Monodentate s-N and Bidentate s-N,s-N' Coordination of 1,1-Bis(N-p-tolylimino)-diphenylphosphoranyl)ethane, CHCH3(PPh2=NC6H4-4-CH3)2, to Platinum(II)

Published in:
Inorganic Chemistry

DOI:
10.1021/ic950748w

Link to publication

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Monodentate \(\sigma\)-N and Bidentate \(\sigma\)-N,\(\sigma\)-N' Coordination of 1,1-Bis(\((N-p\text{-tolylimino})\)diphenylphosphoranyl)ethane, CHCH\(_3\)(PPh\(_2\)=NClH\(_4-4\)-CH\(_3\))\(_2\), to Platinum(II)

Mandy W. Avis,† Cornelis J. Elsevier,*† Nora Veldman,† Huub Kooijman,† and Anthony L. Spek*†

Van’t Hoff Research Institute, Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and Bijvoet Center for Biomolecular Research, Vakgroep Kristal- en Structuurchemie, Universiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received June 15, 1995

The new ligand, 1,1-bis(\((N-p\text{-tolylimino})\)diphenylphosphoranyl)ethane (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 \(\text{PtX}_2(\text{PR}_3)_2\) with \(1\) readily afforded \(\sigma\)-N monodentate complexes, \([\text{PtCl}(\text{PR}_3)\{1,1\text{-BIPE-}\sigma\text{N}\}]\) \(\{\text{2a}, \text{PR}_3 = \text{PEt}_3; \text{2b}, \text{PR}_3 = \text{PMe}_2\text{Ph}\}\). Conversion of 2 into the six-membered platinacycle \([\text{PtCl}(\text{PR}_3)\{1,1\text{-BIPE-}\sigma\text{N',}\sigma\text{N''}\}]\) \(\{\text{3a}, \text{PR}_3 = \text{PEt}_3; \text{3b}, \text{PR}_3 = \text{PMe}_2\text{Ph}\}\) took place after prolonged stirring, its reaction rate being strongly dependent on the type of phosphine (5 days for \(2\) in the presence of NaBF\(_4\), 1 hr for \(2\)) and the metal-to-ligand ratio. The compounds \(1, 2, \) and \(3\) have been fully characterized by \(^1\)H, \(^{31}\)P\(^\text{[\(\text{H}\)]}\), and \(^{13}\)C\(^\text{[\(\text{H}\)]}\) NMR and IR spectroscopy, elemental analysis, or FAB mass spectroscopy. The molecular structures of CHCH\(_3\)PPh\(_2\)-tolylimino)diphenylphosphoranyl)ethane (1,1-BIPE), \(1\) and \([\text{PtCl}(\text{PMep}_2\text{Ph})\{(\text{N}(\text{Pt})=\text{PPh}_2)\text{CHCl}_3\}]\) \(\{\text{Cl}\}^{-}\) \(\{\text{3b}\}\) 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, \(\beta = 105.069(4)^\circ\), \(V = 3649.1(3)\) 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, \(\beta = 109.544(5)^\circ\), \(V = 4712.7(5)\) Å\(^3\), and \(Z = 4\). The structure refinement converged to \(R_1 = 0.057, \) \(R_w = 0.122\). 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), \(\text{H}_2\text{C}=\text{N}(\text{NR})=\text{N'}(\text{R'})\), 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 (II). Previous reports have shown that reactions of N\(\text{SiMe}_3\)-substituted BIPM ligand with \(\text{WX}_6\) \((X = \text{Cl, F})\) and OsO\(_4\) resulted in the formation of \(\text{N,N}'\)-coordinated six-membered metallasycles by splitting of the reactive \(\text{N} = \text{Si}\) bonds.\(^1,2\) Reaction of \(\text{N} = \text{aryl}\) substituted BIPM with halide bridged Rh and Ir dimers, however, gave mixtures of two products, in which the ligand acts as a \(\sigma\)-N, \(\sigma\)-N' chelate in one isomer and as a \(\text{N,C}\) chelate in the other.\(^5\) Interestingly, similar reactions of BIPM \((\text{R} = \text{aryl})\) with \(\text{PtX}_2(\text{PR}_3)_2\) \((X = \text{Cl, Br; PR}_3 = \text{PEt}_3, \text{PMe}_2\text{Ph})\) proceeded much more selectively, since stable \(\text{N,C}\) chelated four-membered platinacycles (Scheme 1, \(D\)) were formed exclusively.\(^2\)

Monitoring the reactions by NMR revealed that the initial step in the formation of the \(\text{N,C}\) chelates involves a nucleophilic attack by a nitrogen donor atom, giving an intermediate \([\text{PtX}_2(\text{PR}_3)_2(\text{N'}(\text{R'})=\text{PPh}_2\text{CHCl}_3\text{R})]\) \(\{\text{A}\}\), containing \(\sigma\)-N monodentate BIPM (Scheme 1),\(^4\) which reacts further by a 1,3-H-shift from the methylene carbon atom in \(\text{A}\) to the noncoordinated nitrogen atom, giving intermediate \(\text{B}\) (not observed) and subsequent fast dissociation of the ligand isomer (\(\text{C}\)). The final product \(\text{D}\) is formed by recombination of \(\text{C}\) with \(\text{PtX}_2(\text{PR}_3)_2\).\(^-4\)

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 \(\sigma\)-N-coordinated \(\text{N=P}\) group in \(\text{A}\), 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 \(\text{N,C}\) 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 \(\text{N,N}'\) 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 \(\text{N,N}'\) 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
Scheme 1. Reaction Sequence in the Formation of Four-Membered Platinacycles (D), Containing N,C-Coordinated BIPM

\[ \frac{1}{2} \]

\[ X \]

\[ X \]

\[ R_3P \]

\[ PR_3 \]

\[ \text{BIPM} \]

\[ P \]

\[ N' \]

\[ R' \]

\[ \text{Pt} \]

\[ \text{C} \]

\[ \text{H} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]

\[ \text{Pt} \]

\[ \text{Cl}_3 \]

\[ \text{PR}_3 \]

\[ \text{X} \]

\[ \text{Ph}_2 \]

\[ \text{Pb}_2 \]

\[ \text{Ph}_2 \]

\[ \text{N} \]

\[ \text{Ph} \]

\[ \text{P} \]

\[ \text{X}^- \]
approximately 23% 3a and 77% 2a. Continued stirring of this mixture in CH₂Cl₂ with freshly added NaBF₄ (ca. 100 mg) gave 77% 3a and 23% 2a and some decomposition after 5 days. Compound 2a was completely washed out with Et₂O (2 × 20 mL), giving a residue consisting of 3a and some decomposition. Recrystallization out of CH₂Cl₂/EtOH (1:3) at 20 °C gave 155 mg of pure 3a (23%). IR (KBr): ν= 1247 and 1225 cm⁻¹. Anal. Calcd. for C₁₀H₉N₂P₂: C, 60.59; H, 4.04; N, 2.77; P, 12.24. Found: C, 60.61; H, 4.07; N, 2.75; P, 12.26.

\[
\text{[PtCl₂PeS₃]Cl} \text{[Cl] (3a).} \]

To a solution of 106.2 mg (0.17 mmol) of 1 in 15 mL of CH₂Cl₂ was added 134.0 mg (0.17 mmol) of PtCl₂(PeS₃), and the mixture was stirred for 18 h. Evaporation of the solvent resulted in a yellow powder, 240 mg (35.3 mmol, 99.9% of 3a). IR (Nujol): ν= 1248 and 1219 cm⁻¹. FAB mass found: m/z = 957.3 (M⁺, calcd for C₁₅H₁₄N₂P₃Cl₂PtCl₂).

Crystal Structure Determinations of 1 and 3b. Crystal data and experimental procedures on both crystal structures are collected directly using the SHELXS86 program system; Technical report of the Crystallography Laboratory; University of Cambridge, Cambridge, 1976.

Table 1. Crystallographic Data for 1-Toluene and 3b-THF

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/w</td>
<td>564.77</td>
<td>1084.94</td>
</tr>
<tr>
<td>temp</td>
<td>293 K</td>
<td>293 K</td>
</tr>
<tr>
<td>space group</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>a, Å</td>
<td>8.9521(5)</td>
<td>12.4021(7)</td>
</tr>
<tr>
<td>b, Å</td>
<td>19.1961(12)</td>
<td>16.9705(11)</td>
</tr>
<tr>
<td>c, Å</td>
<td>21.9740(9)</td>
<td>23.7602(2)</td>
</tr>
<tr>
<td>β, deg</td>
<td>105.069(4)</td>
<td>109.544(5)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>3649.1(3)</td>
<td>4712.6(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dₐ₀,C</td>
<td>1.192</td>
<td>1.529</td>
</tr>
<tr>
<td>F(000)</td>
<td>1388</td>
<td>2192</td>
</tr>
<tr>
<td>μ, cm⁻¹</td>
<td>13.1 (Cu Kα)</td>
<td>32.6 (Mo Kα)</td>
</tr>
<tr>
<td>data set</td>
<td>−117.0, 0.24, −27.27</td>
<td>−100.0, 0.22, −30.28</td>
</tr>
<tr>
<td>R₁</td>
<td>0.080 (for 5234 F &gt; 2σ(F))</td>
<td>0.057 (for 6850 F &gt; 2σ(F))</td>
</tr>
<tr>
<td>Rₑ</td>
<td>1.091</td>
<td>0.1215</td>
</tr>
<tr>
<td>wRₑ</td>
<td>1.28</td>
<td>1.00</td>
</tr>
<tr>
<td>R̃₀</td>
<td>0.996</td>
<td>0.998</td>
</tr>
<tr>
<td>σ(θ)</td>
<td>0.122 for all 10778 reflections</td>
<td></td>
</tr>
</tbody>
</table>

For 3b, the F₁ wRₑ was calculated with F₁, which was unweighted and corrected for Lorentz, polarization, and absorption effects (an empirical absorption/extension correction was applied (DIFABS) correction range 0.725–1.00) and averaged into a unique set of reflections. Total data of 15022 reflections were collected of which 10778 were independent (Rint = 0.0382).

The structure was solved by automatic Patterson methods and subsequent difference Fourier synthesis (DIRDIF-92).** Refinement on F² was carried out by full-matrix least-squares techniques (SHELXL-93)** final R1 value of 0.057 for 555 parameters and 6850 reflections with I > 2σ(I), wR₂ = 0.122 for all 10778 reflections, S = 0.996 and w = 1/(σ²(F₀) + 0.00154P²) where P = (Max(F²)+2F₂)/3. All

---


reflections were considered 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 parameter of the carrier atoms. Weights were introduced in the final refinement cycles. A final difference Fourier showed no residual parameter of the carrier atoms.

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), was used to synthesize the new 1,1-bis(N-p-tolylimino)diphenylphosphanyl)ethane ligand (1,1-BIPE, 1), containing a methyl substituent on the carbon atom bridging the two P=N moieties.

\[
\text{Ph}_2\text{PCH(Me)PPh}_3 + 2\text{p-tolyl-N}_3 \rightarrow \text{p-Tol-}N=\text{Ph}_2\text{PCH(Me)PPh}_3 = \text{N-p-Tol} + 2\text{N}_2
\]

Compound 1 was obtained in quantitative yield. Other methods, through deprotonation of BIPM by NaH, and subsequent reaction with 1 equiv Me2S, as has been reported earlier for the synthesis of CHMe(PR2),2 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 Et2O, but not soluble in apolar solvents like pentane. In the solid state, 1 is thermostable for at least 1 year when stored under N2 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, 31P{1H}, and 13C{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 Pt2Cl4(PR3)2 (PR3 = PEt3, PMe2Ph) 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 platamycles 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, CH2Cl2, CHCl3, toluene, benzene, and Et2O 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 H2O and CO2. The platinum complexes 2a,b and 3a,b′,b′ have been fully characterized by 1H, 31P{1H}, and 13C{1H} NMR, infrared, and FAB mass spectroscopy, elemental analysis, and an X-ray crystal structure determination of 3b.

Complexes 2a and 2b, [PtCl2(PR3){1,1-BIPE-σN}], represent the first isolable complexes in which the potentially bi- or even tridentate bis(phosphinimine) ligand of the type R′N=PR2-CHR′PR2=NR′ is monodentate coordinated. Recently, the formation of an analogous thermally less stable Pt complex, [PtCl2(PEt3)2{BIPM-σN}] (A, Scheme 1), containing a σ-N monodentate coordinated bis((N-p-tolylimino)diphenylphosphanylmethylene) ligand (BIPM), has been observed by NMR. Although many coordination complexes containing related

---

ligands of the type X=PR₃CHR(PR₃)ᵦ, with X=Y=S, O, and Se; R = alkyl, aryl; and R' = H, Me, and PR₃=X are known.¹⁻²⁹ to our knowledge only two similar types of stable monodentate coordinated species have been reported, i.e. \( \text{C₆F₅}_₂\text{Au}\{\text{S}=\text{PPh₂CH₂PPh₂=S}\}^{29a} \) and \( \text{Fe(C₆H₅)(CO)}₂\{-\text{X}=\text{PPh₂(CH₂)_nPPh₂=X}\}\text{BF₄}^- \) (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 (PR₃ = PE₃) is stable in solution; no further reaction is observed within 24 h at 20 °C. Treatment of a solution of 2a with NaBF₄ resulted in only 23% conversion into the six-membered platinacycle 3a after 24 h. In contrast, complex 2b (PR₃ = PMe₂Ph) converts completely within 1 h (in CH₂Cl₂ 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 dimethylphosphine (cone angle = 122°).³⁰ which slows down the substitution of chlorides cis to PE₃ 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 (PR₃ trans to the Pt−C1 bond) is unlikely because this would have resulted in a faster dissociation of the Pt−C1 bond in 2a relative to 2b, as the trans effect of PE₃ > PMe₂Ph.

When the metal-to-ligand (M:L) ratio of the reaction is changed to 2:1, the ionic dinuclear complexes \([\text{PtCl(PR₃)}\text{C}_{29} \cdots \text{C}_{29} \cdots \text{C}_{29}] \) is stable in solution; no further reaction of BIPM with PtCl₂(PR₃)₂ resulted in a faster dissociation of the Pt−Cl bond. In fact, two diastereomeric complexes 3a,b or 3a,c or 3b,c 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 PtCl₂(PR₃)₂ resulted in the exclusive formation of four-membered platinacycles by N,C coordination of BIPM.³ 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.³⁴ We have not found such a conversion for the six-membered platinacycles 3a,b, 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.

X-ray Crystal Structure of CH₂Cl₂(PPh₂=NC₆H₄-4-Ch₃)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 enantiopure (p-tolylmino)diphenylphosphoranylidene 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(iminophosphoranylidene)methane (BIMP) compounds, i.e. in CH₃(PR₃)=NC₆H₄-4-R' (1.566−1.568 Å for R = Ph and R' = Me, or 1.580(4) Å for R = Me and R' = NO₂),²² but are comparable with the P−N distances normally found for other phosphorus nitriles, ranging from 1.50 to 1.64 Å.³² The P−Calkyl

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

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

#### Bond Lengths

<table>
<thead>
<tr>
<th>Bond</th>
<th>Esd's (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)−N(1)</td>
<td>1.559(3)</td>
</tr>
<tr>
<td>P(1)−C(6)</td>
<td>1.820(4)</td>
</tr>
<tr>
<td>P(1)−C(14)</td>
<td>1.814(4)</td>
</tr>
<tr>
<td>P(1)−C(20)</td>
<td>1.827(3)</td>
</tr>
<tr>
<td>N(1)−C(1)</td>
<td>1.380(4)</td>
</tr>
<tr>
<td>C(20)−C(21)</td>
<td>1.529(5)</td>
</tr>
</tbody>
</table>

#### Bond Angles

<table>
<thead>
<tr>
<th>Bond</th>
<th>Esd's (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)−P(1)−C(1)</td>
<td>133.4(2)</td>
</tr>
<tr>
<td>N(1)−P(1)−C(8)</td>
<td>117.95(16)</td>
</tr>
<tr>
<td>N(1)−P(1)−C(14)</td>
<td>106.57(15)</td>
</tr>
<tr>
<td>N(1)−P(1)−C(20)</td>
<td>105.14(16)</td>
</tr>
<tr>
<td>N(1)−P(1)−C(29)</td>
<td>105.42(16)</td>
</tr>
<tr>
<td>C(14)−P(1)−C(20)</td>
<td>104.42(16)</td>
</tr>
<tr>
<td>C(14)−P(1)−C(21)</td>
<td>107.61(16)</td>
</tr>
<tr>
<td>C(1)−P(2)−C(20)</td>
<td>113.0(2)</td>
</tr>
<tr>
<td>C(1)−P(2)−C(21)</td>
<td>119.5(2)</td>
</tr>
</tbody>
</table>

#### Torsion Angles

<table>
<thead>
<tr>
<th>Torsion</th>
<th>Esd's (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)−P(1)−C(20)−P(2)</td>
<td>−53.8(2)</td>
</tr>
<tr>
<td>N(1)−P(1)−C(21)−P(2)</td>
<td>−177.5(2)</td>
</tr>
<tr>
<td>N(1)−P(1)−C(20)−N(2)</td>
<td>−174.5(3)</td>
</tr>
<tr>
<td>N(1)−P(1)−C(21)−N(2)</td>
<td>−166.3(3)</td>
</tr>
</tbody>
</table>

bonds (1.380(4) and 1.393(5) Å) are almost similar to the ones reported for the analogous BIPM compounds (1.81–1.83 Å),\textsuperscript{22} or the P–C single bonds in \( \text{Me}_2\text{Si}:\text{C} \equiv \text{PPh}_2: \text{CH}(\text{SiMe}_3)_2 \) (1.762(4) and 1.821(4) Å),\textsuperscript{33} but are shorter than the average P–C bonds in, for instance, [HC(\text{PR}_2)_2\text{C}]= (1.883 Å).\textsuperscript{34} The geometry around the two phosphorus atoms and C(20) is approximately tetrahedral. The Pt(1)–C(20)–P(2) angle (112.39(19)°) is somewhat smaller than found for BIPM (115.2(1)°),\textsuperscript{22} due to the steric effect of the methyl group on C(20).

X-ray Crystal Structure of \( \text{PtCl(PMe}_2\text{Ph})(\text{N}(\text{p-Tol})= \text{PPh}_2)(\text{CHCH}_3)] \text{Cl}_2 (3b) \). The atom labeling scheme and the structure of a single molecule of 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 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(iminophosphanyl)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 PMe2Ph 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)x]–(S=PPh2)2C)].\textsuperscript{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.\textsuperscript{31,33,36}

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, \( \Theta \) of 82.2(2)°, and \( \phi \) of 338.1(2)°, in agreement with the description as a twisted boat conformation.\textsuperscript{37}

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)=PPh2)2CH2]3+.\textsuperscript{38} Within the N,N′-coordinated 1,1-BIPe ligand in 3b both N=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.\textsuperscript{49,49,50} 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)=PPh2)2CH2]3+ and [Rh(COD)(S=PPh2)=CH2]3+\textsuperscript{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

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Around Pt} & \textbf{Pt–P(3)} & 2.234(2) \textbf{Pt–N(1)} & 2.052(5) \\
\hline
\textbf{Within Phosphine} & \textbf{Pt–Cl(1)} & 2.293(3) \textbf{Pt–N(2)} & 2.131(7) \\
\hline
\textbf{P(3)–C(41)} & 1.813(8) & \textbf{P(3)–C(48)} & 1.819(7) \\
\hline
\textbf{P(3)–C(47)} & 1.802(9) & & \\
\hline
\textbf{Within Ligand} & \textbf{P(1)–N(1)} & 1.611(5) & \textbf{P(2)–N(2)} & 1.618(6) \\
\hline
\textbf{P(1)}–\textbf{C(6)} & 1.806(7) & \textbf{P(2)}–\textbf{C(28)} & 1.795(7) \\
\hline
\textbf{P(1)}–\textbf{C(14)} & 1.806(8) & \textbf{P(2)}–\textbf{C(22)} & 1.826(7) \\
\hline
\textbf{P(1)}–\textbf{C(20)} & 1.821(7) & \textbf{P(2)}–\textbf{C(20)} & 1.828(5) \\
\hline
\textbf{N(1)}–\textbf{C(1)} & 1.443(8) & \textbf{N(2)}–\textbf{C(34)} & 1.433(10) \\
\hline
\textbf{C(20)–C(21)} & 1.545(10) & & \\
\hline
\end{tabular}
\caption{Selected Interatomic Distances (Å) and Angles (deg) for 3b (Esd’s in Parentheses)}
\end{table}


Table 4. $^{31}$P NMR Data for the Compounds 1–3$^a$

<table>
<thead>
<tr>
<th>compd</th>
<th>solvent/ temp, K</th>
<th>$\delta$(P)</th>
<th>$\delta$(P-A, $^1$J(P,P-A))</th>
<th>$\delta$(P, $^1$J(P,P))</th>
<th>$\delta$(P, $^2$J(P,P))</th>
<th>$\delta$(P, $^2$J(P,P))</th>
<th>$\delta$(P, $^3$J(P,P))</th>
<th>$\delta$(P, $^3$J(P,P))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CD$_2$Cl$_2$/293</td>
<td>6.6 (s)</td>
<td>3.3 (d)</td>
<td>3.3 (d)</td>
<td>3.3 (d)</td>
<td>3.3 (dd)</td>
<td>3.3 (dd)</td>
<td>3.3 (dd)</td>
</tr>
<tr>
<td>2a</td>
<td>CD$_2$Cl$_2$/293</td>
<td>1.0 (d)</td>
<td>34.55</td>
<td>39.4 (dd)</td>
<td>61.0 (d)</td>
<td>6.1 (d)</td>
<td>13.1 (d)</td>
<td>14.5 (d)</td>
</tr>
<tr>
<td>2b</td>
<td>CD$_2$Cl$_2$/293</td>
<td>-24.5 (d)</td>
<td>3490</td>
<td>40.3 (dd)</td>
<td>62.0 (d)</td>
<td>6.5 (d)</td>
<td>14.5 (d)</td>
<td>4.0 (d)</td>
</tr>
<tr>
<td>3a</td>
<td>CD$_2$Cl$_2$/293</td>
<td>1.2 (d)</td>
<td>3579</td>
<td>27.9 (dd)</td>
<td>61.0 (d)</td>
<td>6.1 (d)</td>
<td>3.6 (d)</td>
<td>12.4 (d)</td>
</tr>
<tr>
<td>3a$^b$</td>
<td>CD$_2$Cl$_2$/293</td>
<td>2.1 (d)</td>
<td>3554</td>
<td>28.3 (dd)$^e$</td>
<td>31.8 (d)$^f$</td>
<td>2.8 (d)</td>
<td>2.5 (d)</td>
<td>12.1 (d)</td>
</tr>
<tr>
<td>3b</td>
<td>CD$_2$Cl$_2$/293</td>
<td>-20.4 (s)$^g$</td>
<td>3650</td>
<td>28.9 (d)$^e$</td>
<td>32.3 (d)$^f$</td>
<td>32.4 (d)$^g$</td>
<td>21.4 (d)$^h$</td>
<td>12.1 (d)</td>
</tr>
<tr>
<td>3b$^e$</td>
<td>CD$_2$Cl$_2$/293</td>
<td>-20.4 (s)$^g$</td>
<td>3650</td>
<td>28.9 (d)$^e$</td>
<td>32.3 (d)$^f$</td>
<td>32.4 (d)$^g$</td>
<td>21.4 (d)$^h$</td>
<td>12.1 (d)</td>
</tr>
</tbody>
</table>

$^a$ 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. $^1$H NMR Data for 1–3$^a$

<table>
<thead>
<tr>
<th>compd</th>
<th>$\delta$(alkyl–P)$^b$</th>
<th>$\delta$(CH–CH$_3$)$^c$</th>
<th>$\delta$(CH)$^d$</th>
<th>$\delta$(CH$_2$–N)$^e$</th>
<th>$\delta$(C=H–N)$^f$</th>
<th>$\delta$(Ph/Ar- o, m, p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^i$</td>
<td>1.42 (d, 7.4, 16.7)</td>
<td>3.72 (m)</td>
<td>2.15 (s)</td>
<td>6.36 (d, 4H)</td>
<td>7.4 (m, 12H)</td>
<td></td>
</tr>
<tr>
<td>2a$^i$</td>
<td>1.15 (dt)</td>
<td>1.77 (dt, 7.0, 17.4)</td>
<td>5.57 (m)</td>
<td>2.01 (d)</td>
<td>6.58 (d, 2H)</td>
<td>6.9–8.1 (m, 18H)</td>
</tr>
<tr>
<td>2b$^i$</td>
<td>1.80 (d)</td>
<td>(o)</td>
<td>5.50 (m)</td>
<td>2.04 (s)</td>
<td>(o)</td>
<td>6.5–7.9 (m, 26H)</td>
</tr>
<tr>
<td>3a$^j$</td>
<td>1.03 (dt)</td>
<td>1.34 (dt, 7.3, 17.8)</td>
<td>5.75 (m, 19.1)</td>
<td>2.23 (s)</td>
<td>6.94 (d, 2H)</td>
<td>7.28 (d, 1H)</td>
</tr>
<tr>
<td>233K</td>
<td>1.28 (d, 7.1, 17.9)</td>
<td>6.71 (m, 18.7)</td>
<td>2.19 (s)</td>
<td>6.16 (d, 1H)</td>
<td>8.46 (d, 1H)</td>
<td>7.0–8.3 (m, 22H)</td>
</tr>
<tr>
<td>3a$^j$</td>
<td>1.00 (dt)</td>
<td>1.45 (br)</td>
<td>5.8 (br)</td>
<td>2.21 (s)</td>
<td>(o)</td>
<td>6.8–8.4 (m, 28H)</td>
</tr>
<tr>
<td>233K</td>
<td>1.01 (dt)</td>
<td>1.45 (o)</td>
<td>5.72 (m)</td>
<td>2.19 (s)</td>
<td>6.05 (d, 1H)</td>
<td>8.50 (d, 1H)</td>
</tr>
<tr>
<td>3b$^j$</td>
<td>1.68 (d)</td>
<td>1.41 (br)</td>
<td>(o)</td>
<td>2.18 (s)</td>
<td>(o)</td>
<td>6.5–8.8 (m, 33H)</td>
</tr>
<tr>
<td>223K</td>
<td>1.32 (d, 7.0, 18.2)</td>
<td>6.78 (m, 19.2)</td>
<td>2.15 (s)</td>
<td>5.66 (d, 1H)</td>
<td>6.8–8.8 (m, 30H)</td>
<td></td>
</tr>
<tr>
<td>3b$^j$</td>
<td>1.28 (d)</td>
<td>1.41 (br)</td>
<td>5.72 (m)</td>
<td>2.19 (s)</td>
<td>6.05 (d, 1H)</td>
<td>8.50 (d, 1H)</td>
</tr>
<tr>
<td>213K</td>
<td>1.37 (d, 6.9, 18.2)</td>
<td>nr</td>
<td>2.17 (s)</td>
<td>5.47 (d, 1H)</td>
<td>8.56 (d, 1H)</td>
<td>6.8–8.6 (m, 34H)</td>
</tr>
</tbody>
</table>

$^a$ 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 = triplet of quartet, $^b$ For Et$_2$P: $\delta$(P–CH$_2$–CH$_3$) (d) and $\delta$(P–CH$_2$–CH$_3$) (m) are given successively, with coupling constants $^1$J(H/H) = 7.5 Hz, $^2$J(H/H) = 15.0 Hz, and $^3$J(H/P) = nr. For Me$_2$PhP: $\delta$(P–CH$_2$–CH$_3$) (d) with $^2$J(H/P) = 6.7–11.8 Hz, $^3$J(H/H) and $^3$J(P/H) are given in parentheses. $^c$ For B: Me$_3$P–P: for the countercation [PtCl$_2$(PPh$_3$)]$^-$ is found at 1.17 (d) and 1.90 (dq). $^d$ $\delta$(P–alkyl) for the countercation [PtCl$_2$(PMe$_2$Ph)$_2$] is found at 1.81 (d). $^e$ Measured at 500.13 MHz. $^f$ Measured at 100.13 MHz. $^g$ BF$_3$ salt. $^h$ $\delta$(P–alkyl) for the countercation [PtCl$_2$(PPh$_3$)]$^-$ is found at 1.17 (d) and 1.90 (dq). $^i$ $\delta$(P–alkyl) for the countercation [PtCl$_2$(PMe$_2$Ph)$_2$] is found at 1.81 (d). $^j$ $\delta$(P–alkyl) for the countercation [PtCl$_2$(PMe$_2$Ph)$_2$] is found at 1.81 (d). $^k$ $\delta$(P–alkyl) for the countercation [PtCl$_2$(PMe$_2$Ph)$_2$] is found at 1.81 (d).

3$^1$P NMR Spectroscopy. 1,1-BIPE shows a $^{31}$P resonance frequency at 7 ppm, which is higher than that of BIPPM (0 ppm). A similar trend has also been found for CHCl$_3$–(PPh$_2$)$_2$–S$_2$: $\delta$(P) = 46.6 ppm) relative to CH$_2$(PPh$_2$)–S$_2$: $\delta$(P) = 34.6 ppm). The 3$^1$P NMR of complexes 2, where three resonances are found, shows strong similarities to the 3$^1$P NMR data of the analogous o-N coordinated Pt–BIPPM complex reported earlier. The low frequency doublet resonance with $^1$J(P,P) of 3455–3490 Hz and $^3$J(P,P) of ca. 14 Hz is unambiguously assigned to the phosphate P$_3$R$_3$ trans to the coordinated N=P$_3$ group. The doublet at about 6.3 ppm lies at approximately the same 3$^1$P frequency as the free ligand 1 and is therefore directly assigned to the noncoordinated P$_3$N group.

Spectroscopic Characterization of Compounds 1–3. $^{31}$P, $^{1}$H, and $^{13}$C($^{1}$H) 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.
The high frequency resonance, a doublet of doublet at ca. 40 ppm, is attributed to P_C of the coordinated P_C-N group, based on the observed \( J(P,P) \) coupling of 61–62 Hz, and mutual spin–spin couplings with P_C and P_B. The large high frequency shift of \( \Delta \delta(P_C) \approx 33 \) 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') \(^3\)P resonances at 293 K. The signals at 32.5 ppm (3a,3b') or 31.8 ppm (3a',3b) 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. Further proof for the trans Pt-P=Pt-N=PR disposition is supplied by the Pt complexes 3a and 3a' (P_B=PR = PEt\(_3\)), which show small \( J(P,P) \) of about 3 Hz. For related six-membered platinacycles of the type [Pt(PPh\(_3\))\(_2\)N(PR\(_2\)=CHPh\()_2\)], similar \( J(P,P) \) trans couplings of 2.7–2.8 Hz have been reported, whereas cis couplings range from 0.1 to 0.9 Hz.

The two resonances in the high frequency region between 28 and 33 ppm are slightly broadened at 293 K (for 3a,3b), whereas \( J(P,P) \) coupling of 6.6 Hz has been reported, 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 doublet 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\(_2\)Ph ligand on Pt are diastereotopic due to the chirality of the central C atom of the \( \sigma-N \)- and the \( \sigma-N,\sigma-N' \)-coordinated 1,1-BIPE ligands in 2b and 3a,b,a',b', respectively. Interestingly, for the \( \sigma-N \) 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 intermittent 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\(_2\)\( \{N\equiv\text{PPh}_2\}C(\text{Ph})\equiv\text{CHO}R\}_3\)](NCP_{Ph})\], 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.\(^43\)

\(^{41}\) Katti, K. V.; Cavell, R. G. Organometallics 1991, 10, 539.


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$_2$Ph ligand over the whole temperature range from 213 to 330 K, an $N^1,N^2$ 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 $\leftrightarrow$ 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 $\leftrightarrow$ 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 (I), 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 platinacaycles 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 PMe$_2$Ph signals (c and d), since F is a diastereomer of E. As mentioned before, only two sharp doublets (a and b) for PMe$_2$Ph 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$_3$)$_2$(N(pTol)=PPh$_2$)$_2$CH$_2$–N,N‘}{PtCl$_4$(PEt$_3$)$_2$}], 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 $3a,b,3a'$ and $3b'$ (Table 5 and Figure 3) show that two doublets (a,b) appear at 8.5 and ca. 7.3 ppm (observed) and two doublets (a',b') in the region 5.5–6.8 ppm, the doublet splitting being due to $^1$H(CH$_3$)$_2$ coupling within a C$_6$H$_4$ moiety as established by $^1$H($^{31}$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$_{pho}$ atoms (H$_4$) 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$_6$H$_4$ moiety have become anisochronous. Fast rotation of the $p$-tolyl group at temperatures $\geq 293$ K results in coalescence to give broad

---

**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.

---

signals at 7.0 ppm (asv) and 6.7 ppm (bsv, obscuring δ(CHJ)), found at the approximate average chemical shifts of Hα, Hα′ and Hδ, Hδ′.

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 [PtCl2(N≡PPh3)2] and [PtCl3(N≡PPh3)2], due to the larger steric effect of the bridging CHCH3 group in 3.

13C NMR Spectroscopy (Table 6). The 13C[1H] NMR spectrum of 1 shows a triplet at 36.8 ppm (δ(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)25 and the bis-sulfide analogue of 1,1-BIPE, CHCH3 in 3δ in the boat conformers of [PtCl2(N≡PPh3)2] and [PtCl3(N≡PPh3)2]13, due to the larger steric effect of the bridging CHCH3 group in 3.

The assignment of the 13C resonance signals, belonging to the noncoordinated PPh3=N-N-Pt part (C3–C11) and coordinated PPh3=N-N-Pt moiety (C13–C21) in complex 2a, is in agreement with relevant 13C NMR data of 1 and the structurally related complex, trans-[PtCl2(N≡CPh)(N≡PPh3)]13.

Figure 4. Representation of the pTol−N=PPh3.CH(Me)PPh3=N−pTol ligand (1), viewed through the P−C−P plane.

The 13C NMR spectrum of 3a shows that C1 has shifted to an even lower frequency as compared to 1 and 2a. The Ph3P=N−pTol part (C13–C21), which is coordinated trans to PEt3 in 3a, has virtually the same 13C 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 1H NMR (vide supra). For the newly coordinated Ph3P=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 PEt3. 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=NN) stretch vibrations in the region 1282–1344 cm−1 reported for (N-aryl)phosphiniminates20b,41 and the bisiminophosphoranyl)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=NN) of 1 and earlier reported σ-N coordinated Pt- and Pd-phosphinimine complexes, e.g. trans-[PtCl2{(N≡PPh3)2}2] and [PtCl3{(N≡PPh3)2}],43 [PdCl{(μ-Cl){N≡PPh3}2}]48 and [PdCl2 {(N≡PPh3)2}2]48 with absorptions between 1238 and 1296 cm−1.

For the complexes 3, two signals are found for ν(P=NN) 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)diphenylphosphoranylene-ethane ligand resembles the structure of the bisiminophosphoranyl)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 α-N monodentate 1,1-BIPE (2) and α,N′-chelated 1,1-BIPE

(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 PMe3Ph and Pt.


(3) could be isolated, which is in sharp contrast to the instability of analogous Pt–BIPM complexes.\textsuperscript{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).\textsuperscript{4}

**Acknowledgment.** This work was supported in part (A.L.S. and N.V.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). M.W.A. and C.J.E. wish to thank Prof. K. Vrieze for his support of this work and Prof. K. V. Katti and co-workers of the Radiology and Chemistry Department of the University of Missouri–Columbia for helpful discussions and use of their facilities.

**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.

IC950748W