned deep brown. After stirring for 0.5 h the volume was reduced to 2 mL and investigated by  ${}^{31}P{}^{1}H{}$  NMR. **2a**, **2b**,  ${}^{t}Bu_2P-PH-P{}^{t}Bu_2$  (small signals) and Et<sub>3</sub>P were found. Then the

solution was evaporated to 1 mL and stored for 2 d at 4 °C. Yellow crystals deposited (0.121 g,  $\sim 60 \%$ ) (2a).

Elemental analysis (**2a** and small amount of **2b**),  $C_{22}H_{51}CIP_4Pd$ : C 46.0 (calc. 45.45); H 9.02 (8.88) %.

**2a:** <sup>1</sup>**H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, atom labelling see Fig. 2):  $\delta = 0.95$  (dt,  ${}^{3}J_{P1,H} = 15.8$  Hz,  ${}^{2}J_{H,H} = 7.6$  Hz,  $H_{3}CCH_{2}P1$ ); 1.76-1.72 (m,  ${}^{2}J = 7.6$  Hz,  $H_{3}CCH_{2}P1$ ); 1.79 (d,  ${}^{3}J_{H,P3} = 11.8$  Hz,  $H_{3}CCP3$ ); 1.48 ppm (d,  ${}^{3}J_{H,P3} = 10.6$  Hz,  $H_{3}CCP3$ ); 1.22 (dd,  ${}^{3}J_{H,P4} = 15.1$  Hz,  ${}^{4}J_{H,P2} = 1.5$  Hz,  $H_{3}CCP4$ ); 1.54 (dd,  ${}^{3}J_{H,P4} = 16.4$  Hz,  ${}^{4}J_{H,P2} = 1.2$  Hz,  $H_{3}CCP4$ ).  ${}^{13}C1^{1}H$ } **NMR** (62.9 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 33.5 \cdot 32.5$  (m, C(CH<sub>3</sub>)<sub>3</sub>); 32.5 \cdot 31.5 (m, C(CH<sub>3</sub>)<sub>3</sub>); 18.28 (d,  ${}^{1}J_{CP} = 20.0$  Hz, PCH<sub>2</sub>CH<sub>3</sub>); 9.66 (s, PCH<sub>2</sub>CH<sub>3</sub>).  ${}^{3}P{H}$  **H NMR** (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 22.6$  (dd, P1); -103.4(ddd, P2); 26.2 (dd, P3); 110.3 (ddd, P4);  ${}^{2}J_{P1,P2} = 108.5$  Hz,  ${}^{3}J_{P1,P3} \sim 0$  Hz,  ${}^{2}J_{P1,P4} = 21.7$  Hz,  ${}^{1}J_{P2,P3} = -248.0$  Hz,  ${}^{1}J_{P2,P4} = -550.8$  Hz,  ${}^{2}J_{P3,P4} = 33.9$  Hz.

**2b:** <sup>1</sup>**H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, the resonances are partially overlapped by 2a):  $\delta = 1.04 - 1.15$  (m,H<sub>3</sub>CCH<sub>2</sub>P1); 1.73-1.81 (m, H<sub>3</sub>CCH<sub>2</sub>P1); 1.59 (d, <sup>3</sup>J<sub>H,P3</sub> = 11.8 Hz, H<sub>3</sub>CCP3, overlapped); 1.42 (d, <sup>3</sup>J<sub>H,P4</sub> 15.0 Hz, H<sub>3</sub>CCP4, overlapped). <sup>13</sup>C{<sup>1</sup>H} **NMR** (62.9 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 17.73$  (d, <sup>1</sup>J<sub>C-P</sub> = 17.4 Hz, PCH<sub>2</sub>CH<sub>3</sub>); 8.96 (s,  $\delta$ PCH<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} **NMR** (121.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta = 10.7$  (dd, P1); -74.5 (ddd, P2); 28.8 (dd, P3); 79.2 (ddd, P4); <sup>2</sup>J<sub>P1,P2</sub> = 15.3 Hz, <sup>3</sup>J<sub>P1,P3</sub> ~ 0, <sup>2</sup>J<sub>P1,P4</sub> = 270.0 Hz, <sup>1</sup>J<sub>P2,P3</sub> = -241.0 Hz, <sup>1</sup>J<sub>P2,P4</sub> = -534.0 Hz, <sup>2</sup>J<sub>P3,P4</sub> = 34.9 Hz.

The mother liquor was stored for 3 weeks at ambient temperature. Then, **2c**,  $({}^{t}Bu_{2}P)_{3}P$  and  ${}^{t}Bu_{2}P-P=PEt_{3}$  were found additionally.

**2c:** <sup>31</sup>**P**{<sup>1</sup>**H**} **NMR** (101.3 MHz, THF, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 11.2 (ddd, P1); -34.2 ppm (ddd, P2); -51.5 (ddd, P3); -83.5 (ddd, P4); J<sub>P1,P2</sub> = 4.4 Hz, J<sub>P1,P3</sub> = -403.3 Hz, J<sub>P1,P4</sub> = 4.4 Hz, J<sub>P2,P3</sub> = 51.6 Hz, J<sub>P2,P4</sub> = -298.6 Hz, J<sub>P3,P4</sub> = -285.6 Hz.

**'Bu<sub>2</sub>P3-P2=P1Et<sub>3</sub>:** <sup>31</sup>P{<sup>1</sup>H} **NMR** (101.3 MHz, THF, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 39.0 (dd, P1); -215.8 (dd, P2); 27.0 (dd, P3);  ${}^{1}J_{P1,P2} = -531.1$  Hz,  ${}^{2}J_{P1,P3} = 88.3$  Hz,  ${}^{1}J_{P2,P3} = -243.1$  Hz [20].

# Reaction of $[cis-(Et_3P)_2PtCl_2]$ with ${}^tBu_2P-PLi-P{}^tBu_2{}^2THF.$

A solution of  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2{}\cdot 2THF$  (0.070 g, 0.15 mmol) in THF (4 mL) was added at room temperature in 20 min to a solution of [*cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>] (0.066 g, 0.13 mmol) in THF (10 mL). The solution turned slowly yellow. The mixture was stirred for 5 h and then evaporated at 0.002 Torr, dissolved in THF (8 mL), filtered, concentrated to 2 mL and stored for 2 d at 4 °C. Small yellow crystals deposited. The mother liquor was investigated by  ${}^{31}P{}^{1}H{}$  NMR (101.3 MHz, THF, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta = 13.4$  (s,  ${}^{1}J_{P,Pt} = 2428 \text{ Hz}$ , [*trans*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>]); 10.2 (s,  ${}^{1}J_{P,Pt} = 3473 \text{ Hz}$  [*cis*-(Et<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>]); -19.8 (s, Et<sub>3</sub>P);  ${}^{1}Bu_2P-PH-P{}^{1}Bu_2$  [19].

# Reaction of $[(Ph_3P)_2PtCl_2]$ with ${}^tBu_2P - PLi - P{}^tBu_2{}\cdot 2THF$ .

A solution of  ${}^{t}Bu_2P-PLi-P{}^{t}Bu_2{}^{\cdot}2THF$  (0.131 g, 0.29 mmol) in THF (3 mL) was added at room temperature in 6 h to a dispersion of [(Ph\_3P)\_2PtCl\_2] (0.088 g, 0.12 mmol) in THF (17 mL). The mixture turned very slowly orange. The mixture was stirred for 5 d at room temp. and 2 d at 50 °C. Then the solution was evaporated at 0.002 Torr to dryness, dissolved in THF (5 mL), filtered, evaporated to 2 mL, investigated with  ${}^{31}P{}^{1}H{}$  NMR (101.3 MHz, THF, C<sub>6</sub>D<sub>6</sub>, 25 °C). Only  ${}^{t}Bu_2P-PH-P{}^{t}Bu_2$  and a small amount of Ph<sub>3</sub>P were found. Orange crystals (needles) deposited by means of diffusion of pentane into a THF solution. The quality of these crystals did not allow for a X-ray structure analysis. The solid deposit was dissolved in THF and again crystallized by means of diffusion of

pentane into a THF solution. The deposited colourless solid was not crystalline.

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