C−Cl and Si−Cl Activation by *P*,*N*-Chelated Pt^{II} Complexes

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Keywords: Platinum / Silicon / Hemilabile ligands / Oxidative addition / Halogen compounds

The complex [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]$PtMe_2$ reacts with chlorinated hydrocarbons such as CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl by oxidative addition of the C–Cl bond. In the reaction with CCl_4, the complexes [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]Pt(Me)Cl, [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]$Pt(Me)_3Cl$, and [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]Pt(CCl=CH_2)Cl are obtained. The analogous *P,P*-chelated complex [(κ^2-*P,P*)-$Ph_2CH_2CH_2PPh_2$]$PtMe_2$ does not react under the same conditions. Reaction of [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]$PtMe_2$ with $ClSiMe_2Ph$ results in the formation of $Ph_2Me_4Si_2$ along with [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]Pt(Me)Cl and [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]$Pt(Me)_3Cl$.

Introduction

The oxidative addition of organic halides to several complexes of the type (*N,N*-chelate)$PtMe_2$ to form Pt^{IV} derivatives has been described. While bromides and iodides react readily, simple alkyl chlorides were not employed since they react poorly.[1] The reason is probably the carbon−halogen bond strength, which increases in the sequence C−I (56 kcal·mol^{-1} for CH_3I), C−Br (70 kcal·mol^{-1}), C−Cl (84 kcal·mol^{-1}), and C−F (109 kcal·mol^{-1}). While the *thermal* reaction of chlorocarbons is not straightforward, Zelewsky et al. reported *photochemical* oxidative additions of chlorinated hydrocarbons to Pt^{II} complexes with hemilabile C,N ligands.[2]

In previous studies on the oxidative addition of organosilanes to Pt^{II} complexes, we found that the reactivity the complexes is strongly enhanced by hemilabile *P,N*-chelating ligands.[3,4] In this paper, we report that this is also true for reactions with chlorocarbons. The presence of the hemilabile ligands allows the *thermal* reactions of chloromethane derivatives with Pt^{II} complexes.

Results and Discussion

Reaction of ($P^\cap N$)$PtMe_2$ with CCl_4

When CCl_4 was added to a solution of [(κ^2-*P,N*)-$Ph_2PCH_2CH_2NMe_2$]$PtMe_2$ (**1**) (the chelating ligand $Ph_2PCH_2CH_2NMe_2$ is abbreviated as $P^\cap N$) in C_6D_6 at room temperature, a colorless precipitate was immediately formed. The reaction was complete within 2 min. In contrast, no reaction occurred with the bis(phosphane) complexes [(κ^2-*P,P*)-$Ph_2PCH_2CH_2PPh_2$]$PtMe_2$ or $(PhMe_2P)_2$-$PtMe_2$.

The course of the reaction was monitored by ^{31}P, ^{1}H, and ^{195}Pt NMR spectroscopy. Three new sets of signals are observed in the ^{31}P and ^{195}Pt NMR spectra, with characteristic coupling constants (Table 1).

Table 1. ^{31}P and ^{195}Pt NMR spectra of complexes **2−4** (in [D$_6$]acetone; δ in ppm, *J* in Hz)

Complex	δ(^{195}Pt)	$^1J_{PtP}$	δ(^{31}P)
2	−4243	4678	27.29
3	−3905	4363	25.5
4	−2976	1213	9.33

The precipitate was spectroscopically characterized as ($P^\cap N$)Pt(Me)Cl (**2**) and independently synthesized by reaction of ($P^\cap N$)$PtMe_2$ with HCl or from (norbornadiene)Pt(Me)Cl and $Ph_2PCH_2CH_2NMe_2$, as described for [(κ^2-*P,P*)-$Ph_2PCH_2CH_2CH_2PPh_2$]Pt(Me)Cl.[5] Complex **2** was only sparingly soluble in benzene, and therefore part of the formed **2** precipitated from the reaction solution.

After separation of **2** and addition of petroleum ether to the clear solution, the additional complex **3** crystallized. Compound **3** was identified by an X-ray crystal structure analysis as ($P^\cap N$)Pt(CCl=CH_2)Cl (Figure 1 and Table 2). The vinylic protons in the ^1H NMR spectrum of isolated **3** have chemical shifts and $^3J_{PtH}$ coupling constants similar to those reported in the literature.[6,7] $^4J_{PH}$ and geminal $^2J_{H,H}$ were not observed.

In **3**, Pt^{II} has the typical square-planar coordination. The Pt−P(1) distance of 220.19(8) pm and the Pt−N(16) distance of 218.1(2) pm are in the same range as observed for (silyl)Pt^{II} complexes with such ligands.[4] The chloro ligand is located *trans* to the phosphorus atom; the Pt−Cl(1) distance of 236.64(8) pm is typical for this arrangement.[8] The only other related structure is a methyl-substituted complex (PTFA)Pt(CH_3)Cl [PTFA: (η^5-cyclopentadienyl)(η^5-4-*endo*-

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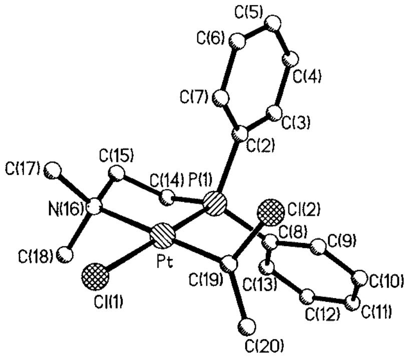
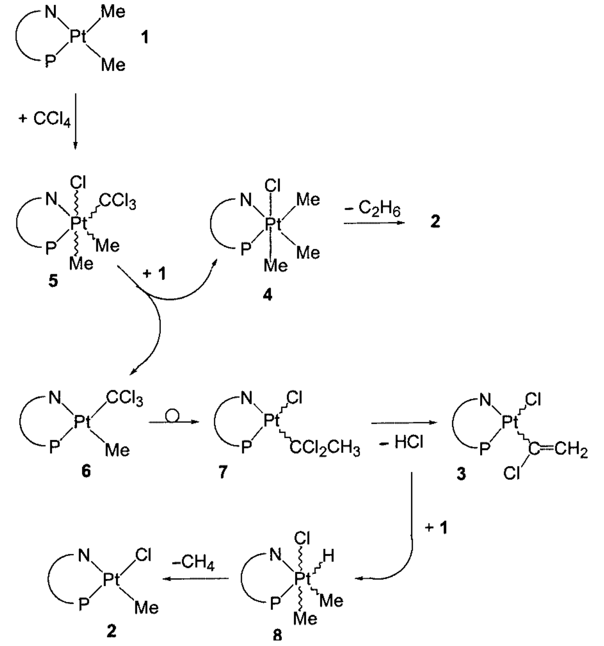


Figure 1. Molecular structure of $[(\kappa^2\text{-}P,N)\text{-}Ph_2PCH_2CH_2NMe_2]Pt(CCl{=}CH_2)Cl$ (**3**); the asymmetric unit also contains three benzene molecules that are not shown in this figure

Table 2. Selected bond lengths [pm] and angles [°] for **3**

Pt−Cl(1)	236.64(8)	C(19)−Pt−Cl(1)	89.61(8)
Pt−P(1)	220.19(8)	Cl(1)−Pt−P(1)	175.28(2)
Pt−N(16)	218.1(2)	C(2)−P(1)−C(8)	105.66(13)
Pt−C(19)	200.2(3)	C(2)−P(1)−C(14)	104.03(13)
P(1)−C(2)	181.6(3)	C(8)−P(1)−C(14)	107.84(13)
P(1)−C(8)	181.1(3)	C(15)−N(16)−C(17)	107.9(2)
P(1)−C(14)	182.8(3)	C(17)−N(16)−C(18)	108.7(2)
Cl(2)−C(19)	168.9(4)	C(15)−N(16)−C(17)	108.9(2)
N(16)−Pt−P(1)	85.32(7)	C(20)−C(19)−Pt	124.7(2)
C(19)−Pt−P(1)	94.03(8)	C(20)−C(19)−Cl(2)	117.7(2)
C(19)−Pt−N(16)	179.34(9)	Cl(2)−C(19)−Pt	117.61(18)
N(16)−Pt−Cl(1)	91.04(7)		



Scheme 1

dimethylamino-3-diphenylphosphanyl-4,5,6,7-tetrahydro-1*H*-indenyl)iron].[9] A chlorovinyl-substituted bis(phosphane)Pt^{II} complex $(Me_2PhP)_2Pt(CCl{=}CH_2)_2$ was reported in the literature with a Pt−C bond length of 205.3(5) pm.[10] In comparison, the Pt−C bond length in **3** is rather short [Pt−C(19), 200.2(3) pm]. However, the accuracy of the bond lengths in the chlorovinyl ligand of **3** is rather low because the Cl and C positions are disordered. The position Cl(2) (Figure 1) has an occupation of 70% Cl and 30% C, and that of C(20) vice versa.

The ^{1}H NMR spectrum of the original reaction solution shows four $Pt{-}CH_3$ signals with characteristic $^2J_{PtH}$ and $^3J_{PH}$ coupling constants. One of them is assigned to the PtMe group of complex **2**. Since **3** contains no methyl ligands, the remaining three signals with equal intensity must belong to a single complex. This complex is spectroscopically identified as $(P^{\cap}N)Pt(Me)_3Cl$ (**4**) by comparison with an authentic sample of **4** obtained by another route (see below). An X-ray structure analysis of **4** was performed.

The postulated sequence of reactions starting with **1** and CCl_4 is shown in Scheme 1.

CCl_4 probably attacks $(P^{\cap}N)PtMe_2$ (**1**) by oxidative addition of one C−Cl bond in the first step of the reaction. Kuyper reported the oxidative addition of CCl_4 to $(bpy)PtMe_2$ yielding the stable product $(bpy)Pt(Me)_2Cl(CCl_3)$.[11] In contrast, we did not observe the corresponding Pt^{IV} complex **5**. It can therefore be assumed that subsequent reductive elimination to Pt^{II} complexes is fast. It appears that the hemilabile $(P^{\cap}N)$-chelate ligand facilitates both the oxidative addition and the reductive elimination from the Pt complex. There are three possibilities of reductive elimination from complex **5**: (i) Elimination of $Me{-}CCl_3$ to give complex **2**. This possibility can be excluded because there is no NMR spectroscopic evidence for $MeCCl_3$. (ii) Elimination of MeCl to give complex **6**. (iii) Elimination of ethane. There is no experimental evidence for the formation of ethane.

A bis(phosphane) complex analogous to **6**, $[(\kappa^2\text{-}P,P')\text{-}Ph_2PCH_2CH_2PPh_2]Pt(CCl_3)Me$, was reported to rearrange by a CCl_2 shift, followed by the elimination of HCl.[12] The same mechanism leads to the formation of **7** and the isolated vinylidene complex **3**. The eliminated HCl can react with the starting complex **1** to give complex **8**, followed by the elimination of methane to give complex **2**. The latter reaction sequence was confirmed by the reaction of $(P^{\cap}N)PtMe_2$ (**1**) with a solution of HCl in diethyl ether, which resulted in the formation of **2**.

Complex **1** does not react with the methyl chloride eliminated in the second step under the conditions at which the reaction with CCl_4 was performed (room temperature) to form the observed product **4** (**4** is only formed at elevated temperatures, see below). We therefore propose a methyl transfer reaction between complexes **1** and **5** to give **4** and **6**. The elimination of ethane from **4** can be assumed as another source of complex **2** in the reaction scheme above. This was proven by another experiment described below.

Due to the different donor/acceptor properties of the two Lewis basic centers of the $(P^{\cap}N)$ ligand, the reactions described above are highly selective, and no isomers of the complexes **2**−**4** were observed.

When the deuterated complex $(P^{\cap}N)Pt(CD_3)_2$ is used for the reaction with CCl_4, the ^{31}P NMR spectrum is unchanged. The $Pt{-}CH_3$ signals of complexes **2** and **4** and the $={CH_2}$ signals of complex **3** are not detected in the ^{1}H

NMR spectrum. The ^{2}H NMR spectrum shows three Pt−CD$_3$ signals of equal intensity for the deuterated complex **4**, and one Pt−CD$_3$ signal for deuterated **2**. There is one additional peak at δ = 0.11 ppm in the ^{1}H NMR spectrum. This may belong to deuterated ethane, proving the formation of **2** from **4** by reductive elimination. Only one =CD$_2$ signal of the deuterated form of **3** is detected. The experiment was repeated in C_6H_6 since the second peak may be hidden by the broad signal of the solvent C_6D_6. However, no further peak is detected. The lack of the second =CD$_2$ signal may be due to exchange effects.[13]

Reaction of (P∩N)PtMe$_2$ with CHCl$_3$

(P∩N)PtMe$_2$ was much more reactive towards CCl$_4$ than towards CHCl$_3$. While the reaction with CCl$_4$ was complete within 2 min at room temperature, no reaction was observed with CHCl$_3$ after 1 d under the same conditions. However, (P∩N)Pt(Me)Cl (**2**) crystallized from a CHCl$_3$/petroleum ether solution of (P∩N)PtMe$_2$ after several weeks. For a reasonable reaction rate, it was necessary to heat the mixture to 60 °C. At this temperature, the reaction was complete in about 10 h.

Three new signals are observed in the ^{31}P NMR spectrum when a mixture of (P∩N)PtMe$_2$ and CHCl$_3$ in a 1:2 ratio was heated in C_6D_6. Comparison of the spectra with those of the products obtained in the reaction of (P∩N)PtMe$_2$ with CCl$_4$ shows that complexes **2** and **4** are also formed in the reaction with CHCl$_3$. The concentrations of **2** and **4** increase simultaneously, while the concentration of **1** decreases. The new complex **9** with a large $^{1}J_{PtP}$ coupling constant, indicating a chlorine atom *trans* to the phosphorus atom, is detected in small quantities only after a reaction time of about 6 h. No Pt−Me resonances are observed in the ^{1}H NMR spectrum, other than those of complexes **4** and **2**. According to the reaction mechanism shown in Scheme 1, complex **9** could be (P∩N)Pt(Cl)(CH=CH$_2$). There are signals between δ = 5 and 6 ppm in the ^{1}H NMR spectrum, which may arise from the vinyl group of **9**. The signals are very weak probably due to the H−H, H−P, and H−Pt coupling, and unequivocal identification is therefore not possible. We were not able to separate **9** from the reaction mixture.

When (P∩N)Pt(CD$_3$)$_2$ is treated with CHCl$_3$, no Pt−CH$_3$ signals are observed in the ^{1}H NMR spectrum, and the ^{2}H NMR spectrum shows a signal for deuterated **2** and three signals of equal intensity for deuterated **4**.

Reaction of (P∩N)PtMe$_2$ with CH$_2$Cl$_2$

The reactivity of CH$_2$Cl$_2$ was lower than that of CHCl$_3$. At 60 °C in C_6D_6, **2** and **4** were formed after a few days, along with decomposition products, which were not identified, and a black precipitate. In contrast to the reaction with CCl$_4$ and CHCl$_3$, no other P-containing platinum complex is observed by ^{31}P NMR spectroscopy.

The sequence of reactivity of the halogenated hydrocarbons, i.e. CCl$_4$ > CHCl$_3$ > CH$_2$Cl$_2$, is related to the C−Cl bond strength in these compounds (CCl$_4$ −248 kJ·mol^{-1}, CHCl$_3$ −280 kJ·mol^{-1}, CH$_2$Cl$_2$ −304 kJ·mol^{-1}, CH$_3$Cl −328 kJ·mol^{-1}).

Reaction of (P∩N)PtMe$_2$ with CH$_3$Cl

CH$_3$Cl does not fit into the sequence as it reacted with (P∩N)PtMe$_2$ in a hot C_6D_6 solution to form complex **4** and traces of **2**. The reaction was complete within 12 h. The amount of **2** increased on further heating, indicating reductive elimination of ethane from **4**. At room temperature no reaction occurred after 1 h (see above). Again, the analogous *P,P*-chelated complex (dppe)PtMe$_2$ did not react with CH$_3$Cl at 60 °C in C_6D_6 after 24 h.

Complex **4** was structurally characterized and has a distorted octahedral geometry (Figure 2 and Table 3). The asymmetric unit contains only half of the molecule with Pt, C(20), C(21), C(8) N(10), and P(1) in a crystallographic mirror plane. Therefore, the positions of Cl and C(22A) are disordered and hence have a mixed occupancy. The C(9) atom of the ethylene bridge is also disordered. The Pt−C distances of the equatorial methyl substituents [Pt−C(20):

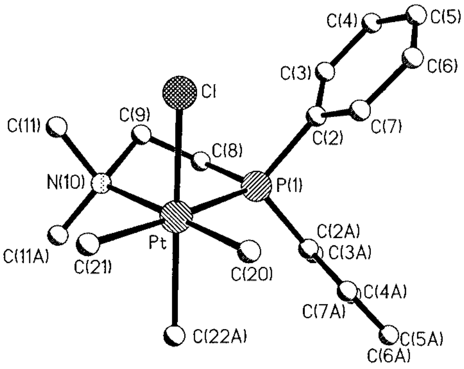


Figure 2. Molecular structure of [(κ^{2}-*P,N*)-Ph$_2$PCH$_2$CH$_2$NMe$_2$]-Pt(Me)$_3$Cl (**4**)

Table 3. Selected bond lengths [pm] and angles [°] measured for **4** and calculated for **4b**. The asterisks refer to symmetry-equivalent atoms

	4	**4b**
Pt−C(20)	206.3(10)	207.2
Pt−C(21)	208.2(9)	208.6
Pt−N(10)	230.4(8)	230.8
Pt−P(1)	236.9(2)	244.7
Pt−Cl	240.9(3)	252.8
Pt−C(22)*	240.9(3)	208.3
C(20)−Pt−C(21)	85.4(5)	87.9
N(10)−Pt−C(20)	178.1(4)	177.6
N(10)−Pt−C(21)	92.7(4)	91.7
P(1)−Pt−C(20)	99.5(3)	100.0
P(1)−Pt−C(21)	175.1(4)	171.5
P(1)−Pt−N(10)	82.4(2)	80.2
Cl−Pt−C(20)	87.55(8)	94.7
Cl−Pt−C(21)	88.36(7)	90.1
Cl−Pt−N(10)	92.40(8)	82.9
Cl−Pt−P(1)	91.84(7)	86.1
C(2)−P(1)−C(8)	105.9(3)	
C(11)−N(10)−C(11)*	105.4(10)	
C(9)−N(10)−C(11)	87.3(9)	

206.3(10) pm; Pt−C(21): 208.2(9) pm] are in the same range as for corresponding Pt^{II} complexes with a P−N-chelating ligand.[14] Due to the disorder of the axial positions, an average distance of only 240.9(3) pm was found.

In order to estimate the Pt−Cl and Pt−C distances, in spite of the disorder of the axial ligands, an ab initio calculation was performed. The phenyl and methyl groups of the chelate ligand were substituted by hydrogen to reduce calculation time. The geometry optimization of this simplified molecule **4b** resulted a Pt−C(22) distance of 208.3 pm and a Pt−Cl distance of 252.8 pm. Additional bond lengths and angles are given in Table 2. Most bond lengths and angles are in good agreement with the measured values of complex **4**. The calculated bond lengths are typical for hexacoordinated Pt compounds and are in agreement with those found in an iodotrimethylplatinum(IV) complex.[15]

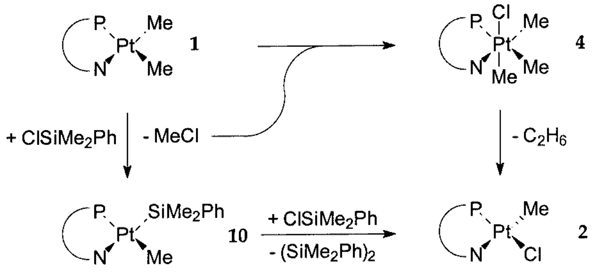
Elimination of Ethane from (P∩N)Pt(Me)$_3$Cl (4) on Heating

A sample of the isolated complex **4** was dissolved in [D$_8$]toluene and heated in an NMR tube. At 60 °C, formation of **2** was detected in the ^{1}H and ^{31}P NMR spectra, but the reaction rate was quite low. Therefore, the temperature was increased to 90 °C, at which temperature the reaction was complete in about 12 h. At this temperature the two Pt−CH$_3$ signals of **4** at $\delta = 0.59$ and 1.92 ppm are extremely broad, while the third Pt−CH$_3$ signal of **4** at $\delta =$ 1.49 ppm remains unchanged. Comparison of the Pt−CH$_3$ resonances of **4** with that of complexes **1**, **2**, and a (PhMe$_2$P)$_2$PtMe$_3$Cl isomer[16] analogous to **4**, allows for the assignment of the Pt−Me signal at $\delta = 0.59$ ppm to the methyl group *trans* to Cl, the signal at $\delta = 1.92$ ppm to the methyl group *trans* to the nitrogen atom, and the signal at $\delta = 1.49$ ppm to the methyl group *trans* to the phosphorus atom. The broadening of the two methyl resonances appears to be related to the start of the reductive elimination of ethane, i.e. ethane is probably formed from the methyl groups *trans* to the nitrogen atom and *trans* to the chlorine atom. The formation of ethane was proven by mass spectrometry.

(P∩N)Pt(CD$_3$)$_2$ was analogously treated to check whether the addition of CH$_3$Cl is stereospecific. However, no difference is seen in the ^{31}P NMR spectra compared with those of the experiments with (P∩N)PtMe$_2$. The ^{1}H NMR spectrum shows three Pt−CH$_3$ signals of **4** with equal intensities. Instead of three singlets with satellites, there are three doublets of doublets with satellites. The additional line splitting may be due to an H−D coupling, or due to the different chemical shifts of the structural isomers. Corresponding signals, also with equal intensity, are seen in the ^{2}H NMR spectrum, indicating a statistical distribution of the added CH$_3$ group to the three possible positions of complex **4**. An intermolecular exchange reaction, or rearrangement via a five-coordinate complex with an intermediate and the reversible opening of the (P∩N)-chelate ligand may be responsible for the scrambling reaction. Thermolysis of (P∩N)Pt(CD$_3$)$_2$(Me)Cl results in the formation of both C$_2$H$_6$ and C$_2$H$_3$D$_3$, as found by mass spectrometry.

Reaction of (P∩N)PtMe$_2$ with ClSiMe$_2$Ph

(P∩N)PtMe$_2$ not only exhibited a strongly increased reactivity towards C−Cl bonds in comparison with related (P∩P)PtMe$_2$ complexes, but was also able to activate the stronger Si−Cl bond of ClSiMe$_2$Ph. When a solution of (P∩N)PtMe$_2$ was heated in C$_6$D$_6$ with a stoichiometric amount of ClSiMe$_2$Ph, the disilane Ph$_2$Me$_4$Si$_2$ was the only silicon-containing product. Complexes **4** and **2** were formed in this reaction in a ratio of about 1:4. The amount of **2** increased after complete conversion of the chlorosilane, indicating a reductive elimination of ethane from **4**, forming **2**. The products were identified by spectroscopic comparison with independently prepared samples. A possible reaction mechanism is shown in Scheme 2. Although the intermediate complex **10** was not observed, this mechanism appears plausible because the formation of both **4** and **10** would correspond to the formation of complexes **4**−**5** in the reaction of **1** with CCl$_4$ (Scheme 1). A rearrangement similar to **6** → **7** is obviously less favored than the substitution of the second methyl ligand.



Scheme 2

Conclusions

The reactivity of Pt^{II} complexes with the chelating P∩N ligands towards chlorinated hydrocarbons and chlorinated silanes is greatly enhanced relative to the corresponding chelating bis(phosphane) complexes. This reactivity enhancement may have two reasons: (i) The nitrogen donor group of the P∩N ligands can be reversibly de-coordinated, i.e. the ligand is hemilabile. In comparison, the de-coordination of a phosphorus donor center chelating bis(phosphane) complexes is much more difficult. Hemilabile ligands are known to promote both oxidative addition and reductive elimination reactions. (ii) Due to the different donor/acceptor properties of the two Lewis basic centers in the P∩N ligands, the electronic difference *trans* to the nitrogen atom is different to that *trans* to the phosphorus atom, i.e. the bond strengths of the *trans* ligands are greatly influenced.

Experimental Section

General: All reactions were performed under dried argon. All reagents were of best commercial grade. The complexes (P∩N)PtMe$_2$, (P$^{\cap}$P)PtMe$_2$, and (PhMe$_2$P)$_2$PtMe$_2$ were prepared as previously described.[4] Solids were used without further purification, liquids were dried with molecular sieves (4 Å) for 24 h and argon-saturated by freeze-pump-thaw. NMR spectra were recorded with a Bruker DPX 300 Avance spectrometer (^{1}H and ^{29}Si NMR spectroscopy, TMS as an external standard. ^{31}P NMR spectroscopy, 85% H_3PO_4 as an external standard; ^{195}Pt NMR spectroscopy, Na_2PtCl_6 in D_2O as an external standard). ^{29}Si NMR spectra were recorded with an INEPT pulse sequence.

Computational Details: The geometry optimization of the equilibrium geometry of **4b** was carried out using the B3LYP version of DFT, which is comprised of Becke's hybrid three-parameter exchange functional,[17] and the correlation functional of Lee, Yang, and Parr.[18] The structure was characterized as minima by computing the Hessian matrices. The ab initio calculation was performed with the Gaussian98 program package.[19] From the available ECP basis sets in Gaussian98, the SDD basis set was used for platinum and the 6-311++G(d) basis set for all the other atoms.

General Procedure for the Reaction of Pt Complexes with Halogenated Compounds: All reactions were performed under argon in NMR or Schlenk tubes. The reaction vessels were flame-dried and argon-saturated before addition of the Pt complex. After addition of the solvent and the liquid halogenated compound, the vessel was closed and put into a thermostatically controlled oil bath or into the thermostatically controlled NMR spectrometer immediately. Experiments with silanes were performed in an NMR Teflon liner.

Reaction of (P$^{\cap}$N)PtMe$_2$ with CCl$_4$ in C$_6$D$_6$: CCl$_4$ (11.4 µL, 0.12 mmol) was added to a solution of **1** (28.7 mg, 0.06 mmol) in 0.7 mL of C$_6$D$_6$. A colorless solid precipitated immediately. It was separated by decanting the liquid phase and washed twice with cold benzene. The NMR spectra were identical with that of an independently prepared sample of **2** (see below). The supernatant solution was decanted and analyzed by NMR spectroscopy. ^{1}H NMR (C$_6$D$_6$, 27 °C): δ = 0.61 (d, $^{3}J_{\mathrm{PH}}$ = 7.7, $^{2}J_{\mathrm{PtH}}$ = 71 Hz, Pt−CH$_3$, **4**), 1.39 (d, $^{3}J_{\mathrm{PH}}$ = 3.0, $^{2}J_{\mathrm{PtH}}$ = 75 Hz, Pt−CH$_3$, **2**), 1.61 (d, $^{3}J_{\mathrm{PH}}$ = 8.1, $^{2}J_{\mathrm{PtH}}$ = 57 Hz, Pt−CH$_3$, **4**), 1.89 (s, $^{3}J_{\mathrm{PtH}}$ = 13.8 Hz, NMe$_2$, **4**), 2.03 (d, $^{3}J_{\mathrm{PH}}$ = 7.0, $^{2}J_{\mathrm{PtH}}$ = 73 Hz, Pt−CH$_3$, **4**), 2.56 (s, $^{3}J_{\mathrm{PtH}}$ = 13 Hz, NMe$_2$, **3**), 2.64 (s, $^{3}J_{\mathrm{PtH}}$ = 11 Hz, NMe$_2$, **2**), 2.69 (s, $^{3}J_{\mathrm{PtH}}$ = 10 Hz, NMe$_2$, **4**), 5.04 (s, $^{3}J_{\mathrm{PtH}}$ = 34 Hz, *cis* =CH, **3**), 6.18 (s, $^{3}J_{\mathrm{PtH}}$ = 89 Hz, *trans* =CH, **3**) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 27 °C): δ = 8.11 (s, $^{1}J_{\mathrm{PtP}}$ = 1185 Hz, **4**), 24.43 (s, $^{1}J_{\mathrm{PtP}}$ = 4375 Hz, **3**), 26.45 (s, $^{1}J_{\mathrm{PtP}}$ = 4677 Hz, **2**) ppm. ^{195}Pt{^{1}H} NMR (C$_6$D$_6$, 27°C): δ = −4243 (d, $^{1}J_{\mathrm{PtP}}$ = 4678 Hz, **2**), −3905 (d, $^{1}J_{\mathrm{PtP}}$ = 4363 Hz, **3**), −2976 (d, $^{1}J_{\mathrm{PtP}}$ = 1213 Hz, **4**) ppm. After the addition of some petroleum ether (boiling range 30−50°C)) to the decanted reaction solution, crystals of **3** suitable for a crystal structure analysis were formed within a few days. **3**: ^{1}H NMR ([D$_6$]acetone, 27 °C): δ = 2.65−2.85 (m, 4 H, CH$_2$), 2.87 (s, $^{3}J_{\mathrm{PtH}}$ = 14 Hz, 6 H, NCH$_3$), 4.39 (s, $^{3}J_{\mathrm{PtH}}$ = 36 Hz, 1 H, *cis* =CH), 5.43 (s, $^{3}J_{\mathrm{PtH}}$ = 90 Hz, 1 H, *trans* =CH), 7.50−7.95 (m, 10 H, C$_{\mathrm{arom}}$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 27 °C): δ = 24.33 (s, 4376 Hz) ppm. ^{31}P{^{1}H} NMR ([D$_6$]-acetone, 27°C): δ = 25.5 (s, $^{1}J_{\mathrm{PtP}}$ = 4369 Hz) ppm.

Synthesis of (P$^{\cap}$N)Pt(Cl)Me (2) by Reaction of (P$^{\cap}$N)PtMe$_2$ with HCl: A solution of HCl (0.1 mL, 0.10 mmol) in diethyl ether was added to a solution of (P$^{\cap}$N)PtMe$_2$ (23.9 mg, 0.05 mmol) in 0.7 mL of C$_6$D$_6$. The volatile compounds were then removed from the solution, and (P$^{\cap}$N)Pt(Me)Cl (**2**) remained as a colorless powder in a quantitative yield. ^{1}H NMR (CDCl$_3$, 27 °C): δ = 0.63 (d, $^{3}J_{\mathrm{PH}}$ = 2.8, $^{2}J_{\mathrm{PtH}}$ = 73 Hz, Pt−CH$_3$, **2**), 2.3−2.7 (m, CH$_2$CH$_2$), 2.87 (s, $^{3}J_{\mathrm{PtH}}$ = 11 Hz, NMe$_2$), 7.4−7.8 (m, PPh$_2$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 27 °C): δ = 27.28 (s, $^{1}J_{\mathrm{PtP}}$ = 4700 Hz) ppm. $C_{17}H_{23}ClNPPt$ (475.4): calcd. C 40.61, H 4.70, N 2.56; found C 41.39, H 4.70, N 2.56.

Synthesis of (P$^{\cap}$N)Pt(Cl)Me (2) by Reaction of (nbd)PtMeCl[5] with P$^{\cap}$N: A solution of [2-(diphenylphosphanyl)ethyl]dimethylamine (P$^{\cap}$N)[20] (282 mg, 1.09 mmol) in 10 mL of CH$_2$Cl$_2$ was added slowly to a solution of (nbd)Pt(Me)Cl (365 mg, 1.08 mmol) in 40 mL of CH$_2$Cl$_2$. After the mixture was stirred for 1 h, the colorless product was filtered and washed with benzene (3 × 5 mL) and pentane (3 × 5 mL). Yield 543 mg (85%).

Reaction of (P$^{\cap}$N)Pt(CD$_3$)$_2$ with CCl$_4$ in C$_6$D$_6$: CCl$_4$ (8.7 µL, 0.09 mmol) was added to a solution of (P$^{\cap}$N)Pt(CD$_3$)$_2$ (22 mg, 0.045 mmol) in 0.7 mL of C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$, 27 °C): δ = 1.83 (s, $^{3}J_{\mathrm{PtH}}$ = 14.3 Hz, NMe$_2$, **4**), 2.59 (s, $^{3}J_{\mathrm{PtH}}$ = 13 Hz, NMe$_2$, **3**), 2.64 (s, $^{3}J_{\mathrm{PtH}}$ = 10.7 Hz, NMe$_2$, **2**), 2.69 (s, $^{3}J_{\mathrm{PtH}}$ = 9.6 Hz, NMe$_2$, **4**) ppm. ^{2}H{^{1}H} NMR (C$_6$D$_6$, 27 °C): δ = 0.43 (s, $^{2}J_{\mathrm{PtD}}$ = 10.1 Hz, Pt−CD$_3$, **4**), 1.18 (s, $^{2}J_{\mathrm{PtD}}$ = 10.0 Hz, Pt−CD$_3$, **2**), 1.40 (s, $^{2}J_{\mathrm{PtD}}$ = 7.5 Hz, Pt−CD$_3$, **4**), 1.83 (s, $^{2}J_{\mathrm{PtD}}$ = 10.9 Hz, Pt−CD$_3$, **4**), 4.89 (s, =CD$_2$, **3**) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 27 °C): δ = 8.67 (s, $^{1}J_{\mathrm{PtP}}$ = 1180 Hz, **4**), 24.72 (s, $^{1}J_{\mathrm{PtP}}$ = 4381 Hz, **3**), 26.89 (s, $^{1}J_{\mathrm{PtP}}$ = 4679 Hz, **2**) ppm.

Reaction of (P$^{\cap}$N)PtMe$_2$ with CHCl$_3$ in C$_6$D$_6$: CHCl$_3$ (7.8 µL, 0.095 mmol) was added to a solution of **1** (23 mg, 0.05 mmol) in 0.7 mL of C$_6$D$_6$. After addition, the sample was heated to 60 °C. ^{1}H NMR (C$_6$D$_6$, 60 °C): δ = 0.59 (d, $^{3}J_{\mathrm{PH}}$ = 7.7, $^{2}J_{\mathrm{PtH}}$ = 71.0 Hz, Pt−CH$_3$, **4**), 1.34 (d, $^{3}J_{\mathrm{PH}}$ = 3.5, $^{2}J_{\mathrm{PtH}}$ = 75.1 Hz, Pt−CH$_3$, **2**), 1.53 (d, $^{3}J_{\mathrm{PH}}$ = 8.3, $^{2}J_{\mathrm{PtH}}$ = 58.0 Hz, Pt−CH$_3$, **4**), 1.91 (s, $^{3}J_{\mathrm{PtH}}$ = 14.1 Hz, NCH$_3$, **4**), 1.94 (d, $^{3}J_{\mathrm{PH}}$ = 6.9, $^{2}J_{\mathrm{PtH}}$ = 73.1 Hz, Pt−CH$_3$, **4**), 2.60 (s, $^{3}J_{\mathrm{PtH}}$ = 12.6 Hz, NCH$_3$, **9**), 2.64 (s, $^{3}J_{\mathrm{PtH}}$ = 11.5 Hz, NMe$_2$, **2**), 2.70 (s, $^{3}J_{\mathrm{PtH}}$ = 9.3 Hz, NMe$_2$, **4**) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 60 °C): δ = 7.57 (s, $^{1}J_{\mathrm{PtP}}$ = 1175 Hz, **4**), 26.15 (s, $^{1}J_{\mathrm{PtP}}$ = 4657 Hz, **2**), 27.95 (s, $^{1}J_{\mathrm{PtP}}$ = 4559 Hz, **9**) ppm.

Reaction of (P$^{\cap}$N)Pt(CD$_3$)$_2$ with CHCl$_3$ in C$_6$D$_6$: CHCl$_3$ (19.5 µL, 0.24 mmol) was added to a solution of **1** (58.6 mg, 0.12 mmol) in 0.7 mL of C$_6$D$_6$. The sample was then heated to 60 °C. ^{1}H NMR (C$_6$D$_6$, 60 °C): δ = 1.93 (s, $^{3}J_{\mathrm{PtH}}$ = 13.9 Hz, NCH$_3$, **4**), 2.59 (s, $^{3}J_{\mathrm{PtH}}$ = 12.4 Hz, NCH$_3$, **9**), 2.64 (s, $^{3}J_{\mathrm{PtH}}$ = 11.8 Hz, NMe$_2$, **2**), 2.72 (s, $^{3}J_{\mathrm{PtH}}$ = 9.2 Hz, NMe$_2$, **4**). ^{2}H{^{1}H} NMR (C$_6$D$_6$, 60 °C): 0.45 (s, $^{2}J_{\mathrm{PtD}}$ = 10.4 Hz, Pt−CD$_3$, **4**), 1.26 (s, $^{2}J_{\mathrm{PtD}}$ = 10.0 Hz, Pt−CD$_3$, **2**), 1.48 (s, $^{2}J_{\mathrm{PtD}}$ = 7.5 Hz, Pt−CD$_3$, **4**), 1.86 (s, $^{2}J_{\mathrm{PtD}}$ = 11.0 Hz, Pt−CD$_3$, **4**) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 60 °C): δ = 7.93 (s, $^{1}J_{\mathrm{PtP}}$ = 1180 Hz, **4**), 26.63 (s, $^{1}J_{\mathrm{PtP}}$ = 4679 Hz, **2**), 28.41 (s, $^{1}J_{\mathrm{PtP}}$ = 4562 Hz, **9**) ppm.

Reaction of (P$^{\cap}$N)PtMe$_2$ with CH$_2$Cl$_2$ in C$_6$D$_6$: CH$_2$Cl$_2$ (29.4 µL, 0.445 mmol) was added to a solution of **1** (21.5 mg, 0.045 mmol) in 0.7 mL of C$_6$D$_6$. After addition, the sample was heated to 60 °C. ^{31}P{^{1}H} NMR (C$_6$D$_6$, 60 °C): δ = 7.33 (s, $^{1}J_{\mathrm{PtP}}$ = 1167 Hz, **4**), 26.60 (s, $^{1}J_{\mathrm{PtP}}$ = 4681 Hz, **2**) ppm.

Formation of (P$^{\cap}$N)Pt(Me)$_3$Cl (4) by Reaction of (P$^{\cap}$N)PtMe$_2$ with CH$_3$Cl in C$_6$D$_6$: A gentle stream of methyl chloride was bubbled through a solution of **1** (108 mg, 0.22 mmol) in 2 mL of C$_6$D$_6$. After 1 h, the ^{1}H NMR spectrum showed an intensive CH$_3$Cl signal at δ = 2.48 ppm, but no formation of new complexes. The CH$_3$Cl saturated solution was then heated to 60 °C and a finely divided colorless solid precipitated. After 12 h, the conversion into **4** was approximately 95%. After 24 h, conversion was complete and only traces of **1** were observed. Crystallization from a saturated benzene solution yielded pure **4** as colorless crystals, some of them suitable for a X-ray structure analysis. ^{1}H NMR (C$_6$D$_6$, 60 °C): δ = 0.59 (d, $^{3}J_{\mathrm{PH}}$ = 7.7, $^{2}J_{\mathrm{PtH}}$ = 70.8 Hz, Pt−CH$_3$), 1.51 (d, $^{3}J_{\mathrm{PH}}$ = 8.2, $^{2}J_{\mathrm{PtH}}$ = 57.6 Hz, Pt−CH$_3$), 1.89 (s, $^{3}J_{\mathrm{PtH}}$ = 14.1 Hz, NCH$_3$), 1.93

Table 4. Crystallographic data for **3** and **4**

Compound	**3**	**4**
Empirical formula	$C_{30}H_{26}Cl_2NPPt$	$C_{19}H_{22}ClNPPt$
Formula mass	697.48	525.89
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	*Pnma*
Unit cell dimensions		
a [pm]	832.3(3)	900.36(4)
b [pm]	1300.8(4)	1359.59(6)
c [pm]	1492.4(5)	1655.71(7)
α [°]	68.069(5)°	90
β [°]	81.566(6)°	90
γ [°]	81.455(6)°	90
Volume [pm^3]	$1474.8(8)\times10^6$	$2026.79(15)\times10^6$
Z	2	4
Calculated density [g cm^{-3}]	1.571	1.723
Absorption coefficient [mm^{-1}]	5.011	7.132
F(000)	680	1012
Crystal size [mm]	0.60 × 0.16 × 0.16	0.32 × 0.28 × 0.08
θ range [°]	1.81−28.35	1.94−26.37
Reflections collected/unique	10116/7137 [$R(\text{int}) = 0.0183$]	11350/2143 [$R(\text{int}) = 0.0373$]
Completeness to θ [%]	97.0	99.0
Max. and min. transmission	0.5011, 0.1530	0.5992, 0.2087
Data/restraints/parameters	7137/0/317	2143/0/119
Goodness-of-fit on F^2	1.033	1.213
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0208$, $wR_2 = 0.0534$	$R_1 = 0.0312$, $wR_2 = 0.0792$
R indices (all data)	$R_1 = 0.0229$, $wR_2 = 0.0543$	$R_1 = 0.0335$, $wR_2 = 0.0803$
Weighting scheme $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 0.16P]$	$w = 1/[\sigma^2(F_o^2) + 9.69\ P]$
Extinction coefficient	0.0014(2)	0.00040(15)
Largest diff. peak/hole [e·A^{-3}]	1.147/−1.131	0.888/−1.130

(d, $^2J_{PtH}$ = 7.2, $^3J_{PH}$ = 73.1 Hz, Pt−CH$_3$), 2.70 (s, $^3J_{PtH}$ = 9.4 Hz, NCH$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 60 °C): δ = 8.01 (s, $^1J_{PtP}$ = 1166 Hz) ppm. $C_{19}H_{29}ClNPPt$ (525.9): found C 42.82, H 5.48, N 2.63; found C 42.81, H 5.37, N 2.65.

Reaction of (P∩N)Pt(CD$_3$)$_2$ with CH$_3$Cl in C$_6$D$_6$: A gentle stream of methyl chloride was bubbled through a solution of (P∩N)Pt(CD$_3$)$_2$ (27.5 mg, 0.056 mmol) in 0.6 mL of C_6D_6. The CH$_3$Cl-saturated solution was heated to 60 °C for 24 h. The conversion was complete yielding (P∩N)Pt[(CH$_3$)/(CD$_3$)]$_3$Cl, with a statistical distribution of the added CH$_3$ group. (P∩N)Pt(CH$_3$)(CD$_3$)$_2$Cl: ^{1}H NMR (C_6D_6, 60 °C): δ = 0.59 (dd, *J* = 1.0, $^3J_{PH}$ = 7.7, $^2J_{PtH}$ = 71.0 Hz, Pt−CH$_3$), 1.49 (dd, *J* = 1.1, $^3J_{PH}$ = 8.1, $^2J_{PtH}$ = 57.0 Hz, Pt−CH$_3$), 1.92 (dd, *J* = 1.0, $^3J_{PH}$ = 7.0, $^2J_{PtH}$ = 72.6 Hz, Pt−CH$_3$) ppm. ^{2}H NMR (C_6D_6, 27 °C): δ = 0.45 ($^3J_{PD}$ = 1.1, $^2J_{PtD}$ = 10.7 Hz, Pt−CD$_3$), 1.36 ($^3J_{PD}$ = 1.7, $^2J_{PtD}$ = 6.9 Hz, Pt−CD$_3$), 1.84 ($^3J_{PD}$ = 1., $^2J_{PtD}$ = 10.8 Hz, Pt−CD$_3$) ppm. ^{31}P{^{1}H} NMR (C_6D_6 60 °C): δ = 8.01 (s, $^1J_{PtP}$ = 1161 Hz) ppm.

Reaction of (P∩N)PtMe$_2$ with ClSiMe$_2$Ph in C$_6$D$_6$: ClSiMe$_2$Ph (26 μL, 0.156 mmol) was added to a solution of (P∩N)PtMe$_2$ (37.5 mg, 0.078 mmol) in 0.5 mL of C_6D_6 in a Teflon liner. The sample was then heated to 60 °C. Because of the Teflon liner, the resolution of the ^{1}H NMR spectrum was very low, and resolution of the Pt complexes was not possible. ^{1}H NMR (C_6D_6, 60 °C): δ = 0.39 [s, (SiMe$_2$Ph)$_2$] ppm. ^{29}Si{^{1}H} NMR (C_6D_6, 60 °C): δ = −21.45 ppm. ^{31}P{^{1}H} NMR (C_6D_6, 60 °C): δ = 7.87 (s, $^1J_{PtP}$ = 1168 Hz, **4**), 26.24 (s, $^1J_{PtP}$ = 4665 Hz, **2**) ppm.

X-ray Structure Analyses: Crystal data and experimental details are given in Table 4. The X-ray data were collected at 294 K with a Siemens SMART CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), a nominal crystal-to-detector distance of 4.40 cm and 0.3° ω-scans frames. Corrections for Lorentz polarization, and an empirical absorption correction with the program SADABS were applied. The structures were solved by direct methods (SHELXS-86) and refined by the full-matrix least-squares method based on F^2 (SHELXL-93). All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. CCDC-174589 (**3**) and -174590 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the Fonds zur Förderung wissenschaftlicher Forschung (FWF) for the support of this work.

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Received March 7, 2002
[I02122]