A PCN Ligand System. Exclusive C−C Activation with Rhodium(I) and C−H Activation with Platinum(II)

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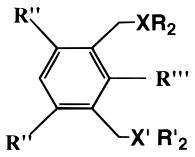
Reaction of the new aromatic aminophosphine ligand 1-((diethylamino)methyl)-3-((di-*tert*-butylphosphino)methyl)-2,4,6-trimethylbenzene (**4**) with $[Rh(COE)_2Cl]_2$ (COE = cyclooctene) or with $[Rh(ethylene)_2Cl]_2$ at room temperature results in selective carbon−carbon bond activation, yielding the complex $ClRh(CH_3)[C_6H(CH_3)_2(CH_2N(C_2H_5)_2)(CH_2P(t\text{-}Bu)_2)]$ (**5**). No competing C−H activation was observed during the course of the reaction. When **4** was reacted with $(COD)PtCl_2$ (COD = cyclooctadiene), selective C−H activation of the methyl group situated between the phosphine and amine groups took place, with concomitant intramolecular H transfer to the amine ligand, resulting in the zwitterionic Pt(II) complex $Cl_2PtCH_2(C_6H(CH_3)_2(CH_2NH(C_2H_5)_2)(CH_2P(t\text{-}Bu)_2)$ (**11**).

Introduction

Late-transition-metal complexes containing a rigid T-shaped X−C−X (X = N, P) ligand frame are of substantial interest in organometallic chemistry.[1−8] van Koten and co-workers have extensively studied complexes of the NCN ligand frame[1] (A1). Such complexes with hard chelating N donors exhibit unusual stoichiometric and catalytic properties. It was also shown that the amine groups are not always spectator ligands and can participate in metal-centered reactions.[1g]

On the other hand, complexes containing the softer PCP type ligands (A2) exhibit high chelate stability. PCP-ligand-based complexes were utilized in studies of polyhydride and dihydrogen complexes,[2] complexes of molecular nitrogen and other small molecules,[3] carbene species,[4] carbon−carbon bond cleavage,[5] methylene transfer reactions,[6] and various catalytic transformations.[7] Our recent studies have shown that Rh(I) and Ir(I) are capable of selective insertion at room temperature into a strong aryl-CH_3 C−C bond situated between the two phosphine "arms" and that this insertion is *thermodynamically* and *kinetically preferred* over the competing C−H activation process[8] (Scheme 1).



A

R,R'=alkyl, aryl; R''=H,CH_3; R'''= H, CH_3, C_2H_5 (1) X=X'=N (NCN); (2) X=X'=P (PCP).; (3) X=P, X'=N (PCN)

It is conceivable that a mixed PCN type ligand (A3) could benefit from advantages of both the NCN and PCP ligand systems. The influence of an N donor in a PCN ligand vs a P donor in a PCP ligand on C−H and C−C activation processes was our primary subject of interest. The expected more labile coordination of the amine "arm" in comparison to the phosphine[9] could provide the system with additional reactivity patterns. Here we report the synthesis of a new phosphinoamine PCN-type ligand and the results of our studies on its reactivity with Rh and Pt precursors.

Results and Discussion

Ligand Synthesis. The new PCN-type ligand **4** was synthesized from bis(dibromomethyl)mesitylene, which was obtained by bromomethylation of mesitylene, according to a literature procedure.[10] Reaction of the resulting dibromide[11] with 1 equiv of di-*tert*-butylphosphine yields a mixture of mono- and diphosphonium

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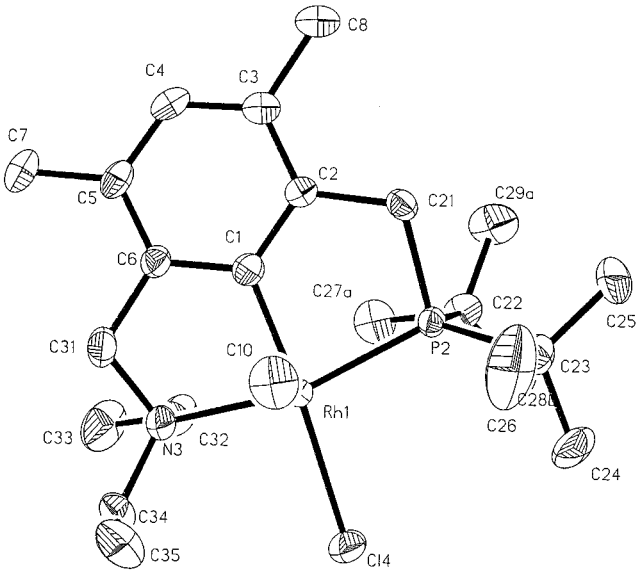


Figure 1. Perspective view of a molecule of **5**. Hydrogen atoms are omitted for clarity.

Scheme 1

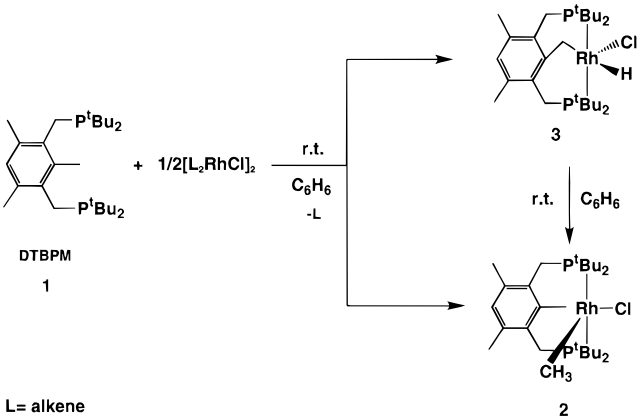


Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 5

Rh(1)−C(1)	1.970(4)	Rh(1)−P(2)	2.2307(11)
Rh(1)−C(10)	2.044(4)	Rh(1)−Cl(4)	2.4576(10)
Rh(1)−N(3)	2.186(3)		
C(1)−Rh(1)−C(10)	80.9(2)	N(3)−Rh(1)−P(2)	160.16(10)
C(1)−Rh(1)−N(3)	81.41(14)	C(1)−Rh(1)−Cl(4)	170.04(11)
C(1)−Rh(1)−P(2)	83.52(11)	C(10)−Rh(1)−Cl(4)	107.62(14)
C(10)−Rh(1)−N(3)	96.2(2)	N(3)−Rh(1)−Cl(4)	92.32(9)
C(10)−Rh(1)−P(2)	94.07(14)	P(2)−Rh(1)−Cl(4)	100.69(4)

salts, which was treated with a 10-fold excess of diethylamine (Scheme 2). Separation of the resulting **4** and the diphosphine **1** was achieved by chromatography on a silica column.

C−C Bond Activation by Rhodium. When a benzene solution of **4** (2 equiv) was added to $[Rh(COE)_2Cl]_2$ (COE = cyclooctene; 1 equiv), quantitative formation of the C−C activation product **5** was observed after 5 h at room temperature or after 15 min at 45 °C (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of **5** shows a doublet at 78.31 ppm (J_{RhP} = 160.8 Hz). In the ^1H NMR spectrum the signal due to CH_3Rh appears at 1.58 ppm as a doublet of doublets (J_{RhH} = 2.9 Hz; J_{PH} = 1.2 Hz). In the $^{13}C\{^1H\}$ NMR spectrum the CH_3Rh group gives rise to a doublet of doublets centered at −2.24 ppm (J_{RhC} = 34.4 Hz; J_{PC} = 8.3 Hz) and the ipso carbon atom exhibits a doublet of doublets at 170.04 ppm (J_{RhC} = 32.0 Hz; J_{PC} = 4.2 Hz). The fact that the two methyl groups of the diethylamine unit ($N(CH_2CH_3)_2$) have different chemical shifts indicates that the amine arm is coordinated to the metal. The chemical shifts of the methyl group bound to the metal center in both ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **5** are very close to those of the Rh-Me group in the C−C activated rhodium complex **2**.[8]

Orange prismatic crystals of **5** suitable for a single-crystal X-ray analysis were obtained by recrystallization from pentane. The rhodium atom is located in the center of a distorted square pyramid with the methyl group occupying the position *trans* to the empty coordination site (Figure 1), the whole structure being similar to that of **2**. The rhodium−methyl carbon bond length of 2.044(4) Å is significantly shorter than that observed in **2** (2.17(2) Å)[8] as well as that of the PMe_2 analog (2.114 Å).[5b] Also, the Rh−Cl bond length (2.4576(10) Å) is very close to that in **2** (2.470(4) Å). The shorter N−Rh bond as compared with P−Rh forces the rhodium atom to tilt toward the amine ligand. This results in asymmetry of the PCN system in **5**, with some interesting consequences (vide infra). Selected bond lengths and bond angles are given in Table 1.

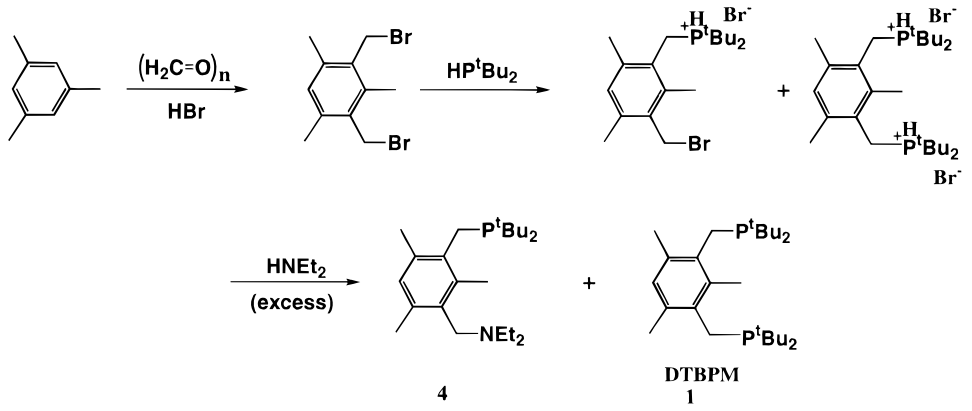
Complex **5** was also obtained by reaction of **4** with the ethylene complex $[Rh(C_2H_4)_2Cl]_2$, the reaction being complete within a few minutes at room temperature. A similar considerable rate increase upon decrease in the bulk of the coordinated alkene was observed in reactions of **1**.[8] This phenomenon is due to the easier substitution of the smaller alkene ligand by the associative mechanism expected for 16e square-planar rhodium(I) complexes.

Remarkably, whereas reaction of the ligand **1** with $[Rh(C_2H_4)_2Cl]_2$ resulted in formation of both the C−C- and C−H-activated complexes **2** and **3**, respectively, (Scheme 2), only complex **5** was observed immediately after mixing of **4** with $[Rh(C_2H_4)_2Cl]_2$ at room temperature. Similarly, no complex resulting from C−H activation was observed upon monitoring the reaction at −50 °C by $^{31}P\{^1H\}$ NMR. Although complex **3** undergoes facile C−H reductive elimination followed by C−C oxidative addition to yield complex **2**, it is long-lived enough in solution to allow its unambiguous characterization.

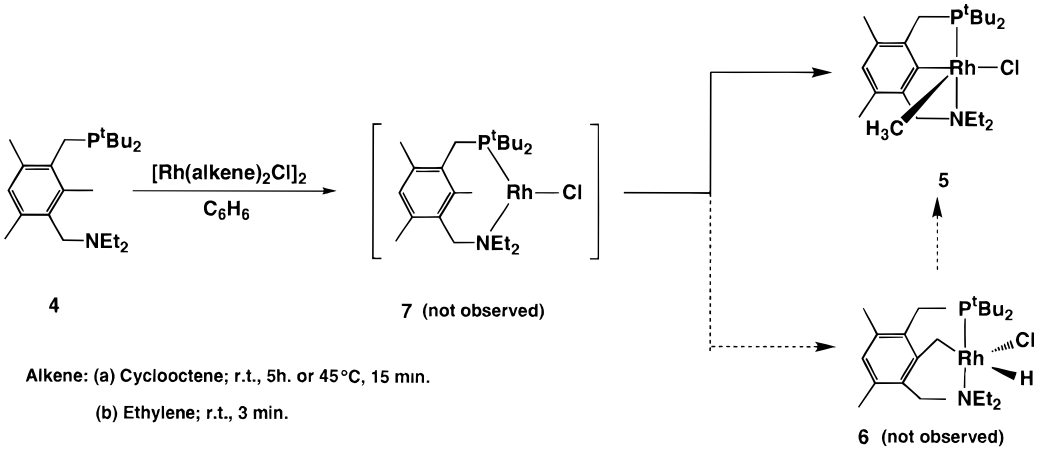
The fact that the C−H activation product **6** was not observed in the case of the PCN ligand **4** could be the result of a significantly lower activation barrier of the C−C vs C−H oxidative addition or, alternatively, a consequence of very rapid C−H reductive elimination in **6** that makes its detection impossible.

We have previously demonstrated that carbon−carbon activation by rhodium in a PCP ligand system proceeds via an intermediate in which both phosphine groups are coordinated to the metal, bringing the metal center into the proximity of the C−C bond to be cleaved (Scheme 1).[8] In the case of the PCN ligand, precoordination of both the phosphine and the amine groups in **4** seems to be required as well, giving the proposed intermediate **7**. This intermediate differs from the analogous PCP-based one by a nonsymmetrical positioning of the metal center and a shorter distance between Rh and the ipso carbon. Also, substitution of $-P^tBu_2$ (in the PCP ligand) for $-NEt_2$ (in the PCN ligand) results in a sterically less crowded metal center

Scheme 2



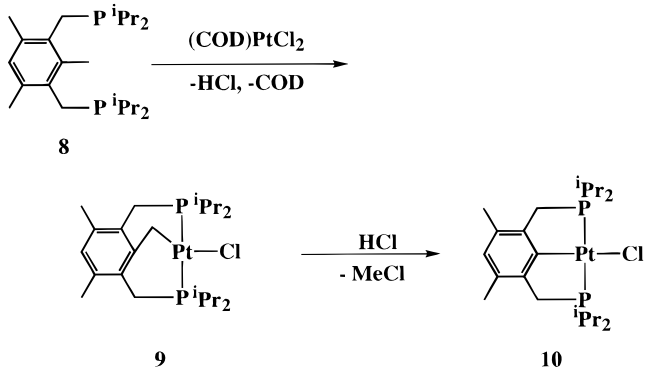
Scheme 3



in the intermediate **7** (e.g., compare cone angles: 160° for $EtP(^tBu)_2$[12a] vs 150° for NEt_3[12b]). These factors play an important role in bringing the Rh center into closer proximity with the Ar−Me bond to be cleaved, lowering the activation barrier of the C−C vs the C−H activation. The electronic influence of exchanging the soft phosphine ligand with a hard amine may also influence the reactivity of the metal center in the C−C vs C−H oxidative addition.

However, the possibility of a fast C−H reductive elimination in complex **6** cannot be discounted. This could result in a very short lifetime for the C−H-activated complex on the NMR time scale, and **6** would not be observed. A likely reason for such a fast C−H reductive elimination (in comparison to the PCP system) may be a rapid, reversible on/off dissociation of the amine. It was shown that rapid coordination/dissociation of an amine ligand to a Rh center occurs even at low temperatures,[13] and a number of chemical processes were explained by this phenomenon.[13,14] Such dissociation of the amine ligand in our case would lower the electron density on the Rh center and promote the C−H reductive-elimination process.[15]

Scheme 4



In any case, the PCN system seems to be *optimal* for carbon−carbon activation with Rh(I), resulting in *exclusive* C−C *activation*.

C−H Bond Activation by Platinum. As recently communicated,[5d] the Pt(II) complex **9**, obtained from the reaction of **8** with $Pt(COD)Cl_2$, reacts with an acid, giving upon heating the C−C activation product **10** with elimination of methyl chloride. A plausible mechanism for this transformation involves the formation of a $HPt^{IV}X$ intermediate, followed by C−H reductive elimination and metal insertion into the carbon−carbon bond (Scheme 4).

Interestingly, when **4** was reacted with $Pt(COD)Cl_2$ in THF at 130 °C for 2 days, quantitative formation of

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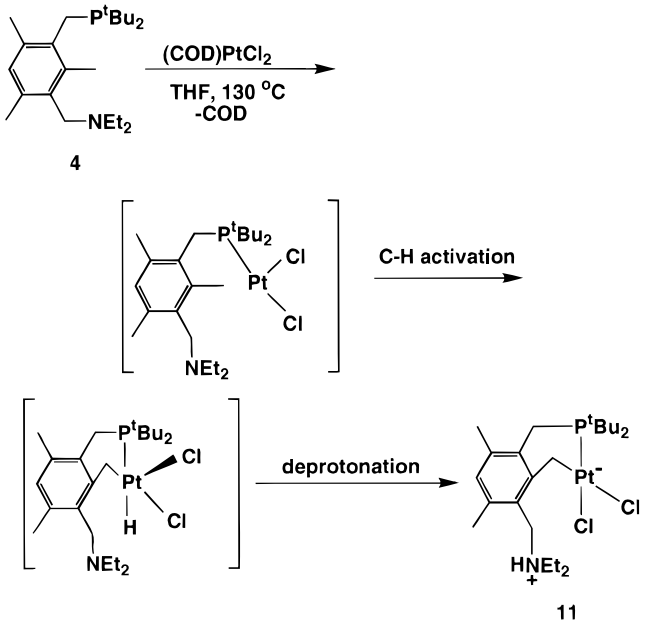
Scheme 5



11 was observed (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum of **11** exhibits a single resonance at 84.23 ppm with $^{195}Pt-P$ satellites with $J = 5119.6$ Hz. The ammonium proton appears in the ^1H NMR spectrum as a broad singlet at 10.02 ppm.

Recrystallization of **11** from hot THF resulted in colorless prisms, which were subjected to a single-crystal X-ray analysis. Complex **11** exhibits a square-planar structure with a practically symmetrical arrangement of the four ligands around the Pt atom (Figure 2). The Pt(1)−Cl(4) bond distance of 2.406(6) Å is slightly longer than that of Pt(1)−Cl(3) (2.380(6) Å), due to the stronger *trans* influence of the carbon ligand vs that of phosphorus. The NH···Cl(3) distance of 2.409 Å indicates the presence of quite a strong intramolecular hydrogen bond for a metal-bound halide ligand.[16] Selected bond lengths and bond angles are given in Table 2.

It is noteworthy that no carbon−carbon bond activation in **11** occurred even after 2 days of heating at 160 °C.

As reported, C−H activation can take place in similar systems having only one coordinated phosphine.[17] Also, proton transfer from a Pt center to a noncoordinated amine ligand has recently been reported.[14b,18] On the basis of these considerations we believe that the probable mechanism for the formation of **11** involves the precoordination of only the phosphine group to the platinum center. The formed intermediate undergoes reversible C−H bond activation, whereas the noncoordinated amine group drives the overall reaction toward **11** by deprotonation of the Pt(IV) center.[19]

Significantly, only the methyl group located between the two ligand arms undergoes C−H activation; the *other two aryl−methyl groups remain unaffected*. This fact demonstrates an important role of the amine, as an internal Lewis base, in the selective C−H activation of a specific methyl group.

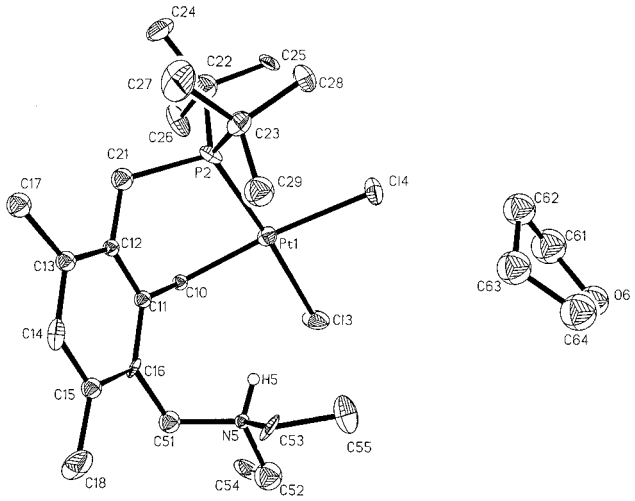


Figure 2. Perspective view of a molecule of **11**. Hydrogen atoms (except N*H*) are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 11

Pt(1)−C(10)	2.08(2)	Pt(1)−Cl(3)	2.380(6)
Pt(1)−P(2)	2.208(6)	Pt(1)−Cl(4)	2.408(6)
C(10)−Pt(1)−P(2)	87.5(7)	C(10)−Pt(1)−Cl(4)	174.3(7)
C(10)−Pt(1)−Cl(3)	88.5(7)	P(2)−Pt(1)−Cl(4)	98.2(2)
P(2)−Pt(1)−Cl(3)	175.4(3)	Cl(3)−Pt(1)−Cl(4)	85.8(2)

Summary

A novel mixed phosphino−amine (PCN) ligand was synthesized and its reactivity with Rh and Pt precursors was studied. The PCN−Rh system demonstrates a unique preference for C−C activation. The C−C-activated product is the only one observed in the reaction system. Reaction of the PCN ligand with Pt(II) results in selective C−H activation assisted by a noncoordinated internal amine.

Experimental Section

General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The complexes $[Rh(COE)_2Cl]_2$,[20] $[Rh(C_2H_4)_2Cl]_2$,[21] and $(COD)PtCl_2$[22] were prepared according to literature procedures.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 400, 100, and 162 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 23 °C. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm down-

(16) For other examples of such a bond, see: (a) Fryzuk, M. D.; MacNeil, P. A.; Retting, S. *J. Am. Chem. Soc.* **1987**, *109*, 2803. (b) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Am. Chem. Soc.* **1990**, *112*, 6411. (c) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; Kooijman, H.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Am Chem. Soc.* **1992**, *114*, 9916.

(17) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 2562.

(18) (a) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van der Sluis, P.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1990**, 1367. (b) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484.

(19) Alternatively, the reversible C−H activation can take place in an intermediate with coordinated P and N donors, resulting in a six-coordinate complex. At this point the amine "arm" undergoes dissociation followed by deprotonation of the Pt center to give **11**, thereby preventing C−H reductive elimination.

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(21) Cramer, R. *Inorg. Chem.* **1962**, *1*, 722.

(22) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

field from tetramethylsilane. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.15 ppm, benzene; 7.24 ppm, chloroform). In ^{13}C-{^{1}H} NMR measurements the signal of C_6D_6 (128.00 ppm) was used as a reference. ^{31}P NMR chemical shifts are reported in parts per million downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet.

Synthesis of $C_6H(CH_3)_3(CH_2N(C_2H_5)_2)(CH_2P(t\text{-}Bu)_2)$ (4). A mixture of di-*tert*-butylphosphine[23] (2.386 g, 16.34 mmol) and 2,6-bis(bromomethyl)mesitylene (5.0 g, 16.34 mmol) in acetone (20 mL) was heated under reflux with stirring for 2 h.[11] After this mixture was cooled to room temperature, the white precipitate that was obtained was filtered and washed with ether to remove unreacted starting material. The resulting mixture of diphosphonium and monophosphonium salts was dissolved in 35 mL of methanol, and a 10-fold excess of diethylamine (11.93 g, 0.163 mol) was added. The resulting reaction mixture was heated for 2 h (60 °C) with stirring. The solvent was evaporated under vacuum, and the residue was extracted with ether (3 × 20 mL). The ether fractions were combined, and the solvent was evaporated, yielding a mixture of compounds **1** and **4** in the ratio 2:1 which were separated by column chromatography on silica (gradient of solvent: from hexane to 4% THF−96% hexane) gave the clean PCN ligand **4** as a white solid in 35% yield. ^{31}P{^{1}H} NMR (benzene-d_6): 26.47 (s). ^{1}H NMR (benzene-d_6): 6.83 (s, 1H, Ar), 3.49 (s, 2H, Ar−CH_2−N), 2.87 (d, J_{PH} = 1.8 Hz, singlet in ^{1}H{^{31}P} spectrum, 2H, Ar−CH_2−P), 2.74 (s, 3H, Ar−CH_3), 2.51 (s, 3H, Ar−CH_3), 2.41 (q, J_{HH} = 7.1 Hz, 4H, 2 CH$_3$−CH_2−N), 2.33 (s, 3H, Ar−CH_3), 1.12 (d, J_{PH} = 10.2 Hz, singlet in ^{1}H{^{31}P} spectrum, 18 H, 2 (CH_3)$_3$C−P), 0.96 (t, J_{HH} = 7.1 Hz, 6H, 2 CH_3CH$_2$−N). ^{13}C{^{1}H} NMR (benzene-d_6): 137.12 (bs, Ar), 135.94 (d, J_{PC} = 6.5 Hz, Ar), 134.97 (bs, Ar), 134.85 (d, J_{PC} = 1.73 Hz, Ar), 134.42 (bs, Ar), 130.91 (d, J_{PC} = 0.7 Hz, Ar), 52.92 (s, Ar−CH$_2$−N), 46.55 (s, 2 CH$_3$$CH_2$−N), 32.31 (d, J_{PC} = 26.5 Hz, 2 (CH$_3$)$_3$$C$−P), 29.97 (d, J_{PC} = 13.3 Hz, 2 (CH_3)$_3$C−P), 24.28 (d, J_{PC} = 29.4 Hz, Ar−CH$_2$−P), 22.28 (d, J_{PC} = 8.6 Hz, Ar−CH$_3$), 20.67 (s, Ar−CH$_3$), 18.23 (d, J_{PC} = 9.5 Hz, Ar−CH$_3$), 12.55 (s, 2 CH$_3$CH$_2$−N) (assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). Anal. Calcd: C, 76.05; H, 11.56. Found: C, 75.28; H, 11.44.

Reaction of the PCN Ligand 4 with $[Rh(olefin)_2Cl]_2$. Formation of $ClRh(CH_3)[C_6H(CH_3)_2(CH_2N(C_2H_5)_2)(CH_2P(t\text{-}Bu)_2)]$ (5). (a) Reaction with $[Rh(COE)_2Cl]_2$. To a solution of ligand **4** (20 mg, 0.055 mmol) in benzene (2 mL) was added 2 mL of a benzene solution of $[Rh(COE)_2Cl]_2$ (20 mg, 0.028 mmol). The mixture was stirred at room temperature for 5 h, after which the color changed to deep orange and ^{31}P{^{1}H} NMR showed quantitative formation of **5** as a single product. (The same result was achieved by heating the mixture at 45°C for 15 min.)

(b) Reaction with $[Rh(ethylene)_2Cl]_2$. When a benzene solution (2 mL) of **4** (20 mg, 0.055 mmol) was mixed with a solution of $[Rh(ethylene)_2Cl]_2$ (11 mg, 0.028 mmol) in benzene (2 mL), complex **5** was obtained already after 3 min at room temperature.

(c) Characterization of 5. ^{31}P{^{1}H} NMR (benzene-d_6): 78.31 (d, J_{RhP} =160.8 Hz). ^{1}H NMR (benzene-d_6): 6.58 (s, 1H, Ar), 3.75 (m, 1H, CH$_3$CH_2−N), 3.67 (d, J_{HH} = 15.1 Hz, 1H, Ar−CH_2−N), 3.54 (d, J_{HH} = 15.1 Hz, 1H, Ar−CH_2−N), 3.00 (m, 1H, CH$_3$CH_2−N), 2.98 (m, 1H, Ar−CH_2−P), 2.89 (m, 1H, Ar−CH_2−P), 2.84 (m, 1H, CH$_3$CH_2−N), 2.66 (m, 1H, CH$_3$CH_2−N), 2.20 (s, 3H, CH$_3$−Ar), 2.08 (s, 3H, CH$_3$−Ar), 1.59 (dd, J_{RhH} = 2.9 Hz, J_{PH} = 1.2 Hz, doublet in ^{1}H{^{31}P} NMR, 3 H, Rh−CH_3), 1.27 (d, J_{PH} = 13.0 Hz, singlet in ^{1}H{^{31}P} NMR, 9 H, (CH_3)$_3$C−P), 1.19 (d, J_{PH} = 12.3 Hz, singlet in ^{1}H{^{31}P} NMR, 9 H, (CH_3)$_3$C−P), 1.04 (t, J_{HH} = 7.4 Hz, 3 H, CH_3CH$_2$−N), 0.86 (t, J_{HH} = 7.2 Hz, 3 H, CH_3CH$_2$−N) (assignment of ^{1}H NMR signals was confirmed by ^{13}C−^{1}H 2D correlation spectrum). ^{13}C{^{1}H} NMR (benzene-d_6): 170.04 (dd, J_{RhC} = 32.1 Hz, $J_{PC,cis}$ = 4.2 Hz, C_{ipso}, Rh−Ar), 143.75 (dd, J_{PC} = 12.0 Hz, J_{RhC} = 3.2 Hz, Ar), 143.04 (s, Ar), 130.79 (dd, J_{PC} = 16.1 Hz, J_{RhC} = 1.9 Hz, Ar), 129.71 (s, Ar), 126.23 (s, Ar), 62.07 (bd, J_{RhC} = 2.1 Hz, Ar-CH$_2$-N), 49.46 (bd, J_{RhC} = 1.4 Hz, CH$_3$-CH$_2$−N), 48.82 (bd, J_{RhC} = 2.1 Hz, CH$_3$CH_2−N), 30.92 (dd, J_{PC} = 26.4 Hz, J_{RhC} = 3.5 Hz, Ar−CH_2−P), 30.57 (d, J_{PC} = 3.2 Hz, (CH_3)$_3$C−P), 29.12 (d, J_{PC} = 2.5 Hz, (CH_3)$_3$C−P), 21.11 (s, CH$_3$−Ar), 19.88 (s, CH$_3$−Ar), 11.27 (s, CH$_3$CH$_2$−N), 7.71 (s, CH$_3$CH$_2$−N), −2.24 (dd, J_{RhC} = 34.4 Hz, J_{PC} = 8.3 Hz, Rh−CH$_3$). Anal. Calcd: C, 55.07; H, 8.37. Found: C, 55.37; H, 8.29.

Reaction of the PCN Ligand 4 with (COD)$PtCl_2$. Formation of $Cl_2PtCH_2(C_6H(CH_3)_2(CH_2NH(C_2H_5)_2)(CH_2P(t\text{-}Bu)_2)$ (11). To a THF suspension (3 mL) of (COD)$PtCl_2$ (COD = cyclooctadiene; 30 mg, 0.08 mmol) was added 29 mg (0.08 mmol) of ligand **4** in THF (3 mL). The mixture was vigorously stirred at 130 °C for 2 days, resulting in a light yellow solution. ^{31}P{^{1}H} NMR revealed formation of **11**. The solvent was evaporated, and the resulting yellowish solid was recrystallized from boiling THF, yielding 42 mg (83%) of **11** as white crystals.

Selected NMR data are as follows. ^{31}P{^{1}H} NMR ($CDCl_3$): 84.23 (s, J_{PPt} = 5119.6 Hz). ^{1}H NMR ($CDCl_3$): 10.02 (bs, 1H, N−H), 6.65 (s, 1H, Ar), 4.46 (d, J_{HH} = 13.6 Hz, 1H, Ar−CH_2−N, left part of AB quartet), 3.92 (d, J_{HH} = 13.3 Hz, 1H, Ar−CH_2−N, right part of AB quartet), 2.27 (s, CH_3−Ar), 2.18 (s, CH_3−Ar), 1.48 (d, J_{PH} = 16.3 Hz, 9H, P−C(CH_3)$_3$), 1.43 (t, J_{HH} = 7.3 Hz, 3H, 1 CH_3CH$_2$−N), 1.30 (t, J_{HH} = 7.3 Hz, 3H, 1 CH_3-CH$_2$−N), 1.08 (d, J_{PH} = 16.3 Hz, 9H, P−C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 51.29 (s, Ar−CH$_2$−N), 48.29 (s, 1 CH$_3$$CH_2$−N), 43.96 (s, 1 CH$_3$$CH_2$−N), 29.90 (bs, 1 P−C(C$H_3$)$_3$), 29.15 (bs, 1 P−C(C$H_3$)$_3$), 20.33 (s, CH$_3$−Ar), 19.81 (s, CH$_3$−Ar), 17.55 (d, J_{PC} = 30.5 Hz, Ar−CH$_2$−P), 8.99 (s, CH$_3$−CH$_2$−N), 7.86 (s, 1 CH$_3$−CH$_2$−N), 2.67 (d, J_{PC} = 4.7 Hz, Ar−CH$_2$−Pt). Anal. Calcd: C, 46.24; H, 7.13. Found: C, 46.02; H, 7.19.

X-ray Structural Analysis of 5. Complex **5** was crystallized by slow evaporation of the solvent from a pentane solution at room temperature to give orange crystals.

Crystal Data: $C_{23}H_{42}NPClRh$, orange prism, 0.3 × 0.2 × 0.2 mm^3, monoclinic, $P2_1/c$ (No. 14), a = 12.392(2) Å, b = 12.701(3) Å, c = 15.991(3) Å, β = 107.33(3)°, from 25 reflections, T = 110 K, V = 2402.6(8) Å^3, Z = 4, fw = 501.9, D_c = 1.388 Mg/m^3, μ = 0.897 mm^{-1}.

Data Collection and Treatment: Rigaku AFC5R four-circle diffractometer, Mo Kα, graphite monochromator (λ = 0.710 73Å), total of 11 222 reflections collected, 1.72° ≤ θ ≤ 27.51°, −16 ≤ h ≤ 16, 0 ≤ k ≤ 16, −20 ≤ l ≤ 20, ω-scan method, scan width 1.2°, scan speed 8°/min, typical half-height peak width 0.45°, 3 standards were collected 61 times each, with a 4% change in intensity, 5528 independent reflections (R_{int} = 0.0367).

Solution and Refinement: structure solved by direct methods (SHELXS-92), full-matrix least-squares refinement based on F^2 (SHELXL-93), hydrogens calculated in idealized positions and refined in a riding mode, 279 parameters with no restraints, final R_1 = 0.0453 (based on F^2) for data with $I > 2\sigma(I)$ and R_1 = 0.0610 for all data based on 5518 reflections, goodness of fit on F^2 1.129, largest electron density 2.433 e/Å^{-3}. The *tert*-butyl groups on phosphorus have large thermal motion and have been modeled as discretely disordered.

X-ray Structural Analysis of 11. Complex **11** was recrystallized from hot THF to give colorless crystals.

Crystal Data: $C_{23}H_{42}Cl_2PNPt$ + C_4H_8O, colorless prisms, 0.05 × 0.05 × 0.05 mm^3, monoclinic, $P2_1/c$ (No. 14), a = 10.576-(2) Å, b = 19.385(4) Å, c = 14.473(3) Å, β = 98.35(3)°, from 25 reflections, T = 110 K, V = 2935.7(10) Å^3, Z = 4, fw = 629.19, D_c = 1.587 Mg/m^3, μ = 5.036 mm^{-1}.

(23) For the synthesis of di-*tert*-butylphosphine, see: Hoffmann, H.; Schellenbeck, P. *Chem. Ber.* **1966**, *99*, 1134.

Data Collection and Treatment: Rigaku AFC5R four-circle diffractometer, Mo Kα, graphite monochromator (λ = 0.710 73Å), total of 8972 reflections collected, 1.77° ≤ θ ≤ 24.01°, $-12 \le h \le 9$, $0 \le k \le 22$, $-16 \le l \le 16$, ω-scan method, scan width 1.2°, scan speed 6°/min, typical half-height peak width 0.35°, 3 standards collected 47 times each, with a 5% change in intensity, 4608 independent reflections (R_{int} = 0.1076).

Solution and Refinement: structure was solved by the Patterson method (SHELXS-92), full-matrix least-squares refinement based on F^2 (SHELXL-93), hydrogens calculated in idealized positions and refined in a riding mode, 226 parameters with 11 restraints on anisotropic factors, final R_1 = 0.0767 (based on F^2) for data with $I > 2\sigma(I)$ based on 3153 reflections, R_1 = 0.1596 for all data, goodness of fit on F^2 = 1.164, largest electron density 1.356 e/Å^{-3}.

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for **5** and **11** (12 pages). Ordering information is given on any current masthead page.

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