4092 *Inorg. Chem.* **1995,** *34,* 4092−4105

Selective Formation of Four-Membered Metallacyclic Pt−N−P−C Compounds from Reactions of Bis((*N*-arylimino)phosphoranyl)methanes with Halide-Bridged Platinum(II) Phosphine Dimers. X-ray Crystal Structures of $[PtCl(PMe_2Ph)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)(PPh_2NHC_6H_4\text{-}4\text{-}CH_3)\}]^+Cl^-$ and $[PtCl(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)(PPh_2NHC_6H_4\text{-}4\text{-}CH_3)\}]^+[PtCl_3(PEt_3)]^-$

Mandy W. Avis,[†] Kees Vrieze,[†] Huub Kooijman,[‡] Nora Veldman,[‡] Anthony L. Spek,[‡,§] and Cornelis J. Elsevier[*,†]

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 November 29, 1994[®]

Bridge-splitting reactions of $Pt_2X_4(PR_3)_2$ (X = Cl, Br; PR_3 = PEt_3, PMe_2Ph) with bis(iminophosphoranyl)methanes $CH_2(PPh_2{=}NC_6H_4\text{-}4\text{-}R')_2$ (BIPM: **1a**, R′ = Me; **1b**, R′ = OMe) produced Pt(II) complexes, in which the BIPM ligand is N,C-coordinated: $[PtX(PR_3)\{CH\text{-}(PPh_2{=}N\text{-}C_6H_4\text{-}4\text{-}R')(PPh_2\text{-}NH\text{-}C_6H_4\text{-}4\text{-}R')\}]^+Y^-$ (**2a−f**, R′ = CH_3, OCH_3, Y = Cl, Br, BF_4, CF_3CO_2; **2g**, R′ = CH_3, PR_3 = PEt_3, Y = $PtCl_3PEt_3$). In the N,C-coordinated BIPM, a net 1,3-H-shift from the bridging methylene group to the noncoordinated N-atom has taken place. NMR studies have revealed a monodentate σ-N-coordinated species $PtX_2(PR_3)\{N(C_6H_4\text{-}4\text{-}R'){=}PPh_2CH_2PPh_2{=}NC_6H_4\text{-}4\text{-}R'\}$, **A**, as the first intermediate in the formation of **2**. The complex formation is strongly dependent on the metal to ligand ratio, M:L. For M:L = 2:1, compound **2g**^{i} was formed, a N,N′-coordinated six-membered platinacycle, followed by conversion into the N,C chelate **2g**, whereas at M:L = 1:2 two new products were obtained; a deprotonated Pt(II) complex with N,C-coordinated BIPM, $[PtX(PR_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}R')_2\}]$ (**3**; X = Cl, PR_3 = PEt_3, R′ = CH_3), and the HCl salt of the ligand $[HC(PPh_2NHC_6H_4\text{-}4\text{-}R')_2]^+Cl^-$ (**4**). The molecular structures of $[PtCl(PMe_2Ph)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)(PPh_2N'HC_6H_4\text{-}4\text{-}CH_3)\}]^+(Cl)^-$ (**2d**) and $[PtCl(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)(PPh_2N'HC_6H_4\text{-}4\text{-}CH_3)\}]^+(PtCl_3PEt_3)^-$ (**2g**) have been determined by X-ray crystallography. Crystal data for **2d**: trigonal, space group $P\bar{1}$, with a = 14.3852(11) Å, b = 15.4886(9) Å, c = 20.190(2) Å, α = 100.580(7)°, β = 92.223(8)°, γ = 99.508(6)°, V = 4350.1(6) Å^3, and Z = 4. Crystal data for **2g**: trigonal, space group $P\bar{1}$, with a = 10.1970(8) Å, b = 14.5045(9) Å, c = 20.5471(19) Å, α = 96.154(7)°, β = 103.993(7)°, γ = 107.548(6)°, V = 2757.8(4) Å^3, and Z = 2. The structure refinement converged to R_w = 0.0432, R = 0.0436 for **2d** and $wR2$ = 0.1247, R1 = 0.501 for **2g**. The structure of the cationic parts of **2d** and **2g** comprises a distorted square planar Pt(II) environment, the coordination sites taken by PR_3, Cl, and the N and C atoms of the BIPM ligand. The structure of the anionic part of **2g**, $PtCl_3(PEt_3)$, is almost perfectly square-planar and is linked with the cationic part via a NH···Cl hydrogen bond.

Introduction

Since the first reports on the synthesis of bis(iminophosphoranyl)methane (BIPM) $[CH_2(PR_2{=}NR')_2]$[1] by means of a Staudinger reaction, only a few investigations toward its reactivity and coordination behavior have been published.[1d,2] However, the versatile coordination possibilities of methylene-bridged phosphinimines $R_2PCH_2PR_2{=}NR'$, $R'N{=}R_2PCH_2PR_2{=}NR'$ to coordinate to early as well as late transition metals have caused an increasing academic interest lately.[2a,b,3,4] In particular, the development of the extended α,ω-diphosphinoalkanes $R_2P(CH_2)_nPR_2$ (n = 1−4) or even triphosphinoalkanes $RC(PR_2)_3$, through oxidation of one, two, or three phosphorus(III) sites, has created a brand new field of research. Examples are known of $R_2P(CH_2)_nPR_2{=}X$,[3a,d, 5] $X{=}R_2P(CH_2)_nPR_2{=}Y$[1,2de,4b,6] and $X{=}R_2PCH(PR_2{=}Y)_2$[7] (with X,Y = N−aryl, $NSiMe_3$, S, O, Se, and CR'_2) and several other functionalized systems, in which the bridging hydrocarbon group between the phosphorus atoms can be varied. One of the interesting features

---

[*] To whom correspondence should be addressed.

[†] Universiteit van Amsterdam.

[‡] Universiteit Utrecht.

[§] To whom correspondence on the crystallography should be addressed.

[®] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) (a) Gilyarov, V. A.; Kovtun, V. Yu; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *5*, 1159. (b) Kovtun, V. Yu; Gilyarov, V. A.; Kabachnik, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, *11*, 2612. (c) Aquiar, A. M.; Beisler, J. *J. Org. Chem.* **1964**, *29*, 1660. (d) Appel, R.; Ruppert, I. *Z. Anorg. Allg. Chem.* **1974**, *406*, 131.

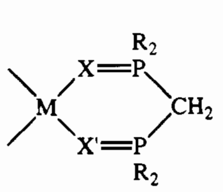
(2) (a) Katti, K. V.; Roesky, H. W.; Rietzel, M. *Z. Anorg. Allg. Chem.* **1987**, *553*, 123. (b) Katti, K. V.; Seseke, U.; Roesky, H. W. *Inorg. Chem.* **1987**, *26*, 814. (c) Aquiar, A. M.; Aquiar, H. J.; Archibald, T. G. *Tet. Lett.* **1966**, *31*, 87. (d) Appel, R.; Ruppert, I. *Chem. Ber.* **1975**, *108*, 919.

(3) (a) Katti, K. V.; Cavell, R. G. *Organometallics* **1988**, *7*, 2236. (b) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 413. (c) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 3033. (d) Katti, K. V.; Cavell, R. G. *Organometallics* **1989**, *8*, 2147. (e) Katti, K. V.; Batchelor, R. J.; Einstein, F. W. B.; Cavell, R. G. *Inorg. Chem.* **1990**, *291*, 808. (f) Katti, K. V.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem.* **1991**, *30*, 2631. (g) Katti, K. V.; Cavell, R. G. *Organometallics* **1991**, *10*, 539.

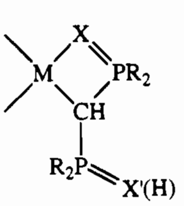
(4) (a) Imhoff, P.; Elsevier, C. J. *J. Organomet. Chem.* **1989**, *361*, C61. (b) Imhoff, P.; van Asselt, R.; Elsevier, C. J.;Vrieze, K.; Goubitz, K.; van Malssen, K. F.; Stam, C. H. *Phosphorus Sulfur* **1990**, *47*, 401. (c) Elsevier, C. J.; Imhoff, P. *Phosphorus Sulfur* **1990**, *49−50*, 405. (d) Imhoff, P.; van Asselt, R.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chim. Acta* **1991**, *184*, 73. (e) Imhoff, P.; van Asselt, R.; Ernsting, J. M.; Vrieze, K.; Elsevier, C. J. *Organometallics* **1993**, *12*, 1523. (f) Imhoff, P.; Gülpen, J. H.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L.; Elsevier, C. J. *Inorg. Chim. Acta*, in press.

0020-1669/95/1334-4092$09.00/0

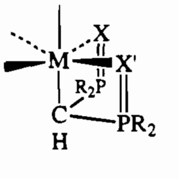
of the methylene-bridged, bisoxidized ligands is their ability to coordinate in various multidentate modes (**I**−**IV**): (i) chelation by both X σ-donor functions[2ab,4abc,6a,8,9,10] seems most likely, but also (ii) ylide C,X coordination by H-shift from the methylene carbon to one of the X,X′ entities, or by deprotonation, may occur,[4a-e,9,10] and (iii) even terdentate X,X′,C coordinations have been reported.[4f,8]



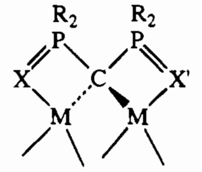
(I)



(II)



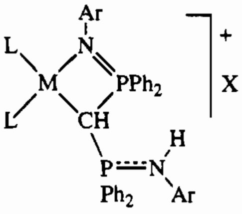
(III)



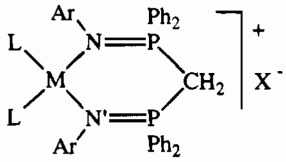
(IV)

In some cases fluxional behavior within these organometallic complexes has been observed, which offers considerable scope for applicability in homogeneous catalysis. Until now, complexes of the type $RhCl(CO)(PPh_2CH_2CH_2PPh_2{=}O)$, containing a fluxional P,O ligand,[11] and related complexes containing $R_2P(CH_2)_nPR'_2{=}NR''$ ligands,[12a] have proven to be active catalysts in the carbonylation of methanol, whereas iridium complexes of $[C(PPh_2{=}O)_3]^-$ are under investigation as catalysts in alkyne hydrosilylation.[12b]

We studied the coordination and organometallic chemistry of bis(iminophosphoranyl)methanes (BIPM) with rhodium(I) and iridium(I) a couple of years ago, the multifunctional properties of which have resulted in some interesting reactivities. The two highly polarized P=N groups cause the methylene hydrogen atoms to be acidic,[4b] consequently deprotonation reactions are easy processes, as is well known for isoelectronic $CH_2(CR{=}O)_2$ and methylenebis(phosphinoxides). The terminal σ-donor nitrogen atoms are suitable for coordination to electron-poor and electron-rich transition metals, depending on the substituent on N. First, BIPM ligands containing N-$SiMe_3$ moieties react with d^0 transition metals like WX_6 (X = Cl, F)[2b] and OsO_4[2a] under formation of the bis-imide complexes with concomitant loss of $XSiMe_3$ and formation of Os-$OSiMe_3$ moieties, respectively, whereas no reaction takes place with d^8 transition metal complexes of Rh and Ir.[3d] Second, N-aryl substituted ligands have proven to be more suitable in reaction with platinum metals like Rh, Ir,[4d] and, as described in this paper, Pt. The coordinating BIPM ligands can undergo a 1,3-H-shift, from the methylene carbon to one of the basic imino N-atoms, which has been an essential feature in the formation of four-membered Rh- and Ir-metallacycles.[4a,c,d] Bridge-splitting reactions of $[M(L_2)Cl]_2$ (M = Rh, Ir; L_2 = COD, NBD, $(CO)_2$) with $CH_2(PPh_2{=}N\text{-}Ar)_2$ (Ar = *p*-tolyl, *p*-anisyl) have resulted in a mixture of two products in which the ligand has adopted a N,C and a N,N′ coordination mode, for the compounds **V** and **VI**, respectively.[4a,c,d]



(V)



(VI)

X = Cl, PF_6, PF_2O_2, BF_4, CF_3CO_2, ML_2Cl_2.

In this paper we describe the reactivity of N-aryl substituted bis(iminophosphoranyl)methanes with $Pt_2X_4(PR_3)_2$ (X = Cl, Br; PR_3 = PEt_3, PMe_2Ph). The synthesis, characterization and crystal structures of newly formed four-membered Pt-N-P-C metallacycles will be presented. Furthermore, the effect of the metal to ligand ratio, M:L on the product formation will be discussed.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques at ambient temperatures, unless stated otherwise. The solvents were dried and distilled prior to use. Data relating to the characterization of the complexes are given in Table 2, under Results, and in the preparative descriptions below. ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ NMR spectra were obtained on Bruker AC 100 and AMX 300 instruments (operating at 100.13/300.13 MHz, 40.53/121.50 MHz and 25.18/75.48 MHz, respectively) using $SiMe_4$, 85% H_3PO_4, and $SiMe_4$ as the external standards, with positive shifts being to high frequency of the standard in all cases. Elemental analysis were carried out by Dornis und Kolbe Mikroanalytisches Laboratorium (Mülheim a. d. Ruhr, Germany). FAB mass spectrometry was carried out by the Institute for Mass Spectroscopy at the University of Amsterdam. $Pt_2X_4(PR_3)_2$ (with X = Cl, Br; PR_3= PEt_3, PMe_2Ph)[13] and the bis(iminophosphoranyl)methanes $H_2C(PPh_2{=}NC_6H_4\text{-}4\text{-}R')_2$[1a,4b] (**1a**, R′ = Me; **1b**, R′ = OMe) were synthesized according to literature procedures.

Synthesis of 2a−d: $[PtX(PR_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}R')(PPh_2NHC_6H_4\text{-}4\text{-}R')\text{-}C,N\}]X$ with PR_3 = PEt_3, PMe_2Ph; X = Cl, Br; R′ = CH_3, OCH_3. These complexes were obtained by reaction of the appropriate ligand $H_2C(PPh_2{=}NC_6H_4\text{-}4\text{-}R')_2$ (**1a,b**) with the halide-bridged dimers $Pt_2X_4(PR_3)_2$. The method of preparation described below is representative for the synthesis of compounds **2a**−**d**.

---

(5) (a) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1975**, *14*, 656. (b) Higgins, S. J.; Taylor, R.; Shaw, B. L. *J. Organomet. Chem.* **1987**, *525*, 285. (c) Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W. *Can. J. Chem.* **1988**, *66*, 1272. (d) Colquhoun, I. J.; Grim, S. O.; McFarlane, M.; Mitchell, J. D.; Smith, P. H. *Inorg. Chem.* **1981**, *20*, 2516. (e) Katti, K. V.; Barnes, C. L. *Inorg. Chem.* **1992**, *31*, 4231.

(6) (a) Wheatland, D. A.; Clapp, C. H.; Waldron, R. W. *Inorg. Chem.* **1972**, *11*, 10, 2340. (b) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982. (c) Appel, R.; Haubrich, G.; Knoch, F. *Chem. Ber.* **1984**, *117*, 2063. (d) Schmidbaur, H. *Pure Appl. Chem.* **1980**, *52*, 1057. (e) Browning, J.; Bushnell, G. W.; Dixon, K. R. *Inorg. Chem.* **1981**, *20*, 3912.

(7) (a) Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456. (b) Browning, J.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R. *Inorg. Chem.* **1986**, *25*, 1987. (c) Grim, S. O.; Nittolo, S.; Amon, H. L.; Smith, P. A.; Colquhoun, I. J.; McFarlane, M.; Holden, J. R. *Inorg. Chim. Acta.* **1983**, *77*, L241. (d) Grim, S. O.; Sangokoya, S. A.; Rheingold, A. L.; McFarlane, M.; Colquhoun, I. J.; Gilardi, R. D. *Inorg. Chem.* **1991**, *30*, 2519. (e) Grim, S. O.; Kettler, P. B.; Thoden, J. B. *Organometallics* **1991**, *30*, 2399. (f) Grim, S. O.; Kettler, P. B.; Merola, J. S. *Inorg. Chim. Acta* **1991**, *85*, 57. (g) Grim, S. O.; Kettler, P. B. *J. Chem. Soc., Chem. Commun.* **1991**, 979.

(8) Browning, J.; Dixon, K. R.; Hilts, D. W. *Organometallics* **1989**, *8*, 552.

(9) Browning, J.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Inorg. Chem.* **1983**, *22*, 16, 2226.

(10) Laguna, A.; Laguna, M.; Rojo, A.; Fraile, M. N. *J. Organomet. Chem.* **1986**, *315*, 269.

(11) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun.* **1987**, 189.

(12) (a) Cavell, R. G.; Katti, K. V. *Can. Pat. Appl.* CA 2,024,284 (Cl. CO7F15/00) March 01, 1992, 30 pages. (b) Tanke R. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1056.

(13) (a) Goodfellow, R. J.; Venanzi, L. M. *J. Chem. Soc.* **1965**, 7533. (b) Baratta, W; Pregosin, P. S. *Inorg. Chim. Acta* **1993**, *209*, 85.

A solution of $\mathrm{H_2C(PPh_2{=}NC_6H_4\text{-}4\text{-}R')_2}$ (**1**) (0.42 mmol) in 10 mL of THF or dichloromethane was added to a stirred solution of $\mathrm{Pt_2X_4(PR_3)_2}$ (0.21 mmol) in 10 mL of THF or dichloromethane. After 4 h at ambient temperature, the yellow solution was evaporated to approximately 5 mL. Subsequent addition of 20 mL of pentane caused precipitation of a pale yellow product. The colorless upper layer was removed with a syringe and the precipitate was washed with pentane (2 × 20 mL). After drying in vacuo a pale yellow powder was obtained in 70−95% yield. Crystals of $\mathrm{PtCl(PMe_2Ph)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}Me)(PPh_2N'HC_6H_4\text{-}4\text{-}Me)\text{-}C,N\}Cl}$ (**2d**) suitable for X-ray structure determination were obtained from a similar reaction, carried out in toluene. The reaction mixture was stirred for only 10 min and then set aside against ether for 2 days, allowing slow diffusion of ether into the solution.

$\mathbf{[PtCl(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}Me)(PPh_2NHC_6H_4\text{-}4\text{-}Me)\}]Cl}$ (2a). Anal. Calcd for $\mathrm{C_{45}H_{51}Cl_2N_2P_3Pt}$: C, 55.21; H, 5.25; N, 2.86; P, 9.49. Found: C, 55.08; H, 5.24; N, 2.94; P, 9.56. ^{1}H NMR ($\mathrm{C_6D_6}$): N−*H*, δ 10.9 (br, 1H, ${}^2J_{\mathrm{PH}}$ = nr); phenyl rings, δ 6.9, 8.2, 9.2 (m, 20H); N-C_6H_4, δ 6.56, 6.85, (d, 8H, ${}^3J_{\mathrm{HH}}$ = 8 Hz); Pt-*CH*, δ 4.58 (br m, 1H, ${}^2J_{\mathrm{PtH}}$ = 57 Hz); $\mathrm{C_6H_4}$-4-CH_3, δ 2.04, 1.81 (s, 6H); P-CH_2-$\mathrm{CH_3}$, δ 1.05 (dq, 6H); $\mathrm{PCH_2}$$CH_3$, δ 0.69 (dt, 9H). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): Pt−*C*, δ −3.98 (vt, ${}^1J_{\mathrm{PC}}$ = 59 Hz, ${}^1J_{\mathrm{PtC}}$ = 535 Hz).

$\mathbf{[PtCl(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}OMe)(PPh_2NHC_6H_4\text{-}4\text{-}OMe)\}]Cl}$ (2b). Anal. Calcd for $\mathrm{C_{45}H_{51}Cl_2N_2O_2P_3Pt}$: C, 53.46; H, 5.08; N, 2.77; P, 9.19. Found: C, 53.55; H, 5.18; N, 2.82; P, 9.08. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): N-*H*, δ 10.4 (brd, 1H, ${}^2J_{\mathrm{PH}}$ = 4.5 Hz); phenyl rings, δ 7.6, 8.3, 8.7 (m, 20H); N-C_6H_4, δ 6.54, 6.45 (vs, 8H, ${}^3J_{\mathrm{HH}}$ = n.r); Pt-*CH*, δ 4.21 (ddd, 1H; ${}^2J_{\mathrm{PtH}}$ = 57 Hz, ${}^2J_{\mathrm{PH}}$ = 1.7, 5.3, 12.1 Hz); $\mathrm{C_6H_4}$-4- OCH_3, δ 3.65, 3.58 (s, 6H); P-CH_2-$\mathrm{CH_3}$, δ 1.35, 1.22 (m, 6H); P-$\mathrm{CH_2}$-CH_3, δ 0.88 (dt, 9H). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): Pt-*C*, δ −4.12 (vt, ${}^1J_{\mathrm{PC}}$ = 60 Hz, ${}^1J_{\mathrm{PtC}}$ = 538 Hz).

$\mathbf{[PtBr(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}Me)(PPh_2NHC_6H_4\text{-}4\text{-}Me)\}]Br}$ (2c). FAB mass found: *m*/*z* = 987 ($\mathrm{M^+}$, calculated for $\mathrm{C_{45}H_{51}BrN_2P_3Pt}$ = 987.1). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): N−*H*, δ 9.24 (br d, 1H, ${}^2J_{\mathrm{PH}}$ = 4.1 Hz); phenyl rings, δ 8.7, 8.3, 7.6 (m, 20H); N−C_6H_4, δ 6.78, 6.71, 6.49, 6.41 (d, 8H, ${}^3J_{\mathrm{HH}}$ = 8 Hz); Pt−*CH*, δ 4.33 (m, 1H, ${}^2J_{\mathrm{PtH}}$ = 54 Hz, ${}^2J_{\mathrm{PH}}$ = nr); $\mathrm{C_6H_4}$-4-CH_3, δ 2.18, 2.09 (s, 6H); P$CH_2$$\mathrm{CH_3}$, δ 1.45, 1.20 (m, 6H); $\mathrm{PCH_2}$$CH_3$, δ 0.87 (dt, 9H). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): Pt−*C*, δ −2.16 (vt, ${}^1J_{\mathrm{PC}}$ = 60 Hz, ${}^1J_{\mathrm{PtC}}$ = 536 Hz).

$\mathbf{[PtCl(PMe_2Ph)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}Me)(PPh_2NHC_6H_4\text{-}4\text{-}Me)\}]Cl}$ (2d). Anal. Calcd for $\mathrm{C_{47}H_{47}Cl_2N_2P_3Pt}$: C, 56.51; H, 4.74; N, 2.80; P, 9.30. Found: C, 56.56; H, 4.85; N, 2.87; P, 9.15. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): N−*H*, δ 10.4 (br d, 1H, ${}^2J_{\mathrm{PH}}$ = nr); phenyl rings, δ 7.4, 8.1, 8.7 (m, 20H); N−C_6H_4, δ 6.82, 6.70, 6.58, 6.39 (d, 8H, ${}^3J_{\mathrm{HH}}$ = 8 Hz); Pt−*CH*, δ 4.31 (ddd, 1H, ${}^2J_{\mathrm{PtH}}$ = 57 Hz, ${}^2J_{\mathrm{PH}}$ = 2.5, 5.1, 11.9 Hz); $\mathrm{C_6H_4}$-4-CH_3, δ 2.08, 2.19 (s, 6H); P−CH_3, δ 1.45 (d, 3H, ${}^2J_{\mathrm{PH}}$ = 10.9 Hz); P−CH_3, δ 1.35 (d, 3H, ${}^2J_{\mathrm{PH}}$ = 10.9 Hz). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): Pt−*C*, δ −3.12 (vt, ${}^1J_{\mathrm{PC}}$ = 59 Hz, ${}^1J_{\mathrm{PtC}}$ = 534 Hz).

Substitution of the anions in the above described compounds (**2a**−**d**) can be accomplished by reaction of **1a**,**b** with $\mathrm{Pt_2X_4(PR_3)_2}$ in the presence of the appropriate sodium salt, or preferably by reacting the in situ formed complexes **2a**−**d** with the appropriate sodium salt.

$\mathbf{[PtCl(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}OMe)(PPh_2NHC_6H_4\text{-}4\text{-}OMe)\}]BF_4}$ (2e). A 5-fold excess (0.81 mmol) of $\mathrm{NaBF_4}$ was added to a solution of **2b** (161.8 mg, 0.16 mmol) in dichloromethane (20 mL) and stirred for 1.5 h. The cloudy yellow solution was filtered to remove the excess unreacted $\mathrm{NaBF_4}$ and the precipitated NaCl. The filtrate was evaporated to dryness to give 166.6 mg (98%) of pale yellow **2e**. Anal. Calcd for $\mathrm{C_{45}H_{51}BClF_4N_2O_2P_3Pt}$: C, 50.88; H, 4.84. Found: C, 50.60; H, 5.13. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): N-*H*, δ 7.2 (br, 1H, ${}^2J_{\mathrm{PH}}$ = nr); phenyl rings, δ 8.5, 8.4, 8.0, 7.4 (dd, 8H, ortho) and δ 7.8−7.2 (m, 12H, meta and para); N-C_6H_4, δ 6.63, 6.59, 6.50, 6.32 (d, 8H, ${}^3J_{\mathrm{HH}}$ = 9 Hz); Pt−*CH*, δ 3.37 (br m, 1H, ${}^2J_{\mathrm{PtH}}$ = 60 Hz); $\mathrm{C_6H_4}$-4-OCH_3, δ 3.67, 3.61 (s, 6H); P$CH_2$$\mathrm{CH_3}$, δ 1.39, 1.12 (m, 6H); $\mathrm{PCH_2}$$CH_3$, δ 0.86 (dt, 9H). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): Pt-*C*, δ −3.76 (vt, ${}^1J_{\mathrm{PC}}$ = 59 Hz, ${}^1J_{\mathrm{PtC}}$ = 532 Hz).

$\mathbf{[PtCl(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}OMe)(PPh_2NHC_6H_4\text{-}4\text{-}OMe)]CF_3CO_2}$ (2f). A procedure similar to the synthesis of **2e** was used, employing 97.6 mg of **2b** (0.097 mmol) and a 5-fold excess of $\mathrm{CF_3COONa}$, yielding 105.7 mg (99.9%) of pale yellow **2f**. Anal. Calcd for $\mathrm{C_{47}H_{51}ClF_3N_2O_4P_3Pt}$: C, 51.87; H, 4.73; N, 2.57; P, 8.54. Found: C, 51.66; H, 4.70; N, 2.64; P, 8.61. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): N−*H*, δ 10.5 (br d, 1H, ${}^2J_{\mathrm{PH}}$ = 7 Hz); phenyl rings, δ 8.5, 8.2, 7.5, 7.2 (m, 20H); N−C_6H_4, δ 6.59, 6.54, 6.45, 6.33 (d, 8H, ${}^3J_{\mathrm{HH}}$ = 9 Hz); Pt−*CH*, δ 3.88 (br m, 1H, ${}^2J_{\mathrm{PtH}}$ = 63 Hz); $\mathrm{C_6H_4}$-4-OCH_3, δ 3.65, 3.58 (s, 6H); P$CH_2$$\mathrm{CH_3}$, δ 1.40, 1.12 (m, 6H); $\mathrm{PCH_2}$$CH_3$, δ 0.91 (dt, 9H). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): Pt−*C*, δ −6.16 (vt, ${}^1J_{\mathrm{PC}}$ = 60 Hz, ${}^1J_{\mathrm{PtC}}$ = 539 Hz); CF_3, δ nr; $\mathrm{CF_3}$$CO_2$ δ 161.78 (q, ${}^2J_{\mathrm{CF}}$ = 27 Hz).

Following the Reaction Sequence in the Formation of 2a. In Benzene or Toluene. A mixture of $\mathrm{Pt_2Cl_4(PEt_3)_2Cl_4}$ (27.4 mg, 0.036 mmol) and $\mathrm{H_2C(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)_2}$ (**1a**) (42.4 mg, 0.071 mmol) in 0.6 mL $\mathrm{C_6D_6}$ or toluene-d_8 was stirred for 5 min at 293 K, which left both reactants completely dissolved. The reaction mixture was then transferred via a syringe into a 5 mm NMR tube and preserved at approximately 0 °C until the measurement was carried out. The first NMR experiment was performed at 20 °C, after a 10 min initial reaction time. Both ^{1}H and ^{31}P NMR data were collected at regular intervals of about 30 min at constant temperature (20 °C).

In $\mathbf{CD_2Cl_2}$. A similar reaction as described above was carried out in $\mathrm{CD_2Cl_2}$. Both reactants were dissolved at ambient temperature, and within 1 min transferred into a cooled NMR tube (−40 °C). NMR measurements were performed at −40 °C and between measurements the NMR tube was removed from the probe to warm to 20 °C in order to let the reaction proceed.

Intermediate A. ^{1}H NMR (toluene-d_8, after 10 min at 20 °C): phenyl rings, δ 8.3, 7.7, 6.7 (m, 20H); N-C_6H_4, δ 7.47, 6.58, 6.56, 6.44 (d, 8H, ${}^3J_{\mathrm{HH}}$ = 8 Hz); PCH_2P, δ 5.39 (dd, 2H, ${}^2J_{\mathrm{PH}}$ = 12.6, 18.5 Hz); $\mathrm{C_6H_4}$-4-CH_3, δ 1.99, 1.79 (s, 6H); P$CH_2$$\mathrm{CH_3}$, δ 1.57 (dq, 6H, ${}^2J_{\mathrm{PH}}$ = 10.8 Hz); $\mathrm{PCH_2}$$CH_3$, δ 0.82 (dt, 9H, ${}^3J_{\mathrm{HH}}$ = 7.9 Hz, ${}^3J_{\mathrm{PH}}$ = 16.8 Hz). ^{31}P NMR ($\mathrm{C_6D_6}$): $\mathrm{P_AEt_3}$, δ 0.9 (d, ${}^1J_{\mathrm{PtP}}$ = 3514 Hz, ${}^3J_{\mathrm{PP}}$ = 12.4 Hz); $\mathrm{P_B{=}N}$, δ 29.4 (dd, ${}^2J_{\mathrm{PtP}}$ = 64 Hz, ${}^3J_{\mathrm{PP}}$ = 12.4 Hz, ${}^2J_{\mathrm{PP}}$ = 2.7 Hz); $\mathrm{P_C{=}N}$, δ −5.7 (d, ${}^2J_{\mathrm{PP}}$ = 2.7 Hz).

Intermediate C. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −40 °C): N*H*, δ 9.5 (br); C_6H_4, δ 6.8 (vs); $\mathrm{C_6H_4}$-4-CH_3, δ 2.16 (s); all other signals are obscured by ^{1}H resonances of **A** and **2a**. ^{31}P NMR ($\mathrm{C_6D_6}$, 20 °C): P=N/P=NH, δ 26.1 (s). ^{31}P NMR ($\mathrm{CD_2Cl_2}$, −40 °C): P=N/P=NH, δ 25.7 (s).

Synthesis of $\mathbf{[PtCl(PEt_3)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)(PPh_2N'HC_6H_4\text{-}4\text{-}CH_3)\text{-}}\boldsymbol{C,N}\mathbf{\}]^+[PtCl_3(PEt_3)]^-}$ (2g). A mixture of $\mathrm{H_2C(PPh_2{=}N\text{-}C_6H_4\text{-}4\text{-}CH_3)_2}$ (**1a**) (0.39 mmol, 229.2 mg) and $\mathrm{Pt_2Cl_4(PEt_3)_2}$ (0.39 mmol, 296.1 mg) in 20 mL of toluene was stirred for 4 h at 60 °C and a pale yellow precipitate formed. The solvent was evaporated to about 10 mL, and 20 mL of pentane was added, resulting in the complete precipitation of a yellow solid, which could be isolated after filtration, washing with pentane (2 × 20 mL), and drying in vacuo. Yield: 531 mg, 100%. Crystals of **2g** were obtained from a similar reaction carried out in $\mathrm{CH_2Cl_2}$. A clear yellow mixture was stirred for only 3 h at 20 °C and put aside against pentane in a closed system. Over a period of 2 weeks yellow needle-shaped crystals were formed, which were suitable for X-ray crystal structure analysis. Anal. Calcd for $\mathrm{C_{51}H_{66}Cl_4N_2P_4Pt_2}$ (**2g**): C, 44.94; H, 4.88; N, 2.06; P, 9.09. Found: C, 45.06; H, 4.94; N, 2.11; P, 9.16. ^{1}H NMR ($\mathrm{CDCl_3}$): N−*H*, δ nr; phenyl rings, δ 8.73, 8.45, 8.30 (dd, 6H) and δ 7.5, 7.4, 7.3 (m, 12H); N−C_6H_4, δ 6.80, 6.51 (d, 4H, ${}^3J_{\mathrm{HH}}$ = 8.1 Hz) and δ 6.72, 6.64 (d, 4H, ${}^2J_{\mathrm{HH}}$ = 8.4 Hz); Pt−*CH*, δ 3.74 (br m, 1H, ${}^2J_{\mathrm{PtH}}$ = 62 Hz); $\mathrm{C_6H_4}$-4-CH_3, δ 2.18, 2.09 (s, 6H); P$CH_2$$\mathrm{CH_3}$, δ 1.91 (dq, 6H, anion) and δ 1.40, 1.10 (m, 6H, cation); $\mathrm{PCH_2}$$CH_3$, δ 1.13, 0.76 (dt, 18H, anion, cation resp.). ^{13}C NMR ($\mathrm{CD_2Cl_2}$): Pt−*C*, δ −2.93 (vt, ${}^1J_{\mathrm{PC}}$ = 57 Hz, ${}^1J_{\mathrm{PtC}}$ = 532 Hz).

Synthesis of $\mathbf{[PtCl(PEt_3)\{CH_2(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)_2\text{-}}\boldsymbol{N,N'}\mathbf{\}]^+[PtCl_3(PEt_3)]^-}$ ($\mathbf{2g^i}$): An Intermediate in the Formation of 2g. A solution of $\mathrm{H_2C(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)_2}$ (**1a**) (0.07 mmol, 40.2 mg) in dry toluene (5 mL) was added to a suspension of $\mathrm{Pt_2Cl_4(PEt_3)_2}$ (0.07 mmol, 51.9 mg) in 10 mL of toluene. The mixture was stirred for 17 h at 20 °C, which gave a clear yellow solution. The solvent was evaporation to 5 mL, and 20 mL of pentane was added, resulting in the precipitation of a yellow solid. After removal of the colorless upper layer, the precipitate was washed with pentane (2 × 10 mL) and dried in vacuo, yielding 92 mg of a yellow powder (96%). The product is contaminated with circa 5% **2g**. ^{1}H NMR ($\mathbf{2g^i}$, tol-$\mathrm{d_8}$, 293 K): phenyl rings, δ 6.9−9.0 (m, 22H); N−C_6H_4, δ 7.42, 6.71, 6.65 (d, 6H, ${}^3J_{\mathrm{HH}}$ = 8 Hz); PCH_2P, δ 5.53 (br t, 2H, ${}^2J_{\mathrm{PH}}$ = 12.2 Hz); $\mathrm{C_6H_4}$-4-CH_3, δ 1.91, 1.89 (s, 6H); P$CH_2$$\mathrm{CH_3}$, δ 1.68 (m, 6H, anion) and 1.26 (m, 6H, cation); $\mathrm{PCH_2}$$CH_3$, δ 0.93 (dt, 9H, anion) and 0.71 (dt, 9H, cation).^{1}H NMR (toluene-d_8, 233 K): phenyl rings, δ 8.9, 8.2, 7.7, 7.0−7.4 (m, 20H); N−C_6H_4, δ 7.55, 6.74 (d, 4H, ${}^3J_{\mathrm{HH}}$ = 8 Hz) and 6.6 (m, 4H): P$CH_{eq/ax}$P,

Table 1. Crystallographic Data for **2d** and **2g**

compounds	**2d**	**2g**
formula	$C_{47}H_{47}Cl_2N_2P_3Pt$	$C_{52}H_{68}Cl_6N_2P_4Pt_2$
mol wt	998.81	1447.9
space group	$P\bar{1}$	$P\bar{1}$
crystal system	triclinic	triclinic
a, Å	14.3852(11)	10.1970(8)
b, Å	15.4886(9)	14.5045(9)
c, Å	20.190(2)	20.5471(19)
α, deg	100.580(7)	96.154(7)
β, deg	92.223(8)	103.993(7)
γ, deg	99.508(6)	107.548(6)
V, Å^3	4350.1(6)	2757.8(4)
Z	4	2
ϱ_{calcd}, g cm^{-3}	1.5250(2)	1.7436(3)
$F(000)$	2000	1424
$\mu_{\mathrm{Mo\ K}\alpha,\ \mathrm{cm}^{-1}}$	35.2	55.1
data set	−18:18, −20:20, −26:26	−13:12, −12:18, −26:26
R^a	0.0436 [for 10625 $F_o > 5.0\sigma F_o$]	0.0501 [for 9008 $F_o > 4.0\sigma F_o$]
R_w^b	0.0432	
$wR2^c$		0.1247
S	3.25	0.99

[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] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

δ 5.75 (m, 1H) and δ 5.47 (dt, 1H, $^2J_{HH}$ = 16.5 Hz, $^2J_{PH}$ = 15.8 Hz); C_6H_4-4-CH_3, δ 1.94, 1.87 (s, 6H); PCH_2CH$_3$, δ 1.66 (m, 6H, anion) and 1.17 (m, 6H, cation); PCH$_2$$CH_3$, δ 0.91 (dt, 9H, anion) and 0.66 (dt, 9H, cation). ^{1}H NMR (CD_2Cl_2, 233 K): P−$CH_{eq/ax}$-P, δ 5.09 (dt, 1H, $^2J_{HH}$ = 15.7 Hz, $^2J_{PH} \approx$ 16 Hz) and δ 4.47 (m, 1H). FAB mass found: m/z = 943 (M$^+$, calculated for $C_{45}H_{51}ClN_2P_3Pt$ = 943.61).

Synthesis of PtCl(PEt$_3$){CH(PPh$_2$=NC$_6$H$_4$-4-CH$_3$)$_2$-*C,N*} (3). Method A: Reaction of Pt$_2$Cl$_4$(PEt$_3$)$_2$ with 4 equiv of 1a. To a suspension of $Pt_2Cl_4(PEt_3)_2$ (0.12 mmol, 92.7 mg) in 20 mL of toluene was added 4 equiv (0.48 mmol, 286.9 mg) of the ligand $H_2C(PPh_2{=}NC_6H_4\text{-}4\text{-}CH_3)_2$ (**1a**). After 20 h of stirring, a white precipitate formed which was separated from the clear yellow solution by filtration. The yellow filtrate was then completely evaporated, leaving an oily residue. Addition of 40 mL of cold pentane gave a yellow solid (**3**). Yield: 195 mg (0.21 mmol; 86%). The remaining white precipitate on the filter was washed with pentane (2 × 20 mL) and dried in vacuo, yielding a white powder, the HCl salt of the ligand, $[HC(PPh_2NHC_6H_4\text{-}4\text{-}CH_3)_2]^+(Cl^-)$ (**4**). Yield: 145 mg (0.23 mmol; 96%).

Method B: Reaction of 2a with 1 equiv of 1a. A solution of $H_2C(PPh_2{=}N\text{-}C_6H_4\text{-}4\text{-}CH_3)_2$ (**1a**) (0.04 mmol, 24 mg) was added to a stirred solution of **2a** (0.04 mmol, 39 mg) in toluene. After 20 h a white precipitate was formed and the products were isolated as described above.

Compound 3. Anal. Calcd for $C_{45}H_{50}ClN_2P_3Pt$: C, 57.34; H, 5.35; N, 2.97; P, 9.86. Found: C, 57.28; H, 5.55; N, 2.85; P, 9.81. ^{1}H NMR (CD_2Cl_2): phenyl rings, δ 8.4, 7.0−8.0 (m, 20H); N−C_6H_4, δ 7.77, 6.66, 6.48, 6.24 (br d, 8H, $^3J_{HH}$ = nr); Pt−CH, δ 2.47 (br m, 1H, $^2J_{PtH}$ = 59 Hz); C_6H_4-4-CH_3, δ 2.18, 2.11 (s, 6H); PCH_2CH$_3$, δ 1.93, 1.66 (m, 6H); PCH$_2$$CH_3$, δ 0.99 (dt, 9H). ^{13}C NMR (CD_2Cl_2): Pt−C, δ 1.67 (dd, $^1J_{PC}$ = 70, 93 Hz, $^1J_{PtC}$ = nr).

Compound 4. ^{1}H NMR ($CDCl_3$): N−H, δ 9.5 (br, 2H, $^2J_{PH}$ = nr); phenyl rings, δ 7.65, 7.35, 7.23 (m, 20H); N−C_6H_4, δ 6.81, 6.75 (d, 8H, $^3J_{HH}$ = 8.3 Hz); P(CH)P, δ 1.95 (br t, 1H, $^2J_{PH}$ = 4.0 Hz); C_6H_4-4-CH_3, δ 2.11 (s, 6H). ^{31}P NMR ($CDCl_3$): −Ph_2PNHpTol, δ 26.1 ppm (s). ^{13}C NMR (CD_2Cl_2): PCHP, δ 14.9 (t, $^1J_{PC}$ = 131 Hz). FAB mass found: m/z = 595 (M$^+$, calculated for $C_{39}H_{37}N_2P_2$ = 595.7).

X-ray Crystallography on Compounds 2d and 2g. Crystal data and experimental procedures on both crystal structures are collected in Table 1. Yellowish crystals, 0.1 × 0.1 × 0.2 mm (0.05 × 0.20 × 0.38 mm for **2g**) suitable for X-ray structure determination were mounted on a Lindemann-glass capillary and immediately placed on an Enraf-Nonius CAD4-T diffractometer on a rotating anode: **2d** at 298 K; **2g** in the cold dinitrogen stream (150 K). Data were collected in the $\omega/2\theta$ mode, λ(Mo Kα) 0.71073 (monochromator), θ in the range 1.0−27.5°. Scan angle was $\Delta\omega = a + 0.35 \tan \theta°$ with a = 0.61 and 0.85 for **2d** and **2g**, respectively. Unit-cell dimensions and standard deviations were obtained by least-squares fit (SET4)[14] of the setting angles from 25 reflections in the range 11.5° < θ < 13.9° and 10.5° < θ < 14.0° (for **2d** and **2g**, respectively). Reduced-cell calculations did not indicate higher lattice symmetry.[15] Three standard reflections were monitored periodically and showed approximately 8% (4% for **2g**) variation in intensity during data collection. The data were scaled accordingly. Intensity data were corrected for Lorentz, polarization and absorption effects (an empirical absorption/extinction was applied (DIFABS)[16] 0.392−1.000 (0.279−1.000 for **2g**)) and averaged into a unique set of reflections. Total data of 23 149 and 14 714 reflections were collected of which 19 953 and 12 646 were independent (R_{int} = 0.0337 and 0.0621) for **2d** and **2g**, respectively.

Structure **2d** was solved by automatic direct methods (SHELXS86).[17] Refinement on F was carried out by full-matrix least-squares techniques (SHELX76);[18] final R value 0.044, R_w = 0.043, $w = 1/[\sigma^2(F) + 0.000178F^2]$, S = 3.25 (based on the variance), for 993 parameters and 10 625 reflections with $I > 2.5\sigma(I)$. 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 two common isotropic displacement parameters. Weights were introduced in the final refinement cycles. The unit cell contains two small potential solvent accessible areas (21 and 24 Å^3), but a difference Fourier showed no residual density in that region. The final difference Fourier showed no residual density outside −1.09 and +2.04 e Å^{-3}, close to Pt. Neutral atom scattering factores were taken from Cromer and Mann,[19] with anomalous dispersion corrections from Cromer and Liberman.[20]

Structure **2g** was solved by automatic Patterson methods and subsequent difference Fourier synthesis (DIRDIF-92).[21] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93):[22] final $R1$ value 0.0501 for 603 parameters and 9008 reflections with $I > 2.0\sigma(I)$, $wR2$ = 0.1247 for all 12646 reflections, S = 0.99,

---

(14) de Boer, J. L.; Duisenberg, A. J. M. *Acta Crystallogr.* **1984**, *A40*, C410.

(15) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(16) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(17) Sheldrick, G. M. SHELXS86 Program for crystal structure determination. University of Göttingen, Germany, 1986.

(18) Sheldrick, G. M. SHELX76 Program for crystal structure determination. University of Cambridge, Cambridge, 1976.

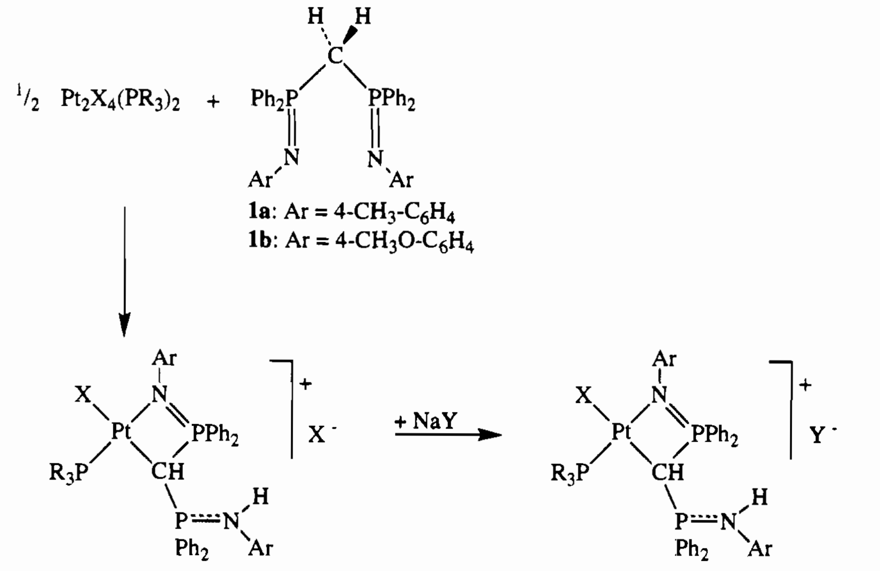
(19) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(20) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(21) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system, Technical report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

(22) Sheldrick, G. M. SHELXL-93 Program for crystal structure refinement. University of Göttingen, Germany, 1993.

Scheme 1



2a: $PR_3 = PEt_3$, X = Cl, Ar = 4-CH_3-C_6H_4
2b: $PR_3 = PEt_3$, X = Cl, Ar = 4-CH_3O-C_6H_4
2c: $PR_3 = PEt_3$, X = Br, Ar = 4-CH_3-C_6H_4
2d: $PR_3 = PMe_2Ph$, X = Cl, Ar = 4-CH_3-C_6H_4

2e: $PR_3 = PEt_3$, X = Cl,
Ar = 4-CH_3O-C_6H_4, Y = BF_4
2f: $PR_3 = PEt_3$, X = Cl,
Ar = 4-CH_3O-C_6H_4, Y = CF_3CO_2

and $w = 1/[\sigma^2(F_o^2) + (0.0724P)^2]$ where $P = (\max((F_o^2, 0) + 2F_c^2)/3$. All reflections were considered observed during refinement. An observance criterion was only applied for calculation of *R1*. 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 or 1.2 times the value of the equivalent isotropic thermal parameters of their carrier atoms, for methyl hydrogen and all other hydrogen atoms, respectively. Weights were introduced in the final refinement cycles. A final difference Fourier showed no residual density outside −2.04 and +1.58 e Å^{-3}, near Pt. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 23.

All geometrical calculations and ORTEP illustrations were performed with PLATON.[24] Positional parameters are listed in Tables 3 and 4. Computing was conducted on a DEC-station 5000 cluster.

Results

Synthesis and Spectroscopic Identification of Complexes 2a−f. The *b*is(*i*mino-*p*hosphoranyl)*m*ethane (BIPM) ligands $CH_2(PPh_2{=}NC_6H_4\text{-}4\text{-}R')_2$, **1a,b** (with R′ = CH_3, OCH_3), reacted cleanly with the halide-bridged platinum dimers $Pt_2X_4(PR_3)_2$ (with X = Cl, Br; PR_3 = PEt_3, PMe_2Ph) to afford new four-membered platinacycles **2a−d** in good yields (70−95%). Subsequent anion metathesis of **2b** gave compounds **2e,f** quantitatively (Scheme 1).

The bridge-splitting reaction proceeds under mild conditions in dichloromethane or tetrahydrofuran within 4 h at 20 °C. In toluene, the product precipitates spontaneously from the solution after 6 h of stirring. This advantage was used to grow crystals of **2d**, which were suitable for X-ray structure determination. In the case of **1c** (R′ = NO_2), in view of the decreased nucleophilicity of the N atoms, no complex formation but only decomposition was observed.

Compounds **2a−f** are air-stable pale yellow solids, readily soluble in THF, CH_2Cl_2, and $CHCl_3$, moderately soluble in toluene, and insoluble in apolar solvents. They are monomeric in solution. Decomposition occurs when these solutions are exposed to air or when they are heated above 70 °C (in benzene). No blackening (Pt^0) is observed, but several unidentified decomposition products are formed.

Proof for the N,C coordination of BIPM in **2a−f** was obtained from ^1H, ^{13}C and ^{31}P NMR (see Experimental Section and Table 2) and X-ray crystal structure determination of **2d** (Figure 1, Table 5). Characteristically, for the methine proton at δ 3.4−4.6 ppm a doublet of double doublet multiplicity was observed due to coupling with three inequivalent ^{31}P nuclei. Taken together with $^2J_{PtH}$ of about 60 Hz, observed by measuring $^1H\{^{31}P\}$NMR spectra, these data implicate the presence of a $P_APtCHP_BP_C$ unit. Further support was derived from $^{13}C\{^1H\}$ spectra, where a triplet was found at values between −2.2 and −6.2 ppm with $^1J_{PC}$ of ca. 60 Hz and Pt satellites ($^1J_{PtC}$ of about 535 Hz). The presence of an PNH(Ar) moiety, by 1,3-H shift from the methylene carbon to the noncoordinated N, was inferred from ^1H NMR where a broad (doublet) NH resonance was found at 9.2−10.9 ppm (**2a−d** and **2f**) or at 7.2 ppm (**2e**). Interestingly, for compound **2d**, two sets of signals are observed for the diastereotopic PMe groups in the ^1H and ^{13}C NMR, since N,C coordination of the aminophosphonium (iminophosphoranyl)methanide ligand to Pt induces chirality on the sp^3-C atom bonded to platinum.

The ^{31}P NMR spectra invariably exhibit three resonances at characteristic positions; a singlet with Pt-satellites ($^1J_{PtP_A}$ = 3560−3680 Hz) for P_A and two doublets for P_B and P_C ($^2J_{P_BP_C}$ = 9−13 Hz, $^2J_{PtP_B}$ = 383−409 Hz, $^2J_{PtP_C}$ = 101−125 Hz). These data indicate that P_A is *trans* to N[25−29] and, in view of

---

[23] Wilson, A. J. C. (ed.), *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

[24] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(25) (a) Hartley, F. R. *Chem. Soc. Rev.* **1973**, *2*, 163. (b) Verkade, J. G., Quin, L. D., Eds. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, Organic Compounds and Metal Complexes*; VCH: Weinheim, Germany, 1987; pp 439, 513.

(26) Albinati, A.; Lianza, F.; Muller, B.; Pregosin, P. S. *Inorg. Chim. Acta* **1993**, *208*, 119.

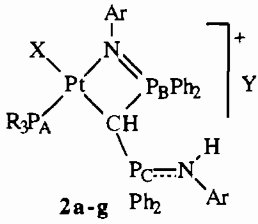
(27) van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1980**, *19*, 1145.

(28) Chivers, T.; Doxsee, D. D.; Hilts, R. W.; Meetsma, A.; Parvez, M.; van de Grampel, J. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1330.

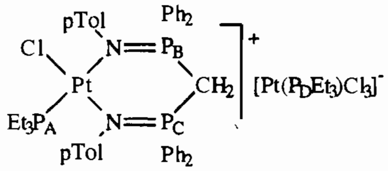
Table 2. ^{31}P NMR Data for the Complexes **2a–g**, **2g^i**, and **3**^{a}

compd	solvent	$\delta(P_A)$	$\delta(P_B)$	$\delta(P_C)$	$^1J_{PtP_A}$	$^2J_{PtP_B}$	$^2J_{PtP_C}$	$^2J_{P_BP_C}$
2a	$CDCl_3$	0.5(s)	26.4(d)	28.2(d)	3610	402	108	12.2
	C_6D_6	0.8(s)	24.1(d)	27.5(d)	3645	397	109	12.6
2b	CD_2Cl_2	0.3(s)	29.3(d)	28.3(d)	3595	395	107	11.5
	C_6D_6	0.7(s)	23.9(d)	27.3(d)	3640	399	125	12.9
2c	$CDCl_3$	−0.3(s)	26.0(d)	27.0(d)	3566	388	107	12.0
	CD_2Cl_2	−0.4(s)	28.3(d)	28.0(d)	3562	405	101	11.7
2d	$CDCl_3$	−22.3(s)	30.0(d)	27.6(d)	3679	406	119	12.0
	C_6D_6	−22.4(s)	26.4(d)	28.0(d)	3679	392	114	11.7
2e	CD_2Cl_2	−0.3(s)	27.2(d)	29.9(d)	3576	400	117	10.2
	C_6D_6	0.4(s)	22.8(d)	29.1(d)	3611	397	111	11.1
2f	CD_2Cl_2	0.1(s)	32.1(d)	29.5(d)	3575	409	103	9.3
	C_6D_6	0.3(s)	28.7(vs)	28.7(vs)	3610	404	103	10.0
2g^b	CD_2Cl_2	0.3(s)	26.5(d)	29.2(d)	3589	399	112	11.6
2g^i^{c}	C_6D_6	1.4(d)^d	23.7(dd)^d	29.9(d)	3620	nr	71	24.1
3	CD_2Cl_2	0.4(s)	31.1(br s)	6.3(br s)	3756	425	112	nr
	CD_2Cl_2^{e}	0.7(s)	32.5(d)	8.0(d)	3740	426	114	3.9

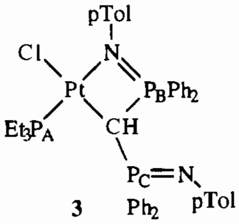
^{a} Measured at 40.5 or 121.5 MHz at 293K, unless noted otherwise. The atom labeling scheme is shown below. Multiplicity labels and abbreviations: br = broad, s = singlet, d = doublet, dd = doublet of doublet, vs = virtual singlet, nr = not resolved. ^{b} Pt(PEt$_3$)Cl$_3$ anion in **2g**: $\delta(PEt_3)$ = 3.1 ppm (s), $^1J_{PtP_D}$ = 3767 Hz. ^{c} Pt(PEt$_3$)Cl$_3$ anion in **2g^i**: $\delta(PEt_3)$ = 1.9 ppm (s), $^1J_{PtP_D}$ = 3804 Hz. ^{d} $^3J_{P_AP_B}$ = 2.4 Hz. ^{e} Measured at 253 K.



2a-g



2g^i



3

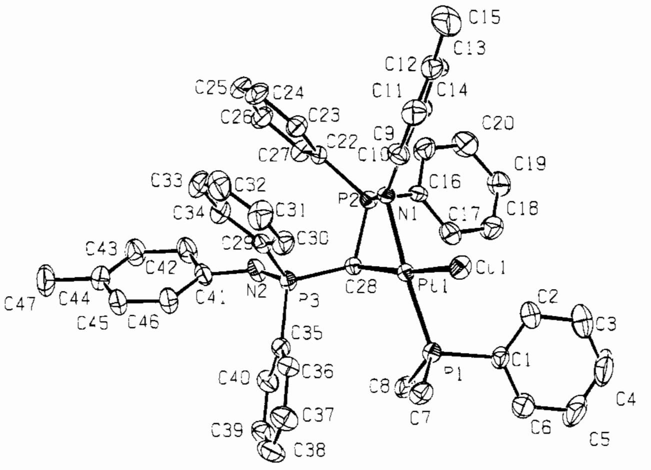


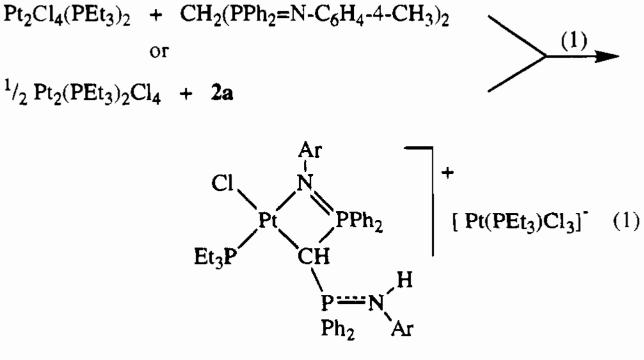
Figure 1. ORTEP 30% problability plot of **2d** (PLATON).[24] Hydrogen atoms have been omitted for clarity.

the larger $^2J_{PtP_B}$ as compared to $^2J_{PtP_C}$ and, by comparison with data for similar complexes PtCl(PEt$_3$){CH(PPh$_2$=X)-(PPh$_2$=Y)},[29,30] that P$_B$ is contained within the four-membered platinacycle. The relative $\delta(P_B)$ and $\delta(P_C)$ positions in the range 22.8–32.1 ppm are not fixed, but can interchange when different deuterated solvents are used (Table 2).

Unfortunately, several attempts to coordinate the bis(iminophosphoranyl)methane ligands to palladium by using Pd$_2$Cl$_4$(PR$_3$)$_2$ (PR$_3$ = PEt$_3$, PMe$_2$Ph) failed. The mixture of products formed in each reaction are mostly involved in complex exchange processes, probably due to the weaker coordination of the ligand toward palladium. Attempts to stabilize palladium complexes by addition of sodium or silver salts of large anions were unsuccessful.

Synthesis of Compounds 2g, 3, and 4; Dependence on the Metal-to-Ligand Ratio. The outcome of the reaction between CH$_2$(PPh$_2$=NC$_6$H$_4$-4-R′)$_2$ and Pt$_2$X$_4$(PR$_3$)$_2$ is thermodynamically determined; the order in which the two reactants are added, or other variations in the reaction conditions such as the solvent (benzene, toluene, dichloromethane, tetrahydrofuran) or longer reaction time have an effect neither on the composition of the reaction mixture nor on the structure of the product. The metal-to-ligand (M:L) ratio, however, does have an enormous influence on the types of product formed.

A metal-to-ligand (Pt:BIPM) ratio of 2:1 in the reaction of the ligand **1a** or the complex **2a** with Pt$_2$Cl$_4$(PEt$_3$)$_2$ in toluene at 60 °C leads to the binuclear ionic compound **2g** (eq 1), the single X-ray crystal structure of which was determined (see below). The structure of **2g** is similar to the structures of **2a–f**, except for the [PtCl$_3$(PEt$_3$)]$^-$ counterion.



(1)

2g: Ar = 4-CH$_3$-C$_6$H$_4$

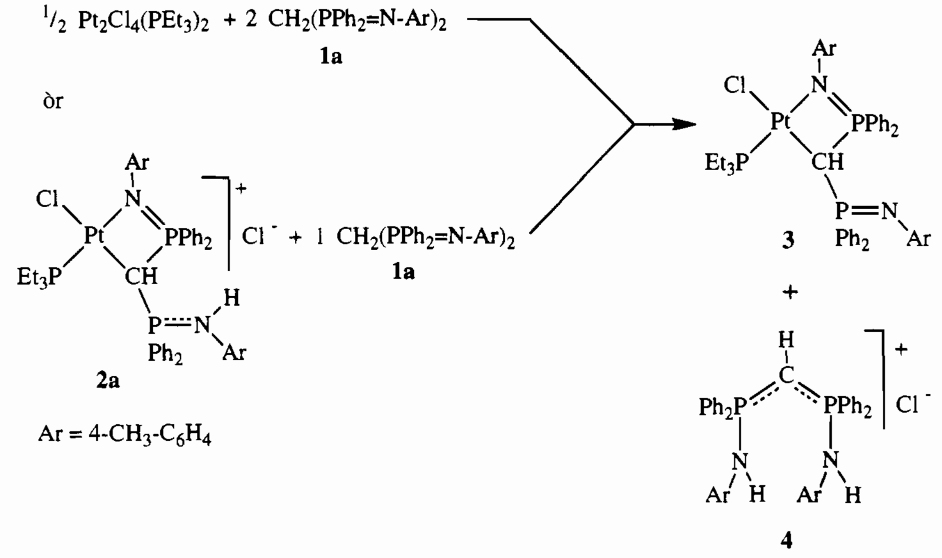
When using a Pt:BIPM = 1:2 ratio, the neutral metallacyclic compound **3** containing an N,C-coordinated bis(iminophos-

---

(29) Avis, M. W.; Ernsting, J. M.; Vrieze, K.; Elsevier, C. J.; Kooijman, H.; Veldman, N.; Spek, A. L.; Katti, K. V.; Barnes, C. L. To be submitted for publication.

(30) Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W.; Pidcock, A. *Inorg. Chem.* **1992**, *31*, 1479.

Scheme 2. Formation of **3** Containing an Anionic Bis(iminophosphoranyl)methanide Ligand by Reaction with Excess BIPM, M:L = 1:2



phoranyl)methanide, the anion of BIPM, is formed. Compound **3** is formed irrespective of whether 1 equiv of **1a** is added to a solution of **2a**, or a one-pot reaction of $Pt_2(PEt_3)_2Cl_4$ with 2 equiv of **1a** is carried out. Obviously, the additional ligand behaves as a base, abstracting HCl from complex **2a**, forming the deprotonated platinum complex $Pt(PEt_3)Cl\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}Me)(PPh_2{=}NC_6H_4\text{-}4\text{-}Me)\text{-}C,N\}$ (**3**) and the HCl salt of BIPM: $[CH(PPh_2NHC_6H_4\text{-}4\text{-}Me)_2]^+Cl^-$ (**4**) (Scheme 2).

This reaction is best performed in toluene, since the precipitation of **4** pulls the reaction to completion. The neutral four-membered metallacyclic compound **3** is similar to the earlier reported Rh– and Ir–bis(iminophosphoranyl)methanide complexes.[4e] One of the iminophosphorane entities remains non-coordinated, as was clearly established by $^{31}P\{^1H\}$ NMR spectroscopy.

The ^{31}P, ^1H, and ^{13}C NMR spectra indicate an N,C chelating coordination mode of the BIPM ligand in **2g** and its anionic derivative in **3**, as most of the data are similar to those found for **2a–f**. For **2g** an additional resonance is observed at 3.1 ppm ($^1J_{PtP_D}$ = 3767 Hz) in the ^{31}P NMR as well as an additional set of P_DEt_3 signals in the ^1H and ^{13}C NMR.

For the neutral compound **3**, slightly broadened resonances are observed in the ^1H, ^{31}P and ^{13}C NMR at room temperature, indicating that complex **3** exhibits fluxional behavior. The fluxionality of **3** is best illustrated by the ^{31}P NMR data at 293 K (Table 2), showing two broad singlets at 31.1 and 6.3 ppm, with $^2J_{PtP}$ = 425 Hz and $^2J_{PtP}$ = 112 Hz, belonging to P_B and P_C, respectively. When the solution of **3** is cooled to 253 K, the signals belonging to the two P=N functions sharpen up into doublets, due to mutual $^2J_{P_BP_C}$ of 3.9 Hz. The $\delta(P_C)$ and $^2J_{P_BP_C}$, $^2J_{PtP_C}$ are significantly different in **3** from those in **2a–g**, and their values are in agreement with a pendant, nonprotonated $Ph_2P{=}NAr$ moiety, and is circumstantially confirmed by the absence of NH in the ^1H NMR. At 293 K, a slow exchange between the coordinated and the non-coordinated P=N groups takes place. Coalescence of the two signals P_B and P_C could not be reached upon raising the temperature, as a continuing reaction within the complex takes place.[31] Unfortunately, in the ^{13}C NMR, $^1J_{PtC}$ is not observed for **3** due to line broadening for this resonance (even at 253 K).

The ^1H NMR spectrum of **4** shows a broad NH resonance at 9.5 ppm and a triplet for the CH resonance with $^2J_{PH}$ = 4 Hz at 1.95 ppm; the relative integrals of these signals indicate the presence of two NH and one CH proton, respectively. In the ^{13}C NMR, a triplet at 14.9 ppm with $^1J_{P_BC} = {}^1J_{P_CC}$ = 131 Hz is observed, whereas the free ligand **1a** exhibits its CH_2 resonance at 30.5 ppm with $^1J_{PC}$ = 63.5 Hz.[4b] The spectra point to a symmetric compound, since a singlet resonance in ^{31}P NMR at 26.1 ppm, and one set of resonances for the $4\text{-}MeC_6H_4N$ groups in ^1H and ^{13}C NMR are found. Together with FAB mass spectroscopy the formulation of **4** is established as $[CH\{PPh_2N(H)C_6H_4\text{-}4\text{-}Me\}_2]^+Cl^-$.

X-ray Crystal Structures of 2d and 2g. The X-ray crystal structures of both $[PtCl(PMe_2Ph)\{CH(PPh_2{=}NpTol)(PPh_2NH\text{-}pTol)\}]^+[Cl^-]$ **2d**, and the dinuclear $[PtCl(PEt_3)\{CH(PPh_2{=}NpTol)(PPh_2NH\text{-}pTol)\}]^+[PtCl_3(PEt_3)^-]\cdot CH_2Cl_2$ **2g** have been determined (Tables 1, 3–6, Figures 1 and 2).

The molecular structures of the cationic part show close similarities and will be treated together as much as possible. For **2d** two crystallographically independent molecules are present in the unit cell. Only one of them will be discussed here. Deviating crystallographic data for the other molecule will be noted.[32] The coordinations around the platinum centers are approximately square-planar in both complexes, with the five atoms Pt, Cl(1), N(1), P(1), and C(28) (**2d**) or C(26) (**2g**) having deviations of +0.065(1), +0.074(2), −0.095(2), −0.116(6), and 0.095(8) Å (**2d**)[32a] and −0.064(1), −0.026(2), +0.067(6), +0.057(2), and −0.035(8) Å (**2g**), respectively, from the least-squares planes.

In both structures $CH_2(PPh_2{=}NpTol)_2$ acts as a N,C chelating ligand in its tautomeric form, giving rise to cationic four-membered Pt–N–P–C metallacycles. The Pt–N(1) bond distances of 2.099(6) Å (**2d**) and 2.128(6) Å (**2g**) are characteristic for σ-donor interactions *trans* to PR_3 ligands,[26,28,33–36] but are longer than the only other known Pt-phosphinimine

---

(31) These results fall outside the context of this paper and will be published in an forthcoming paper, concerning deprotonated Pt– and Pd–bis(iminophosphoranyl)methanide systems.[29]

(32) (a) The independent enantiomer has deviations of −0.073(1), −0.042(2), +0.079(2), +0.091(6), and −0.056(8) Å from the least-squares plane through Pt(51), Cl(51), N(51), P(51), and C(78). (b) C(66)–C(71) is the atom labeling for the corresponding phenyl group of the other enantiomer. (c) The other enantiomer has a folding angle of 34.9(5)°.

(33) van der Poel, H.; van Koten, G.; Vrieze, K.; Kokkes, M.; Stam, C. H. *J. Organomet. Chem.* **1979**, *175*, C21.

(34) Chivers, T.; McGregor, K.; Parvez, M. *Inorg. Chem.* **1993**, *32*, 5119.

Table 3. Fractional Coordinates for **2d**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}^{a}	atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}^{a}
Pt(1)	1.02141(2)	0.40836(2)	0.34953(2)	0.0363(1)	Cl(51)	0.37281(16)	0.09538(16)	0.05148(12)	0.0591(9)
Cl(1)	1.10757(16)	0.40877(16)	0.45013(11)	0.0580(8)	P(51)	0.57085(15)	0.17853(15)	0.12359(12)	0.0458(8)
P(1)	0.91008(15)	0.30966(15)	0.38082(11)	0.0433(8)	P(52)	0.38625(15)	0.04432(14)	0.26734(11)	0.0429(8)
P(2)	1.07723(14)	0.44658(14)	0.22889(11)	0.0387(7)	P(53)	0.57115(16)	−0.02672(15)	0.24197(12)	0.0507(8)
P(3)	0.89190(14)	0.51058(14)	0.26115(11)	0.0415(8)	N(51)	0.3392(5)	0.0087(4)	0.1924(3)	0.050(3)
N(1)	1.1268(4)	0.4833(4)	0.3041(3)	0.039(2)	N(52)	0.5994(5)	−0.0269(5)	0.3207(3)	0.067(3)
N(2)	0.8585(4)	0.5085(5)	0.1825(3)	0.051(3)	C(51)	0.5369(6)	0.2860(6)	0.1160(4)	0.048(3)
C(1)	0.9506(6)	0.2067(5)	0.3885(4)	0.050(3)	C(52)	0.4558(7)	0.3094(7)	0.1417(5)	0.068(4)
C(2)	1.0386(7)	0.1909(7)	0.3710(5)	0.069(4)	C(53)	0.4326(8)	0.3924(8)	0.1396(6)	0.089(5)
C(3)	1.0646(9)	0.1107(8)	0.3766(6)	0.095(6)	C(54)	0.4914(9)	0.4497(8)	0.1098(7)	0.088(5)
C(4)	1.0066(11)	0.0464(9)	0.3983(8)	0.123(8)	C(55)	0.5724(8)	0.4273(7)	0.0843(6)	0.083(5)
C(5)	0.9181(10)	0.0590(8)	0.4150(7)	0.105(6)	C(56)	0.5958(6)	0.3466(6)	0.0893(5)	0.062(4)
C(6)	0.8906(7)	0.1394(7)	0.4106(5)	0.070(4)	C(57)	0.6180(6)	0.1422(6)	0.0448(5)	0.066(4)
C(7)	0.8639(6)	0.3464(6)	0.4602(4)	0.060(3)	C(58)	0.6733(5)	0.2132(5)	0.1817(5)	0.058(3)
C(8)	0.8088(5)	0.2704(6)	0.3227(5)	0.060(4)	C(59)	0.2447(6)	−0.0292(5)	0.1662(5)	0.049(3)
C(9)	1.2207(6)	0.5191(5)	0.3245(4)	0.041(3)	C(60)	0.2302(6)	−0.0751(6)	0.1010(5)	0.056(3)
C(10)	1.2423(6)	0.5722(6)	0.3887(5)	0.055(3)	C(61)	0.1413(8)	−0.1174(7)	0.0734(6)	0.079(5)
C(11)	1.3347(7)	0.6098(6)	0.4125(6)	0.071(4)	C(62)	0.0648(7)	−0.1129(7)	0.1117(7)	0.077(5)
C(12)	1.4090(7)	0.5965(7)	0.3709(7)	0.072(5)	C(63)	0.0796(7)	−0.0645(7)	0.1757(6)	0.074(5)
C(13)	1.3882(6)	0.5421(7)	0.3093(6)	0.068(4)	C(64)	0.1665(6)	−0.0237(6)	0.2033(5)	0.061(4)
C(14)	1.2957(6)	0.5031(6)	0.2853(5)	0.054(3)	C(65)	−0.0317(7)	−0.1653(8)	0.0805(8)	0.142(8)
C(15)	1.5099(7)	0.6420(8)	0.3959(7)	0.118(6)	C(66)	0.3634(5)	0.1523(5)	0.3104(4)	0.043(3)
C(16)	1.1024(5)	0.3424(5)	0.1833(4)	0.043(3)	C(67)	0.4071(7)	0.1989(6)	0.3665(5)	0.080(4)
C(17)	1.0601(6)	0.2638(6)	0.1989(5)	0.062(3)	C(68)	0.3854(9)	0.2812(7)	0.3954(6)	0.100(5)
C(18)	1.0861(7)	0.1839(6)	0.1695(5)	0.072(4)	C(69)	0.3223(8)	0.3161(7)	0.3661(6)	0.075(5)
C(19)	1.1498(7)	0.1813(7)	0.1218(5)	0.070(4)	C(70)	0.2779(8)	0.2740(7)	0.3061(7)	0.097(6)
C(20)	1.1904(7)	0.2610(7)	0.1052(5)	0.080(5)	C(71)	0.2975(7)	0.1920(6)	0.2766(5)	0.082(4)
C(21)	1.1659(6)	0.3407(6)	0.1354(5)	0.067(4)	C(72)	0.3563(6)	−0.0332(6)	0.3216(4)	0.051(3)
C(22)	1.1005(5)	0.5254(5)	0.1733(4)	0.041(3)	C(73)	0.3136(6)	−0.1188(6)	0.2974(5)	0.060(3)
C(23)	1.1471(6)	0.6106(6)	0.2015(5)	0.055(3)	C(74)	0.2960(7)	−0.1817(6)	0.3366(5)	0.076(4)
C(24)	1.1615(6)	0.6731(6)	0.1602(6)	0.069(4)	C(75)	0.3220(8)	−0.1605(7)	0.4034(6)	0.090(5)
C(25)	1.1338(6)	0.6510(6)	0.0925(5)	0.063(4)	C(76)	0.3669(13)	−0.0787(9)	0.4314(6)	0.165(8)
C(26)	1.0853(6)	0.5676(6)	0.0662(5)	0.059(4)	C(77)	0.3838(12)	−0.0132(8)	0.3889(6)	0.143(8)
C(27)	1.0692(6)	0.5042(6)	0.1062(4)	0.051(3)	C(78)	0.5052(5)	0.0632(5)	0.2441(4)	0.041(3)
C(28)	0.9605(5)	0.4226(5)	0.2569(4)	0.040(3)	C(79)	0.5029(6)	−0.1330(5)	0.2028(5)	0.051(3)
C(29)	0.9561(5)	0.6191(5)	0.2995(4)	0.048(3)	C(80)	0.4616(6)	−0.1476(6)	0.1374(5)	0.061(4)
C(30)	0.9972(6)	0.6375(6)	0.3645(5)	0.064(4)	C(81)	0.4095(7)	−0.2311(7)	0.1079(6)	0.077(4)
C(31)	1.0428(7)	0.7225(7)	0.3923(6)	0.086(5)	C(82)	0.3988(8)	−0.3015(7)	0.1424(7)	0.093(6)
C(32)	1.0522(8)	0.7866(7)	0.3540(8)	0.097(6)	C(83)	0.4397(8)	−0.2859(7)	0.2071(7)	0.091(6)
C(33)	1.0153(8)	0.7690(7)	0.2901(7)	0.092(6)	C(84)	0.4916(6)	−0.2031(7)	0.2371(6)	0.073(4)
C(34)	0.9689(6)	0.6851(6)	0.2606(6)	0.072(4)	C(85)	0.6794(5)	−0.0057(5)	0.1995(5)	0.051(3)
C(35)	0.7882(5)	0.4879(5)	0.3070(4)	0.043(3)	C(86)	0.6833(6)	−0.0282(6)	0.1305(4)	0.055(3)
C(36)	0.7877(6)	0.5111(6)	0.3762(5)	0.059(4)	C(87)	0.7691(7)	−0.0070(7)	0.1030(5)	0.076(4)
C(37)	0.7068(7)	0.4893(7)	0.4087(5)	0.074(4)	C(88)	0.8479(6)	0.0349(7)	0.1423(6)	0.084(5)
C(38)	0.6254(7)	0.4458(8)	0.3705(7)	0.087(5)	C(89)	0.8449(7)	0.0554(7)	0.2106(6)	0.073(4)
C(39)	0.6250(7)	0.4235(7)	0.3019(6)	0.075(5)	C(90)	0.7613(7)	0.0365(6)	0.2392(5)	0.062(4)
C(40)	0.7055(6)	0.4438(6)	0.2695(5)	0.058(4)	C(91)	0.6529(7)	−0.0829(7)	0.3497(5)	0.065(4)
C(41)	0.8038(6)	0.5630(6)	0.1542(5)	0.051(3)	C(92)	0.6452(9)	−0.0833(8)	0.4174(5)	0.110(6)
C(42)	0.8080(6)	0.5592(7)	0.0849(5)	0.067(4)	C(93)	0.6942(10)	−0.1368(8)	0.4500(6)	0.117(7)
C(43)	0.7578(7)	0.6120(7)	0.0543(5)	0.074(5)	C(94)	0.7531(8)	−0.1888(7)	0.4156(6)	0.081(5)
C(44)	0.7031(7)	0.6664(6)	0.0898(5)	0.064(4)	C(95)	0.7570(7)	−0.1890(6)	0.3499(6)	0.074(4)
C(45)	0.7004(6)	0.6682(6)	0.1588(5)	0.063(4)	C(96)	0.7097(6)	−0.1374(6)	0.3144(5)	0.065(4)
C(46)	0.7496(6)	0.6165(6)	0.1898(5)	0.061(4)	C(97)	0.8055(8)	−0.2446(8)	0.4518(6)	0.113(6)
C(47)	0.6490(7)	0.7212(7)	0.0560(6)	0.094(5)	Cl(2)	0.62738(17)	0.15586(18)	0.41500(13)	0.0729(10)
Pt(51)	0.45253(2)	0.08328(2)	0.15117(2)	0.0392(1)	Cl(52)	0.85927(17)	0.32845(16)	0.08808(13)	0.0670(10)

[a] U_{eq} = one-third of the trace of the orthogonalized **U**.

complex, *trans*-[PtCl$_2${N(=PPh$_3$)CPh=CHCO$_2$Et}(NCPh)] (2.034(5) Å).[37] A similar type of coordination mode is found for the corresponding rhodium complex [Rh(COD){CH(PPh$_2$=NpTol)(PPh$_2$NH-pTol)}]$^+$, with a Rh−N bond distance of 2.081(8) Å.[4a] The Pt−C(sp^3) bonds (2.098(8) and 2.099(8) Å for **2d** and **2g**, respectively) are similar to those found in the neutral N,C- and S,C-coordinated complexes [PtCl(PMe$_2$Ph){CMe(PPh$_2$=NpTol)(PPh$_2$=N′-pTol)}] (2.116(4)Å)[29] and [PtCl(PEt$_3$){CH(PPh$_2$=S)(PPh$_2$=S′)}] (2.101(12) Å),[9] respectively, with the Pt−C(sp^3) bonds also *trans* to a Pt−Cl bond.

The complexes **2d** and **2g** are chiral, and both enantiomers are present in the unit cell. For **2d** a different orientation of the phenyl rings C(16)−C(21) and C(66)−C(71)[32b] is observed for the two crystallographically independent enantiomers. The perpendicular orientation (angle between the least-squares planes is 83.9(5)°) is commonly found for phenyl−phenyl interactions (distance between the center of gravities is 4.881 Å).

The rather small N(1)−Pt−C angles, 73.2(3)° (**2d**), 72.9(3)° (**2g**), and the folding angles of the metallacycles around the N(1)··C(sp^3) axis, 32.7(4)° [32c] and 36.4(4)°, respectively, are normal features of four-membered metallacycles.[29,38,39] For the

---

(35) Clark, H. C.; Ferguson, G.; Jain, V. K. Parvez, M. *Inorg. Chem.* **1986**, *25*, 3808.

(36) Kaufmann, W.; Venanzi, L. M.; Albinati, A. *Inorg. Chem.* **1988**, *27*, 1178, and references therein.

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

Table 4. Fractional Coordinates for **2g**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Pt(1)	0.54415(3)	0.78137(2)	0.28630(2)	0.0160(1)
Cl(1)	0.3611(2)	0.64517(13)	0.29335(11)	0.0250(6)
P(1)	0.5929(2)	0.83691(14)	0.39786(11)	0.0242(6)
P(2)	0.6950(2)	0.79474(14)	0.19394(10)	0.0164(5)
P(3)	0.6450(2)	0.98684(13)	0.23442(10)	0.0168(5)
N(1)	0.5300(6)	0.7308(4)	0.1829(3)	0.0168(17)
N(2)	0.7683(7)	1.0522(5)	0.2030(3)	0.0207(19)
C(1)	0.5815(10)	0.7397(6)	0.4474(4)	0.031(3)
C(2)	0.6750(11)	0.6782(6)	0.4373(5)	0.037(3)
C(3)	0.7761(11)	0.9219(7)	0.4377(5)	0.040(3)
C(4)	0.8108(14)	0.9693(8)	0.5119(6)	0.061(4)
C(5)	0.4772(12)	0.8998(7)	0.4227(5)	0.042(4)
C(6)	0.3180(12)	0.8469(9)	0.3868(6)	0.055(4)
C(7)	0.4437(8)	0.6398(5)	0.1398(4)	0.020(2)
C(8)	0.2959(8)	0.6135(6)	0.1245(4)	0.022(2)
C(9)	0.2066(9)	0.5245(6)	0.0824(4)	0.028(2)
C(10)	0.2604(9)	0.4590(6)	0.0535(4)	0.029(3)
C(11)	0.4083(9)	0.4879(6)	0.0677(5)	0.029(3)
C(12)	0.4981(9)	0.5751(6)	0.1104(4)	0.026(3)
C(13)	0.1634(11)	0.3625(7)	0.0070(6)	0.048(3)
C(14)	0.8275(8)	0.7408(6)	0.2297(4)	0.022(3)
C(15)	0.8526(10)	0.7301(7)	0.2977(5)	0.035(3)
C(16)	0.9438(11)	0.6815(8)	0.3249(6)	0.045(4)
C(17)	1.0122(10)	0.6426(7)	0.2833(6)	0.040(3)
C(18)	0.9904(9)	0.6546(7)	0.2181(5)	0.036(3)
C(19)	0.8991(9)	0.7016(6)	0.1904(5)	0.027(3)
C(20)	0.7306(8)	0.8293(6)	0.1173(4)	0.021(2)
C(21)	0.6198(9)	0.8006(6)	0.0563(4)	0.027(2)
C(22)	0.6426(10)	0.8311(7)	−0.0028(5)	0.033(3)
C(23)	0.7789(10)	0.8908(6)	−0.0014(4)	0.030(3)
C(24)	0.8898(9)	0.9207(6)	0.0589(4)	0.027(3)
C(25)	0.8669(8)	0.8894(5)	0.1174(4)	0.020(2)
C(26)	0.7030(8)	0.8886(5)	0.2603(4)	0.0159(19)
C(27)	0.4760(8)	0.9434(5)	0.1706(4)	0.018(2)
C(28)	0.3514(8)	0.8954(6)	0.1856(4)	0.024(3)
C(29)	0.2232(9)	0.8590(6)	0.1336(5)	0.032(3)
C(30)	0.2177(9)	0.8684(6)	0.0675(5)	0.032(3)
C(31)	0.3420(9)	0.9146(7)	0.0524(5)	0.031(3)
C(32)	0.4719(9)	0.9534(6)	0.1029(4)	0.026(3)
C(33)	0.6403(8)	1.0663(5)	0.3076(4)	0.020(2)
C(34)	0.5169(9)	1.0804(6)	0.3160(4)	0.026(3)
C(35)	0.5250(9)	1.1451(6)	0.3732(5)	0.030(3)
C(36)	0.6584(11)	1.1924(7)	0.4205(5)	0.035(3)
C(37)	0.7796(10)	1.1805(7)	0.4120(5)	0.036(3)
C(38)	0.7728(9)	1.1161(6)	0.3546(5)	0.028(3)
C(39)	0.7685(8)	1.1382(5)	0.1743(4)	0.020(2)
C(40)	0.8706(8)	1.1709(5)	0.1392(4)	0.021(2)
C(41)	0.8695(9)	1.2501(6)	0.1079(4)	0.030(2)
C(42)	0.7740(9)	1.2999(6)	0.1112(5)	0.027(3)
C(43)	0.6774(9)	1.2673(6)	0.1468(4)	0.027(3)
C(44)	0.6737(9)	1.1852(6)	0.1789(4)	0.026(2)
C(45)	0.7741(10)	1.3849(7)	0.0757(5)	0.039(3)
Cl(2)	0.0670(2)	0.01540(15)	0.28966(12)	0.0317(6)
Cl(3)	0.2304(3)	0.1269(2)	0.18471(11)	0.0339(7)
Cl(4)	0.1522(2)	0.2307(2)	0.38708(11)	0.0337(6)
P(4)	0.3203(2)	0.33508(15)	0.28417(11)	0.0248(6)
C(46)	0.3896(9)	0.4214(6)	0.3645(4)	0.026(3)
C(47)	0.5048(9)	0.3991(6)	0.4169(4)	0.028(3)
C(48)	0.2108(10)	0.3882(7)	0.2261(5)	0.037(3)
C(49)	0.0928(11)	0.4051(7)	0.2518(6)	0.043(3)
C(50)	0.4750(10)	0.3470(7)	0.2527(5)	0.038(3)
C(51)	0.5715(12)	0.4516(7)	0.2575(6)	0.046(4)
Cl(5)	0.1638(5)	0.5501(4)	0.4433(2)	0.0984(17)
Cl(6)	−0.1279(6)	0.4313(5)	0.3703(4)	0.143(3)3
C(52)	0.0329(17)	0.4391(15)	0.4356(13)	0.144(12)

related Rh−N−P−C ring a N−Rh−C angle of 73.1(1)° has been reported[4a] and the folding angle is 33.6°,[40] whereas for the Pt−S−P−C ring an S−Pt−C angle of 82.3(3)° and 23.06° folding around the S⋅⋅⋅C axis have been found.[9]

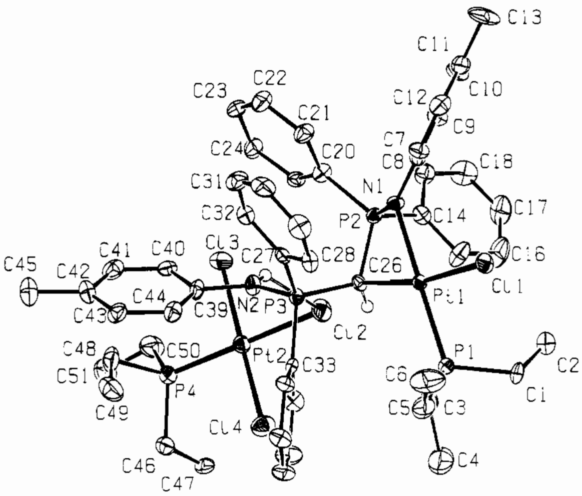


Figure 2. ORTEP 50% probablility plot of **2g** (PLATON).[24] Hydrogen atoms have been omitted except for the hydrogen atoms on C(26) and N(2).

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for **2d**

	Distances		
	Around Pt		
Pt−P(1)	2.219(2)	Pt−C(28)	2.098(8)
Pt−Cl(1)	2.336(2)	Pt−N(1)	2.099(6)
	Within Phosphine		
P(1)−C(7)	1.791(8)	P(1)−C(1)	1.816(8)
P(1)−C(8)	1.784(9)		
	Within Ligand		
P(2)−N(1)	1.613(6)	P(3)−N(2)	1.634(6)
N(1)−C(9)	1.388(10)	N(2)−C(41)	1.421(11)
P(2)−C(28)	1.795(8)	P(3)−C(28)	1.802(8)
P(2)−C(16)	1.804(8)	P(3)−C(29)	1.798(8)
P(2)−C(22)	1.805(8)	P(3)−C(35)	1.806(8)
	Angles		
	Around Pt		
Cl(1)−Pt−P(1)	87.03(8)	N(1)−Pt−C(28)	73.2(3)
Cl(1)−Pt−C(28)	171.5(2)	P(1)−Pt−N(1)	169.40(17)
Cl(1)−Pt−N(1)	98.48(17	P(1)−Pt−C(28)	101.4(2)
	Within Ligand		
Pt−N(1)−P(2)	93.8(3)	Pt−C(28)−P(2)	88.7(3)
Pt−N(1)−C(9)	131.9(5)	Pt−C(28)−P(3)	115.6(4)
P(2)−N(1)−C(9)	129.5(5)	P(3)−N(2)−C(41)	130.4(6)
P(2)−C(28)−P(3)	115.8(4)		
N(1)−P(2)−C(28)	94.4(3)	N(2)−P(3)−C(28)	104.5(4)
N(1)−P(2)−C(16)	117.7(3)	N(2)−P(3)−C(29)	110.4(4)
N(1)−P(2)−C(22)	113.4(4)	N(2)−P(3)−C(35)	108.7(3)
C(16)−P(2)−C(28)	106.5(4)	C(28)−P(3)−C(29)	114.0(4)
C(22)−P(2)−C(28)	119.1(4)	C(28)−P(3)−C(35)	111.0(4)
C(16)−P(2)−C(22)	106.0(4)	C(29)−P(3)−C(35)	108.1(4)

The P(2)−N(1) distances of 1.613(6) Å (**2d**) and 1.604(7) Å (**2g**) are normal values for coordinated phosphinimine groups,[3e,4a,d,e,29,37,41] and are approximately 0.045 Å longer than in the free ligand.[4b] The P(3)−N(2) bond distances of 1.634(6) Å (**2d**) and 1.644(7) Å (**2g**) of the remote aminophosphonium group is elongated as a result of protonation of the N′ atom, however shorter by about 0.019 Å when compared to the same P−N bond in the corresponding Rh complex.[4a,d] The

---

(38) Kemmitt, R. D. W.; Mason, S.; Moore, M. R.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1990**, 1535 and references therein.

(39) Henderson, W.; Kemmitt, R. D. W.; Prouse, L. J. S.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1990**, 1853 and references therein.

(40) Unpublished results by P. Imhoff: folding angle within the Rh−N−P−C metallacycle, around N⋅⋅⋅C axis, is 33.6°. Whereas for the related complex, Rh(COD){N(pTol)=PPh$_2$CH$_2$},[41] a similar folding of 30.4° has been observed.

(41) Imhoff, P.; Nefkens, S. C. A.; Elsevier, C. J.; Vrieze, K.; Goubitz, K.; Stam, C. H. *Organometallics* **1991**, *10*, 1421.

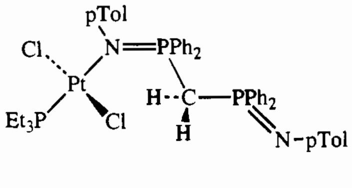
Table 6. Selected Interatomic Distances (Å) and Angles (deg) for **2g**

	Distances		
	Around Pt(1) (Cation)		
Pt(1)−P(1)	2.228(2)	Pt(1)−C(26)	2.099(8)
Pt(1)−Cl(1)	2.319(2)	Pt(1)−N(1)	2.128(6)
	Around Pt(2) (Anion)		
Pt(2)−P(4)	2.217(2)	Pt(2)−Cl(3)	2.305(2)
Pt(2)−Cl(2)	2.389(2)	Pt(2)−Cl(4)	2.298(2)
	Within Ligand		
P(2)−N(1)	1.604(7)	P(3)−N(2)	1.644(7)
N(1)−C(7)	1.405(9)	N(2)−C(39)	1.435(10)
P(2)−C(26)	1.789(8)	P(3)−C(26)	1.784(8)
P(2)−C(14)	1.805(9)	P(3)−C(27)	1.778(8)
P(2)−C(20)	1.789(8)	P(3)−C(33)	1.813(8)
	Within Phosphine (Cation)		
P(1)−C(1)	1.818(9)	P(1)−C(5)	1.823(12)
P(1)−C(3)	1.826(11)		
	Within Phosphine (Anion)		
P(4)−C(46)	1.803(8)	P(4)−C(50)	1.814(11)
P(4)−C(48)	1.826(10)		
	Angles		
	Around Pt(1) (Cation)		
Cl(1)−Pt(1)−P(1)	89.42(8)	N(1)−Pt(1)−C(26)	72.9(3)
Cl(1)−Pt(1)−C(26)	168.5(2)	P(1)−Pt(1)−N(1)	171.62(19)
Cl(1)−Pt(1)−N(1)	95.59(17)	P(1)−Pt(1)−C(26)	101.9(2)
	Around Pt(2) (Anion)		
Cl(2)−Pt(2)−Cl(3)	89.38(9)	Cl(3)−Pt(2)−P(4)	90.03(9)
Cl(2)−Pt(2)−Cl(4)	88.47(9)	Cl(4)−Pt(2)−P(4)	92.13(9)
Cl(2)−Pt(2)−P(4)	179.34(9)	Cl(3)−Pt(2)−Cl(4)	176.92(10)
	Within Ligand		
Pt−N(1)−P(2)	91.8(3)	Pt−C(26)−P(2)	87.8(3)
Pt−N(1)−C(7)	128.8(5)	Pt−C(26)−P(3)	112.4(4)
P(2)−N(1)−C(7)	130.4(6)	P(3)−N(2)−C(39)	127.0(6)
P(2)−C(26)−P(3)	117.0(4)		
N(1)−P(2)−C(26)	95.4(4)	N(2)−P(3)−C(26)	105.9(4)
N(1)−P(2)−C(14)	116.8(4)	N(2)−P(3)−C(27)	109.3(4)
N(1)−P(2)−C(20)	113.2(4)	N(2)−P(3)−C(33)	107.6(3)
C(14)−P(2)−C(26)	106.9(4)	C(26)−P(3)−C(27)	112.3(4)
C(20)−P(2)−C(26)	118.5(4)	C(26)−P(3)−C(33)	110.7(4)
C(14)−P(2)−C(20)	106.2(4)	C(27)−P(3)−C(33)	110.9(4)

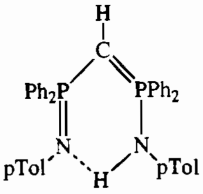
free aminophosphonium entity is pointing away from the Pt center with torsion angles P(2)−C−P(3)−N(2) of +75.6(5) and −70.6(5)° and Pt−C−P(3)−N(2) of 177.4(4) and −170.0(4)° for **2d** and **2g**, respectively.

The counterion $Cl(52)^-$ in compound **2d** is interacting with the cationic part of the molecule through a hydrogen bond with the free aminophosphonium entity: Cl(52)···H−N(2) = 2.176(8) Å. For **2g** a similar type of hydrogen bonding is found between the NH group with Cl(2) (*trans* to $Pt-PEt_3$) belonging to the anionic $PtCl_3(PEt_3)$ species: Cl(2)···H−N(2) = 2.628(7) Å. The bond distances within this metal anion are similar to those reported previously for $[PtCl_3(PEt_3)][NEt_4]$.[42] The Cl(3) and Cl(4) of the anion in **2g** are also involved in hydrogen-bridging interactions with the cocrystallized CH_2Cl_2 molecule.

Sequence of Reactions in the Formation of 2a. In order to investigate the sequence of events in the reaction of $Pt_2Cl_4(PEt_3)_2$ with 2 molar equiv of the ligand $CH_2(PPh_2{=}NpTol)_2$ (**1a**), small scale reactions were performed in 0.6 mL of deuterated benzene or toluene (at 20 °C) or CD_2Cl_2 (at −40 °C) in a 5 mm NMR tube. At 20 °C, within 5 min in toluene or benzene, complete conversion into an intermediate **A** was observed by ^1H and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum shows only three phosphorus resonances; a doublet at 0.9 ppm, $\delta(P_A)$, with $^1J_{PtP_A} = 3508$ Hz and a relatively large $^3J_{P_AP_B}$ of 12.2 Hz, confirming the *trans* $Et_3P_APtN{=}P_B$ geometry. A doublet of doublet was found at 29.4 ppm, δ (P_B), with $^2J_{P_BP_C} = 3.0$ Hz, $^3J_{P_AP_B} = 12.2$ Hz, and $^2J_{PtP_B} = 64$ Hz, due to the coordinated $P_B{=}NPt$ function, and a doublet at −5.8 ppm, δ (P_C), with $^2J_{P_BP_C} = 3.0$ Hz and no observable coupling with platinum, occurring more or less at the frequency of the free ligand[4b] and evidently belonging to a noncoordinated iminophosphorane entity. The presence of a CH_2 resonance was established by a resonance at δ 5.6 ppm (dd, $^2J_{PH} = 12.5$ and 18.3 Hz) having a relative integral of two protons in the ^1H NMR. These data are in agreement with a monodentate σ-N-coordinated BIPM ligand in $[(PEt_3)Cl_2Pt\{NpTol{=}PPh_2CH_2\text{-}PPh_2{=}NpTol\}]$ (**A**), which represents the first example of such a species observed for these bis(iminophosphoranyl)methane ligands.



A



C

The *trans* $Et_3P\text{-}Pt\text{-}N$ geometry around the Pt(II) center is clearly a direct consequence of the *trans* labilizing effect of the phosphine in the chloro-bridged Pt precursor. Complex **A** is stable for about 30 min in toluene when kept between 0 and 10 °C, after which the presence of another intermediate (**C**) is observed, as evidenced by the appearance of a sharp singlet at circa 26 ppm in the ^{31}P NMR lacking coupling to platinum and exhibiting a characteristic NH resonance at 9.5 ppm in the ^1H NMR. Its CH resonance is obscured. Within minutes another NH resonance at 10.4 ppm and a broad CH resonance at 4.5 ppm appear, which belong the the final product **2a**. The ^{31}P resonances of the P=N groups in complex **2a** are somewhat broadened at first, but sharpen up into doublets when the reaction proceeds.

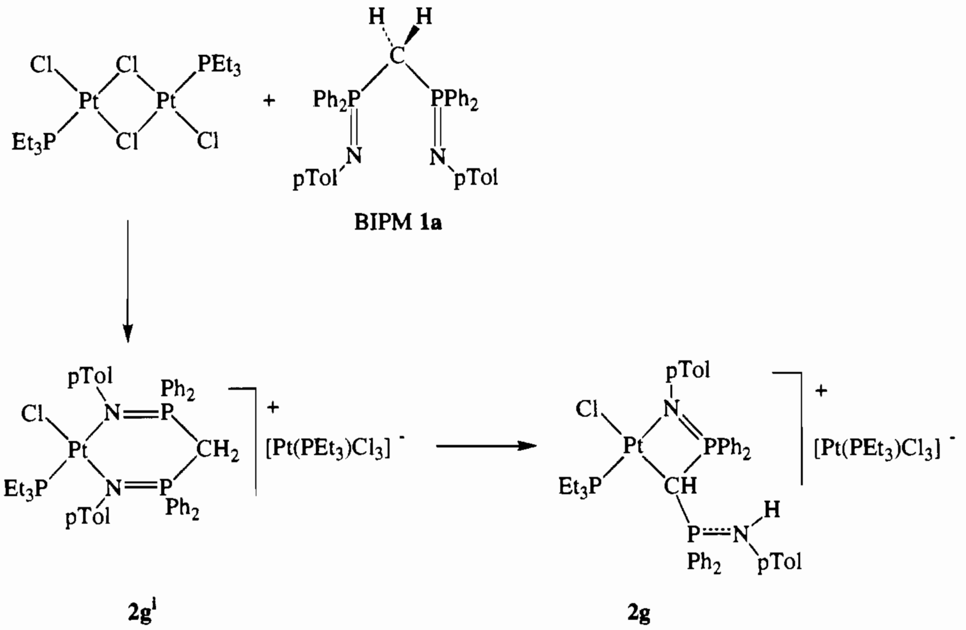
Similar observations are found when the reaction is carried out in CD_2Cl_2 at −40 °C, showing the formation of the monodentate **A**, the intermediate **C**, and complex **2a**, but also some small signals were found which could not be identified and disappeared when the reaction proceeded and therefore probably belong to other intermediates. Even at −40 °C, the singlet resonance of **C** in the ^{31}P NMR shows no Pt satellites, which proves that **C** is an organophosphorus compound containing a NH group, i.e. $[HC(PPh_2{=}NpTol)(PPh_2NH\text{-}pTol)]$, which shows only one signal in the ^{31}P NMR probably as a result of π-delocalization and H-bridge formation between the two N atoms. The spectroscopic data for intermediate **C** are very similar to the data observed for compound **4** (vide supra), which suggests that the electron distribution in $[CH(PPh_2{=}NpTol)(PPh_2N(H)\text{-}pTol)_2]$ (**C**) and $[CH\{PPh_2N(H)\text{-}pTol\}_2]^+Cl^-$ (**4**) is practically the same. The difference in solubility in toluene, however, (**C** is soluble, **4** is insoluble) clearly indicates that we are dealing with two different compounds. As should be expected, together with the observation and conversion of intermediate **A** into **C**, also the species $[PtCl_3(PEt_3)]^-$ has been identified at 2.5 ppm ($^1J_{PtP} = 3830$ Hz) in the reaction mixture.[43]

Isolation and Characterization of an Intermediate in the Formation of 2g. When the reaction of $Pt_2Cl_4(PEt_3)_2$ with an equimolar amount of **1a** was carried out for 17 h in toluene at 20 °C, an intermediate (**2g'**) could be isolated (Scheme 3). Complex **2g'** slowly converts into **2g** when redissolved in a more

---

[42] Bushnell, G. W.; Pidcock, A. S.; Smith, M. A. R *J. Chem. Soc., Dalton Trans.* **1975**, 572.

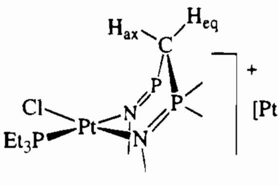
Scheme 3. Sequence in the Formation of **2g**



polar solvent like CH_2Cl_2 or when stirred in toluene for 4 h at 60 °C (vide supra).

The ^1H NMR spectrum of $\mathbf{2g^i}$ at ambient temperature is quite different from that of **2g**, showing a broad triplet CH_2-resonance at 5.53 ppm, with $^2J_{PH}$ = 12.2 Hz, the relative integrals confirming the presence of two protons on the central carbon atom of coordinated BIPM. The CH_3 resonances of the 4-$CH_3C_6H_4N$ group appear as two singlets at 1.91 and 1.89 ppm, respectively, indicating that the intermediate is non-symmetric. The ^{31}P NMR shows two inequivalent resonances for the phosphinimine groups: a doublet at 29.9 ppm, (P_C) and a doublet of doublet at 23.7 ppm (P_B) with $^2J_{P_BP_C}$ = 24.1 Hz and $^3J_{P_AP_B}$ = 2.4 Hz, which show an unusually large two-bond P_B,P_C coupling constant.[44] The three-bond P_A,P_B coupling can also be obtained from the doublet P_AEt_3 resonance at 1.4 ppm, with $^1J_{PtP_A}$ = 3620 Hz and $^3J_{P_AP_B}$ = 2.4 Hz, which establishes the *trans* $Et_3P_APtN{=}P_B$ geometry. Although the magnitude of the mutual P_A,P_B coupling and its chemical shift (23.7 ppm) indicate that this iminophosphoranyl group is coordinated to Pt, the P_B resonance shows no detectable Pt satellites. This suggests a weak $PtN{=}P_B$ bond, more weakly bonded than for instance the corresponding PtN=P bond in monodentate **A** (vide infra), that is probably caused by the *trans* influence of the phosphine and by strain within the six-membered ring as well. The doublet at 29.9 ppm, belonging to the $P_C{=}N$ moiety, however, does show coupling with ^{195}Pt ($^2J_{PtP_C}$ = 70.5 Hz). The magnitude of this coupling indicates that this phosphinimine group is coordinated *trans* to the Pt–Cl bond, confirming that both N-atoms are bonded to a Pt center, forming a six-membered cationic platinacycle $\mathbf{2g^i}$.[45] The anionic part of $\mathbf{2g^i}$ is formed by a $Pt(P_DEt_3)Cl_3^-$ species, as indicated by the fourth signal at 1.9 ppm (s), δ (P_D), with $^1J_{PtP_D}$ = 3804 Hz, which has comparable chemical shift and coupling with ^{195}Pt as observed for the $Pt(PEt_3)Cl_3^-$ counterion in **2g**.

Low temperature ^1H NMR spectra of $\mathbf{2g^i}$ have supplied additional evidence for the presence of a six-membered chelate ring. At −40 °C the CH_2 resonance resolves into two double triplets, each corresponding to one axial and one equatorial proton on the bridge-head position of the boat conformer of $\mathbf{2g^i}$, as has also been reported for other six-membered pallada- and platinacycles, containing flexible bidentate nitrogen donor ligands.[46]



Boat-conformer of $\mathbf{2g^i}$.
Aryl-substituents on P and N have been omitted for clarity

Unfortunately, it is impossible to determine which of the two resonances belong to the axial and which to the equatorial H atom, since their chemical shifts are solvent dependent, but normally the axial H is found at relative higher frequency as a result of its proximity to platinum.[46] At temperatures above −40 °C boat-to-boat inversion of the chelate ring occurs and leads to coalescence of the methylene proton resonances at −10 °C and also significant broadening of the aromatic protons is observed.

Discussion

Numerous examples of normally complexed monophosphinimine[47] and bis(phosphinimine) complexes[2ab,4] of transition

---

(43) Recombination of a "$PtCl_2(PEt_3)$" fragment with Cl^- from **2a**. We have verified the formation of the tautomer **C** by carrying out a similar reaction between $PtCl_2$ and a 4-fold excess of BIPM (**1a**), which results in the exclusive formation of **C** and indicates that the tautomerization of BIPM into **C** is initiated by the presence of a Pt center, since it is not observed for the free ligand.[4b]

(44) The analogue complex $[Pt(PEt_3)Cl\{N(pTol){=}PPh_2\}_2CHCH_3\}]^+$ has a ^2J(P,P) of circa 12 Hz,[45] whereas other related cationic complexes, i.e. $[Pt(PEt_3)Cl\{S{=}PPh_2)_2CH_2\}]^+$ have much smaller couplings, ^2J(P,P) = 8Hz.[30] However, for a neutral S,S′ chelate $[Pt(PEt_3)Cl\text{-}\{(S{=}PPh_2)_2C(PPh_2{=}S'')\}]$ a two-bond P,P coupling of 27.9 Hz, between the two phosphorus atoms in the six-membered ring, has been reported.[7b]

(45) Complex $\mathbf{2g^i}$ shows a strong resemblance to $[PtCl(PMe_2Ph)\text{-}\{(N(pTol){=}PPh_2)_2CHMe\}]Cl$, a stable compound of which an X-ray crystal structure has been determined: Avis, M. W.; Elsevier, C. J.; Kooijman, H.; Veldman, N.; Spek, A. L. To be submitted for publication.

(46) (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.

metals have been recently reported including some studies of Pt[37] and Pd.[3e,g,48] Also, a couple of Pt and Pd complexes, containing closely related phosphazenes are known.[49,50]

The results described in this paper show that the reactions of the methylene-bridged bis(phosphinimines) with platinum(II) have in all cases led to the exclusive formation of four-membered Pt–N–P–C platinacycles, by N,C coordination of the ligand. This is in sharp contrast to the observations for reactions of BIPM with Rh and Ir compounds, where both N,N′ and N,C coordination were found in an approximate 1:1 ratio.[4d] The preference for the formation of N,C-coordinated Pt(II)-BIPM complexes can be explained by taking two aspects into consideration. First, the stronger polarization in the Pt(II)N=P bonds compared to the Rh(I)/Ir(I)N=P bonds in the initially formed σ-N monodentates (**A** in Scheme 4), gives rise to more acidic character of the methylene protons, which will facilitate the proton transfer to the terminal nitrogen atom and eventually results in only N,C coordination in the case of the former. This kinetic effect has also been previously established by substitution of the cyclooctadiene ligand in Rh- or Ir(COD){BIPM}$^+$ for the more electron withdrawing CO ligands, which resulted in a preference for the N,C chelate (**V**).[4d] Second, the formation of a Pt–C σ-bond is thermodynamically more favourable than formation of a Pt–N σ-donor bond. Unlike earlier investigations involving Rh- and Ir(BIPM)-complexes,[4d] addition of sodium salts did not result in the formation of N,N′-coordinated Pt–bis(iminophosphoranyl)methane complexes (simple anion exchange took place), which corroborates the preference of M–C over M–N bond formation in the case of the Pt complexes as compared to those of Rh and Ir.

Our results also show considerable differences with the earlier reports by Dixon and co-workers on the coordination behavior of the closely related ligands bis(thiophosphoranyl)methane, $CH_2(PR_2{=}S)_2$ and tris(thiophosphoranyl)methane $CH(PR_2{=}S)_3$ with platinum(II), which showed that these neutral ligands coordinate as S,S′ chelates only.[8,9] The fact that in these cases no S,C-coordinated complexes were formed can be ascribed to the lower basicity of the sulfur atom as compared to the nitrogen atoms in the bis(iminophosphoranyl)methane ligands. However, S,C coordination of $CH_2(PR_2{=}S)_2$ and related ligands has been reported when the methylene proton is abstracted by an external base, resulting in four-membered Pt–S–P–C metallacycles[7b,30] which are very similar to the complexes we found.

Due to the N,C chelate coordination mode of the aminophosphonium(iminophosphoranyl)methanide ligand in **2a–f**, in which one of the methylene protons has shifted to the noncoordinated nitrogen atom, chirality is introduced on the carbon atom of the platina(iminophosphoranyl)methanide ring. This is nicely demonstrated by complex **2d**, containing the prochiral phosphine PMe_2Ph, of which the methyl groups have become diastereotopic.

The positive charge of these cationic complexes **2a–f** is probably localized on the pentavalent phosphorus of the remote aminophosphonium $-Ph_2P_CN(H)Ar$ entity, as can be deduced from the high frequency $\delta(P_C)$ (see Table 2) and δ(NH) values. This causes considerable acidic character of the NH group, which is verified by the observed acid–base reactivity of the complexes **2a–f**. For example, the reaction of **2a** with additional ligand **1a** results in the formation of deprotonated complexes **3**. Also the related N,C-coordinated Rh(I)– and Ir(I)–bis(iminophosphoranyl)methane complexes (**V**, see Introduction) showed a similar acidic character of the NH group; however, the deprotonation by an external BIPM ligand has not been observed previously.[4d] The relatively low NH resonance frequency of compound **2e** might indicate that no hydrogen bridge exists between the NH group and the BF_4 anion, whereas all other cationic complexes **2a–f** and **2g** show a much higher NH frequency due to hydrogen bridges with the anions (Cl, Br, CF_3CO_2, $PtCl_3(PEt_3)$) as established by the X-ray crystal structures of **2d** and **2g**.

Sequence of Reactions in the Formation of 2a. Bridge-splitting reactions of bimetallic species with bidentate ligands usually lead to a great variety of complexes, depending strongly on the metal-to-ligand ratio and reaction conditions.[4d,5c,6e,9,27,28,30,35,36,41a] For $CH_2(PPh_2{=}N{-}aryl)_2$ ligands in particular, the reactivity toward $[ML_2Cl]_2$ (with M = Rh^I and Ir^I, L_2 = COD, NBD, $(CO)_2$) has been well established,[4d] but the influence of the metal, co-ligands, anions, or metal-to-ligand ratio on the product distribution in that case already exemplified the complexity of the reaction mechanism. In the case of the Pt–bis(iminophosphoranyl)methane complexes, the existence of the initial intermediate **A** (Scheme 4), containing a σ-N monodentate coordinated BIPM with N *trans* to the Pt–PEt_3 bond, was established.

A similar intermediate has been suggested for the Rh– and Ir–BIPM systems, but has never been observed.[4d] For the related $CH_2(PR_2{=}S)_2$ ligand a few examples of monodentate coordination have been reported,[51] and for $CH_2(PR_2{=}O)_2$ an exchange between σ-O monodentate coordinations to "Ga(^{t}Bu)$_3$" has been demonstrated.[52] So, intermediate **A** is a perfectly logical first product arising from substitution of the chloride *trans* to the phosphine in the initial Pt dimer.

The following steps in the reaction have not been fully clarified, but we have found spectroscopic evidence for an intermediate **C**, which was identified as a tautomer of BIPM (Scheme 4), which is present in relatively large quantities during the reaction. The organophosphorus compound **C** is probably formed by (b) reversible H-migration from the methylene group to the noncoordinated N atom in **A** giving the tautomeric form **B** and (c) reversible subsequent dissociation of **C** from the platinum center.[43] The dissociation/association equilibria b and c (Scheme 4) are very fast, since **B** is not seen. A simple substitution of X in **B** by coordination of the ylide C atom to Pt might directly lead to **2a** (e), but we have found that the formation of **2a** directly starts after **C** is formed, which indicates that a reaction proceeding through steps c and d might occur also. We have found no evidence for the formation of the six-membered platinacycle **D**, containing N,N′-coordinated BIPM, when a Pt:BIPM ratio of 1:1 is used.

This reaction sequence is largely in agreement with previous descriptions of the sequences proposed for the formation of

---

(47) (a) Imhoff, P.; Elsevier, C. J.; Stam, C. H. *Inorg. Chim. Acta* **1990**, *175*, 209. (b) Abel, E. W.; Mucklejohn, S. A. *Phosphorus Sulfur* **1981**, *9*, 235. (c) Dehnicke, K.; Strähle, J. *Polyhedron* **1989**, 8, 6, 707.

(48) (a) Fukui, M.; Itoh, K.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 7, 2044. (b) Kiji, J.; Matsumura, A.; Haishi, T.; Okazaki, S.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1975**, *50*, 10, 2731. (c) Alper, H. *J. Organomet. Chem.* **1977**, *127*, 385. (d) Abel, E. W.; Mucklejohn, S. A. *Inorg. Chim. Acta* **1979**, *37*, 107.

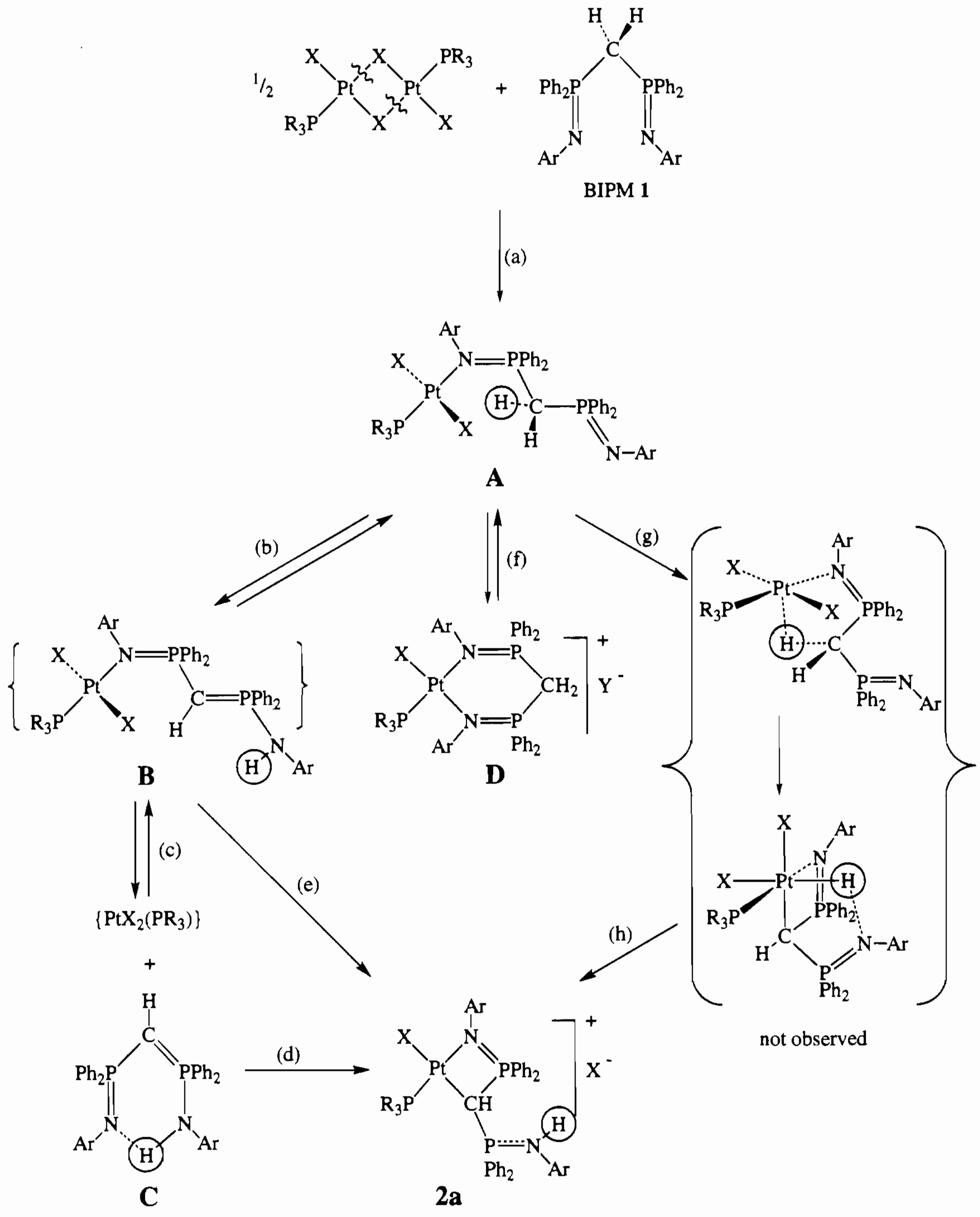
(49) (a) Roesky, H. W.; Scholz, U.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1989**, *576*, 255. (b) Scherer, O. J.; Nahrsted, A. *J. Organomet. Chem.* **1979**, *166*, C1. (c) Chandrasekaran, A.; Krishnamurthy, S. S.; Nethji, M. *Inorg. Chem.* **1994**, *33*, 3085. (d) Balakrishna, M. S.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1994**, *33*, 3079.

(50) $Ph_3P{=}NSiMe_3$ has been shown to react with $[M(L_2)Cl]_2$ (M = Rh, Ir) when L_2 is $(CO)_2$ instead of COD, indicating a preference for binding to electron-poor metal centers.[47a]

(51) (a) Ainscough, E. W.; Brodie, A. M.; Furness, A. R. *J. Chem. Soc., Chem. Commun.* **1973**, 2360. (b) Schumann, H. J. *Organometallics* **1987**, *320*, 145.

(52) Power, M. B.; Ziller, J. W.; Barron, A. R. *Organometallics* **1993**, *12*, 4908.

Scheme 4. Reaction Pathways in the Formation to **2a**



C is observed for M:L = 1:1 reactions.
D (**2g**^{i},with Y = PtCl$_3$(PEt$_3$)) is observed for the 2:1 reacton.

analogous Rh and Ir compounds, which resulted in cationic four-membered metallacycles by N,C coordination of the BIPM ligand.[4d]

Alternatively, pathways g and h, through cyclometalation of the methylene group in **A**, could also lead to **2a**. Then, equilibria involving **B** and **C** would be nonproductive. However, this alternative seems unlikely as it was found that formation of **2a** starts immediately after **C** is formed. Furthermore, in contrast to the reported mechanism for the formation of Rh– and Ir–BIPM complexes,[4d] we have never observed any intermediate Pt–hydrides.

Reaction Sequence in the Formation of Complex 2g. The 2:1 (Pt:BIPM) reaction in toluene has revealed that a relatively stable intermediate **2g**^{i} is formed, in which the ligand is σ-N,σ-N′ chelated, previous to the conversion into the stable product **2g** (Scheme 3), which is similar to **2a**. The formation of Pt(PEt$_3$)Cl$_3^-$ counterions, as in **2g**^{i} and **2g**, have been previously observed in other reactions.[42,53] The earlier reported bridge-splitting reactions of BIPM with [ML$_2$Cl]$_2$ (M = Rh, Ir; L$_2$= COD, NBD, (CO)$_2$) also resulted in the formation of complexes of the type [ML$_2$(BIPM)]$^+$[ML$_2$Cl$_2$]$^-$.[4d] The formation of **2g**^{i}, however, was rather surprising, because a N,N′-coordinated

---

(53) (a) Schmid, B.; Venanzi, L. M.; Albinati, A.; Mathey, F. *Inorg. Chem.* **1991**, *30*, 4693. (b) Gosling, R.; Tobe, M. L. *Inorg. Chem.* **1983**, *22*, 1235. (c) Tobe, M. L.; Treadgold, A. T. *J. Chem. Soc., Dalton. Trans.* **1988**, 2347.

species is not observed in the reaction sequence of $Pt_2Cl_4(PEt_3)_2$ with 2 equiv of BIPM (vide supra). Obviously, the formation of a cationic six-membered metallacycle is stabilized by the large $PtCl_3(PEt_3)$ anion. This is in agreement with the results obtained by Imhoff et al. where substitution of a Cl anion for a larger anion like BF_4, PF_6 resulted in the formation of more N,N′ chelate relative to the amount of N,C chelate.[4d] We think that an equilibrium between a monodentate species, similar to **A**, and the N,N′ chelate **2g**^{i} (**D**, in Scheme 4) is involved, which is lying at the side of **D** in the case of a 2:1 (Pt:BIPM) reaction and at the side of **A** for a 1:1 reaction. The conversion of the N,N′ coordinated complex **2g**^{i} into the N,C chelate **2g** is taking place much faster in CH_2Cl_2 (<4 h, 20 °C) than in toluene (>17 h, 20 °C), which could indicate that the equilibruim between **A** and **D** shifts to the side of compound **A** in polar solvents. For the analogous Rh− and Ir−bis(iminophosphoranyl)methane complexes interconversion between the N,C chelate and the N,N′ chelate has not been found.[4d]

Formation of Compounds 3 and 4. When the reaction is performed in a 1:2 (Pt:BIPM) molar ratio, a deprotonation of the cationic four-membered platinacycle **2a** by the excess ligand is observed. The final product formation to **3** is independent of the reaction path followed, both the reaction of BIPM (**1a**) with 1 equiv of **2a** or with 0.5 equiv of $Pt_2Cl_4(PEt_3)_2$ lead to the same product **3** (Scheme 2). This finding is different from similar reactions of BIPM with $[M(L_2)Cl]_2$ (M = Rh, Ir and L_2 = COD, NBD, $(CO)_2$), where at higher ligand concentrations a preference for the N,N′-coordinated complex has been found and slight changes in the product distribution between N,C or N,N′ coordination have been ascribed to exchange processes between free and coordinated BIPM.[4d] One of the reasons why a deprotonation reaction by the excess BIPM does occur here for Pt may be the fact that due to a different solvent, toluene instead of CH_2Cl_2, compound **4** precipitates and shifts the equilibrium to the right hand side.

Closely related, so-called transylidation reactions have been reported by Schmidbaur et al.[54] For instance, reactions of $PtCl_2$ with 4 equiv of $(CH_3)_3P{=}NP(CH_3)_2{=}CH_2$ or $(CH_3)_3P{=}C{=}P(CH_3)_3$ yielded the HCl salts of these ligands, $(CH_3)_3P{=}N{=}P(CH_3)_3]^+Cl^-$ or $(CH_3)_3P{=}CH{=}P(CH_3)_3]^+Cl^-$, respectively, together with their deprotonated Pt−chelate complexes. Deprotonation of bis(iminophosphoranyl)methane and its W, Rh, and Ir complexes has been reported previously;[2b,4a−e] however in those cases, strong bases like NaH, LDA (lithium diisopropylamide) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were used to carry out the deprotonation.

As established by variable temperature ^{31}P NMR, the neutral complex **3** exhibits fluxional behavior, in which both P=N groups are involved. In analogy with the dynamic processes which have been described for other related complexes, e.g. $[M(L_2)\{CH(PPh_2{=}NC_6H_4\text{-}4\text{-}R')_2\}]$ (M = Rh, Ir; L_2 = COD, NBD, $(CO)_2$; R′ = CH_3, OCH_3), $[Pt(PEt_3)Cl\{CH(PPh_2{=}S)_2\}]$,[9] $[Pt(PEt_3)Cl\{C(PPh_2{=}S)_3\}]$,[7b] $[Rh(COD)\{(O{=}PPh_2)_2C(PPh_2{=}S)\}]$,[55a] $[Ir(COD)\{(S{=}PPh_2)_3C\}]$[55b] and $[M(COD)\{(O{=}Ph_2)_3C\}]$ (M = Rh, Ir),[55c,d] we have deduced that N,N′ exchange between the coordinated and noncoordinated P=N group is taking place in complex **3**. The Pt complex **3** could not be brought into fast exchange, since an intramolecular reaction takes place at increased temperature. A more detailed description of the structure, fluxionality and reactivity of **3** and several other analogous complexes, $[MX(PR_3)\{CR'(PPh_2{=}NC_6H_4\text{-}4\text{-}R'')_2\}\text{-}C,N]$ (M = Pt, Pd) will be published in a forthcoming paper.[29]

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).

Supporting Information Available: Further details of the structure determination, including crystallographic data, atomic coordinates for the hydrogen atoms, bond lengths and angles, and thermal parameters for **2d** and **2g** (33 pages). Ordering information is given on any current masthead page.

IC9413575

---

(54) (a) Schmidbaur, H.; Füller, H.-J.; Bejenke, V.; Franck, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 3536. (b) Schmidbaur, H.; Gasser, O.; Krüger, C.; Sekutowski, J. C. *Chem. Ber.* **1977**, *110*, 3517.

(55) (a) Grim, S. O.; Kettler, P. B.; Thoden, J. B. *Organometallics* **1991**, *30*, 2399. (b) Grim, S. O.; Kettler, P. B.; Merola, J. S. *Inorg. Chim. Acta* **1991**, *85*, 57. (c) Tanke, R. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1056. (d) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984.