

Reactions of bis(iminophosphoranes) with palladium(II) dichloride: metal-induced tautomerization orthopalladation and unexpected platinum-assisted [2 + 2] cycloaddition of an aryl–nitrile with a phosphinimine moiety

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Abstract

Reactions of bis(iminophosphoranyl)methane, $\text{CH}_2(\text{PPh}_2=\text{N-aryl})_2$, (BIPM; **1a,b**) or 1,1-bis(iminophosphoranyl)ethane (1,1-BIPE; **1c**) with Pd- and Pt-dichlorides containing weakly coordinating ligands (L) such as nitriles or cyclo-octadiene, afforded several products depending on the reaction time, type of ligand (**1a–c**) or nature of the metal. The first reaction observed is a metal-assisted tautomerization of BIPM to aryl–N=PPh₂–CH=PPh₂–NH–aryl. When BIPM reacts with PdCl₂(L)₂, exclusive formation of the C,N-chelate PdCl₂{CH(PPh₂=N–aryl)(PPh₂–NH–aryl)} (**2a,b**) is observed, whereas with 1,1-BIPE (**1c**) a product mixture consisting of a C,N-chelate (**2c**) and an N,N'-chelate (**3**) is found. Orthometallation of the four-membered palladacycle (**2**) took place upon heating, giving the five-membered palladacycle [PdCl₂{2-C₆H₄-PPh(NH[-pTol])–C'H–PPh₂(NH–pTol)–C,C'}] (**4**). The molecular structure of **4** has been determined by X-ray crystallography. Reactions of BIPM (**1a,b**) with PtCl₂(RC≡N)₂ (R = phenyl, *p*-tolyl) afforded entirely different products: the six-membered platinacycles [PtCl(RC≡N){aryl–N=C(R)–N=PPh₂–CH=PPh₂–NH–aryl}–C,N]Cl (**5**) and [PtCl₂{aryl–N=C(R)–N=PPh₂–CH=PPh₂–NH–aryl}–C,N] (**6**), due to an unexpected 2 + 2 cycloaddition of a nitrile with a P=N group.

Keywords: Phosphinimines; Platinum; Palladium; 2 + 2 cycloadditions; Nitriles

1. Introduction

In previous reports, we have shown that phosphinimines of the type R₃P=N–R', R'–N=PR₂–CH₃ and CH₂(PPh₂=N–aryl)₂ are capable of bridge-splitting reactions with [M(L)₂Cl]₂ (M = Rh, Ir) [1–6] and with Pt₂X₄(PR₃)₂ (X = Cl, Br; PR₃ = PEt₃, PMe₂Ph) [7]. Especially the bis(iminophosphoranyl)methane (BIPM) ligand CH₂(PPh₂=N–aryl)₂ and its derived anion demonstrated very interesting coordination behaviour to Rh, Ir, [5,8] Pt and Pd [7,9]. So far, we have not been

able to coordinate neutral BIPM to palladium(II) via the bridge-splitting method [7], and we therefore decided to use a different type of precursor, i.e. PdCl₂(L)₂ (L = MeCN, PhCN or L₂ = COD), as in the few reports on coordination complexes of phosphinimines to palladium(II) and platinum(II) such precursors proved to be suitable [10–13]. It was expected that substitution of the weakly coordinating ligands (L) by the bis(phosphinimines) would give chelated Pd complexes in which at least one nitrogen atom coordinates trans to Pd–Cl, which is likely to be more stable than *trans*-N–Pd–PR₃ complexes formed in bridge-splitting reactions with Pd₂Cl₄(PR₃)₂. Also, carrying out similar reactions between the bis(phosphinimines) and PtCl₂(RCN)₂ seemed interesting to us.

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Furthermore, we were interested to see if these complexes would undergo orthometallation reactions. Several investigators have shown that orthometallation reactions involving phosphinimines or isoelectronic phosphorus ylides $R_3P=CR'R''$ occur readily. For instance, Alper reported on the orthometallation reactions of monophosphinimines $(4-R-C_6H_4)_3P=N$ -aryl with Na_2PdCl_4 [14], and a similar type of reactivity has recently been found for phosphorus ylide complexes of Pt and Pd [15–19]. Moreover, we recently found that four-membered metallacyclic complexes of Pt(II) and Pd(II), $[MX(PR_3)(CH(PPh_2=N-C_6H_4-4-R')_2)]$, containing C,N-coordinated bis(iminophosphoranyl)methanide ligands, orthometallate readily upon prolonged stirring at 20°C or heating, giving C,C'-chelated five-membered metallacycles [9].

In this paper we report on substitution reactions of bis(*N*-aryliminodiphenylphosphoranyl)methane (BIPM, **1a**: aryl = *p*-tolyl; **1b**: aryl = *p*-anisyl) and 1,1-bis(*N*-*p*-tolyliminodiphenylphosphoranyl)ethane (1,1-BIPE, **1c**) with $PdCl_2(L)_2$ ($L = PhC\equiv N$, $MeC\equiv N$ or $L_2 = COD$) and $PtCl_2(RC\equiv N)_2$ ($R = Ph$, *p*Tol), on subsequent orthometallation reactions of a palladium complex and unexpected platinum-assisted 2 + 2 cycloaddition reactions between a tautomer of **1a** and an aryl nitrile.

2. Experimental section

All preparations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques at 20°C, unless stated otherwise. The solvents were dried and distilled prior to use. 1H and ^{31}P (1H) NMR spectra were obtained on Bruker AC 100, AMX 300 and WH 500 (located at the University of Missouri-Columbia, USA) instruments (operating at 100.13, 300.13, 500.14 MHz and 40.53, 121.50, 202.45 MHz respectively) using $SiMe_4$ and 85% H_3PO_4 , respectively, as the external standards, positive shifts to high frequency of the standard in all cases. ^{13}C (1H) NMR data were obtained on a Bruker AMX 300 instrument (operating at 75.48 MHz) using $SiMe_4$ as the external standard. Elemental analysis were carried out by Dornis u. Kolbe Mikroanalytisches Laboratorium (Mülheim a/d Ruhr, Germany). Infrared spectra were recorded with a Perkin-Elmer 283 or a BIO-RAD FFS-7 spectrophotometer. $MCl_2(RCN)_2$ (with $M = Pd, Pt$; $R = Ph, Me, pTol$) [20], $M(COD)Cl_2$ (with $M = Pd, Pt$) [21] and the bis(iminophosphoranyl)alkanes $CHR(PPh_2=N-C_6H_4-4-R')_2$ (**1a**: $R = H, R' = Me$; **1b**: $R = H, R' = OMe$; **1c**: $R = Me, R' = Me$) were synthesized according to literature procedures [22–24]. Data relating to the spectroscopic characterization of the complexes are given in Tables 2 and 3, and in the preparative descriptions below.

2.1. Synthesis of (**2a**): $[PdCl_2\{CH(PPh_2=N-C_6H_4-4-Me)(PPh_2-N'H-C_6H_4-4-Me)\}-C,N]$

A mixture of 190.3 mg (0.32 mmol) $CH_2(PPh_2=N-C_6H_4-4-Me)_2$ (**1a**) and 0.32 mmol of $PdCl_2(RCN)_2$ or $PdCl_2:(COD)$ was stirred in either 20 ml of CH_2Cl_2 , THF or toluene, affording a red solution (only in CH_2Cl_2) or suspension after 1 h. The red product was isolated by evaporation of the solvent, washing the residue with pentane or diethyl ether (2×40 ml), and drying in vacuo, giving 245 mg of an orange red powder (**2a**, 99% yield).

The other palladium complexes (**2b,c**) were synthesized in a similar way in 98–100% yield and were all red to orange. Crystals of **2a–c** were readily obtained from various solvent mixtures (CH_2Cl_2 -pentane, THF-pentane, or alcohols), but they were all unsuitable for X-ray crystal structure determinations owing to their mica-like structure.

Anal. Found: C, 59.41; H, 4.90; N, 3.45; P, 7.65. $C_{39}H_{36}Cl_2N_2P_2Pd$ (**2a**). Calc.: C, 60.68; H, 4.70; N, 3.63; P, 8.02%. FAB mass found: $m/z = 773$ ($M + 1$, 1%), 737 ($M - Cl$, 10%), 699 ($M - 2Cl$, 89%) (M , calc. $C_{39}H_{36}Cl_2N_2P_2Pd$: 772.0). Infrared (CH_2Cl_2): $\nu(N-H) = 3000-3100$ cm^{-1} (br), $\nu(P=N) = 1262$ cm^{-1} , $\nu(P-NH) = 970$ or 915 cm^{-1} . ^{13}C NMR ($CDCl_3$): Pd-C, $\delta -8.3$ (vt, $^1J(P,C) = 81$ Hz); $C_6H_5-4-CH_3$, $\delta 21.3, 21.5$ (s); C_6H_4 : $\delta 136.0, 140.9$ (s, $2C_1$); $\delta 119.8, 124.8$ (d, $2C_6$, $^3J(P,C) = 7$ and 13 Hz, resp.); $\delta 129.4, 130.2$ (s, $2C_m$); $\delta 132.9, 131.6$ (s, $2C_p$); phenyls: $\delta 119.8, 123.2$ (d, $2C_1$, $^1J(P,C) = 98$ and 95 Hz, resp.) other C_1 are obscured; $\delta 132.4, 132.8, 133.0, 135.9$ (d, $4C_6$, $^2J(P,C) = 11$ Hz); $\delta 129.1$ (vt, $2C_m$, $^1J(P,C) = 12$ Hz), $129.8, 130.2$ (d, $2C_m$, $^1J(P,C) = 13$ Hz); $\delta 134.1$ (vs, $2C_p$), $134.6, 135.3$ (vs, $2C_p$).

2.2. $[PdCl_2\{CH(PPh_2=N-C_6H_4-4-OMe)(PPh_2-N'H-C_6H_4-4-OMe)\}-C,N]$ (**2b**)

Anal. Found: C, 57.93; H, 4.78; N, 3.35; P, 7.79. $C_{39}H_{36}Cl_2N_2O_2P_2Pd$ (**2b**). Calc.: C, 58.26; H, 4.51; N, 3.48; P, 7.70%. FAB mass found: $m/z = 805$ ($M + 1$, 5%), 768 ($M - Cl$, 15%), 731 ($M - 2Cl$, 80%) (M , calc. $C_{39}H_{36}Cl_2N_2O_2P_2Pd$: 804.0). Infrared (KBr): $\nu(N-H) = 3053$ cm^{-1} , $\nu(P=N) = 1239$ cm^{-1} , $\nu(P-NH) = 1035$ cm^{-1} .

2.3. $[PdCl_2\{CMe(PPh_2=N-C_6H_4-4-Me)(PPh_2-N'H-C_6H_4-4-Me)\}-C,N]$ (**2c**)

The reaction procedure described above yielded an approximate 1:1 mixture of complex **2c** and **3**, but **2c** was purified by recrystallization from THF-PhCN. Anal. Found: C, 60.98; H, 4.96; N, 3.63; P, 7.75. $C_{40}H_{38}Cl_2N_2P_2Pd$ (**2c**). Calc.: C, 61.12; H, 4.88; N,

3.56; P, 7.88%. FAB mass found: $m/z = 787$ ($M + 1$, 4%), 749 ($M - \text{Cl}$, 15%), 713 ($M - \text{Cl}_2$, 81%) (M , calc. $\text{C}_{40}\text{H}_{38}\text{Cl}_2\text{N}_2\text{P}_2\text{Pd}$: 786.0). Infrared (Nujol): $\nu(\text{N-H}) = 2990 \text{ cm}^{-1}$, $\nu(\text{P=N}) = 1250 \text{ cm}^{-1}$, $\nu(\text{P-NH}) = 1022 \text{ cm}^{-1}$.

2.4. Synthesis of $[\text{PdCl}_2\{\text{CHMe}(\text{PPh}_2 = \text{N-C}_6\text{H}_4\text{-4-Me})_2\}\text{-N,N'}]$ (**3**)

Complex **3** was obtained as a mixture with **2c** from the above-described reaction and could not be obtained in pure form. Characterization is based on ^1H and ^{31}P NMR spectroscopy at variable temperature (see Section 3). Infrared (Nujol): $\nu(\text{P=N}) = 1256 \text{ cm}^{-1}$.

2.5. Synthesis of $[\text{PdCl}_2\{2\text{-C}_6\text{H}_4\text{-PPh}(\text{NH-C}_6\text{H}_4\text{-4-Me})\text{-CH-PPh}_2(\text{NH-C}_6\text{H}_4\text{-4-Me})\}\text{-C,C'}]$ (**4**)

A mixture of 190.9 mg (0.32 mmol) **1a** and 83.6 mg (0.32 mmol) $\text{PdCl}_2(\text{MeCN})_2$ was suspended in 30 ml toluene and was heated at 90°C . The red solution, consisting of complex **2a**, was stirred for 24 h, which resulted in the formation of a pale white precipitate. The suspension was evaporated to 10 ml and 80 ml of diethyl ether was added. After filtration, the white residue was washed with pentane ($2 \times 20 \text{ ml}$) and dried in vacuo, yielding 241 mg of a white powder (97%). Complex **4** was also synthesized from a reaction of **1a** with $\text{PdCl}_2(\text{PhCN})_2$ in THF at 80°C . Crystals suitable for an X-ray crystal structure determination were obtained from acetonitrile at 20°C . Anal. Found: C, 60.45; H, 4.76; N, 3.73; P, 7.97. $\text{C}_{39}\text{H}_{36}\text{Cl}_2\text{N}_2\text{P}_2\text{Pd}$ (**4**). Calc.: C, 60.68; H, 4.70; N, 3.63; P, 8.02%. Infrared (KBr): $\nu(\text{N-H}) = 3060 \text{ cm}^{-1}$ (br), $\nu(\text{P-N}) = 1285 \text{ cm}^{-1}$ (s), 1223 cm^{-1} (s) and/or 951 cm^{-1} (s).

2.6. Synthesis of $[\text{PtCl}(\text{N}=\text{CPh})\{\text{CH}(\text{PPh}_2 = \text{N-C}_6\text{H}_4\text{-4-Me})(\text{PPh}_2\text{-N'H-C}_6\text{H}_4\text{-4-Me})\}\text{-C,N/Cl}]$ (**5a**)

To a solution of 273.0 mg (0.58 mmol) $\text{PtCl}_2(\text{PhCN})_2$ in 30 ml THF was added 343.7 mg (0.58 mmol) of $\text{H}_2\text{C}(\text{PPh}_2 = \text{N-C}_6\text{H}_4\text{-4-Me})_2$ (**1a**). After 48 h stirring at 20°C , the yellow solution was concentrated to 15 ml, at $10\text{--}20^\circ\text{C}$. Removal of the stirring rod and careful addition of 20 ml hexane, without mixing the two layers, resulted in the formation of pale-yellow crystals after 24 h at 20°C . The crystals were isolated by filtration and were washed with diethyl ether ($2 \times 20 \text{ ml}$) and pentane (20 ml) and dried in vacuo, giving 223 mg of complex **5a** (0.22 mmol, 38% yield). The crystals of **5a** were unsuitable for X-ray crystal structure determinations owing to their mica-like structure. Anal. Found: C, 58.90; H, 4.61; N, 4.61; P, 6.59. $\text{C}_{53}\text{H}_{46}\text{Cl}_2\text{N}_4\text{P}_2\text{Pt}$ (**5a**). Calc.: C, 59.66; H, 4.35; N, 5.25; P, 5.81%. FAB mass found: $m/z = 1031$ (M^+ , 45%), 994 ($M^+ - \text{Cl}$,

55%) (M^+ , calc. $\text{C}_{53}\text{H}_{46}\text{ClN}_4\text{P}_2\text{Pt}$: 1031.0). Infrared (KBr): $\nu(\text{N-H}) = 3140 \text{ cm}^{-1}$ (w), $\nu(\text{C}\equiv\text{N}) = 2280 \text{ cm}^{-1}$ (w), $\nu(\text{P=N}) = 1395, 1285$ or 1230 cm^{-1} (m), $\nu(\text{P-N}) = \text{n.r.}$ ^{13}C NMR (CDCl_3): Pt-C, $\delta -10.2$ (dd, $^1J(\text{P,C}) = 57, 33 \text{ Hz}$, $^1J(\text{Pt,C}) = \text{n.r.}$); $\text{C}_6\text{H}_4\text{-4-CH}_3$, $\delta 21.0, 21.4$ (s); N-C $_6\text{H}_4$: $\delta 137.3$ (d, C_i , $^2J(\text{P,C}) = 5 \text{ Hz}$) and 147.4 (s, C_i); $\delta 120.6$ (d, 1C_o , $^3J(\text{P,C}) = 7 \text{ Hz}$), other C_o is obscured; $\delta 132.5, 134.5$ (s, 2C_p); phenyls: $\delta 118.7$ (d, 1C_i , $^1J(\text{P,C}) = 95$) other C_i are obscured; $\delta 127\text{--}136$ (overlapping $\text{C}_{o,m,p}$); PhC=N: $\delta 139.2$ (d, C_i , $^3J(\text{P,C}) = 20 \text{ Hz}$); $\delta 170.4$ (d, C=N, $^2J(\text{P,C}) = 10 \text{ Hz}$); PhC≡N: $\delta 110.4$ (s, C_i); $\delta 118.6$ (s, C≡N).

2.7. Synthesis of $[\text{PtCl}_2\{\text{CH}(\text{PPh}_2 = \text{N-C}(\text{Ph})=\text{N-C}_6\text{H}_4\text{-4-Me})(\text{PPh}_2\text{-N'H-C}_6\text{H}_4\text{-4-Me})\}\text{-C,N}]$ (**6a**)

To a solution of 117.1 mg (0.25 mmol) $\text{PtCl}_2(\text{PhCN})_2$ in 30 ml THF was added 147.5 mg (0.25 mmol) **1a** and the mixture was stirred at 80°C for 24 h. The yellow solution was cooled to room temperature and was set aside against pentane in a closed system for 2 days, which resulted in the formation of yellow crystals, 108 mg **6a** (0.11 mmol, 45% yield). The supernatant contained complex **6a** contaminated with small amounts of **5a** and some decomposition products. Normal work-up procedures, e.g. evaporation of the solvent and subsequent addition of pentane, resulted in the precipitation of both complexes, **5a** as well as **6a**. FAB mass found: $m/z = 928$ ($M - \text{Cl}$, 34%), 891 ($M - 2\text{Cl}$, 64%) (M , calc. $\text{C}_{46}\text{H}_{41}\text{Cl}_2\text{N}_3\text{P}_2\text{Pt}$: 963.8). Infrared (KBr): $\nu(\text{N-H}) = 3140 \text{ cm}^{-1}$ (w), $\nu(\text{P=N}) = 1390$ or 1260 cm^{-1} (s), $\nu(\text{P-N}) = 1030 \text{ cm}^{-1}$. ^{13}C NMR (CDCl_3): Pt-C, $\delta -8.1$ (dd, $^1J(\text{P,C}) = 59, 102 \text{ Hz}$, $^1J(\text{Pt,C}) = \text{n.r.}$); $\text{C}_6\text{H}_4\text{-4-CH}_3$, $\delta 21.1, 21.5$ (s); C_6H_4 : $\delta 148.4, 136.2$ (s, 2C_i); $\delta 119.7$ (d, 1C_o , $^3J(\text{P,C}) = 6 \text{ Hz}$), other C_o is obscured; $\delta 132.6, 133.9$ (s, 2C_p); phenyls: $\delta 120.5, 124.1$ (d, 2C_i , $^1J(\text{P,C}) = 102$ and 85 Hz , resp.) other C_i are obscured; $\delta 126\text{--}135$ (overlapping $\text{C}_{o,m,p}$); Ph-C=N: $\delta 139.8$ (d, C_i , $^3J(\text{P,C}) = 19 \text{ Hz}$); $\delta 167.5$ (d, C=N, $^2J(\text{P,C}) = 10 \text{ Hz}$).

2.8. Synthesis of **5b** and **6b**

To a solution of 145.4 mg (0.29 mmol) $\text{PtCl}_2(\text{pTolCN})_2$ in 10 ml THF was added 172.8 mg (0.29 mmol) of **1a** and the mixture was stirred at 25°C for 24 h. The yellow solution was evaporated to dryness and 40 ml of diethyl ether was added. The yellow precipitate was washed with diethyl ether (20 ml) and pentane ($2 \times 20 \text{ ml}$) and dried in vacuo. The ^1H and ^{31}P NMR spectra showed the presence of 65% **5b**, 10% **6b** and 25% of the intermediate compound **C** (vide infra). Recrystallization was carried out by slow diffusion of pentane into a THF- CH_2Cl_2 mixture for 7 days at 20°C , yielding 40 mg (0.04 mmol, 14%) pure **6b**.

[PtCl₂{CH(PPh₂)=N-C(pTol)=N-C₆H₄-4-Me)(PPh₂-N'H-C₆H₄-4-Me)-C.N]} (6b). Anal. Found: C, 57.44; H, 4.52; N, 4.26; P, 6.23. C₄₇H₄₃Cl₂N₃P₂Pt (6b). Calc.: C, 57.73; H, 4.44; N, 4.30; P, 6.33. FAB mass found: *m/z* = 978 (M + 1, 2%), 942 (M - Cl, 15%), 905 (M - 2 - Cl, 83%) (M, calc. C₄₇H₄₃Cl₂N₃P₂Pt: 977.8). Infrared (KBr): $\nu(\text{N-H}) = 3170 \text{ cm}^{-1}$ (br,m), $\nu(\text{P=N}) = 1388 \text{ cm}^{-1}$ (s), $\nu(\text{P-N}) = 983 \text{ cm}^{-1}$ (m).

2.9. NMR experiments

2.9.1. Reaction of PdCl₂(MeCN)₂ + BIPM (1a)

A mixture of 42.4 mg (0.07 mmol) **1a** and 18.5 mg (0.07 mmol) PdCl₂(MeCN)₂ was suspended in 0.5 ml CD₂Cl₂ at -80°C. The yellow suspension was quickly transferred into a cooled 5 mm NMR tube, with a syringe, but within these few seconds the reaction had already started to give a clear red solution. The first ³¹P and ¹H NMR measurements were carried out at -80°C, and subsequently spectra were recorded between -80°C and 20°C at regular intervals (every 30 min). ³¹P NMR (-80°C, *t* = 1 h): δ 2.8 (s, P=N, BIPM **1a**); δ 28.6 and 32.3 (d, intermediate **B**, ²*J*(P,P) = 18 Hz); δ 25.4 (s, intermediate **C**); δ 25.5 and 33.0 (d, **2a**, ²*J*(P,P) = 15 Hz); δ 22.1, 24.3, 24.9 (remaining small signals). ¹H NMR (-20°C, *t* = 5 h). Intermediate **B** [PdCl₂(MeCN)(N(pTol)=PPh₂-CH=PPh₂-NH(pTol))]: CH, δ 2.92 (dd, ²*J*(P,H) = 7, 16 Hz); NH, δ 11.5 (br). Intermediate **C**: CH δ not resolved; NH δ 9.2 (br). ³¹P NMR (20°C, *t* = 16 h): δ 6.2 (s, small amount of intermediate **C**); δ 24.7 and 33.2 (d, **2a**, ²*J*(P,P) = 14 Hz).

2.9.2. Reaction of PtCl₂(PhCN)₂ + BIPM (1a)

A 1:1 mixture of PtCl₂(PhCN)₂ and **1a** in 0.5 ml CD₂Cl₂ was measured at -50°C (³¹P NMR showed only the free ligand, 1.9 ppm(s)). At 20°C the ligand was converted within 15 min into the intermediate **C** (δ ³¹P, 26.1 ppm (s), no ¹⁹⁵Pt satellites). Subsequently, after approximately 30 min another equivalent of **1a** was added, which was repeated again after 30 min.

2.9.3. Reaction of PtCl₂(COD) + BIPM (1b)

A solution of 0.048 mmol PtCl₂(COD) in 0.4 ml CDCl₃ was put into a 5 mm NMR tube and was frozen in (-100°C); subsequently, a solution of 0.048 mmol **1b** in 0.4 ml CDCl₃ was added on top of the frozen sample. Warming to -30°C, the solution was shaken for about 10 s before the NMR measurements were taken at -30°C. ³¹P NMR (-30°C): δ 26.3 (s, intermediate **C** > 90%), δ 19.4 (decomposition), 75.4 (s, unknown compound).

2.10. Attempted reaction of BIPM (1a) with PhC≡N

A mixture of 100 mg (0.17 mmol) of **1a** and 3 ml PhCN in 25 ml THF was stirred and gave no reaction

after 70 h at 20°C. Refluxing for 4 h gave no reaction either, although some decomposition products were observed.

2.11. Reaction of PtCl₂ + 4 BIPM (1a)

To a suspension of 30.6 mg (0.115 mmol) PtCl₂ in 40 ml THF was added four equivalents of **1a** and the mixture was stirred for 48 h at 20°C. The brown-yellow suspension was filtered through Celite filter aid and the clear yellow filtrate was concentrated to 1 ml. Addition of 20 ml of pentane and washing with pentane (2 × 20 ml) and drying in vacuo, yielded a white powder, consisting of compound **C** and some decomposition products. ¹H NMR (CD₂Cl₂): δ 2.19 (s, CH₃); δ 6.80 (vs, N-C₆H₄); δ 7.1–8.0 (m, Ph); δ 9.4 (br, NH). ³¹P NMR (CDCl₃): δ 26.9 (s, intermediate **C**, 95%), δ 17.7, 22.8, 24.3, 29.0, 32.4 (s, decomposition, 5%). ¹³C NMR (CD₂Cl₂): δ 14.7 (t, P-CH-P, ¹*J*(P,C) = 132 Hz); *p*-tolyl: δ 21.0 (vs, CH₃); δ 120.8 (s, C_o); δ 132.0 (s, C_p); δ 139.2 (s, C_i); C_m is not resolved; phenyls: δ 126.8 (d, C_i, ¹*J*(P,C) = 113 Hz), δ 129–131 (m, C_m); δ 133–135 (m, C_o + C_p).

2.12. Structure determination and refinement of **4**

Crystal data and numerical details of the structure determination are given in Table 1. A colourless block-shaped crystal (0.12 × 0.18 × 0.28 mm³) was glued on a glass-fibre and transferred to an Enraf-Nonius CAD4-T (graphite monochromated MoK α radiation) rotating anode diffractometer for data collection at room temperature. Unit cell parameters were determined from least squares treatment of the SET4 setting angles of 25 reflections in the range 8.5 < θ < 13.5 and were checked for the presence of higher lattice symmetry [25]. All data were collected with ω -2 θ scan mode; data were corrected for Lp and for the observed linear decay (4%) of the intensity control reflections during the 32 h of X-ray exposure time; redundant data were merged into a unique data set. Absorption correction was applied using the DIFABS method (correction range: 0.540–1.538) [26]. The structure was solved with DIRDIF PATTY [27] methods followed by subsequent difference Fourier synthesis. Refinement on *F*² was carried out by full-matrix least squares techniques. H-atoms of the water molecule were located from a difference Fourier map. In view of the limited quality of the data, the water molecule was included in the refinement as a rigid group. Other H-atoms were introduced on calculated positions and included in the refinement on their carrier atoms with isotropic thermal parameters. All non-H atoms were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles.

Neutral atom scattering factors were taken from

Table 1
Crystal data and details of the structure determination

<i>Crystal data</i>	
Formula	C ₃₉ H ₃₆ Cl ₂ N ₂ P ₂ Pd·H ₂ O
Mol. wt.	790.02
Crystal System	monoclinic
Space group	P2 ₁ /c (Nr. 14)
a, b, c (Å)	14.4356(14), 15.870(2), 16.6385(19)
β (deg)	106.37(1)
V (Å ³)	3657.2(7)
Z	4
D _{calc} (g cm ⁻³)	1.4348(2)
F(000)	1616
μ (cm ⁻¹)	7.7
<i>Data collection</i>	
Temperature (K)	298
θ _{min} , θ _{max}	1.27, 23.00
Radiation	MoKα, 0.71073 Å
Δω (°)	1.11 + 0.35 tan θ
Hor. and vert. aperture (mm)	3.79, 4.00
Reference reflections	-2 3 -2, -3 -2 -1, -2 -3 -2
Data set	h - 15:15; k - 17:0; l - 18:14
Total data	6611
Total unique data	5094
Observed data	4168 (F _o ² > 0)
<i>Refinement</i>	
No. of refl. and parms.	4168, 429
Weighting scheme	w = 1.0/[σ ² (F _o ²) + (0.0529P) ²]
Final R ₁ , wR ₂ , S	0.0962, 0.1922, 0.936
(Δ/σ) _{av} in final cycle	0.058
Min. and max. resd.	-0.62, 0.75
dens. (e Å ⁻³)	

Cromer and Mann [28], corrections for anomalous dispersion from Cromer and Liberman [29]. All calculations were performed with SHELXL-93 [30] and the PLA-

TON package [31] (geometrical calculations and illustration) on a DEC-5000 cluster.

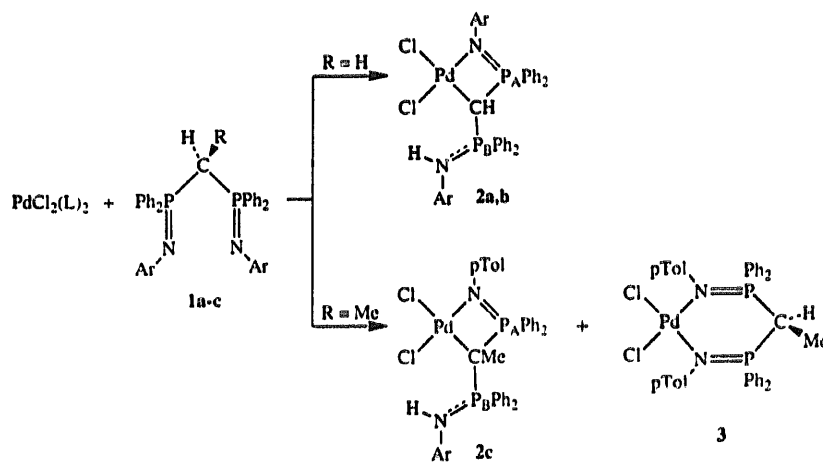
3. Results

3.1. Synthesis and characterization of the palladium(II) complexes 2 and 3

The reactions of BIPM **1a,b** with PdCl₂(RCN)₂ (R = Ph, Me) in CH₂Cl₂, THF or toluene selectively afforded the complexes PdCl₂{CH(PPh₂=N-aryl)(PPh₂NH-aryl)} **2a,b**, containing C,N-coordinated (iminophosphoranyl)(aminophosphonium)methanide, in good yields (99%) by substitution of the weakly coordinated nitriles at the palladium centre. The same complexes were obtained by using PdCl₂(COD) as starting compound. Lower selectivity was observed for the reaction of 1,1-bis(iminophosphoranyl)ethane (1,1-BIPE) ligand **1c**, which resulted in a mixture of the C,N- and N,N'-coordinated isomers PdCl₂{1,1-BIPE} (**2c** and **3** respectively) in an approximate 1:1 ratio (Scheme 1).

The products **2a-c** and **3** are air-stable orange-red solids, soluble in polar solvents like CH₂Cl₂, CHCl₃ and acetone, but insoluble in THF or toluene and other non-polar solvents. In acetone, decomposition of the complexes occurred after 3 days at 20 °C, giving Pd⁰ as a black precipitate.

In the ¹H NMR (Table 2) the Pd-CH resonance is found at 2.3 ppm for **2a,b** and the Pd-CCH₃ resonance at 1.3 ppm for **2c**, which are doublets of doublets as a result of coupling with two anisochronous phosphorus atoms. Their chemical shifts are in agreement with the corresponding data reported previously for related Pt and Pd complexes [7,9]. Furthermore, a broad doublet NH resonance at about 9 ppm is found, characteristic for



L = PhCN, MeCN; (L)₂ = COD
1a/2a: R = H, Ar = *p*-tolyl; **1b/2b**: R = H, Ar = *p*-anisyl; **1c**: R = Me, Ar = *p*-tolyl.

Scheme 1. Reactions of BIPM and 1,1-BIPE with PdCl₂(L)₂. L = PhCN, MeCN; (L)₂ = COD. **1a/2a**: R = H, Ar = *p*-tolyl; **1b/2b**: R = H, Ar = *p*-anisyl; **1c**: R = Me, Ar = *p*-tolyl.

an aminophosphonium group [1,2,5,7]. Higher NH resonance frequencies have been reported for $[\text{PtCl}(\text{PR}_3)(\text{CH}(\text{PPh}_2=\text{N-aryl})(\text{PPh}_2\text{-NH-aryl})\text{-C,N})]^+\text{Cl}^-$ (10.4–10.9 ppm) [7], but similar low NH frequencies between 8.3–9.4 ppm have been found for the corresponding groups in **4** (vide supra) and in *trans*-S–Pt–Cl $[\text{PtCl}(\text{PEt}_3)(\text{CH}(\text{PPh}_2=\text{S})(\text{PPh}_2\text{-NH-aryl})\text{-C,N})]\text{BF}_4$ [32], which could indicate that the P–NH–aryl function in **2a–c** is intramolecularly bridging to a chloride ligand cis to it, as is the case in **4** and the last example.

The ^{31}P NMR spectra (Table 3) for **2a–c** exhibit two doublets, with a remarkably large $^2J(\text{P,P})$ of 28 Hz for **2c**. The low frequency resonance in the range 23 to 28 ppm in the ^{31}P NMR is assigned to the coordinated $\text{P}_\text{A}=\text{N}$ group, since it resembles the ^{31}P frequency observed for complex **3**, containing *N,N'*-coordinated 1,1-BIPE (vide infra). This assignment is confirmed by selective $^1\text{H}\{^{31}\text{P}\}$ decoupling experiments, which showed that the other signal, at about 34 ppm, belonged to the aminophosphonium entity $\text{Ph}_2\text{P}_\text{B}\text{-NH-aryl}$. Also, comparison with the earlier reported data of related cationic four-membered platinacycles $[\text{PtX}(\text{PR}_3)(\text{CH}(\text{PPh}_2=\text{N-aryl})(\text{PPh}_2\text{-NH-aryl})\text{-C,N})]^+$, obtained from the reactions of BIPM with $\text{Pt}_2\text{Cl}_4(\text{PR}_3)_2$ [7], clearly indicate that the ligand is *C,N*-coordinated. The ^{13}C NMR data of **2a** are in agreement with this structural assignment.

The ^{31}P NMR spectrum of complex **3**, showing one broad resonance at 24.5 ppm at 20°C which resolves into a sharp singlet at –30°C, indicates that the ligand

Table 3
 ^{31}P NMR data of the metallacycles 2–6^a

	δP_A	δP_B	$^2J(\text{Pt,P}_\text{A})$	$^2J(\text{Pt,P}_\text{B})$	$^2J(\text{P}_\text{A},\text{P}_\text{B})$
2a	23.6 (d)	33.0 (d)	—	—	14.3
2b	23.4 (d)	33.7 (d)	—	—	14.4
2c	28.0 (d)	34.3 (d)	—	—	28.1
3	24.5 (br) ^b	—	—	—	—
4 ^c	17.0 (d)	31.0 (d)	—	—	6.1
5a	2.7 (d)	32.9 (d)	285	67	3.8
5b	2.3 (d)	32.9 (d)	277	n.r.	3.3
6a	0.7 (d)	29.9 (d)	250	147	15.8
6b	0.4 (d)	29.7 (d)	249	138	15.9

^a Measured at 40.53 MHz or 121.5 MHz in CDCl_3 at 293 K, unless stated otherwise. Atom labelling is shown in Schemes 1 and 2. Multiplicity labels and abbreviations: s = singlet, d = doublet, br = broad, n.r. = not resolved. ^b Measurement at –30°C gave δP_A = 24.8 (s). ^c Measured in CD_2Cl_2 .

is $\sigma\text{-N},\sigma\text{-N}'$ -coordinated forming a six-membered palladacycle wherein the two P-atoms are equivalent.

In the ^1H NMR of **3** the CH resonance is obscured, even at –50°C, but the broad CHCH_3 resonance at 1.4 ppm (at 20°C) resolves into a triplet of doublets at –30°C. Similar features have been observed previously for related six-membered platinacycles, containing *N,N'*-coordinated BIPM [7] or 1,1-BIPE [23], which have been ascribed to boat-to-boat inversion (**3A** ↔ **3B**, Fig. 1) of the six-membered ring at 20°C. From the facts that only one phosphorus resonance is found at low temperature and one signal is observed for Pd–

Table 2
 ^1H NMR data of the metallacycles 2–6^a

Solvent	$\delta(4\text{-R})$ ^b	$\delta(\text{M}=\text{CH})$ ^c	$\delta(\text{N}-\text{C}_6\text{H}_4)$ ^d	$\delta(\text{phenyls})$	$\delta(\text{NH})$ ^e
2a CDCl_3	2.05 (s)	2.25 (dd, 10.5, 2.7)	6.5–6.8 (m)	7.1–8.6 (m, 20 H)	9.12 (br.d, 6.5)
	2.11 (s)				
2b CD_2Cl_2	3.61 (s)	2.32 (dd, 10.6, 2.2)	6.37 (d), 6.47 (d), 6.55 (d), 6.62 (d)	6.8–8.6 (m, 20 H)	8.87 (d, 6.2)
	3.62 (s)				
2c CDCl_3 ^e	2.01 (s)	— ^f	6.12 (d), 6.33 (d), 6.48 (d), 6.59 (d)	6.8–8.7 (m, 20 H)	9.09 (d, 5.8)
	2.08 (s)				
3 CDCl_3 ^e	2.13 (s)	— ^{g,h}	6.80 (d), 7.40 (d)	7.0–8.4 (m, 20 H)	—
	2.09 (s)	4.69 (t, 15.7)	6.50 (d), 6.61 (d), 6.71 (d), 6.87 (d)	6.9–8.5 (m, 19 H)	7.69 (d, 12.1) 9.6 (br)
5a CDCl_3	2.11 (s)				
	2.08 (s)	6.85 (dd, 12.2, 20.1) ⁱ	6.25 (d), 6.54 (d) n.r., 8.20 (d)	6.6–8.7 (m, 32 H)	10.54 (d, 7.2)
5b $^j\text{CDCl}_3$	2.17 (s)	n.r.	6.27 (d), 6.53 (d) 7.26 (d), 8.04 (d)	7.0–8.7 (m)	10.4 (br)
	2.06 (s)				
6a CDCl_3	2.11 (s)	4.82 (dd, 12.3, 20.9) ⁱ	6.3–6.8 (m)	6.8–8.3 (m, 25 H)	8.51 (d, 6.2)
	2.16 (s)				
6b ^h CDCl_3	2.12 (s)	4.79 (dd, 12.2, 20.9) ⁱ	6.35 (d), 6.44 (d) 6.50 (d), 6.62 (d)	6.9–8.4 (m, 20 H)	8.60 (d, 6.3)
	2.16 (s)				

^a Recorded at 300.13 MHz at 20°C, unless noted otherwise; s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, n.r. = not resolved, br = broad. ^b R = Me, OMe. ^c $^2J(\text{H,H})$ Hz are given in parentheses. ^d $^3J(\text{H,H})$ = 8–9 Hz. Not-resolved protons are included under the next column. ^e Measured at 500 MHz. ^f $\delta(\text{Pd}-\text{C}-\text{CH}_3)$ = 1.33 (dd, 16.9, 19.7). ^g At 20°C: $\delta(\text{C}-\text{CH}_3)$ = 1.40 (br), $\delta(\text{CH})$ is not resolved. ^h Measured at –30°C: $\delta(\text{C}-\text{CH}_3)$ = 1.36 (dt, 7.5, 17.4), $\delta(\text{CH})$ is not resolved. ⁱ $^2J(\text{Pt,H})$ is not resolved. ^j *p*-Tolyl–C=N: $\delta(4\text{-CH}_3)$ = 2.31 (s); $\delta(\text{C}_6\text{H}_4)$ = 6.94 (d), 6.99 (d). *p*-Tolyl–C=N: $\delta(4\text{-CH}_3)$ = 2.39 (s); $\delta(\text{C}_6\text{H}_4)$ = 6.68 (t, 4H). ^k *p*-Tolyl–C=N: $\delta(4\text{-CH}_3)$ = 2.25 (s); $\delta(\text{C}_6\text{H}_4)$ = 6.77 (d), 6.80 (d). ^l $^2J(\text{Pt,H})$ = 93 Hz.

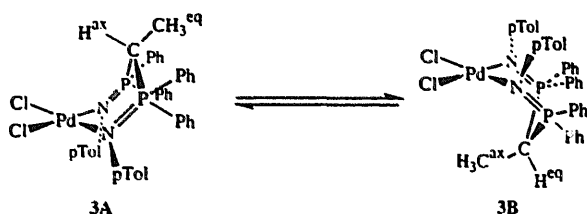
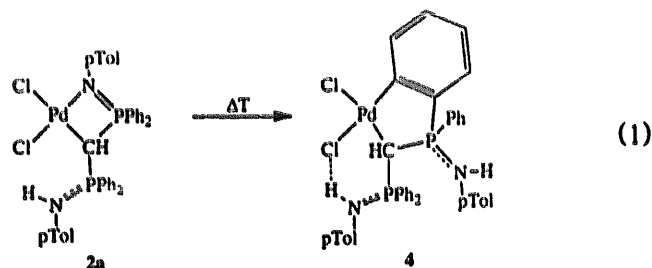


Fig. 1. Exchange involving boat conformers 3A and 3B.

CCH_3 , it is deduced that compound **3** exists as one single boat conformer (**3A**) at -30°C , wherein the methyl group on the central carbon of the N,N' -coordinated 1,1-BIPE ligand is probably in equatorial position, similar to the boat conformation of the related Pt complex $[\text{PtCl}(\text{PMe}_2\text{Ph})\{(\text{N}(\text{pTol})=\text{PPh}_2)_2\text{CHMe}\}-N,N']\text{Cl}$ [23], which has been determined crystallographically.

3.2. Synthesis and characterization of the orthopalladated complex **4**

When a red suspension of complex **2a** is refluxed in toluene or THF, a new white compound **4** is formed after 24 h in high yield (97%) (Eq. (1)). For the mixture of compound **2c** and **3** a similar reaction was carried out, but that resulted in an increase of **3** relative to the amount of **2c** instead of the formation of a new product similar to **4**. Compound **4** is an air-stable white solid, moderately soluble in dmso, CHCl_3 , CH_2Cl_2 and insoluble in MeOH, THF, toluene, diethyl ether and pentane. Crystals suitable for an X-ray crystal structure determination were obtained from acetonitrile.



The ^{31}P NMR spectrum of **4** (Table 3) shows two doublets at 31 ppm and 17 ppm ($^2J(\text{P},\text{P}) = 6.1$ Hz). In the ^1H NMR of complex **4** (Table 2) one observes a triplet CH resonance at 4.0 ppm and two doublet NH resonances at 7.7 ppm and 9.4 ppm. The coupling with the adjacent phosphorus nuclei has been corroborated by $^1\text{H}\{^{31}\text{P}\}$ NMR, by which these signals collapse into singlets. The integrals indicate that 19 aromatic H-atoms are present instead of the 20 phenyl protons in **2**, in agreement with the X-ray crystal structure of **4**, which shows that one of the phenyl groups on P is orthometalated. Clearly, one of the ortho-H atoms has shifted to the nitrogen atom of a previously non-protonated $\text{P}=\text{N}$ group in **2a** (Eq. (1)).

Several attempts to measure ^{13}C NMR failed owing to the moderate solubility of the compound in various solvents and precipitation during measurements.

3.3. X-ray crystal structure of $4 \cdot \text{H}_2\text{O}$

The X-ray crystal structure of $[\text{PdCl}_2\{2\text{-C}_6\text{H}_4\text{-PPh}(\text{NH-C}_6\text{H}_4\text{-4-CH}_3)\text{C}'\text{H}(\text{PPh}_2\text{-NH-C}_6\text{H}_4\text{-4-CH}_3)\}\text{-C,C'}\} \cdot \text{H}_2\text{O}$ (**4**) has been determined. The monoclinic unit cell comprises four molecules of complex **4** and four molecules of H_2O , which originate from water in the acetonitrile used for crystallization. Fractional atomic coordinates are given in Table 4. Selected bond distances and angles are given in Table 5.

Fig. 2 shows the neutral square-planar Pd complex **4** and the adopted numbering scheme. The coordination around Pd is almost perfectly square planar as evidenced by the least squares plane through Pd, Cl(1), Cl(2), C(1) and C(2), which shows only minor deviations of 0.000(1) Å, 0.012(5) Å, $-0.011(5)$ Å, $-0.015(17)$ Å and 0.017(16) Å respectively. Complex **4** represents one of the two orthometalated Pd complexes containing a C,C' -coordinated ligand which have been authenticated by X-ray crystallographically [18]. It is, furthermore, similar to the Pt complex $[\text{PtCl}(\text{PEt}_3)\{2\text{-C}_6\text{H}_4\text{-PPh}(\text{NH-C}_6\text{H}_4\text{-4-CH}_3)\text{C}'\text{H}(\text{PPh}_2\text{-N-C}_6\text{H}_4\text{-4-CH}_3)\}\text{-C,C'}\}$ reported earlier [9]. The five-membered palladacycle in **4** is almost identical to the M-C-C-P-C rings of the crystallographically determined orthometalated complexes $[\text{PdCl}\{2\text{-(4-Me-C}_6\text{H}_3)\text{P}(\text{pTol})_2\text{-CH-Py}\}\text{-C,C'}\}]_2$ [18], and $[\text{Pt}(\mu\text{-Cl})\{2\text{-C}_6\text{H}_4\text{-PPh}_2\text{-CH-C(O)Me}\}\text{-C,C'}\}]_2$ [15].

The orthometalated BIPM ligand in **4** is C,C' -coordinated by the ortho sp^2 -carbon atom C(2) of a phenyl group on P(1), with $\text{Pd-C}(2)$ of 1.974(16) Å, and by the methine-carbon atom C(1), with $\text{Pd-C}(1)$ of

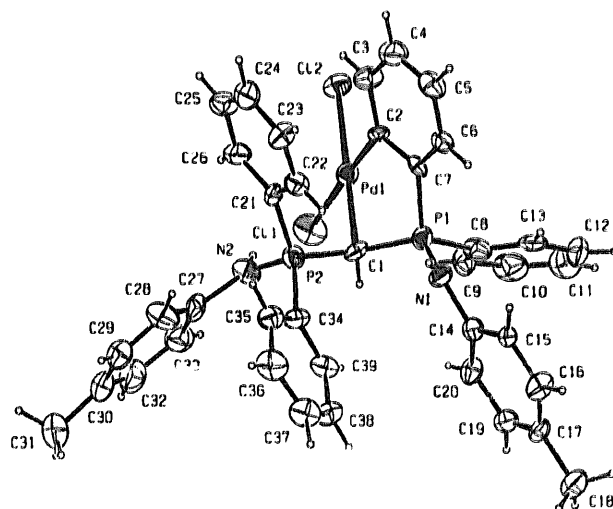


Fig. 2. Thermal ellipsoid plot of **4** at 50% probability, showing the adopted atom labelling. The water molecule was left out for clarity.

Table 4
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **4**

Atom	x	y	z	U_{eq} (Å ²)
Pd (1)	0.24834(10)	0.32606(9)	0.47331(8)	0.0281(4)
Cl (1)	0.1326(4)	0.4128(3)	0.5195(3)	0.049(2)
Cl (2)	0.3153(4)	0.2706(3)	0.6085(3)	0.0382(16)
P (1)	0.299(3)	0.3876(3)	0.3225(3)	0.0267(16)
P (2)	0.1033(3)	0.2985(3)	0.3004(3)	0.0298(16)
N (1)	0.2936(9)	0.3957(8)	0.2219(8)	0.032(4)
N (2)	0.0204(9)	0.3148(8)	0.3491(7)	0.033(4)
C (1)	0.1909(12)	0.3718(10)	0.3503(9)	0.028(5)
C (2)	0.3392(11)	0.2604(10)	0.4290(8)	0.021(4)
C (3)	0.3809(12)	0.1856(11)	0.4579(9)	0.036(5)
C (4)	0.4451(13)	0.1458(11)	0.4238(11)	0.046(6)
C (5)	0.4722(12)	0.1810(12)	0.3545(10)	0.037(5)
C (6)	0.4293(11)	0.2570(10)	0.3239(10)	0.028(5)
C (7)	0.3653(11)	0.2969(9)	0.3588(9)	0.020(5)
C (8)	0.3563(13)	0.4823(10)	0.3733(10)	0.036(5)
C (9)	0.3210(13)	0.5265(11)	0.4300(10)	0.038(5)
C (10)	0.3732(15)	0.5962(12)	0.4658(11)	0.055(6)
C (11)	0.4535(15)	0.6224(13)	0.4483(12)	0.059(6)
C (12)	0.4875	0.5779(12)	0.3911(11)	0.050(6)
C (13)	0.4403(13)	0.5047(10)	0.3555(10)	0.035(5)
C (14)	0.2876(12)	0.4716(11)	0.1728(10)	0.029(5)
C (15)	0.3328(11)	0.4697(11)	0.1107(10)	0.026(5)
C (16)	0.3284(12)	0.5382(11)	0.0594(9)	0.034(5)
C (17)	0.2804(12)	0.6108(10)	0.0680(9)	0.026(5)
C (18)	0.2773(13)	0.6850(11)	0.0134(10)	0.050(6)
C (19)	0.2399(12)	0.6119(10)	0.1329(9)	0.032(5)
C (20)	0.2399(12)	0.5426(10)	0.1858(10)	0.030(5)
C (21)	0.1418(11)	0.1930(10)	0.3105(8)	0.022(5)
C (22)	0.1902(11)	0.1594(11)	0.2562(10)	0.033(5)
C (23)	0.2215(13)	0.0778(12)	0.02638(11)	0.045(6)
C (24)	0.02111(13)	0.0319(12)	0.3309(12)	0.045(6)
C (25)	0.1658(13)	0.0626(11)	0.3849(10)	0.039(5)
C (26)	0.1310(12)	0.1427(11)	0.3746(10)	0.039(5)
C (27)	-0.0807(12)	0.3076(10)	0.3135(10)	0.031(5)
C (28)	-0.1271(14)	0.2546(12)	0.2507(11)	0.046(6)
C (29)	-0.2227(14)	0.2558(12)	0.2148(11)	0.046(6)
C (30)	-0.2828(14)	0.3091(12)	0.2439(12)	0.049(6)
C (31)	-0.3902(13)	0.3113(13)	0.2024(12)	0.075(7)
C (32)	-0.2381(15)	0.3609(12)	0.3094(12)	0.051(6)
C (33)	-0.1367(14)	0.3640(11)	0.3455(11)	0.046(6)
C (34)	0.0542(12)	0.3242(12)	0.1905(10)	0.036(5)
C (35)	0.0270(12)	0.2623(12)	0.1294(10)	0.033(5)
C (36)	-0.0130(13)	0.2826(12)	0.0474(10)	0.044(5)
C (37)	-0.0171(13)	0.3666(12)	0.0252(11)	0.041(5)
C (38)	0.0089(13)	0.4271(12)	0.0866(11)	0.044(6)
C (39)	0.0438(12)	0.4059(11)	0.1692(10)	0.035(5)
O (11)	0.0383(15)	0.5440(11)	0.3546(13)	0.117(6)

U_{eq} is one-third of the trace of the orthogonalized U tensor.

2.109(15) Å, which is bridging the two P–NH–pTol entities. These Pd–C bond lengths are in good agreement with the corresponding values found for other orthometallated Pd-complexes [18,33–35].

The Pd–Cl(1) distance of 2.450(6) Å is significantly longer than the Pd–Cl(2) bond cis to it (2.354(5) Å, which is due to the differences in trans influence of the sp^2 -C(2) > sp^3 -C(1) atoms. The P–N bond distances of 1.644(14) Å and 1.658(14) Å in **4** indicate that both

P–N bonds are elongated due to protonation, since free BIPM [24] and other phosphiminines show much shorter P–N bond lengths of 1.55–1.60 Å [23,36]. They correspond perfectly with the P–N distances (1.63–1.66 Å) of aminophosphonium groups in related Rh-, Ir- [1,5] and Pt-(BIPM) [7] complexes.

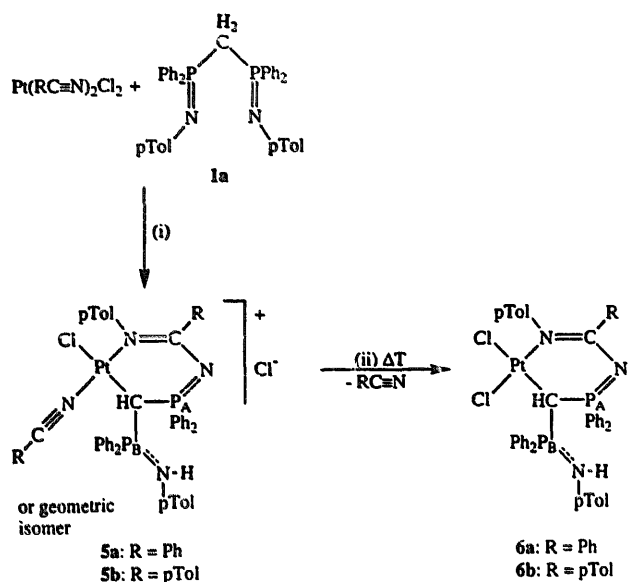
Both nitrogen atoms are protonated and form hydrogen bonds with the Cl ligands on Pd, i.e. an intramolecular N(2)–H(2)···Cl(1) interaction, with an angle of 155.0(14)° and d (H(2)···Cl(1)) of 2.439(13) Å, and an intermolecular N(1)–H(1)···Cl(2) interaction, with an angle of 169.5(15)° and d (H(1)···Cl(2)) of 2.460(14) Å. This is also demonstrated by the torsion angles \angle (Pd–C(1)–P(1)N(1)) of 161.5(6)° and \angle (Pd–C(1)–P(2)–N(2)) of 69.4(8)°, which indicate that only the aminophosphonium group P(2)–N(2) is pointed toward the palladium centre. A different hydrogen bond has been observed for the related orthometallated Pt complex [PtCl(PEt₃)(2-C₆H₄-PPh(NH-C₆H₄-4-CH₃)C'H(PPH₂=N-C₆H₄-4-CH₃))-C,C'], which has an intramolecular N(1)–H···N(2) bond [9].

3.4. Synthesis and characterization of the platinum(II) complexes **5** and **6**

The reaction of BIPM **1a** with Pt(RC≡N)₂Cl₂ in THF resulted in the formation of complex **5a** (R = Ph) or **5b** (R = pTol) after 24 to 48 h stirring at 20°C (Scheme 2, (i)), which is contaminated with an intermediate compound (see Section 3.5, 4.1), and small amounts of compound **6a** or **6b**. Recrystallization from THF–diethyl ether or THF–hexane gave pure **5a**

Table 5
Selected interatomic distances (Å) and angles (deg) for compound **4**

Around Pd			
Pd–Cl(1)	2.450(6)	Pd–Cl(2)	2.109(15)
Pd–Cl(2)	2.354(5)	Pd–C(2)	1.974(16)
Within ligand			
P(1)–N(1)	1.658(14)	P(2)–N(2)	1.644(14)
N(1)–C(14)	1.44(2)	N(2)–C(27)	1.42(2)
P(1)–C(1)	1.769(18)	P(2)–C(1)	1.746(17)
P(1)–C(7)	1.738(16)	P(2)–C(21)	1.757(17)
P(1)–C(8)	1.805(17)	P(2)–C(34)	1.812(17)
Around Pd			
Cl(1)–Pd–Cl(2)	92.46(18)	Cl(2)–Pd–Cl(1)	177.7(5)
Cl(1)–Pd–C(1)	89.7(5)	Cl(2)–Pd–C(2)	91.3(4)
Cl(1)–Pd–C(2)	176.2(4)	C(1)–Pd–C(2)	86.6(6)
Within ligand			
Pd–C(1)–P(1)	99.7(8)	P(1)–N(1)–C(14)	127.9(11)
Pd–C(1)–P(2)	105.4(8)	P(2)–N(2)–C(27)	126.1(10)
P(1)–C(1)–P(2)	123.0(9)		
N(1)–P(1)–C(1)	118.7(7)	N(2)–P(2)–C(1)	101.0(7)
N(1)–P(1)–C(7)	106.3(7)	N(2)–P(2)–C(21)	110.9(7)
N(1)–P(1)–C(8)	107.1(7)	N(2)–P(2)–C(34)	109.3(7)
C(1)–P(1)–C(7)	103.3(8)	C(1)–P(2)–C(21)	115.0(8)
C(1)–P(1)–C(8)	108.4(8)	C(1)–P(2)–C(34)	110.8(8)
C(7)–P(1)–C(8)	113.1(8)	C(21)–P(2)–C(34)	109.5(8)



Scheme 2. Reaction of BIPM with bis(aryl-nitrile)platinum dichloride.

[PtCl(N≡CR){CH(PPh₂=N-C(R)=N-pTol)(PPh₂-N'H-pTol)-C,N}]⁺Cl⁻ (R = Ph), which is an air-stable off-white solid, soluble in THF, acetone, CHCl₃ and CH₂Cl₂, but decomposes slowly in the chlorinated solvents. It is also moderately soluble in toluene and insoluble in diethyl ether or pentane. Compound **5b** (R = pTol) could not be purified and has been characterized in situ as a mixture with **6b** and the intermediate compound (vide infra).

In the ¹H NMR of **5a** (Table 2) a remarkably high frequency CH resonance is observed at 6.85 ppm (dd), with ²J(P,H) = 20.1 and 12.2 Hz; its coupling to ¹⁹⁵Pt is probably obscured by the aromatic protons. Also, a doublet NH resonance is found at 10.54 ppm, which is indicative of an aminophosphonium group. The integral of the aromatic area indicated that two molecules of benzonitrile were present in complex **5a**. A similar observation was made for complex **5b**, which showed four sets of 4-CH₃-C₆H₄ resonance signals, belonging to the two *N*-*p*-tolyl moieties and two other *p*-tolyl groups.

The ¹³C NMR spectrum (Section 2) of **5a** shows the characteristic quaternary carbon resonance frequencies, at 110.4 ppm and 118.6 ppm for the C_{ipso}(Ph) and C≡N respectively, of an end-on coordinated PhC≡N ligand [13]. A typical methine-C resonance is found at -10.2 ppm (dd), which shows a strong resemblance to the methine chemical shift (-3 to -6 ppm) in [PtCl(PR₃){CH(PPh₂=N-aryl)(PPh₂-NH-aryl)-C,N}]⁺ with CH coordinated trans to the Pt-Cl bond [7]. The Pt-satellites in **5a** were not observed due to signal/noise limitations. Furthermore, two doublets are found at 139.2 ppm and 170.4 ppm, with ³J(P,C) = 20 Hz and ²J(P,C) = 10 Hz respectively, belonging to the quater-

nary carbons of the P=N-C(Ph)=N moiety in complex **5a**. The high frequency resonance at 170.4 ppm is clearly indicative of an imine carbon, which lies at a slightly higher frequency than the C=N resonances that have been reported for Pt-diaza-butadienes [37], which indicates that the imine group in **5** is coordinated. Remarkably, only one doublet at 120.6 ppm (with ³J(P,C) = 7 Hz) is found for the ortho-C atoms of a *p*-tolyl group in complex **5a**, whereas usually two characteristic doublets are found in the 119–126 ppm region for bis(*p*-tolyliminophosphoranyl)methane and related complexes [5,7,9,23]. This indicates that the other *p*-tolyl-*N* group is no longer adjacent to P and proves that one PhC≡N has inserted into the Ph₂P=N-pTol group, thus giving rise to a Ph₂P=N-C(Ph)=N-pTol moiety. The ortho-C resonance (singlet) of the last mentioned *p*-tolyl group is obscured by overlap.

The ³¹P NMR spectra of complexes **5a,b** (Table 3) show two doublets, one at ca. 2.5 ppm and the other at 32.9 ppm, with a small ²J(P,P)-coupling of 3 to 4 Hz, which confirms that the P-CP moiety has remained intact, as has also been established in the ¹H and ¹³C NMR. The low frequency resonance, characteristic of a non-coordinated N=P function [8,12,23,24,36], shows a large coupling with ¹⁹⁵Pt (280 Hz), which signifies that P must be coupling with Pt through a Pt-C-P=N linkage. (The ²J(Pt,P)-value for **5** lies exactly between the ²J(Pt,P_A) of ca. 400 Hz and ²J(Pt,P_B) of ca. 100 Hz found for [PtCl(PR₃){CH(P_APh₂=N-aryl)(P_BPh₂-NH-aryl)-C,N}]⁺ [7] and [PtCl(PR₃){CH(P_APh₂=N-aryl)(P_BPh₂=N-aryl)-C,N}] [9] respectively, which also have a Pt-C-P_A as well as a Pt-C-P_B linkage.) The high frequency phosphorus resonance at 32.9 ppm is assigned to a -Ph₂P-NH- group, in agreement with the observation of an accompanying doublet NH resonance in the ¹H NMR, and similar to the data for the corresponding group in **2a-c** and **4**.

The spectroscopic data point to a structure for complexes **5a,b** (Scheme 2), in which a previously coordinated nitrile ligand has been incorporated into a P=N bond of a *C,N*-coordinated BIPM ligand.

Upon heating, complex **5a** converts into **6a** after 24 h in THF in good yields (85%) by loss of the coordinated nitrile (Scheme 2, (ii)), but some decomposition (15%) also occurs. Recrystallization from THF-pentane gave pure **6a**, in approximately 45% yield. Isolation of pure crystalline **6b** was achieved by slow diffusion of pentane into a THF-CH₂Cl₂ solution of the product mixture **5b**, **6b** and an intermediate compound (see Section 3.5, 4.1) after 7 days at 20°C. Complexes **6a,b** are air-stable yellow solids, soluble in THF, CH₂Cl₂, CHCl₃ and acetone, moderately soluble in toluene and insoluble in pentane.

The spectroscopic data (¹H, ³¹P and ¹³C NMR) for **6a,b** are similar to those found for **5a,b**, except for the missing nitrile in **6**. In addition, it must be noted that the

^1H NMR spectra of **6a,b** show a significant shift to lower frequency for both the NH as well as the CH resonance ($\Delta\delta = 2$ ppm) (Table 2), which is probably due to the neutral character of **6a,b** compared with the cationic character of **5a,b**. In contrast to **5a,b** and **6a**, the $^2J(\text{Pt},\text{H})$ -coupling for **6b** (93 Hz) could be observed by $^1\text{H}\{^{31}\text{P}\}$ NMR, which proves the Pt–CH linkage in complexes **6a,b**. Based on the spectroscopic data, the structure as depicted in Scheme 2 is proposed for complex **6**.

3.5. Intermediates in the formation of the complexes **2** and **5**

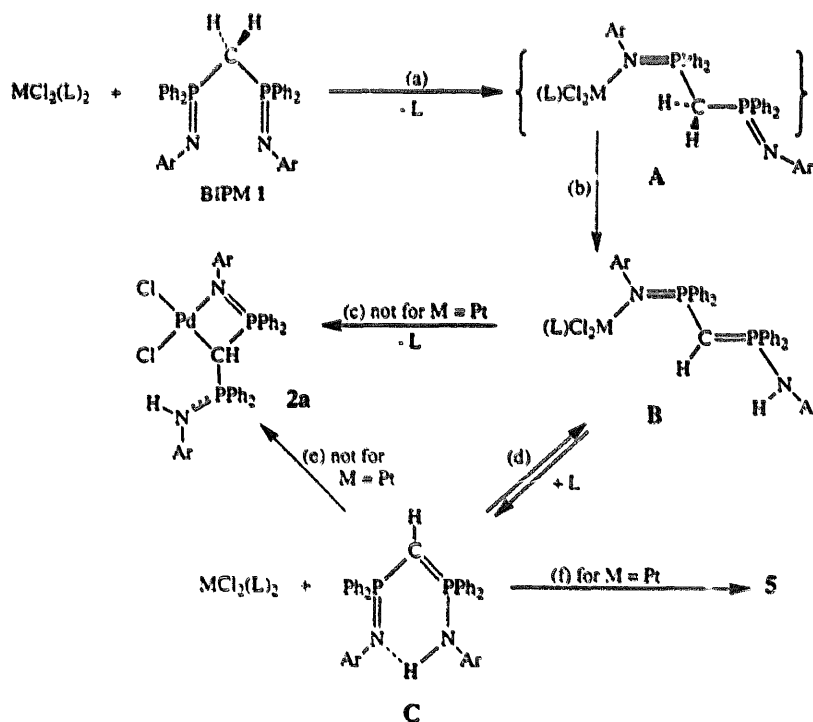
A low-temperature NMR experiment of the reaction between $\text{PdCl}_2(\text{RCN})_2$ and **1a**, started at -80°C , showed that the reaction already proceeds at low temperature to give three products within a few seconds, i.e. the intermediates **B** and **C** and complex **2a** (Scheme 3).

The intermediate **B** shows two doublets in the ^{31}P NMR (-80°C to 0°C) at 28.6 and 32.3 ppm ($^2J(\text{P},\text{P}) = 18$ Hz), which are indicative for coordinated and/or protonated P=N groups [7,9]. This is verified by the ^1H NMR of **B**, showing $\delta(\text{CH})$ at 2.9 ppm (dd) and $\delta(\text{NH})$ at 11.5 ppm (br), the latter being characteristic of a P–NH group. Intermediate **B** is therefore characterized as a palladium complex, wherein one of the nitriles is substituted for a σ -N monodentate coordinated BIPM ligand, in which one of the methylene-H atoms has shifted to the non-coordinated N. The NMR experiment

showed that intermediate **B** slowly disappeared at 0°C with concomitant increase of intermediate **C**, showing a singlet ^{31}P resonance at 26 ppm, and the end-product **2a**. Intermediate **C** was initially thought of as a Pd complex, containing an N,N' -chelated BIPM ligand, but this was rejected after comparison with an identical intermediate, formed in the reactions of BIPM with $\text{PtCl}_2(\text{PhCN})_2$, with other Pt-dichlorides (vide infra), and with $\text{Pt}_2\text{X}_4(\text{PR}_3)_2$ [7].

The ^1H NMR and ^{31}P NMR data for **C** are in agreement with the data reported earlier for this tautomer of BIPM, $\text{aryl-N}=\text{PPh}_2-\text{CH}=\text{PPh}_2-\text{NH-aryl}$, in which a H migration has occurred from the methylene group to one of the terminal nitrogen atoms [7]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **C**, however, is new and reveals a triplet at 14.7 ppm ($^1J(\text{P},\text{C}) = 132$ Hz) for the P–CH–P carbon, indicating that the methine carbon in **C** is more shielded than the methylene carbon atom in BIPM ($\delta(\text{CH}_2) = 30.5$ ppm, $^1J(\text{P},\text{C}) = 63.5$ Hz) and suggests that π -electron delocalization takes place in the P–C–P moiety in **C**.

The reactions with $\text{PtCl}_2(\text{PhCN})_2$ proceeded much slower. Variable-temperature NMR experiments showed that BIPM completely converted into intermediate **C** first, showing a singlet ^{31}P resonance at 26 ppm without Pt satellites (even at -90°C), before it converted slowly into the platinum complex **5**. In order to establish whether **C** was a Pt complex or an organophosphorus compound, several equivalents of the BIPM ligand were added to the reaction mixture. It appeared that the ligand (catalytically) converted completely into the in-



Scheme 3. Reaction pathways in the formation of **2** and **5**. For $\text{M} = \text{Pd}$: **A** is not observed, **B** and **C** are observed; For $\text{M} = \text{Pt}$: only **C** is observed.

intermediate **C** each time new ligand was added, which proves that **C** is an organophosphorus compound and not a Pt complex. It must be noted that the conversion of the extra added BIPM into **C** only occurs before **5** has formed.

As mentioned above, intermediate **C** has also been identified in the previously reported bridge-splitting reactions of BIPM with $\text{Pt}_2\text{X}_4(\text{PR}_3)_2$ [7]. Therefore, several reactions of BIPM with other Pt(II) and Pd(II) precursors were performed in order to determine whether the formation of **C** is a general feature, and to see if it was possible to isolate and further characterize **C**. This was indeed verified by reactions with $\text{PtCl}_2(\text{MeCN})_2$, $\text{PtCl}_2(\text{COD})$, $\text{PtCl}_2(\text{SeEt}_2)_2$, PdCl_2 and PtCl_2 . In all cases **C** was formed as intermediate and in high yield, which proves that formation of **C** is a more general feature and is not restricted to nitrile complexes. Eventually, **C** could be isolated by stirring a suspension of PtCl_2 with four equivalents of BIPM at 20°C for 48 h. There is no evidence that **C** reacts back to BIPM. In solution, **C** decomposes within a few days by reaction with traces of water.

4. Discussion

4.1. Tautomerization of BIPM in the presence of palladium(II) or platinum(II)

Variable-temperature NMR experiments have revealed that a remarkable metal-promoted tautomerization of the BIPM ligand takes place in its reactions with several palladium(II) and platinum(II) dichlorides. As excess of BIPM also tautomerizes into **C** in the presence of small amounts of PtCl_2 and PdCl_2 , the conversion clearly takes place catalytically. For free BIPM such tautomerizations have not been found [24], and neither have they been observed in reactions with Rh(I) and Ir(I) [3]. However, tautomerization has been observed for a related bis(methylenephosphanyl)methane compound, $\text{CH}_2(\text{PPh}_2=\text{C}(\text{SiMe}_3)_2)_2$, but in that case the H-migrations are temperature dependent and occur without involvement of a metal centre [38].

Although the reactions of BIPM with $\text{PdCl}_2(\text{L})_2$ and $\text{PtCl}_2(\text{RC}\equiv\text{N})_2$ afforded entirely different final products, i.e. Pd complexes **2–4** and Pt complexes **5** and **6** respectively, the initial steps leading to **C** must be similar. The sequence of events in the formation of **C**, as determined by means of variable-temperature NMR experiments of the reaction of BIPM **1a** with $\text{PdCl}_2(\text{MeCN})_2$, are depicted in Scheme 3 (vide supra). The initial product **A** wherein BIPM is simply σ -N monodentate coordinated to Pd via substitution of a nitrile ligand (or one of the double bonds when $\text{PdCl}_2(\text{COD})$ is used) is not observed at low temperatures. The conversion of **A** into **B** via an H-shift must

therefore proceed very fast. Earlier investigations on the bridge-splitting reactions of $\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2$ by BIPM, however, showed that an intermediate of the type **A**, $[\text{PtCl}_2(\text{PEt}_3)(\text{N}(\text{pTol})=\text{PPh}_2-\text{CH}_2-\text{PPh}_2=\text{NpTol})]$ is normally relatively stable for about 30 min at 0–10°C [7], but an intermediate similar to **B**, wherein one of the methylene-hydrogens is shifted to the non-coordinated nitrogen atom, has not been observed previously. Obviously, the presence of two Cl ligands on Pd results in a very fast H-migration once the BIPM ligand is coordinated, due to a stronger polarization of the coordinated Pd–N=P moiety. Conversion of **B** into **C** is probably caused by formation of an internal N–H···N hydrogen bridge, resulting in stabilization of tautomer **C**, which dissociates from the metal upon re-coordination of a nitrile ligand (or double bond of COD, or BIPM when present in excess). The Pd complex **2a** could either be formed by (c) coordination of the ylide-carbon in **B** or (e) recombination of **C** with $\text{PdCl}_2(\text{L})_2$.

Complete tautomeric isomerization of BIPM to give **C**, $\text{pTol}-\text{N}=\text{PPh}_2-\text{CH}=\text{PPh}_2-\text{NH}-\text{pTol}$, also takes place in the formation of the Pt complexes **5a** and **5b**, and is assumed to proceed similarly as described above for the analogous Pd reaction (Scheme 3). The relatively long life-time of **C** in solution, when Pt is involved, is probably promoted and stabilized by the tendency of the nitriles (or COD, SeEt_2) to coordinate more strongly to the Pt(II) than to Pd(II), which explains why **C** reacts slowly with $\text{PtCl}_2(\text{RC}\equiv\text{N})_2$ to give **5**.

4.2. Structure of the palladium complexes **2** and **3**

Clearly, BIPM (**1a,b**) prefers to coordinate in a *C,N*-chelating fashion to palladium(II) centres in the complexes **2a,b** rather than in an *N,N'*-coordination mode, similar to the situation observed previously in its reactions with $\text{Pt}_2\text{X}_4(\text{PR}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{PR}_3 = \text{PEt}_3, \text{PMe}_2\text{Ph}$) [7]. The complexes **2** and **3** represent the first examples of stable Pd(II) complexes containing neutral BIPM. This is remarkable, since we have reported previously that reactions with $\text{Pd}_2\text{X}_4(\text{PR}_3)_2$ resulted in a mixture of unidentifiable products [7]. This finding indicates that the presence of two electron-withdrawing Cl ligands on palladium stabilizes the *C,N*-coordination of BIPM, whereas in the case of products arising from bridge-splitting reactions the destabilization is probably caused by the trans influence of the PR_3 ligand. In contrast to the reactions of BIPM with chloro-bridged Rh and Ir dimers, where both coordination modes have been found to occur simultaneously [1,5], selectivity in the reactions with Pt(II) and Pd(II) is much higher, as only *C,N*-coordination takes place. This effect is ascribed to the higher positive charge of the Pt(II) and Pd(II) centres compared with Rh(I) and Ir(I), resulting in a larger polarization of the coordinated N=P moiety,

which subsequently increases the acidity of the adjacent CH_2 group. Migration of a methylene hydrogen atom to the non-coordinated $\text{P}=\text{N}$ part and coordination of the methine carbon will therefore take place more easily in the Pd and Pt compounds.

The substitution reaction of 1,1-BIPE (1c) with $\text{PdCl}_2(\text{L})_2$ not only afforded compound 2c, containing *C,N*-chelated 1,1-BIPE, but also the six-membered palladacycle 3 by $\sigma\text{N},\sigma\text{N}'$ -coordination of the ligand. Formation of 3 was expected, since we recently discovered that bridge-splitting reactions of 1,1-BIPE with $\text{Pt}_2\text{Cl}_4(\text{PR}_3)_2$ exclusively afforded $\sigma\text{-N}$ monodentate and $\sigma\text{-N},\sigma\text{N}'$ chelate Pt(II) complexes [23]. In that case formation of *C,N*-chelates was obstructed due to the electronic-induced effect of the methyl group on the central carbon of 1,1-BIPE (1c), which decreases the acidity of the adjacent methine proton and prevents migration to the non-coordinated nitrogen atom, a prerequisite for *C,N*-coordination [7,23]. However, the presence of two Cl ligands on the palladium(II) centre, instead of Cl and PR_3 ligands, enhances the polarization of the coordinated $\text{P}=\text{N}$ group(s), which makes the hydrogen atom on the central carbon more acidic and results in a shift to one of the basic nitrogen atoms, thus giving rise to the formation of *C,N*-chelate 2c also.

4.3. Structure and formation of the orthopalladated complex 4

Complex 4 is one of the few examples of orthometalated Pd-phosphinimine complexes reported so far. The first report by Alper [14] dealt with complexes of the type $[\text{PdCl}(2\text{-C}_6\text{H}_3\text{R}')\text{PR}_2=\text{N-aryl-C,N}]_2$ which were already formed at room temperature, whereas we recently reported the orthometallation of the neutral Pt and Pd complexes $[\text{MX}(\text{PR}_3)(\text{CH}(\text{PPh}_2=\text{N-aryl})_2)\text{-C,N}]$ by heating, affording $[\text{MX}(\text{PR}_3)(2\text{-C}_6\text{H}_4\text{-PPh}(\text{NH-aryl})\text{CHPPh}_2=\text{N-aryl-C,C'})]$ [9].

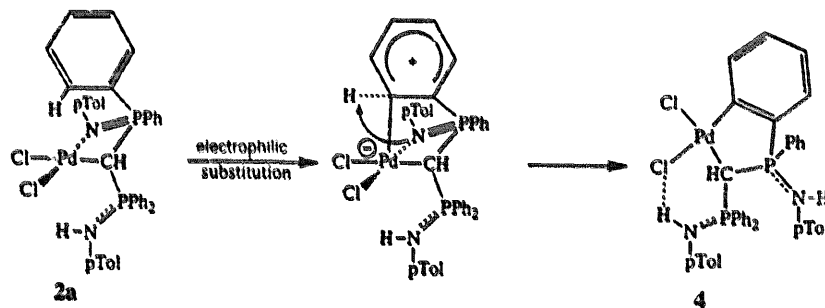
In analogy with the earlier reported orthometallation of neutral four-membered platina- and palladacycles, one of the major driving forces in the conversion of 2a into 4 is probably the formation of a five-membered palladacycle, since the strained four-membered metallacycle 2a has a low internal entropy due to restricted

rotational freedom. The orthometallation is enhanced by the presence of an internal base, the nitrogen atom of a phosphinimine group, which abstracts the ortho-H atom, similar to that which has been found for the four-membered metallacycles $[\text{MX}(\text{PR}_3)(\text{CH}(\text{PPh}_2=\text{N-aryl})_2)\text{-C,N}]$ ($\text{M} = \text{Pt}, \text{Pd}$) [9]. Both the ^1H and X-ray crystal structure of 4 have established that the ortho-H has indeed shifted to one of the N-atoms, presumably the one previously coordinated to the Pd centre in 2a, resulting in dissociation of the Pd–N bond.

Comparison of the reaction-time and -temperature needed for the orthometallation reaction to occur, 24 h at reflux for 2a and 4 h at reflux for *trans*-P–Pd–N $[\text{PdCl}(\text{PR}_3)(\text{CH}(\text{PPh}_2=\text{N-aryl})_2)\text{-C,N}]$ [9], shows that the reactions presented here proceed much slower due to the lower trans effect of Cl in 2a, compared with PR_3 , on the Pd–N bond. Furthermore, it is seen from the crystal structures of the closely related four-membered platinacycles $[\text{PtCl}(\text{PR}_3)(\text{CH}(\text{PPh}_2=\text{N-pTol})(\text{PPh}_2=\text{N}'\text{H-pTol}))\text{-C,N}]^+$ and $[\text{PtCl}(\text{PMe}_2\text{Ph})(\text{CMe}(\text{PPh}_2=\text{N-pTol})_2)\text{-C,N}]$ that the phenyl group on the phosphorus in the four-membered (Pt–N–P–C) ring is always in close proximity of the platina centre [7,9], which makes it acceptable that the corresponding Ph group in complex 2a is also close to Pd. We therefore assume that an intramolecular interaction, followed by electrophilic attack of the Pd(II) centre on the ortho position of the phenyl group, as depicted in Scheme 4, has led to the conversion of 2a into 4.

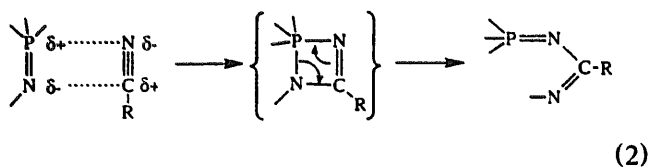
4.4. Structure and formation of the platina complexes 5 and 6

The formation of the complexes 5a,b and 6a,b was rather surprising, since the reaction between BIPM (1a) and $\text{PtCl}_2(\text{RC}\equiv\text{N})_2$ gave no ordinary substitution of the nitriles, as was the case for the analogous reactions with $\text{PdCl}_2(\text{L})_2$ which yielded the Pd complex 2a. The cause of this difference might be directly deduced from the more strongly coordinated nitrile ligands to Pt(II) centres, as evidenced by the presence of an end-on coordinated $\text{RC}\equiv\text{N}$ ligand in 5a ($\text{R} = \text{Ph}$) and 5b ($\text{R} = \text{pTol}$) and its reluctance to dissociate to give 6a and 6b respectively.



Scheme 4. Proposed reaction sequence for orthometallation of 2a.

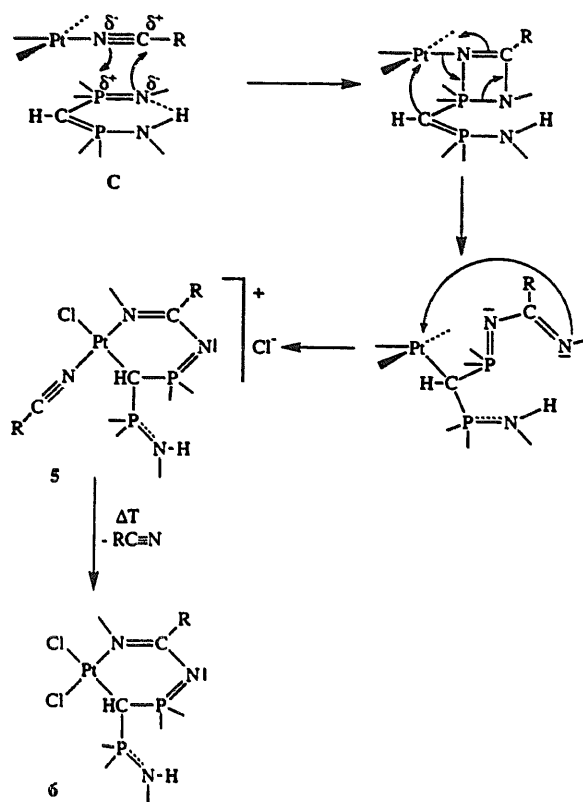
The NMR data revealed another striking structural difference between the Pt complexes **5a,b** and the Pd complexes **2a–c**, **3** and other earlier reported complexes of BIPM [1,2,5,7], namely the incorporation of an RC≡N ligand into a C,N-coordinated BIPM ligand. The ¹H and ³¹P NMR also showed that the nitrile is not simply inserted into the Pt–N bond, but has inserted into the P=N(pTol) bond, giving a P=N–C(R)=N–pTol fragment, which must have occurred via a 2 + 2 cycloaddition reaction (Eq. (2)), similar to the reaction of Li[NMe=PMe₂–NMe] with PtCl₂(PhCN)₂ reported by Scherer and Nahrstedt [39], which gave [Pt(NMe=C(Ph)–N=PMe₂–NMe)₂].



In the literature, few 2 + 2 cycloadditions reactions have been described involving phosphinimines and nitriles [40,41]. For phosphorus ylides, which are isostructural with phosphinimines, similar types of reaction with nitriles have been reported [13,41,42], and it has been shown that strong dipolar interactions are generally required for the reaction to occur. In our case both reactants are activated, the nitrile by coordination to the metal and the BIPM ligand by isomerization to **C** (vide supra). Clearly, the activation of the nitrile by coordination to Pt is very important, as an attempted reaction between BIPM and an excess PhC≡N in the absence of Pt gave no reaction at all after 4h reflux in THF. An explanation for the fact that analogous reactions with Pd (vide supra) did not show any reaction between P=N and RC≡N is found in the smaller extent of polarization of the nitriles coordinated to Pd(II) compared with Pt(II). Furthermore, we have also tried to react BIPM with PtCl₂(MeC≡N)₂, but, despite the fact that tautomerization of BIPM into **C** takes place, no insertion of MeC≡N was observed, which suggests that the nitrile must contain a polarizable (aryl) group.

We propose that the 2 + 2 cycloaddition takes place intermolecularly between non-coordinated **C** and a coordinated RC≡N ligand, as depicted in Scheme 5.

Complexes **5** and **6** represent rare examples of coordination complexes formed by a platinum-assisted reaction of a phosphinimine ligand with a nitrile [39]. Vicente et al. [13] reported a similar reaction between PtCl₂(PhC≡N)₂ and a phosphorus ylide Ph₃P=CHCOOR, which also resulted in a 2 + 2 cycloaddition and subsequent insertion of a PhC≡N group into the P=C bond, yielding the Pt-phosphinimine complex, *trans*-[PtCl₂(PhCN){N(PPh₃)-C(Ph)=CHCOOR}]. Interestingly, for this compound no



Scheme 5. Proposed reaction sequence for the formation of **5** and **6**. The aryl substituents on N and P have been omitted for clarity.

reaction with a second molecule of benzonitrile has been found, which could imply that indeed the phosphinimine must be non-coordinated in order to undergo a dipolar cycloaddition with the coordinated nitrile, as depicted in Scheme 5.

5. Supplementary material

Tables of hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, all bond distances and bond angles and of observed and calculated structure factors are available from A.L.S. on request.

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