Monodentate σ-N and Bidentate σ-N,σ-N′ Coordination of 1,1-Bis((*N*-*p*-tolylimino)diphenylphosphoranyl)ethane, $CHCH_3(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)_2$, to Platinum(II)

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The new ligand, 1,1-*b*is((*N*-*p*-tolyl*i*mino)diphenyl*p*hosphoranyl)*e*thane (1,1-BIPE), **1**, has been synthesized by means of a Staudinger reaction of 1,1-bis(diphenylphosphino)ethane (1,1-dppe) with 2 equiv of *p*-tolylazide. Bridge-splitting reactions of $Pt_2Cl_4(PR_3)_2$ with **1** readily afforded σ-N monodentate complexes, $[PtCl_2(PR_3)\{1,1\text{-BIPE-}\sigma N\}]$ (**2a**, $PR_3 = PEt_3$; **2b**, $PR_3 = PMe_2Ph$). Conversion of **2** into the six-membered platinacycle $[PtCl(PR_3)\{1,1\text{-BIPE-}\sigma N,\sigma N'\}]^+[X]^-$ (**3**) (X = Cl, $PtCl_3(PR_3)$, BF_4) took place after prolonged stirring, its reaction rate being strongly dependent on the type of phosphine (>5 days for **2a** in the presence of $NaBF_4$, 1 h for **2b**) and the metal-to-ligand ratio. The compounds **1**, **2**, and **3** have been fully characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR and IR spectroscopy, elemental analysis, or FAB mass spectroscopy. The molecular structures of $CHCH_3(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)_2$ (**1**) and $[PtCl(PMe_2Ph)\{(N(pTol){=}PPh_2)_2CHCH_3\}]^+[Cl]^-$ (**3b**) have been determined by X-ray crystallography. Crystal data for **1**: space group $P2_1/c$ with $a = 8.9591(5)$ Å, $b = 19.1961(12)$ Å, $c = 21.9740(9)$ Å, $\beta = 105.069(4)°$, $V = 3649.1(3)$ Å^3, and $Z = 4$. The structure refinement converged to $R = 0.080$ and $R_w = 0.109$. Crystal data for **3b**: monoclinic, space group $P2_1/c$ with $a = 12.4021(7)$ Å, $b = 16.9705(11)$ Å, $c = 23.760(2)$ Å, $\beta = 109.544(5)°$, $V = 4712.7(5)$ Å^3, and $Z = 4$. The structure refinement converged to R1 = 0.057, wR2 = 0.122. Variable temperature NMR spectroscopy has revealed that complexes **3** exclusively adopt a twisted boat conformation with the methyl group in equatorial position at low temperature, in agreement with the solid state structure of **3b** as determined by X-ray crystallography. Boat-to-boat inversion is assumed to take place at temperatures above 293 K. Furthermore, for **3**, hindered rotation of one of the *p*-tolyl substituents on nitrogen has been established at low temperatures.

Introduction

In connection with recent investigations on the coordination behavior of bis(iminophosphoranyl)methanes (BIPM), $H_2C(PPh_2{=}NR')_2$ toward the transition metals tungsten(VII),[1] osmium(VIII),[2] rhodium(I), and iridium(I),[3] we have extended this line of research to platinum(II) and palladium(II). Previous reports have shown that reactions of $NSiMe_3$-substituted BIPM ligand with WX_6 (X = Cl, F) and OsO_4 resulted in the formation of N,N′-coordinated six-membered metallacycles by splitting of the reactive N−Si bonds.[1,2] Reaction of N−aryl substituted BIPM with halide bridged Rh and Ir dimers, however, gave mixtures of two products, in which the ligand acts as a σ-N, σ-N′ chelate in one isomer and as a N,C chelate in the other.[3] Interestingly, similar reactions of BIPM (R′ = aryl) with $Pt_2X_4(PR_3)_2$ (X = Cl, Br; $PR_3 = PEt_3$, PMe_2Ph) proceeded much more selectively, since stable N,C chelated four-membered platinacycles (Scheme 1, **D**) were formed exclusively.[4]

Monitoring the reactions by NMR revealed that the initial step in the formation of the N,C chelates involves a nucleophilic attack by a nitrogen donor atom, giving an intermediate $[PtX_2(PR_3)\{N(R'){=}PPh_2CH_2PPh_2{=}N(R')\}]$ (**A**), containing σ-N monodentate BIPM (Scheme 1),[4] which reacts further by a 1,3-H-shift from the methylene carbon atom in **A** to the noncoordinated nitrogen atom, giving intermediate **B** (not observed) and subsequent fast dissociation of the ligand isomer (C). The final product (**D**) is formed by recombination of **C** with $PtX_3(PR_3)^-$.[4]

The selectivity of the reactions of BIPM with Pt(II), in contrast to its reactions with Rh(I) and Ir(I),[3] has been explained in terms of an increased polarity of the σ-N-coordinated N=P group in **A**, resulting in an increased acidity of the methylene hydrogen atoms, which may shift easily to the noncoordinated nitrogen atom.[4] Also the fact that Pt−C bond formations are thermodynamically more favorable than Pt−N bonds probably results in a preference for N,C chelation of BIPM to Pt. This has been confirmed by a reaction where twofold excess of the Pt(II) precursor was used, which afforded a relatively stable six-membered platinacycle by N,N′ coordination of BIPM which finally converted into the thermodynamically more stable four-membered platinacycle.[4]

We have been looking for ways to obtain (if possible exclusively) platinum(II) complexes containing a N,N′ chelating bis(iminophosphoranyl)alkane fragment. Hence, in order to retard the H-shift and subsequent C coordination we have modified the bis(iminophosphoranyl)methane ligand by substituting the bridging CH_2 group by a $CHCH_3$ group. This

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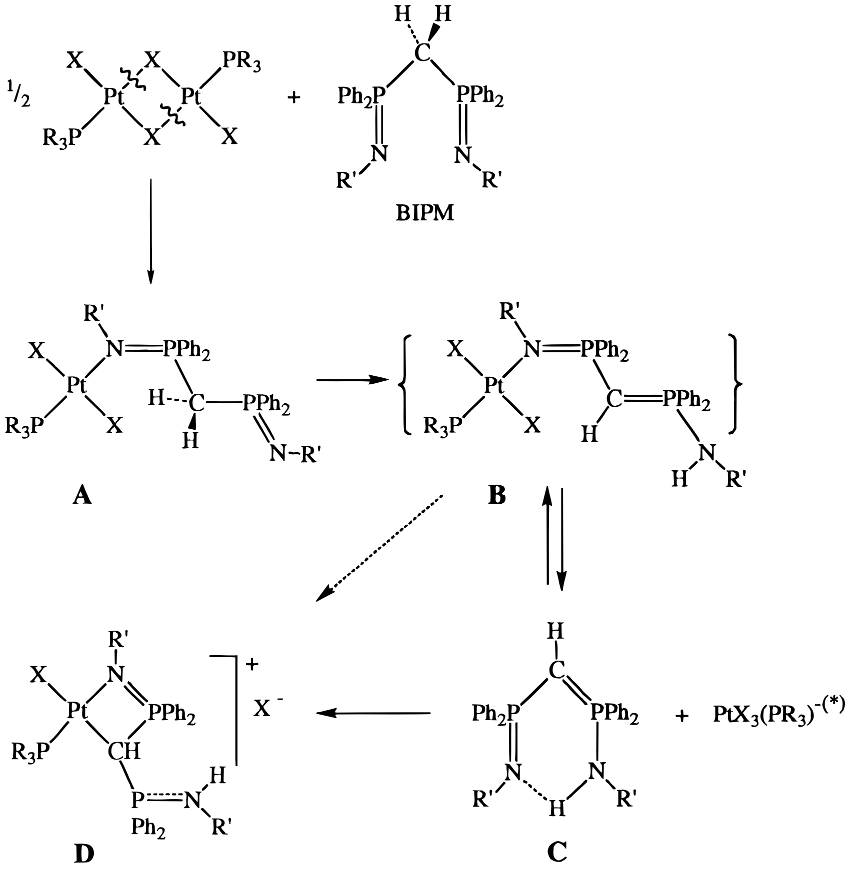
Scheme 1. Reaction Sequence in the Formation of Four-Membered Platinacycles (**D**), Containing N,C-Coordinated BIPM[a]



[a] An asterisk denotes recombination of dissociation fragment $PtX_2(PR_3)$ with X^- of **D**).

modification will introduce more steric hindrance around the central carbon atom and hence favor stabilization of σ-N,σ-N′-coordinated species, and at the same time the inductive electronic effect of the methyl substituent in the $CHCH_3$ moiety will result in a decreased acidity of the methine proton.

In this paper we report the synthesis of 1,1-*b*is(*N*-*p*-tolyl*i*mino)diphenyl*p*hosphoranyl)*e*thane (1,1-BIPE, **1**), $CHCH_3(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_4)_2$, and its reactions with $Pt_2Cl_4(PR_3)_2$.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques at 20 °C, unless stated otherwise. The solvents were dried and distilled prior to use. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on Bruker AC 100, AMX 300, and WH 500[5] instruments (operating at 100.13/300.13/500.14 MHz and 40.53/121.50/202.45 MHz, respectively) using $SiMe_4$ and 85% H_3PO_4, respectively, as the external standards, with positive values (in ppm) to high frequency of the standard in all cases. $^{13}C\{^1H\}$NMR data were obtained on a Bruker AMX 300 instrument (operating at 75.48 MHz) using $SiMe_4$ as the external standard. Elemental analysis were carried out by Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Infrared spectra, using KBr pellets and Nujol mulls, were recorded on a Perkin-Elmer 283 or a Mattson Galaxy 3000 spectrophotometer.[5] FAB Mass spectroscopy was carried out by the Institute for Mass Spectroscopy at the University of Amsterdam. The compounds 1,1-bis(diphenylphosphino)ethane (1,1-dppe),[6] *p*-tolylazide[7] and $Pt_2Cl_4(PR_3)_2$ (PR_3= PEt_3, PMe_2Ph)[8] were synthesized according to literature procedures. Data relating to the characterization of the complexes are given in Tables 4−6 under results, and in the preparative descriptions below.

Synthesis of 1,1-Bis((*N*-*p*-tolylimino)diphenylphosphoranyl)ethane (1,1-BIPE) (1). To a stirred solution of 713 mg (1.79 mmol) of 1,1-dppe in 15 mL of toluene was added dropwise a solution of 480 mg (3.60 mmol) of *p*-tolylazide in 5 mL of toluene at 60 °C. After 4 h at 60 °C, during which N_2 gas evolved, the solvent was removed in vacuo. To the brownish residue 60 mL of pentane was added, which resulted in precipitation of a white solid after 1 h of stirring. The precipitate was washed with pentane (2 × 20 mL) and dried in vacuo, yielding 1.10 g (1.8 mmol, 99%) of a white powder **1**. IR (Nujol): $\nu(P{=}N) = 1341\ cm^{-1}$. Anal. Calcd. for $C_{40}H_{38}N_2P_2$: C, 78.93; H, 6.30; N, 4.60; P, 10.18. Found: C, 78.99; H, 6.34; N, 4.53; P, 10.23. Crystals (colorless needles) suitable for X-ray crystal structure determination were obtained by diffusion of pentane into a toluene solution of **1** after 4 days at 20 °C and 1 atm.

Synthesis of [PtCl$_2$(PEt$_3$){1,1-BIPE-σ*N*}] (2a). To a solution of 37.6 mg (0.05 mmol) of $Pt_2Cl_4(PEt_3)_2$ in 10 mL of CH_2Cl_2 was added 59.6 mg (0.10 mmol) of **1**. After 10 min of stirring at 20 °C, the yellow solution was evaporated to dryness. The residue was washed with cold pentane (0 °C, 2 × 20 mL) and dried in vacuo, yielding 95 mg (98%) of a yellow powder, **2a**. IR(KBr): $\nu(P{=}N) = 1335$ (br) and 1235 cm^{-1} (m). Anal. Calcd. for $C_{46}H_{53}N_2P_3Cl_2Pt$: C, 55.65; H, 5.38; N, 2.82; P, 9.36. Found: C, 55.36; H, 5.48; N, 2.73; P, 9.30. FAB mass found: $m/z = 957$ (M − Cl) (M, calcd for $C_{46}H_{53}N_2P_3Cl_2Pt$: 992.9).

[PtCl$_2$(PMe$_2$Ph){1,1-BIPE-σ*N*}] (2b) was synthesized in the same way, yielding 99% **2b** after 10 min of stirring in CH_2Cl_2 at 20 °C and evaporation to dryness. IR (KBr): $\nu(P{=}N) = 1334$ (br) and 1236 cm^{-1} (m). FAB mass found: $m/z = 977$ (M − Cl) (M, calcd for $C_{48}H_{49}N_2P_3Cl_2Pt$: 1012.9).

Synthesis of [PtCl(PEt$_3$){1,1-BIPE-σ*N*,σ*N′*}]$^+$[BF$_4$]$^-$ (3a). To a solution of 395.7 mg (0.65 mmol) of **1** and 249.7 mg (0.33 mmol) of $Pt_2Cl_4(PEt_3)_2$ in 20 mL of CH_2Cl_2 was added a 10-fold excess of $NaBF_4$, and the mixture was stirred for 24 h at 20 °C. The product, obtained by filtration and subsequent evaporation of the solvent, contained

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[5] Located at the University of Missouri—Columbia.

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approximately 23% **3a** and 77% **2a**. Continued stirring of this mixture in CH_2Cl_2 with freshly added $NaBF_4$ (ca. 100 mg) gave 77% **3a** and 23% **2a** and some decomposition after 5 days. Compound **2a** was completely washed out with Et_2O (2 × 20 mL), giving a residue consisting of **3a** and some decomposition. Recrystallization out of CH_2Cl_2/Et_2O (1:3) at 20 °C gave 155 mg of pure **3a** (23%). IR (KBr): $\nu(P{=}N) = 1247$ and $1225\ cm^{-1}$. Anal. Calcd. for $C_{46}H_{53}BN_2F_4P_3ClPt$: C, 52.91; H, 5.12; N, 2.68; P, 8.90. Found: C, 52.75; H, 5.19; N, 2.75; P, 8.95. FAB mass found: $m/z = 957.3$ (M^+, calcd for $C_{46}H_{53}N_2P_3ClPt$: 957.4).

[PtCl(PEt$_3$){1,1-BIPE-*σN,σN′*}]$^+$[PtCl$_3$(PEt$_3$)]$^-$ (3a′). To a solution of 106.2 mg (0.17 mmol) of **1** in 15 mL of CH_2Cl_2 was added 134.0 mg (0.17 mmol) of $Pt_2Cl_4(PEt_3)_2$, and the mixture was stirred for 18 h. Evaporation of the solvent resulted in a yellow powder, 240 mg (0.35 mmol, 99.9%) of **3a′**. IR (Nujol): $\nu(P{=}N) = 1248$ and $1219\ cm^{-1}$. FAB mass found: $m/z = 957.3$ (M^+, calcd for $C_{46}H_{53}N_2P_3ClPt$: 957.4).

[PtCl(PMe$_2$Ph){1,1-BIPE-*σN,σN′*}]$^+$[Cl]$^-$ (3b). To a solution of 179.1 mg (0.29 mmol) of **1** in 10 mL of CH_2Cl_2 was added 118.9 mg (0.15 mmol) of $Pt_2Cl_4(PMe_2Ph)_2$, and the mixture was stirred for 1 h at 20 °C. The product was obtained by evaporation of the solvent, yielding 294 mg (0.29 mmol, 99%) of **3b**. IR (KBr): $\nu(P{=}N) = 1251$ and $1230\ cm^{-1}$. FAB mass found: $m/z = 977$ (M^+, calcd for $C_{48}H_{49}N_2P_3ClPt$: 977.4). Crystals suitable for X-ray crystal structure determination were obtained by diffusion of pentane into a THF/CH_2Cl_2 solution of **3b** at 20 °C at 1 atm for 7 days.

Alternative Method. Stirring a mixture of 90 mg (0.15 mmol) of **1** and 61 mg (0.07 mmol) of $Pt_2Cl_4(PMe_2Ph)_2$ in 10 mL of THF at 70 °C for 4.5 h gave the same product **3b** after workup with pentane, yielding 111 mg (73%).

[PtCl(PMe$_2$Ph){1,1-BIPE-*σN,σN′*}]$^+$[PtCl$_3$(PMe$_2$Ph)]$^-$ (3b′) was synthesized from 172.4 mg (0.25 mmol) of 1,1-BIPE (**1**) and 229.4 mg (0.25 mmol) of $Pt_2Cl_4(PMe_2Ph)_2$ (M:L = 1:1) in 20 mL of CH_2Cl_2. The solution was stirred for 1 h and evaporated to 5 mL. Addition of 40 mL of pentane resulted in the precipitation of **3b′**, which was washed with pentane (20 mL) and dried in vacuo. Yield: 344 mg (87%). IR (KBr): $\nu(P{=}N) = 1250\ cm^{-1}$ (br). Anal. Calcd.for $C_{56}H_{60}N_2P_4\ Cl_4Pt_2$: C, 47.47; H, 4.72; N, 1.98; P, 8.72. Found: C, 47.28; H, 4.33; N, 1.92; P, 8.61.

Variable temperature NMR studies were carried out on solutions of 0.035 mmol of **3a** in 0.5 mL of $CDCl_3$ at 233−330 K or of 0.035 mmol of **3b** in 0.4 mL of CD_2Cl_2 at 233−293 K. Subsequently, 2.8 μL (0.035 mmol) of pyridine was added to the $CDCl_3$ solution of **3a** at 330 K, which gave no reaction and no exchange processes occurred.

X-ray Crystal Structure Determinations of 1 and 3b. Crystal data and experimental procedures on both crystal structures are collected in Table 1.

Table 1. Crystallographic Data for **1**·Toluene and **3b**·THF

	1	**3b**
formula	$C_{40}H_{38}N_2P_2{\cdot}0.5C_7H_8$	$C_{48}H_{49}Cl_2N_2P_3Pt{\cdot}C_4H_8O$
mw	654.77	1084.94
space group	$P2_1/c$	$P2_1/c$
cryst syst	monoclinic	monoclinic
a, Å	8.9591(5)	12.4021(7)
b, Å	19.1961(12)	16.9705(11)
c, Å	21.9740(9)	23.760(2)
β, deg	105.069(4)	109.544(5)
V, Å^3	3649.1(3)	4712.6(6)
Z	4	4
D_{calcd}, g cm^{-3}	1.192	1.529
$F(000)$	1388	2192
μ, cm^{-1}	13.1 (Cu Kα)	32.6 (Mo Kα)
data set	−11:7, 0:24, −27:27	−10:16, 0:22, −30:28
R^a	0.080 [for 5234$F_o > 5.0\sigma(F_o)$]	0.057 [for 6850 $F_o > 4.0\sigma(F_o)$]
$R_w{}^b$	0.109	
wR2^c		0.1215
S	1.28	1.00

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(||F_o| - |F_c||)^2]/[\sum[w(F_o{}^2)]]^{1/2}$. ^{c} $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

Compound 1. Transparent colorless crystals, 0.3 × 0.3 × 0.6 mm, suitable for X-ray structure determination, were mounted on a Lindemann-glass capillary and placed on an Enraf-Nonius CAD4-F diffractometer at 298 K. Data were collected in $\omega/2\theta$ mode, λ(Cu Kα) = 1.54184 Å (Ni-filtered), with θ in the range 2.1−75.0°. Scan angle was $\Delta\omega = 0.55 + 0.14 \tan\theta°$. Unit cell dimensions and standard deviations were obtained by least-squares fit (SET4)[9] of the setting angles of 25 reflections in the range $18.4° < \theta < 23.7°$. Reduced-cell calculations did not indicate higher lattice symmetry.[10] Three standard reflections were monitored periodically ($\bar{2}14$, $\bar{1}2\bar{4}$, $\bar{2}\bar{1}4$) and showed approximately 14% decay during the 91 h of data collection. The data were scaled accordingly. Intensity data were corrected for Lorentz, polarization, but not for absorption, and averaged into a unique set of reflections. Total data of 11 303 reflections were collected of which 7503 were independent ($R_{int} = 0.0778$). The structure was solved by direct methods (SHELXS86).[11] Refinement on F was carried out by full-matrix least-squares techniques (SHELX76);[12] final R value 0.080, $R_w = 0.109$, $w = 1/\{\sigma^2(F) + 0.000248F^2\}$, $S = 1.28$ (based on the variance), for 404 parameters and 5234 reflections with $F_o > 5\sigma(F_o)$. Hydrogen atoms were included in the refinement on calculated positions (C−H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with one common isotropic displacement parameter. Weights were introduced in the final refinement cycles. The unit cell contains two toluene molecules disordered over the inversion centers. No discrete atom model could be fitted. The BYPASS procedure[13] was used to take this electron density into account. The application of BYPASS made refinement more stable. The solvent accessible areas have a total volume of 550 Å^3. A total density of 100 electrons was counted in this area, consistent with two toluene molecules. The final difference Fourier showed no residual density outside −0.78 and +0.89 e Å^{-3}. Neutral atom scattering factors were taken from Cromer and Mann,[14] with anomalous dispersion corrections taken from Cromer and Liberman.[15]

Compound 3b. Yellowish crystals of **3b**, 0.3 × 0.3 × 0.05 mm, were mounted on a Lindemann-glass capillary and placed on an Enraf-Nonius CAD4-T diffractometer on rotating anode in the cold dinitrogen stream (150 K). Data were collected in $\omega/2\theta$ mode, λ(MoKα) = 0.71073 Å (monochromator), with θ in the range 1.5−27.5°. Scan angle was $\Delta\omega = 0.66 + 0.35 \tan\theta°$. Unit cell dimensions and standard deviations were obtained by least-squares fit (SET4)[9] of the setting angles of 25 reflections in the range $11.6° < \theta < 14.0°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[10] Three standard reflections were monitored periodically ($2\bar{4}\bar{2}$, $2\bar{2}4$, $1\bar{5}\bar{2}$) and showed approximately 4% variation in intensity during the 44 h of data collection. The data were scaled accordingly. Intensity data were corrected for Lorentz, polarization, and absorption effects (an empirical absorption/extinction correction was applied (DIFABS[16] correction range 0.725−1.00)) and averaged into a unique set of reflections. Total data of 15 022 reflections were collected of which 10 778 were independent ($R_{int} = 0.0382$).

The structure was solved by automatic Patterson methods and subsequent difference Fourier synthesis (DIRDIF-92).[17] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93);[18] final R1 value 0.057 for 555 parameters and 6850 reflections with $I > 2.0\sigma(I)$, wR2 = 0.122 for all 10 778 reflections, $S = 0.996$ and $w = 1/\{\sigma^2(F_o) + 0.0514P^2\}$ where $P = (\mathrm{Max}(F_o{}^2,0) + 2F_c{}^2)/3$. All

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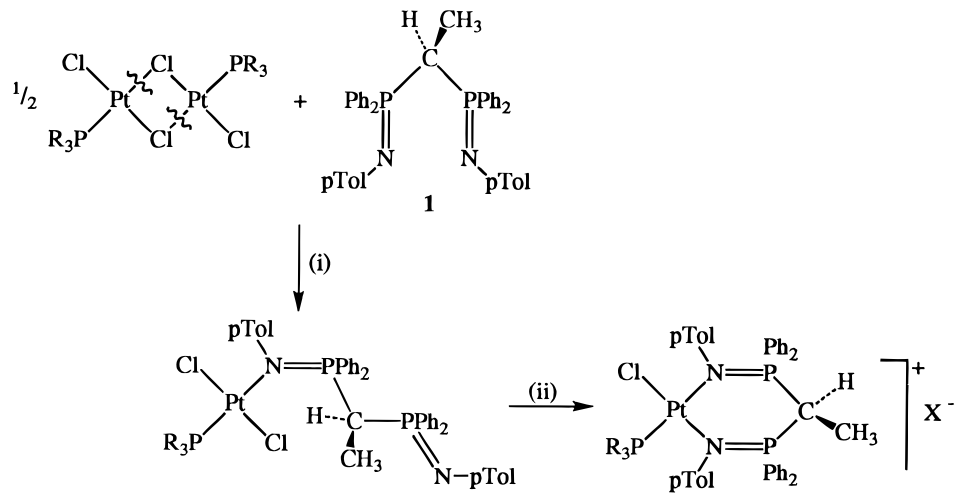
Scheme 2. Complex Formation of **2** and **3**[a]



2a: $PR_3 = PEt_3$
2b: $PR_3 = PMe_2Ph$

3a: $PR_3 = PEt_3$; X = BF_4
3a': $PR_3 = PEt_3$; X = $PtCl_3(PEt_3)$
3b: $PR_3 = PMe_2Ph$; X = Cl
3b': $PR_3 = PMe_2Ph$; X = $PtCl_3(PMe_2Ph)$

[a] Conditions (20 °C): (i) 5 min in CH_2Cl_2; (ii) +$NaBF_4$, more than 5 days in CH_2Cl_2 (**3a**); + 0.5 equiv of $Pt_2Cl_4(PEt_3)_2$, 18 h in CH_2Cl_2 (**3a′**); 1 h in CH_2Cl_2 (**3b**); + 0.5 equiv of $Pt_2Cl_4(PMe_2Ph)_2$ (**3b′**).

reflections were considered observed during refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were included in the refinement cycle at calculated positions, riding on their carrier atoms. The hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.5 (methyl-H) or 1.2 times (all other H's) the value of the equivalent isotropic thermal parameter of the carrier atoms. Weights were introduced in the final refinement cycles. A final difference Fourier showed no residual density outside −0.78 and +2.03 e Å^{-3}. Neutral scattering factors and anomalous dispersion corrections were taken from ref 19.

All geometrical calculations and the ORTEP illustrations were performed with PLATON.[20] Computing was conducted on a DEC-station 5000 cluster.

Results and Discussion

Synthesis of 1,1-BIPE (1). A Staudinger reaction (eq 1), similar as reported previously for the synthesis of analogous bis(iminophosphoranyl)methanes (BIPM),[21,22] was used to synthesize the new 1,1-bis((*N*-*p*-tolylimino)diphenylphosphoranyl)ethane ligand (1,1-BIPE, **1**), containing a methyl substituent on the carbon atom bridging the two P=N moieties.

$$\mathrm{Ph_2PCH(Me)PPh_2} + 2p\text{-tolyl}-\mathrm{N_3} \rightarrow$$
$$p\text{-Tol}-\mathrm{N{=}Ph_2PCH(Me)PPh_2{=}N}-p\text{-Tol} + 2\mathrm{N_2} \quad (1)$$
$$\mathbf{1}$$

Compound **1** was obtained in quantitative yield. Other methods, through deprotonation of BIPM by NaH,[22] and subsequent reaction with 1 equiv MeI, as has been reported earlier for the synthesis of $CHMe(PR_2{=}S)_2$,[23] did not result in methylation of the bridging carbon, but of one of the terminal N atoms instead. 1,1-BIPE is quite soluble in THF, benzene, toluene, chloroform, and dichloromethane, slightly soluble in Et_2O, but not soluble in apolar solvents like pentane. In the solid state, **1** is thermally stable for at least 1 year when stored under N_2 at 20 °C, but decomposition occurs within a couple of weeks when it is exposed to moist air. The 1,1-BIPE ligand (**1**) has been fully characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$-NMR and infrared spectroscopy, elemental analysis, and an X-ray crystal structure determination.

Formation of Complexes 2 and 3. 1,1-BIPE (**1**) reacted rapidly and quantitatively with the halide-bridged platinum dimers $Pt_2Cl_4(PR_3)_2$ ($PR_3 = PEt_3$, PMe_2Ph) in dichloromethane at 20 °C to give mononuclear platinum(II) complexes **2a** or **2b**, in which 1,1-BIPE is σ-N monodentate coordinated (Scheme 2, eq i).

Prolonged stirring of the reaction mixture eventually resulted in the selective formation of cationic six-membered platinacycles **3a**,**3b** or **3a′**,**3b′**, by σ-N,σ-N′ coordination of 1,1-BIPE (Scheme 2, eq ii), irrespective of whether a metal-to-ligand (M:L) ratio of 1:1 or 2:1 is used. The rate of the conversion reaction of **2** into **3** was found to depend strongly on the type of phosphine and the M:L ratio (vide infra).

Complexes **2** and **3** are air-stable yellow solids, readily soluble in THF, CH_2Cl_2, $CHCl_3$, toluene, benzene, and Et_2O and moderately soluble in pentane at 20 °C, but only slightly soluble in pentane when cooled down. In solution, the complexes **2** and **3** decompose in air, by reaction with H_2O and CO_2. The platinum complexes **2a,b** and **3a,b,a′,b′** have been fully characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$NMR, infrared, and FAB mass spectroscopy, elemental analysis, and an X-ray crystal structure determination of **3b**.

Complexes **2a** and **2b**, $[PtCl_2(PR_3)\{$1,1-BIPE-σ*N*$\}]$, represent the first isolable complexes in which the potentially bi- or even tridentate bis(phosphinimine) ligand of the type $R'N{=}PR_2\text{-}CHR''PR_2{=}NR'$ is monodentate coordinated. Recently, the formation of an analogous thermally less stable Pt complex, $[PtCl_2(PEt_3)\{$BIPM-σ*N*$\}]$ (**A**, Scheme 1), containing a σ-N monodentate coordinated bis((*N*-*p*-tolylimino)diphenylphosphoranyl)methane ligand (BIPM), has been observed by NMR.[4] Although many coordination complexes containing related

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ligands of the type $X{=}PR_2CHR'PR_2{=}Y$, with X,Y = S, O, and Se; R = alkyl, aryl; and R′ = H, Me, and $PR_2{=}X$ are known,[24−29] to our knowledge only two similar types of stable monodentate coordinated species have been reported, i.e. $(C_6F_5)_3Au\{S{=}PPh_2CH_2PPh_2{=}S\}$[29a] and $[Fe(C_5H_5)(CO)_2\text{-}\{X{=}PPh_2(CH_2)_nPPh_2{=}X\}]BF_4$ (X = S, Se; $n = 1{-}3$).[29b] The isolation of the complexes **2a,b** has demonstrated that the σ-N-coordinated Pt(1,1-BIPE) complex is thermally more stable than the σ-N-coordinated Pt−BIPM complex, which is clearly caused by the methyl substituent on the central carbon atom in 1,1-BIPE.

Complex **2a** ($PR_3 = PEt_3$) is stable in solution; no further reaction is observed within 24 h at 20 °C. Treatment of a solution of **2a** with $NaBF_4$ resulted in only 23% conversion into the six-membered platinacycle **3a** after 24 h. In contrast, complex **2b** ($PR_3 = PMe_2Ph$) converts completely within 1 h (in CH_2Cl_2 at 20 °C) into complex **3b** (Scheme 2, eq ii). The much slower conversion of **2a** into **3a** as compared to the fast conversion of **2b** into **3b** might be explained by the slightly larger steric hindrance exerted by the triethylphosphine (cone angle = 132°) relative to the dimethylphenylphosphine (cone angle = 122°),[30] which slows down the substitution of chloride *cis* to PEt_3 via intramolecular attack of the second N atom.

Note that the large difference in conversion rate between **2a** and **2b** is true for *trans* complexes only. A *cis* geometry for **2** (PR_3 *trans* to the Pt−Cl bond) is unlikely because this would have resulted in a faster dissociation of the Pt−Cl bond in **2a** relative to **2b**, as the *trans* effect of $PEt_3 > PMe_2Ph$.

When the metal-to-ligand (M:L) ratio of the reaction is changed to 2:1, the ionic dinuclear complexes $[PtCl(PR_3)\text{-}\{(N(pTol){=}PPh_2)_2CHCH_3\text{-}\sigma N,\sigma N'\}][PtCl_3(PR_3)]$ (**3a′**: $PR_3 = PEt_3$) and (**3b′**: $PR_3 = PMe_2Ph$) are formed. Clearly, the reactions of 1,1-BIPE (**1**) with $Pt_2Cl_4(PR_3)_2$ result in the selective formation of six-membered platinacycles **3a,b** or **3a′,b′** as the final products, independent of whether a 1:1 or a 2:1 (M:L) ratio is used. This is in sharp contrast to an earlier report which showed that the reactions of BIPM with $Pt_2Cl_4(PR_3)_2$ resulted in the exclusive formation of four-membered platinacycles by N,C coordination of BIPM.[4] In that case, N,N′ coordination of BIPM only took place in an intermediate complex formed in a 2:1 reaction, which reacted further to give a N,C-coordinated product.[4] We have not found such a conversion for the six-membered platinacycles **3**, not even after reflux, which indicates that N,C coordination of 1,1-BIPE is disfavored by the presence of a methyl substituent on the central carbon atom. Previous investigations have shown that the N,C coordination of BIPM occurs concomitantly with, or is preceded by, a H-shift (Scheme 1), which obviously is not taking place for the complexes **2a,b**. This finding is in keeping with the less acidic character of the methine H atom in the σ-N-coordinated 1,1-BIPE ligand as compared to the methylene H atoms in the Pt−BIPM complex (**A**, Scheme 1), due to the inductive effect of the methyl group on the central carbon. The decreased acidity of free 1,1-BIPE has also been established by its diminished reactivity toward NaH in comparison to BIPM.[31] Furthermore, the steric effect exerted by the Me substituent will disfavor the formation of a four-membered Pt−N−P−C metallacycle.

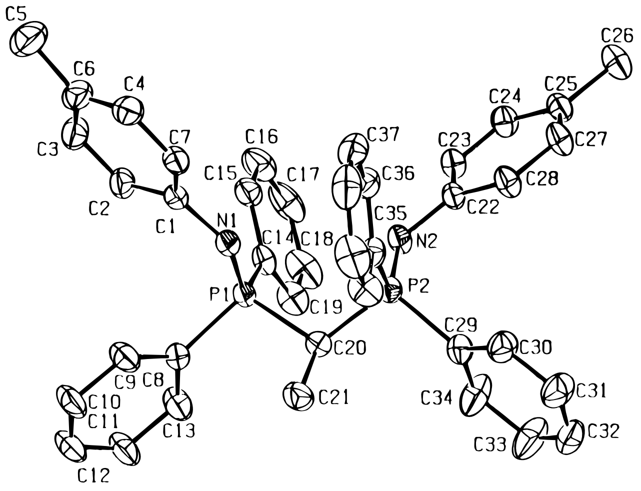

Figure 1. ORTEP 30% probability plot of 1 (PLATON).[20] Hydrogens are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1** (Esd's in Parentheses)

Bond Lengths			
P(1)−N(1)	1.559(3)	P(2)−N(2)	1.553(3)
P(1)−C(8)	1.820(4)	P(2)−C(29)	1.820(4)
P(1)−C(14)	1.814(4)	P(2)−C(35)	1.819(4)
P(1)−C(20)	1.827(3)	P(2)−C(20)	1.835(4)
N(1)−C(1)	1.380(4)	N(2)−C(22)	1.393(5)
C(20)−C(21)	1.529(5)		
Bond Angles			
P(1)−N(1)−C(1)	133.4(2)	P(2)−N(2)−C(22)	130.5(2)
N(1)−P(1)−C(8)	113.54(16)	N(2)−P(2)−C(29)	115.63(16)
N(1)−P(1)−C(14)	117.95(16)	N(2)−P(2)−C(35)	116.17(16)
N(1)−P(1)−C(20)	106.57(15)	N(2)−P(2)−C(20)	105.22(15)
C(8)−P(1)−C(14)	105.14(16)	C(29)−P(2)−C(35)	105.01(16)
C(8)−P(1)−C(20)	105.22(16)	C(20)−P(2)−C(29)	104.42(16)
C(14)−P(1)−C(20)	107.61(16)	C(20)−P(2)−C(35)	109.75(16)
P(1)−C(20)−C(21)	111.0(2)	P(1)−C(20)−P(2)	112.39(19)
P(2)−C(20)−C(21)	113.9(2)		
Torsion Angles			
N(1)−P(1)−C(20)−P(2)	−53.8(2)	P(1)−C(20)−P(2)−N(2)	−50.2(2)
N(1)−P(1)−C(20)−C(21)	75.1(3)	C(21)−C(20)−P(2)−N(2)	−177.5(2)
C(1)−N(1)−P(1)−C(20)	−174.5(3)	C(20)−P(2)−N(2)−C(22)	−166.3(3)

X-ray Crystal Structure of $CHCH_3(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)_2$ (1). The molecular structure of **1** and the adopted numbering scheme are shown in Figure 1. Selected bond distances and angles are listed in Table 2. The unit cell contains four molecules of **1** and two molecules of toluene, which was used as the solvent for crystallization. Compound **1** consists of two enantiotopic (*p*-tolylimino)diphenylphosphoranyl units attached to a prochiral ethane-1,1-diyl moiety. The P−N bond lengths (1.559(3) and 1.553(3) Å) are slightly shorter than found for the related bis(iminophosphoranyl)methane (BIPM) compounds, i.e in $CH_2(PR_2{=}NC_6H_4\text{-}4\text{-}R')_2$ (1.566−1.568 Å for R = Ph and R′ = Me, or 1.580(4) Å for R = Me and R′ = NO_2),[22] but are comparable with the P−N distances normally found for other phosphinimines, ranging from 1.50 to 1.64 Å.[32] The $P{-}C_{alkyl}$

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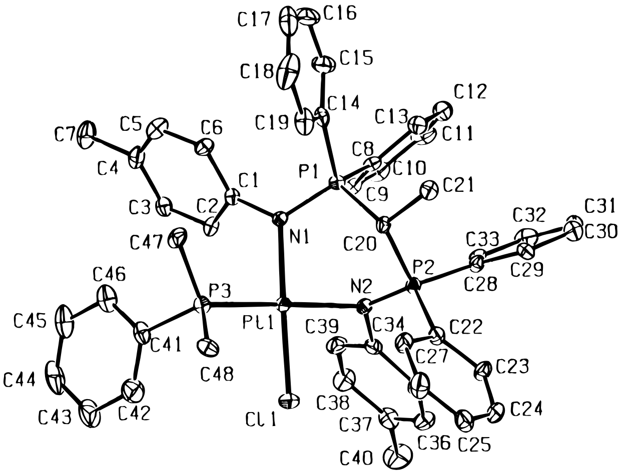

Figure 2. ORTEP 30% probability plot of **3b** (PLATON).[20] The hydrogen atoms, the Cl^- and the THF solvent are omitted.

bonds (1.835(4) and 1.827(3) Å) are almost similar to the ones reported for the analogous BIPM compounds (1.81−1.83 Å),[22] or the P−C single bonds in $(Me_3Si)_2C{=}PPh_2CH{=}PPh_2$-$CH(SiMe_3)_2$ (1.762(4) and 1.821(4) Å),[33] but are shorter than the average P−C bonds in, for instance, $[HC(PR_2{=}S)_3]$ (1.883 Å).[34] The geometry around the two phosphorus atoms and C(20) is approximately tetrahedral. The P(1)−C(20)−P(2) angle (112.39(19)°) is somewhat smaller than found for BIPM (115.2(1)°),[22] due to the steric effect of the methyl group on C(20).

The relatively short N−C bonds (1.380(4) Å and 1.393(5) Å), the wide P−N−C angles (133.4(2)° and 130.5(2)°) and the planarity of the P−N−aryl moiety (the least-squares planes through the *p*-tolyl substituents on the N atoms in **1** make angles of 0.94(17) and 7.82(17)° with the phosphinimine P═N bonds), are features that have been observed also for the related BIPM compounds[22] and other phosphinimines,[32a] indicating that electron delocalization takes place over the P═N bond, which is extended to the π-system of the *p*-tolyl groups on both N atoms in **1**.

X-ray Crystal Structure of $[PtCl(PMe_2Ph)\{(N(p\text{-Tol}){=}PPh_2)_2CHCH_3\}]Cl$ (3b). The atom labeling scheme and the structure of a single molecule of compound **3b** are shown in Figure 2. The unit cell also contains THF, but this has been omitted in the figure. Selected bond distances and angles are listed in Table 3. The planarity of the coordination geometry around platinum has been determined by a least-squares plane analysis through the atoms Pt, Cl(1), P(3), N(1), and N(2), which showed deviations from the plane of −0.021(1), −0.064(2), 0.063(2), −0.069(5), and 0.069(6) Å, respectively. The 1,1-bis(iminophosphoranyl)ethane ligand in **3b** is bidentate coordinated by both N atoms. The Pt−N bonds, 2.052(5) and 2.131(7) Å, differ considerably in length, with the longer bond *trans* to the PMe_2Ph ligand, in keeping with the larger *trans* influence of the phosphine. Such features have been previously observed for the Pt−S bonds in S,S′-coordinated $[PtCl(PEt_3)\{(S{=}PPh_2)_3C\}]$.[24] The Pt−Cl(1), 2.293(3) Å, and Pt−P(3), 2.234(2) Å, bond lengths in **3b** are in agreement with the distances normally found for such bonds *trans* to N σ-donor atoms.[4,31,35,36] The X-ray crystal structure clearly shows that the six-membered chelate ring Pt−N(1)−P(1)−C(20)−P(2)−N(2) has a boat conformation, with the H atom on C(20) in axial and the methyl group in equatorial position. A ring-puckering analysis resulted in a puckering amplitude (Q) of 1.187(5) Å, Θ of 82.2(2)°, and ϕ of 338.1(2)°, in agreement with the description as a twisted boat conformation.[37]

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **3b** (Esd's in Parentheses)

Around Pt			
Pt−P(3)	2.234(2)	Pt−N(1)	2.052(5)
Pt−Cl(1)	2.293(3)	Pt−N(2)	2.131(7)
Within Phosphine			
P(3)−C(41)	1.813(8)	P(3)−C(48)	1.819(7)
P(3)−C(47)	1.802(9)		
Within Ligand			
P(1)−N(1)	1.611(5)	P(2)−N(2)	1.618(6)
P(1)−C(8)	1.806(7)	P(2)−C(28)	1.795(7)
P(1)−C(14)	1.806(8)	P(2)−C(22)	1.826(7)
P(1)−C(20)	1.821(7)	P(2)−C(20)	1.825(8)
N(1)−C(1)	1.443(8)	N(2)−C(34)	1.433(10)
C(20)−C(21)	1.545(10)		
Around Pt			
Cl(1)−Pt−P(3)	88.71(8)	N(1)−Pt−N(2)	88.4(2)
Cl(1)−Pt−N(1)	176.63(15)	P(3)−Pt−N(2)	174.68(15)
Cl(1)−Pt−N(2)	89.12(18)	P(3)−Pt−N(1)	93.95(14)
Within Ligand			
Pt−N(1)−P(1)	118.8(3)	Pt−N(2)−P(2)	110.6(3)
Pt−N(1)−C(1)	118.1(4)	Pt−N(2)−C(34)	118.5(5)
P(1)−N(1)−C(1)	121.2(5)	P(2)−N(2)−C(34)	124.1(5)
N(1)−P(1)−C(8)	113.4(3)	N(2)−P(2)−C(28)	112.9(3)
N(1)−P(1)−C(14)	111.6(3)	N(2)−P(2)−C(22)	116.8(3)
N(1)−P(1)−C(20)	106.3(3)	N(2)−P(2)−C(20)	105.6(3)
C(8)−P(1)−C(14)	106.9(4)	C(28)−P(2)−C(22)	105.9(3)
C(8)−P(1)−C(20)	110.8(3)	C(28)−P(2)−C(20)	108.8(4)
C(14)−P(1)−C(20)	107.6(4)	C(22)−P(2)−C(20)	106.6(3)
P(1)−C(20)−C(21)	114.2(5)	P(1)−C(20)−P(2)	112.3(4)
P(2)−C(20)−C(21)	112.7(5)		

The bite angle N(1)−Pt−N(2), 88.4(2)°, is close to optimum and is similar to the N−Rh−N angle, 88.3(5)°, in N,N′-coordinated $[Rh(COD)\{(N(pTol){=}PPh_2)_2CH_2\}]^+$.[3] Within the N,N′ coordinated 1,1-BIPE ligand in **3b** both P═N bonds (1.611(5) and 1.618(6) Å) are elongated when compared to those in the free ligand **1** and represent normal bond distances for coordinated phosphinimine ligands.[3,4,31,38−40] Most features such as the P(1)−C(20)−P(2) angle of 112.3(4) Å, which is indicative for an approximate tetrahedral geometry around C(20), and the P−C(20) bond lengths are similar to those observed for **1**, $[Rh(COD)\{(N(pTol){=}PPh_2)_2CH_2\}]^+$,[3] and $[Rh(COD)\{(S{=}PPh_2)_2$-$CH_2\}]^+$.[25] The least-squares planes through the *p*-tolyl substituents on the N atoms in complex **3b** are not in plane with the phosphinimine P═N bonds, but make an angle of 44.2(3)° and 21.3(4)° to it, which is in contrast to the almost planarity of the P═N−tolyl moiety in the free ligand **1** (vide supra). Also, a significant lengthening of the N−C bonds has occurred, from

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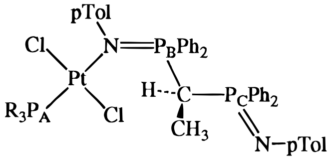
Table 4. ^{31}P NMR Data for the Compounds **1**−**3**[a]



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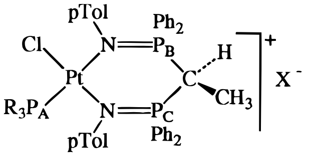


3

compd	solvent/temp, K	δ(P)	$\delta(P_A)$, $^1J(Pt,P_A)$	$\delta(P_B)$, $^2J(Pt,P_B)$	$\delta(P_C)$, $^2J(Pt,P_C)$	$\delta(P_D)$, $^1J(Pt,P_D)$	$^3J(P_A,P_B)$	$^2J(P_B,P_C)$
1	C_6D_6/293	6.6 (s)						
	CD_2Cl_2/293	8.2 (s)						
2a	CD_2Cl_2/293		1.0 (d), 3455	39.4 (dd), 61	6.1 (d)		13.1	4.5
2b	$CDCl_3$/293		−24.5 (d), 3490	40.3 (dd), 62	6.5 (d)		14.5	4.0
3a	CD_2Cl_2/285		1.2 (d), 3579	27.9 (dd)	31.4 (d), 60		3.6	12.4
3a′ [b]	$CDCl_3$/233		2.1 (s),[c] 3554	28.3 (dd)[c]	31.8 (d),[c] nr	2.8 (s), 3690	2.5	12.3
3b	CD_2Cl_2/253		−20.4 (s),[c] 3643	28.9 (d)[c]	32.3 (d),[c] 56			12.1
3b′	$CDCl_3$/253		−20.4 (s),[c] 3650	28.8 (d)[c]	32.4 (d),[c] nr	−21.4 (s), 3790		12.1

[a] Measured at 40.53 or 121.48 MHz, unless noted otherwise. All *J* values in Hz. Multiplicity labels and abbreviations: br = broad, s = singlet, d = doublet, dd = doublet of doublet, nr = not resolved. [b] Recorded at 202.5 MHz. [c] Slightly broadened at 293 K.

Table 5. ^1H NMR Data for **1**−**3**[a]

compd	δ(alkyl−P)[b]	$\delta(CH-CH_3)$[c]	δ(C*H*)[d]	$\delta(4\text{-}CH_3)$	$\delta(C_6H_4\text{-}N)$[e]	δ(Ph/Ar-*o*,*m*,*p*)
1[f]		1.42 (dt, 7.4, 16.7)	3.72 (m)	2.15 (s)	6.36 (d, 4H) 6.73 (d, 4H)	7.4 (m, 12H) 7.7, 7.9 (m, 8H)
2a[g]	1.15 (dt) 1.91 (m)	1.77 (dt, 7.0, 17.4)	5.57 (m)	2.01 (s) 2.23 (s)	6.58 (d, 2H) 6.69 (m, 4H) 6.87 (d, 2H)	6.9−8.1 (m, 18H) 9.18 (dd, 2H-ortho)
2b[h]	1.80 (d) 1.92 (d)	(o)	5.50 (m)	2.04 (s) 2.25 (s)	(o)	6.5−7.9 (m, 26H) 9.27 (m, 2H-ortho)
3a[f,i]	1.03 (dt) 1.44 (m)	1.34 (dt, 7.3, 17.8)	5.75 (tq, 7.3, 19.1)	2.23 (s) 2.25 (s)	6.94 (d, 2H)	7.0−8.3 (m, 22H)
233K	1.00 (dt) 1.36 (m)	1.28 (dt, 7.1, 17.9)	5.71 (tq, 7.1, 18.7)	2.19 (s) 2.21 (s)	6.16 (d, 1H) 6.69 (d, 1H) 6.92 (d, 2H)	7.28 (d, 1H) 8.46 (d, 1H) 7.0−8.3 (m, 22H)
3a′[g,j]	1.00 (dt) 1.53 (br)	1.45 (br)	5.8 (br)	2.21 (vs)	(o)	6.8−8.4 (m, 28H)
233K	1.01 (dt) 1.42 (m)	∼1.4 (o)	5.72 (m)	2.19 (s) 2.22 (s)	6.05 (d, 1H) 6.56 (d, 1H) 6.91 (d, 2H)	8.50 (d, 1H) 6.9−8.4 (m, 23H)
3b[f]	1.68 (d) 1.87 (d)	1.41 (br dt)	(o)	2.18 (s) 2.22 (s)	(o)	6.5−8.8 (m, 33H)
223K	1.58 (d) 1.84 (d)	1.32 (dt, 7.0, 18.2)	6.78 (tq, 7.0, 19.2)	2.15 (s) 2.17 (s)	5.66 (d, 1H) 6.33 (d, 1H) 8.55 (d, 1H)	6.8−8.8 (m, 30H)
3b′ [k]	1.8 (br)	1.47 (br)	nr	2.17 (s) 2.20 (s)	(o)	6.6−8.7 (m)
213K	1.64 (d) 1.70 (d)	1.37 (dt, 6.9, 18.2)	nr	2.16 (s) 2.17 (s)	5.47 (d, 1H) 6.28 (d, 1H) 6.65 (d, 1H)	8.56 (d, 1H) 6.8−8.6 (m, 34H)

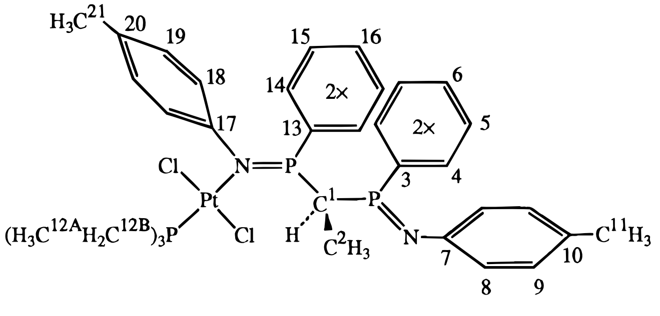
[a] Measured at 300.13 MHz in $CDCl_3$ at 293 K, unless stated otherwise. *J* values in Hz. Multiplicity labels and abbreviations: br = broad, s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, nr = not resolved, o = obscured by overlap, tq = triplet of quartet. [b] For Et_3P: $\delta(P-CH_2\text{-}CH_3)$ (dt) and $\delta(P-CH_2-CH_3)$ (m) are given successively, with coupling constants $^3J(H,H) = 7.5$ Hz, $^3J(P,H) = 15.0$ Hz, and $^2J(P,H)$ = nr. For Me_2PhP: $\delta(P-CH_3)$ (d) with $^2J(P,H) \approx 8.7-11.8$ Hz. [c] $^3J(H,H)$ and $^3J(P,H)$ are given in parentheses. [d] $^3J(H,H)$ and $^2J(P,H)$ are given in parentheses. [e] $^3J(H,H) \approx 6.3-8.3$ Hz. Remaining or obscured protons are included under next column: δ(Ar). [f] Recorded in CD_2Cl_2. [g] Measured at 500.13 MHz. [h] Measured at 100.13 MHz. [i] BF_4 salt. [j] δ(P−alkyl) for the counterion $[PtCl_3(PEt_3)]^-$ is found at 1.17 (dt) and 1.90 (dq). [k] δ(P−alkyl) for the counterion $[PtCl_3(PMe_2Ph)]^-$ is found at 1.81 (d, $^2J(P,H) = 11.9$ Hz).

1.386(5) Å (**1**) to 1.438(9) Å (**3b**) (averages), which is likely due to a shift of electron density from the P=N groups to the metal. These two effects might also be caused by severe steric interference between the aromatic groups on N and the PR_3 and Cl ligand on Pt. The chloride anion, Cl(2), has short nonbonding contact distances with H(19), H(20), H(27), and H(48C). Short intramolecular distances exist between the Pt(1) center and H(20), 2.844(7) Å, Pt···H(2), 2.916(7), Å, and Pt···H(39), 3.141(9) Å.

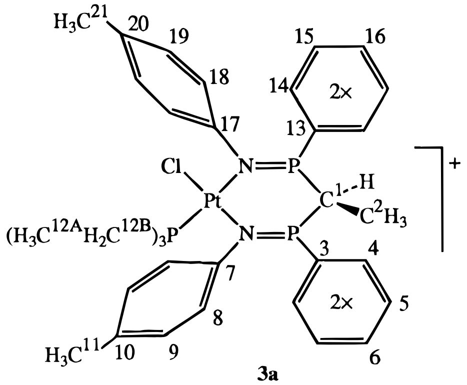
Spectroscopic Characterization of Compounds 1−3. $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR data for the compounds **1**, **2**, and **3** are given in Tables 4−6, respectively. Selected IR data (Nujol, KBr) are given in the experimental section.

^{31}P NMR Spectroscopy. 1,1-BIPE shows a ^{31}P resonance frequency at 7 ppm, which is higher than that of BIPM (0 ppm).[22] A similar trend has also been found for $CHCH_3(PPh_2{=}S)_2$ ($\delta(P) = 46.6$ ppm) relative to $CH_2(PPh_2{=}S)_2$ ($\delta(P) = 34.6$ ppm).[28d] The ^{31}P NMR of complexes **2**, where three resonances are found, shows strong similarities to the ^{31}P NMR data of the analogous σ-N coordinated Pt−BIPM complex reported earlier.[4] The low frequency doublet resonance with $^1J(Pt,P)$ of 3455−3490 Hz and $^3J(P_A,P_B)$ of ca. 14 Hz is unambiguously assigned to the phosphine P_AR_3 *trans* to the coordinated $N{=}P_B$ group. The doublet at about 6.3 pm lies at approximately the same ^{31}P frequency as the free ligand **1** and is therefore directly assigned to the noncoordinated $P_C{=}N$ group.

Table 6. ^{13}C NMR Data for **1**, **2a**, and **3a**[a]



2a



3a

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
1	36.8 (t, 75)	12.3 (s)	130.0 (d, 83) 131.2 (d, 92)	133.4 (vt, 4) 133.9 (vt, 4)[b]	128.9 (m)[b]	132.0 (s) 132.1 (s)	149.1 (s)	123.3 (m, 9)[b]	129.8 (s)	126.6 (s)	20.9 (s)
2a	35.7 (dd, 83, 70)	15.1 (m)	130.8 (d, 93) 131.3 (dd, 73, 7)	133.2 (m)	128.1 (d, 13) 128.7 (d, 13)	131.7 (d, 2) 132.3 (d, 2)	149.1 (d, 3)	123.7 (d, 17)	129.9 (s)	127.0 (s)	21.0 (s)
3a	34.2 (vt, 79)	11.2 (s)	118.1 (d, 87) 118.5 (dd, 88, 3)	135.4 (d, 9) 136.0 (d, 9)	130.8 (d, 12) 131.5 (d, 12)	135.1 (d)[e] 135.5 (d)[e]	145.8 (s)	123.2 (s) 128.6 (d, 12)	131.2 (s)[f]	134.1 (s)	21.4 (s)[g]

	C12A	C12B	C13	C14	C15	C16	C17	C18	C19	C20	C21
2a	15.0 (d, 39)	8.3 (d, 3)	123.5 (d, 87) 124.6 (dd, 90)[d]	135.8 (d, 10) 137.4 (d, 11)	129.0 (d, 12) 129.4 (d, 11)	132.5 (d, 3) 133.2 (d, 3)[c]	148.3 (s)	125.4 (d, 12)	128.5 (s)	128.8 (s)	20.7 (s)
3a	14.6 (d, 38)	8.8 (d, 3)	126.9 (dd, 84, 5) 127.4 (dd, 91, 5)	132.9 (d, 10) 133.3 (d, 10)	129.6 (d, 12) 129.7 (d, 12)	134.6 (d)[e] 134.9 (d)[e]	146.1 (s)	125.4 (d, 13)	129.9 (s)	132.1 (s)	21.4 (s)[g]

[a] Measured at 75.48 MHz in CD_2Cl_2 at 293 K (**1**, **2a**) or 233 K (**3a**). ^nJ(P,C) (in Hz) is given in parentheses. The atom labeling scheme is given above. [b] Second order multiplet: vt = virtual triplet, m = multiplet, virtual couplings are given where possible. [c] C16 obscured by C4. [d] ^3J(P,C) ≤ 2 Hz. [e] ^4J(P,C) was not resolved. [f] One C9 atom of the interacting *p*-tolyl group. The other C9 atom is obscured. [g] C11 and C21 are overlapping.

The high frequency resonance, a doublet of doublet at ca. 40 ppm, is attributed to P_B of the coordinated P_B=N group, based on the observed ^2J(Pt,P) coupling of 61−62 Hz, and mutual spin−spin couplings with P_A and P_C. The large high frequency shift of $\Delta\delta(P_B) \approx 33$ ppm falls within the range usually found for coordination complexes of phosphinimines.[3,4,31,32,38,39,41]

Complexes **3** show three (**3a**,**3b**) or four (**3a′**,**3b′**) ^{31}P resonances at 293 K. The signals at 32.5 ppm ($^2J(Pt,P_C)$ = 56−60 Hz) and 28.5 ppm ($^2J(Pt,P_B) \approx 0$ Hz) are unambiguously assigned to P_C and P_B, respectively, based on normal *trans* influence criteria. This is confirmed by the X-ray crystal structure of **3b**, which has pointed out that the Pt−N bond *trans* to Cl is indeed shorter than that *trans* to PR_3. Further proof for the *trans* P_A−Pt−N=P_B disposition is supplied by the Pt complexes **3a** and **3a′** (P_AR_3 = PEt_3), which show small $^3J(P_A,P_B)$ of about 3 Hz. For related six-membered platinacycles of the type [Pt(PPh_3)$_2${NR=PPh_2N=CPhNR′}],[42] similar ^3J(PPh_3,P) *trans* couplings of 2.7−2.8 Hz have been reported, whereas *cis* couplings range from 0 to 1.9 Hz.

The two resonances in the high frequency region between 28 and 33 ppm are slightly broadened at 293 K (for **3a′**, **3b**, and **3b′**), but do not show significant increases in broadening or coalescence at temperatures up to 330 K. This observation indicates that a slow dynamic process on the NMR time scale might be at hand, indeed the peaks due to P_B and P_C become sharp at low temperature. Addition of 1 equiv of pyridine to a solution of **3a** in $CDCl_3$ in an NMR tube did not result in a broadening of the ^{31}P signals belonging to P_B and P_C, in a temperature range from 293 to 330 K, which indicates that the dynamic process does not involve a substitution or exchange reaction of either of the two P=N groups of the N,N′ coordinated 1,1-BIPE ligand for pyridine. Evidence obtained from ^{1}H NMR (vide infra) points to conformational changes of the six-membered platinacycle at temperatures above 293 K.

^{1}H NMR Spectroscopy (Table 5). In the ^{1}H NMR spectra of the 1,1 BIPE ligand (**1**), a characteristic multiplet (triplet of quartet) is found for the methine-H at 3.72 ppm, which shifts to higher frequencies upon mono- (5.5−5.6 ppm) or bidentate (5.7−6.8 ppm) coordination of the ligand in the complexes **2** and **3**, respectively. The methyl substituent on the central C atom is found as a double triplet at about 1.3−1.8 ppm for **1**−**3**, meaning that its resonance frequency and also its coupling pattern are hardly influenced by the coordination mode of the 1,1-BIPE ligand. As evidenced by the two doublets between 1.80 and 1.92 ppm for **2b**, **3b**, and **3b′**, the methyl groups of the PMe_2Ph ligand on Pt are diastereotopic due to the chirality of the central C atom of the σ-N- and the σ-N,σ-N′-coordinated 1,1-BIPE ligands in **2a,b** and **3a,b,a′,b′**, respectively. Interestingly, for the σ-N monodentate coordinated complexes **2a** and **2b**, a striking high frequency resonance is observed in the region 9.1−9.3 ppm (dd), the integral corresponding to two phenyl-H atoms, which can be understood in terms of intermittant intramolecular interactions of the two H_{ortho} atoms of one phenyl ring on P with a Cl ligand or with the Pt center (by rotation around the P−Ph bond). For a related Pt−phosphinimine complex, reported earlier by Vicente et al., *trans*-[$PtCl_2${N(=PPh_3)C(Ph)=$CHCO_2R$}(NCPh)], an X-ray structural analysis has shown that indeed one of the phenyl groups on P is close to one of the axial positions of the Pt center, resulting in short intramolecular distances between H_{ortho} and Pt.[43]

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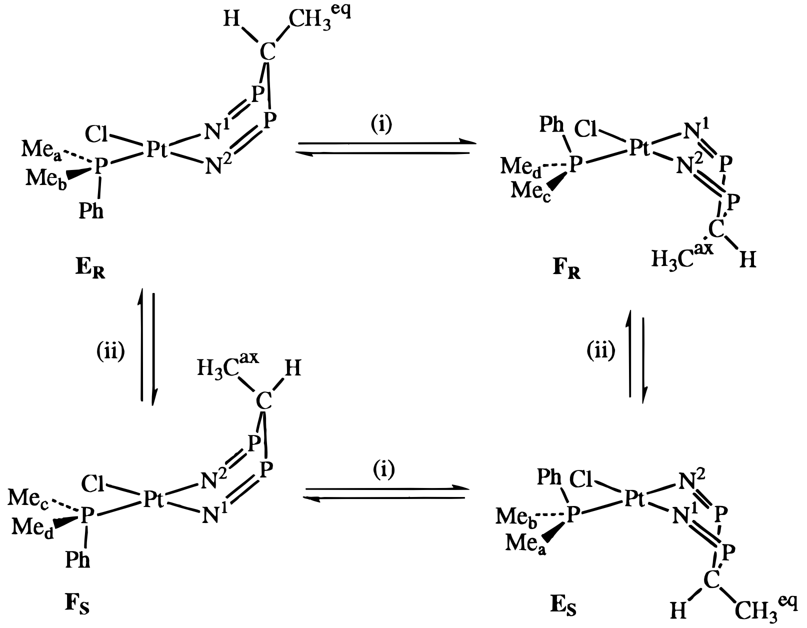
(41) Katti, K. V.; Cavell, R. G. *Organometallics* **1991**, *10*, 539.

(42) Roesky, H. W.; Scholz, U.; Noltemeyer, M. Z. *Z. Anorg. Allg. Chem.* **1989**, *576*, 255.

(43) Vicente, J.; Chicote, M.-T.; Fernández-Baeza, J.; Lahoz, F. J.; López, J. A. *Inorg. Chem.* **1991**, *30*, 3617.

Scheme 3. Possible Dynamic Processes for **3b** and **3b′** [a]



[a] Key: (i) boat-to-boat inversion (occurring) and (ii) N^1,N^2 exchange (not occurring). Substituents on N and P have been omitted for clarity.

The variable temperature ^{1}H NMR spectra (Table 5) for the six-membered platinacycles **3a′**,**b** and **3b′** show slightly broadened signals belonging to the bridging ethane-1,1-diyl group at 293 K accompanying the broadening as observed in the ^{31}P NMR for **3a′**,**b** and **3b′**(vide supra). The signals sharpen up at low temperature. As complexes **3b** and **3b′** show two sharp methyl resonances for the PMe_2Ph ligand over the whole temperature range from 213 to 330K, an N,N′ exchange process as depicted in Scheme 3 by steps (ii) can be excluded, since such a process would lead to inversion of configuration at the methine carbon atom (R ↔ S) and should hence reveal broadening or coalescence of the two diastereotopic P–Me signals at high temperature, which is not observed. This is confirmed by ^{31}P NMR (vide supra).

However, the observations are consistent with a dynamic process involving conformational changes within the six-membered ring as depicted in Scheme 3(i), **E** ↔ **F**. As rotation about the P–N double bonds is blocked, chair-type conformers cannot occur and hence conformational changes are restricted to boat-to-boat inversion only. Such a ring flip results in an exchange of equatorial and axial positions of the hydrogen and methyl group on the central carbon, which accounts for the broadness of these signals in the ^{1}H NMR. The fact that one set of sharp signals is observed for the $CHCH_3$ group at low temperature indicates that one conformer is favored. A boat-to-boat inversion is also consistent with the ^{31}P NMR as P_B and P_C do not average, but minor broadening is expected, also for P_A.

In view of the relatively high CH frequency (5.7–6.8 ppm) and the hardly changing $C-CH_3$ frequency for **3**, as compared to the corresponding signals for 1,1-BIPE (**1**), we have deduced that the most favored species in solution assumes conformation **E**. The axial position of the methine hydrogen atom could cause the observed high frequency shift for this group due to its proximity to the platinum center. The structure in solution is therefore in agreement with the solid state structure, as authenticated by the X-ray crystal structure determination of **3b**. Clearly, the concentration of conformer **F** in solution is too low to be observed, as an axial position of the methyl group in **F** would have resulted in a significant high frequency shift of this methyl and a much lower CH resonance frequency as compared to **E**. Such features have been reported for six-membered platina- and palladacycles containing flexible nitrogen donor ligands bridged by methylene and ethane-1,1-diyl groups.[44] Also, as can be seen from Scheme 3, presence of **E** and **F** in solution would have resulted in additional $P\mathit{Me}_2Ph$ signals (c and d), since **F** is a diastereomer of **E**. As mentioned before, only two sharp doublets (a and b) for $P\mathit{Me}_2Ph$ are observed over the whole temperature range. We therefore infer that the boat-to-boat inversion of **3** is a slow process up to 330 K and that the equilibrium lies completely on the side of conformer **E** at low temperature; i.e., the concentration of conformer **F** is too low to be observed. Comparison with the related complex $[PtCl(PEt_3)\{(N(pTol){=}PPh_2)_2CH_2\text{-}N,N'\}]^+[PtCl_3(PEt_3)]^-$, for which rapid boat-to-boat inversion of the six-membered platinacycle has been demonstrated,[4] shows that the increased steric hindrance around the central carbon atom in complex **3** is responsible for the slow ring-flip to conformer **F**. Molecular CPK models have shown that indeed significant steric interactions between the Me group and the Ph groups on the phosphorus atoms exist during an enforced boat-to-boat inversion. Furthermore, for organic six-membered ring systems it is generally known that an equatorial position of sterically demanding Me-groups is preferred.

The low temperature ^{1}H NMR spectra (Figure 3) of the six-membered platinacycles (**3a**,**b**) revealed another fluxional process too. When the samples are cooled, the ^{1}H NMR spectra of **3a**,**3b**,**3a′** and **3b′** (Table 5 and Figure 3) show that two doublets (a,b) appear at 8.5 and ca. 7.3 ppm (obscured) and two doublets (a′,b′) in the region 5.5–6.8 ppm, the doublet splitting being due to $^3J(H_a,H_b)$ coupling within a C_6H_4 moiety as established by $^1H\{^{31}P\}$ NMR spectroscopy, and each signal corresponding to one proton. It appears that one of the N–*p*-tolyl groups has lost its rotational freedom by intramolecular interaction of either of the H_{ortho} atoms (H_a) with the Cl ligand or with the Pt(II) center, causing the large downfield shift to 8.5 ppm.[45] The remaining three protons of the C_6H_4 moiety have become anisochronous. Fast rotation of the *p*-tolyl group at temperatures ≥293 K results in coalescence to give broad

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[44] (a) Byers, P. K.; Canty, A. J. *Organometallics* **1990**, *9*, 210. (b) Byers, P. K.; Canty, A. J.; Honeyman, R. T.; Watson, A. A. *J. Organomet. Chem.* **1990**, *385*, 429.

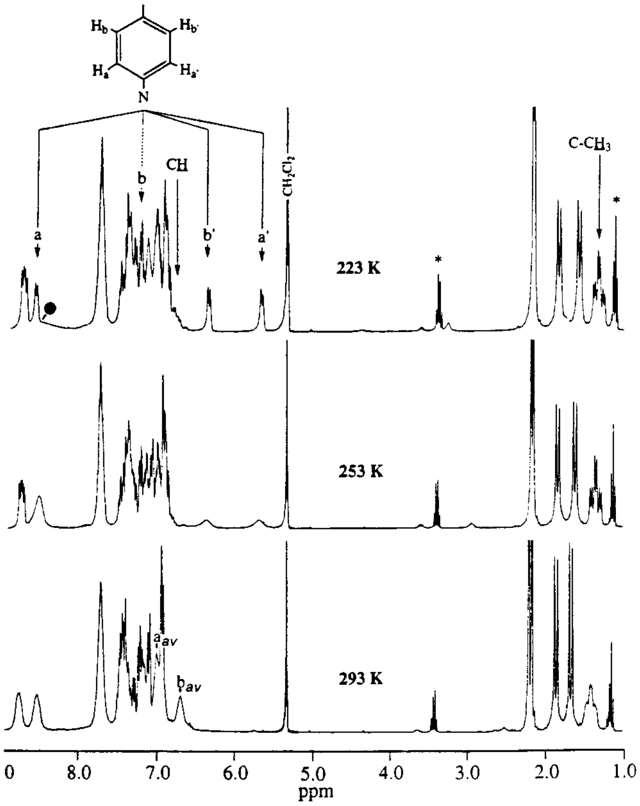

Figure 3. ^{1}H NMR spectra of **3b** at 223, 253, and 293 K showing the anisochronicity of the ortho- and meta-protons of the *p*-tolyl group at low temperatures. Note that at 223 K two signals are found at 8.5 ppm: a broad signal (•) belonging to ortho-H of Ph (see 293 K) and a doublet (a) belonging to one ortho-H of pTol. (* = diethyl ether).

signals at 7.0 ppm (a_{av}) and 6.7 ppm (b_{av}, obscuring δ(C*H*)), found at the approximate average chemical shifts of H_a, H_a' and H_b, H_b'.

Interestingly, for the earlier reported N,N′-coordinated Pt−BIPM complex,[4] no intramolecular interactions as in **3** have been observed, even at low temperature. We suspect that this might be caused by a difference in folding of the six-membered chelate ring in the boat conformers of $[PtCl(PEt_3)\{BIPM\text{-}\sigma N,\sigma N'\}]^+[PtCl_3(PEt_3)]^-$ [4] and $[PtCl(PR_3)\{1,1\text{-BIPE-}\sigma N,\sigma N'\}]^+X^-$ (**3**), due to the larger steric effect of the bridging $CHCH_3$ group in **3**.

^{13}C NMR Spectroscopy (Table 6). The $^{13}C\{^1H\}$ NMR spectrum of **1** shows a triplet at 36.8 ppm (^1J(P,C) = 75 Hz), characteristic for the central carbon atom (C1). Similar values have been reported for the corresponding carbon atom in bis(iminophosphoranyl)methane (BIPM) (30.5 ppm, ^1J(P,C) = 63.5 Hz)[22] and the bis-sulfide analogue of 1,1-BIPE, $CHCH_3(PPh_2{=}S)_2$ (41.1 ppm, ^1J(P,C) = 43 Hz).[26] The C_{ipso},C_{ortho}, and C_{meta} of the P−phenyl groups and also the C_{ortho} atoms of the *p*-tolyl substituent on N show double sets of resonance signals, indicating that these aryl groups are magnetically inequivalent, in keeping with their diastereotopicity (Figure 4).

The assignment of the ^{13}C resonance signals, belonging to the noncoordinated $PPh_2{=}N$-pTol part (C3−C11) and coordinated $PPh_2{=}N$-pTol moiety (C13−C21) in complex **2a**, is in agreement with relevant ^{13}C NMR data of **1** and the structurally related complex, *trans*-$[PtCl_2(N{\equiv}CPh)\{N({=}PPh_3]C(Ph){=}CHCO_2R\}]$, respectively.[43] The shielding of the C_{ipso} atoms on P and N (C13 and C17), as well as the C(1) atom, is obviously the result of a stronger polarization of the coordinated P=N group and concomitant delocalization of electron density in the aryl groups on N and P as compared to the noncoordinated one. Similar observations have been made on going from $Ph_3P{=}NPh$ to $[Ph_3PNHPh]^+[Br]^-$.[46]

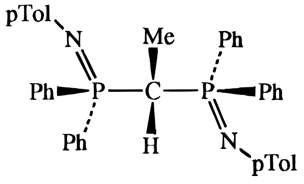

Figure 4. Representation of the $pTol{-}N{=}PPh_2CH(Me)PPh_2{=}N{-}pTol$ ligand (**1**), viewed through the P−C−P plane.

The ^{13}C NMR spectrum of **3a** shows that C1 has shifted to an even lower frequency as compared to **1** and **2a**. The $Ph_2P{=}N{-}pTol$ part (C13−C21), which is coordinated *trans* to PEt_3 in **3a**, has virtually the same ^{13}C resonances as in **2a**, except for the phenyl ortho-carbons (C14) which showed a high frequency shift of 3−4 ppm for **2a** as a result of an intramolecular interaction with the chloride ligand or the platinum center, which is in agreement with the observation in the ^{1}H NMR (vide supra). For the newly coordinated $Ph_2P{=}N{-}pTol$ moiety *trans* to chloride in **3a** an extreme low frequency shift is observed for C3 and a somewhat smaller one for C7, which clearly indicates that the polarization of the P=N bond *trans* to chloride is larger than in the P=N bond *trans* to PEt_3. All other carbons show deshielding effects upon coordination similar as noted above for **2a**.

IR Spectroscopy. The ligand **1** shows a characteristic medium absorption at 1341 cm^{-1}, corresponding well with the ν(P=N) stretch vibrations in the region 1282−1344 cm^{-1} reported for (*N*-aryl)phosphinimines[21ab,47] and the bis(iminophosphoranyl)methane (BIPM) ligands.[22]

Complexes **2** show absorptions at 1330 and 1235 cm^{-1}, corresponding to the noncoordinated and coordinated P=N groups, respectively, when compared to ν(P=N) of **1** and earlier reported σ-N coordinated Pt- and Pd-phosphinimine complexes, e.g. *trans*-$[PtCl_2\{N({=}PPh_3)C(Ph){=}CHCO_2R\}(N{\equiv}CPh)]$,[43] $[PdCl(\mu\text{-}Cl)\{N(aryl){=}PPh_3\}]_2$,[48] and $[PdCl_2\{N(aryl){=}PPh_3\}(N{\equiv}CPh)]$[48] with absorptions between 1238 and 1296 cm^{-1}.

For the complexes **3**, two signals are found for ν(P=N) in the region 1219−1251 cm^{-1}. The low frequency shift of 90−122 cm^{-1} is more pronounced than found for the analogous N,N′-coordinated Rh− and Ir−BIPM complexes,[3] but fall within range of other complexes containing phosphinimine ligands, which act as two-electron donors.[38,39,47,48]

Conclusion

The free 1,1-bis((*N*-*p*-tolylimino)diphenylphosphoranyl)ethane ligand resembles the structure of the bis(iminophosphoranyl)methane analogues both in solution and in the solid state, as evidenced by the close similarities in spectroscopic and X-ray crystallographic data. However, a tremendous change in coordination behavior to Pt(II) is observed as a consequence of the presence of an additional methyl group on the central carbon atom in 1,1-BIPE. Stable platinum(II) complexes containing σ-N monodentate 1,1-BIPE (**2**) and σN,σN′-chelated 1,1-BIPE

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(45) Deshielding of aromatic protons by interaction with adjacent halogens is well known,[44] but here an intramolecular interaction with Pt is perhaps more likely, since the X-ray crystal structure analysis of **3b** shows a short distance (2.916(7)Å) between the ortho-H(2) of the *p*-tolyl group *cis* to PMe_2Ph and Pt.

(46) Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *J. Am. Chem. Soc.* **1975**, *97*, 940.

(47) Abel, E. W.; Mucklejohn, S. A. *Phosphorus Sulfur* **1981**, *9*, 235.

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(**3**) could be isolated, which is in sharp contrast to the instability of analogous Pt–BIPM complexes.[4] We have established that the thermal stabilization is largely due to electronic effects of the additional methyl group in 1,1-BIPE, which decreases the relative acidity of the methine proton in 1,1-BIPE as compared to the methylene hydrogen atoms in BIPM, as proven by the reluctance of **2** and **3** to undergo an H-shift from the methine carbon to one of the nitrogen atoms (an essential step in the formation of N,C coordinated four-membered metallacyclic Pt–BIPM complexes).[4]

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Supporting Information Available: Tables giving further details of the structure determination, including crystallographic data atomic coordinates for both the non-hydrogen and the hydrogen atoms, bond lengths and angles, and thermal parameters for **1** and **3b** (18 pages). Ordering information is given on any current masthead page.

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