

Reactions of Sodium Bis(*N*-aryliminophosphoranyl)alkanides with Halide-Bridged Platinum(II) and Palladium(II) Phosphine Dimers Affording Four-Membered M–N–P–C Metallacycles and Orthometalated Platinum(II) and Palladium(II) Complexes

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Reaction of the sodium bis(iminophosphoranyl)alkanide compounds $\text{Na}[\text{CR}''(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2]$ (**1a**, $\text{R}'' = \text{H}$, $\text{R}' = \text{CH}_3$; **1b**, $\text{R}'' = \text{H}$, $\text{R}' = \text{OCH}_3$; **1c**, $\text{R}'' = \text{CH}_3$, $\text{R}' = \text{CH}_3$) with $\text{M}_2\text{X}_4(\text{PR}_3)_2$ ($\text{M} = \text{Pt}$, Pd ; $\text{X} = \text{Cl}$, Br ; $\text{PR}_3 = \text{PEt}_3$, PMe_2Ph) yields the four-membered metallacycles $\text{MX}(\text{PR}_3)\{\text{CR}''(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2\}$ (**2a–f**, $\text{M} = \text{Pt}$; **3a–c**, $\text{M} = \text{Pd}$), containing the bis(iminophosphoranyl)alkanide ligand coordinated in a $\sigma\text{-C}, \sigma\text{-N}$ chelating fashion. The molecular structure of **2e** ($\text{X} = \text{Cl}$, $\text{PR}_3 = \text{PMe}_2\text{Ph}$, $\text{R}'' = \text{CH}_3$, $\text{R}' = \text{CH}_3$) has been determined by X-ray crystallography. The 1,1-bis(iminophosphoranyl)ethanide ligand (**1c**) in **2e** is $\sigma\text{-C}, \sigma\text{-N}$ -chelated toward the square-planar-surrounded Pt, with N coordinated *trans* to PMe_2Ph ($\text{Pt–N} = 2.132(4) \text{ \AA}$) and C *trans* to Cl ($\text{Pt–C} = 2.116(4) \text{ \AA}$), resulting in a puckered M–N–P–C metallacycle and one noncoordinated phosphinimine moiety. In solution the complexes **2** and **3** undergo a dynamic process, involving an intermediate (for **2**) or fast (for **3**) N,N' exchange of coordinated and noncoordinated P=N groups. Heating (to 60–80 °C) or prolonged stirring of solutions of the kinetically obtained four-membered metallacycles **2** and **3** gives the orthometalated complexes $\text{PtX}(\text{PR}_3)\{2\text{-C}_6\text{H}_4\text{PPh}(\text{NHC}_6\text{H}_4\text{R}'-4)\text{CHPPh}_2=\text{NC}_6\text{H}_4\text{R}'-4\}$ (**4a–d,f**) and $\text{PdCl}(\text{PR}_3)\{2\text{-C}_6\text{H}_4\text{PPh}(\text{NHC}_6\text{H}_4\text{Me}-4)\text{CHPPh}_2\text{NHC}_6\text{H}_4\text{Me}-4\}$ (**5a,c**). The X-ray crystal structure of **4a** ($\text{X} = \text{Cl}$, $\text{PR}_3 = \text{PEt}_3$, $\text{R}' = \text{CH}_3$) has been determined. The new mononuclear orthometalated Pt complexes **4** contain a $\sigma\text{-C}, \sigma\text{-C}'$ coordinated $[2\text{-C}_6\text{H}_4\text{PPh}(\text{NHC}_6\text{H}_4\text{R}'-4)\text{CR}''\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4]^-$ ligand, in which the ortho-H (Ph) has shifted to a bridge position between the two noncoordinating nitrogen atoms. The four-membered platinacycles **2a,b** and the orthometalated platinacycles **4a,b** react with 1 equiv of HBF_4 or CF_3COOH to give **6a,b** and **7a,b**, respectively, by protonation of the noncoordinated $\text{P}=\text{NC}_6\text{H}_4\text{R}'-4$ groups only. Addition of CO_2 to **2a,d** and **4c,f** results in an aza-Wittig reaction, giving $\text{PtCl}(\text{PR}_3)\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)(\text{PPh}_2=\text{O})\}$ (**8a,d**) and $\text{PtX}(\text{PR}_3)\{2\text{-C}_6\text{H}_4\text{PPh}(\text{O})\text{-CHPPh}_2\text{NHC}_6\text{H}_4\text{R}'-4\}$ (**9c,f**), respectively, together with aryl isocyanate and bis(aryl)-carbodiimide.

Introduction

The coordination chemistry of phosphorus-containing monoanions **I** (Chart 1), that are structurally related to acetylacetonate (**II**) has been the subject of several studies these last decades.^{1–3} The lithium or sodium

compounds of **I**, which are easily obtained via deprotonation reactions of their neutral derivatives $[\text{CH}_2(\text{PR}_2=\text{X})_2]$ by LDA, NaH, BuLi, or other strong bases, are convenient precursors for transmetalation reactions.

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Chart 1

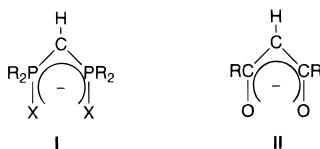


Chart 2

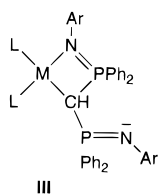
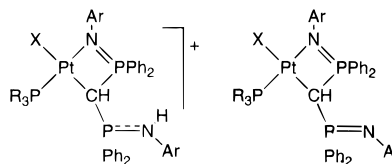
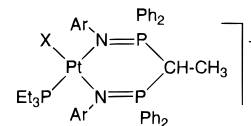


Chart 3



IV:
 $\text{PR}_3 = \text{PEt}_3, \text{PMe}_2\text{Ph}$
 $\text{X} = \text{Cl}, \text{Br}$
 $\text{Ar} = p\text{-tolyl}, p\text{-anisyl}$



V:
 $\text{PR}_3 = \text{PEt}_3, \text{PMe}_2\text{Ph}$
 $\text{X} = \text{Cl}$
 $\text{Ar} = p\text{-tolyl}$

Recently, we reported several new coordination complexes containing a ligand of this type **I**, bis(*N*-aryliminophosphoranyl)methanide, $[\text{CH}(\text{PR}_2=\text{N-aryl})_2]^-$.⁴ In that case $\text{Li}^+[\text{CH}(\text{PR}_2=\text{N-aryl})_2]^-$ reacted with $[\text{MCl}(\text{L})_2]$ to give the four-membered metallacycles **III** ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L}_2 = \text{COD}, \text{NBD}, (\text{CO})_2$; $\text{Ar} = p\text{-tolyl}, p\text{-nitrophenyl}$) (Chart 2) in which the ligand is C,N chelated.⁴

Such a coordination mode was rather peculiar since the closely related bis(chalcogenophosphoranyl)methanide ligands $[\text{CH}(\text{PR}_2=\text{X})(\text{PR}_2=\text{Y})]^-$ ($\text{X}, \text{Y} = \text{O}, \text{S}, \text{Se}$) coordinate exclusively as X, Y chelates to Rh and Ir,^{2a} but C, X and X, Y coordination was observed for these ligands with Pt^{3a,b} and Au.⁵ Furthermore, an entirely different reactivity has been observed for the related *N*-SiMe₃-substituted bis(iminophosphoranyl)methanide ligand $[\text{CH}(\text{PR}_2=\text{NSiMe}_3)_2]^-$, forming planar six-membered metallacycles with WCl_6 or WF_6 under elimination of Me₃Si-halide.⁶

It was therefore interesting to examine whether the bis(*N*-aryliminophosphoranyl)methanide ligands would coordinate to Pt and Pd similarly as found for Rh and Ir,⁴ especially since only a few phosphinimine complexes of Pt⁷ and Pd⁸ have been reported previously, although some related Pt–phosphazene compounds are known.^{9–11}

In a recent report we have already demonstrated that the neutral bis(iminophosphoranyl)methane ligands (BIPM), $\text{CH}_2(\text{PR}_2=\text{N-aryl})_2$, react with $\text{Pt}_2\text{X}_4(\text{PR}_3)_2$ to give cationic or neutral four-membered platinacycles (**IV**) (Chart 3), depending on the metal-to-ligand ratio,

in which the ligand is $\sigma\text{-N}, \sigma\text{-C}$ coordinated.¹² Analogous palladium complexes could not be obtained due to instability.¹² Similar reactions with the modified ligand 1,1-bis(iminophosphoranyl)ethane (1,1-BIPE), which has a 1,1-ethanediyl bridge instead of a methylene bridge between the two $\text{P}=\text{N}$ moieties, resulted in the formation of $\sigma\text{-N}, \sigma\text{-N'}$ -coordinated Pt(II) complexes (**V**).¹³

In view of the ring strain in the above mentioned four-membered M-X-P-C metallacycles ($\text{M} = \text{Rh}, \text{Ir}, \text{Pt}$; $\text{X} = \text{S}, \text{Se}, \text{N-aryl}$)^{3b,4,12} one might expect that ring enlargements via orthometalation, involving metal–carbon bond formation at the *ortho* position of an aromatic group (on P or N in our case) with concomitant M-X bond dissociation, would be favorable. Such reactivity has not been found for these types of four-membered metallacycles so far, but orthometalations of end-on coordinated phosphinimines^{8d} and structurally related phosphorus ylides¹⁴ are known.

In this article we report on the coordination chemistry of the monoanions $[\text{CH}(\text{PR}_2=\text{N-aryl})_2]^-$ and $[\text{CMe}(\text{PR}_2=\text{N-aryl})_2]^-$ toward $\text{Pt}_2\text{X}_4(\text{PR}_3)_2$ and $\text{Pd}_2\text{Cl}_4(\text{PR}_3)_2$. We will show that the kinetically obtained products, the four-membered M-N-P-C metallacycles, readily undergo orthometalation reactions to yield thermodynamically more stable compounds. The reactivity and stability of the kinetic and thermodynamic platinum complexes toward CO_2 and acids will also be described.

Experimental Section

General Comments. All manipulations 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 ³¹P{¹H} NMR spectra were recorded on Bruker AC 100 and AMX 300 instruments (operating at 100.13/300.13 and 40.53/121.50 MHz, respectively), using SiMe₄ and 85% H₃PO₄ as the

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external standards, respectively, positive shifts to high frequency of the standard in all cases. ^{13}C NMR data were obtained from Bruker AMX 300 and ARX 400 spectrometers (operating at 75.48/100.62 MHz, respectively), using SiMe_4 as the external standard. Elemental analyses were carried out by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. $\text{Pt}_2\text{X}_4(\text{PR}_3)_2$, $\text{Pd}_2\text{Cl}_4(\text{PR}_3)_2$ (with $\text{PR}_3 = \text{PEt}_3$, PMe_2Ph ; $\text{X} = \text{Cl}$, Br),¹⁵ the bis(iminophosphoranyl)methanes (BIPM) $\text{CH}_2(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2$ ($\text{R}' = \text{Me}$, OMe),^{16,17} and 1,1-bis(iminophosphoranyl)ethane (1,1-BIPE) $\text{CHCH}_3(\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2$ ¹³ were synthesized according to literature procedures. The deprotonation of these ligands was preferably performed as described previously;¹⁷ e.g. to a solution of 0.45 mmol BIPM in 20 mL of THF was added a 5-fold excess of NaH (washed with ether, dried in vacuo, and stored under nitrogen). After 2 h, during which H_2 gas slowly evolved, the light yellow solution was filtered and the residue washed with THF (2×5 mL). The clear filtrate, containing only sodium bis(iminophosphoranyl)methanide, $\text{Na}^+[\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2]^-$ (**1a**, $\text{R}' = \text{Me}$; **1b**, $\text{R}' = \text{OMe}$)¹⁷ in quantitative amount, was used directly for the preparations described below. For deprotonated 1,1-BIPE, $\text{Na}^+[\text{CCH}_3(\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2]^-$ (**1c**), a different procedure was used; NaH was added to a solution of 1,1-BIPE in THF, and the new solution was stirred for 2.5 h. The orange solution, still containing excess of NaH, was directly used for reaction with $\text{Pt}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_2$ (see **2e**), as removal of NaH by filtration resulted in back-reaction into the neutral ligand.

$\text{Na}^+[\text{CMe}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{Me}-4)_2]^-$ (**1c**). Compound **1c** was isolated by careful removal of the clear orange supernatant by a syringe and subsequent evaporation of the solvent in vacuo for 24 h, yielding a yellow powder. Sampling **1c**, e.g. for NMR purposes, has to be done in extremely dry C_6D_6 , since traces of H_2O result in the formation of 1,1-BIPE. ^1H NMR (C_6D_6): phenyl rings, δ 8.0, 7.1 (m, 20H); NC_6H_4 , δ 6.90, 6.63 (d, 8H, $^3J(\text{H,H}) = 8.1$ Hz); CCH_3 , δ 1.94 (t, 3H, $^3J(\text{P,H}) = 15.5$ Hz); $\text{C}_6\text{H}_4\text{CH}_3-4$, δ 2.20 (s, 6H). ^{31}P NMR (C_6D_6): $\delta(\text{P}) = 23.4$ ppm (s). ^{13}C NMR (C_6D_6 , 75.5 MHz, 293 K): CCH_3 , δ 16.97 (t, $^2J(\text{P,C}) = 8.8$ Hz); CCH_3 , δ not resolved; $\text{C}_6\text{H}_4\text{CH}_3-4$, δ 21.23 (s); C_6H_4 , δ 124.25 (d, C_{ortho} , $^3J(\text{P,C}) = 19.7$ Hz); δ 130.48 (s, C_{meta}); δ 125.14 (s, C_{para}); δ 153.99 (vs, C_{ipso}); phenyls, δ 138.4 (dd, C_{ipso} , $^1J(\text{P,C}) = 105.7$ Hz, $^3J(\text{P,C}) = 11.6$ Hz); δ 133.88 (vs, C_{ortho}); $\delta \sim 128.5$ (obscured by C_6D_6 , C_{meta}); δ 130.61 (s, C_{para}).

Synthesis of 2a–f, $\text{PtX}(\text{PR}_3)\{\text{CR}''(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2\text{-C,N}\}$ ($\text{PR}_3 = \text{PEt}_3$, PMe_2Ph ; $\text{X} = \text{Cl}$, Br ; $\text{R}' = \text{CH}_3$, OCH_3 , $\text{R}'' = \text{H}$, Me). To a stirred solution of freshly prepared $\text{Na}[\text{CR}''(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2]$ (0.45 mmol) in 30 mL of THF was added a solution of $\text{Pt}_2\text{X}_4(\text{PR}_3)_2$ (0.23 mmol) in 10 mL of THF. After 4 h the cloudy yellow solution was filtered through a glass filter (G4), and the residue (precipitated NaX) was washed with 10 mL of THF. The combined clear yellow filtrates were evaporated to dryness, leaving an oily residue. Addition of cold pentane (40 mL) resulted in the solidification of the product, which was washed with pentane (2×20 mL) and dried in vacuo, yielding a yellow powder (84–95%).

PtCl(PEt₃) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2\}$ (2a**).** Anal. Calcd for $\text{C}_{45}\text{H}_{50}\text{ClN}_2\text{P}_3\text{Pt}$: 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. ^{13}C NMR (CD_2Cl_2 , 253 K, 75.48 MHz): δ 1.67 (dd, $\text{Pt}-\text{C}$, $^1J(\text{P,C}) = 70$, 93 Hz, $^1J(\text{Pt,C}) = \text{n.r.}$); δ 8.28 (vs PCH_2CH_3); δ 15.50 (d, PCH_2CH_3 , $^1J(\text{P,C}) = 38$ Hz); $\text{C}_6\text{H}_4\text{CH}_3-4$, δ 20.65 and 20.89 (s, CH_3); δ 142.64 and 149.47 (vs, C_{ipso}); δ 122.56 and 124.14 (d, C_{ortho} , $^3J(\text{P,C}) = 19$ and 14 Hz, respectively); $\delta(\text{C}_{\text{meta}})$ and $\delta(\text{C}_{\text{para}})$ obscured; phenyls, δ 125–135.

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PtCl(PMe₂Ph) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{OCH}_3-4)_2\}$ (2b**).** Anal. Calcd for $\text{C}_{45}\text{H}_{50}\text{ClN}_2\text{O}_2\text{P}_3\text{Pt}$: C, 55.47; H, 5.18; N, 2.87; P, 9.53. Found: C, 55.29; H, 5.28; N, 2.78; P, 8.56. ^{13}C NMR (CD_2Cl_2 , 253 K, 75.48 MHz): δ 1.49 (dd, $\text{Pt}-\text{C}$, $^1J(\text{P,C}) = 59$, 95 Hz, $^1J(\text{Pt,C}) = \text{n.r.}$); δ 8.24 (d, PCH_2CH_3 , $^2J(\text{P,C}) = 3$ Hz); δ 15.50 (d, PCH_2CH_3 , $^1J(\text{P,C}) = 38$ Hz); $\text{C}_6\text{H}_4\text{OCH}_3-4$, δ 55.58 and 55.63 (s, OCH_3); δ 138.40 and 145.58 (vs, C_{ipso}); δ 122.92 and 125.07 (d, C_{ortho} , $^3J(\text{P,C}) = 19$ and 13 Hz, respectively); δ 113.13 and 114.08 (s, C_{meta}); δ 151.11 and 154.86 (s, C_{para}); phenyls, δ 127–134.

PtCl(PMe₂Ph) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2\}$ (2c**).** FAB MS: found, $m/z = 963$ (M, calcd for $\text{C}_{47}\text{H}_{46}\text{ClN}_2\text{P}_3\text{Pt}$, m/z 962.4). ^{13}C NMR (CDCl_3 , 253 K, 75.48 MHz): δ 2.02 (dd, $\text{Pt}-\text{C}$, $^1J(\text{P,C}) = 58$, 71 Hz, $^1J(\text{Pt,C}) = \text{n.r.}$); δ 14.48 (d, PCH_3 , $^1J(\text{P,C}) = 30$ Hz); δ 15.05 (d, PCH_3 , $^1J(\text{P,C}) = 31$ Hz); $\text{C}_6\text{H}_4\text{CH}_3-4$, δ 21.24 and 21.34 (s, CH_3); δ 142.36 (vs, C_{ipso}) and 149.34 (d, C_{ipso} , $^2J(\text{P,C}) = 3$ Hz); δ 123.63 and 123.86 (d, C_{ortho} , $^3J(\text{P,C}) = 18$ and 18 Hz, respectively); $\delta(\text{C}_{\text{meta}})$ and $\delta(\text{C}_{\text{para}})$ obscured; phenyls, δ 125–135.

PtCl(PMe₂Ph) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{OCH}_3-4)_2\}$ (2d**).** FAB MS: found, $m/z = 995$ (M, calcd for $\text{C}_{47}\text{H}_{46}\text{ClN}_2\text{O}_2\text{P}_3\text{Pt}$, m/z 994.4). Further characterization is based on ^1H and ^{31}P NMR spectroscopy.

PtCl(PMe₂Ph) $\{\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2\}$ (2e**).** Anal. Calcd for $\text{C}_{48}\text{H}_{48}\text{ClN}_2\text{P}_3\text{Pt}$: C, 59.05; H, 4.96; N, 2.87; P, 9.52. Found: C, 59.15; H, 5.00; N, 2.94; P, 9.60. Crystals suitable for X-ray diffraction study were obtained by slow evaporation of a solution of **2e** in a 20:1:1 mixture of $\text{Et}_2\text{O}/\text{THF}/\text{hexane}$ at room temperature for 1 week. ^{13}C NMR (CDCl_3 , 293 K, 125.77 MHz): δ 4.82 (dd, $\text{Pt}-\text{C}$, $^1J(\text{P,C}) = 57$, 86 Hz, $^1J(\text{Pt,C}) = \text{n.r.}$); δ 15.27 (s, $\text{Pt}-\text{CCH}_3$); δ 13.50 (d, PCH_3 , $^1J(\text{P,C}) = 37$ Hz); δ 13.93 (d, PCH_3 , $^1J(\text{P,C}) = 42$ Hz); $\text{C}_6\text{H}_4\text{CH}_3-4$, δ 20.20 and 20.47 (s, CH_3); δ 141.76 and 149.62 (vs, C_{ipso}); δ 122.79 and 124.48 (d, C_{ortho} , $^3J(\text{P,C}) = 17$ and 14 Hz, respectively); $\delta(\text{C}_{\text{meta}})$ and $\delta(\text{C}_{\text{para}})$ obscured; phenyls, δ 126–136.

PtBr(PEt₃) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2\}$ (2f**)** is characterized by ^1H and ^{31}P NMR spectroscopy only.

Synthesis of 3a–c, $\text{PdCl}(\text{PR}_3)\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2\text{-C,N}\}$ ($\text{PR}_3 = \text{PEt}_3$, PMe_2Ph ; $\text{R}' = \text{CH}_3$, OCH_3). A solution of $\text{Pd}_2\text{Cl}_4(\text{PR}_3)_2$ (0.23 mmol) in 10 mL of THF was added to a stirred solution of freshly prepared $\text{Na}[\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2]$ (0.45 mmol) in 30 mL of THF. The reaction mixture immediately changes color from yellow to brownish-red and after 30 min into orange. The cloudy solution was stirred for at least 4 h before filtration through a glass filter (G4). The residue (precipitated NaCl) was washed with 10 mL of THF. The combined clear orange filtrates were evaporated to 5 mL. The product was precipitated by the addition of pentane (60 mL) at -30°C , washed with pentane (2×20 mL), and dried in vacuo, yielding a yellow powder (87–92%).

PdCl(PEt₃) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2\}$ (3a**).** Anal. Calcd for $\text{C}_{45}\text{H}_{50}\text{ClN}_2\text{P}_3\text{Pd}$: C, 63.31; H, 5.90; N, 3.28; P, 10.88. Found: C, 63.19; H, 5.95; N, 3.20; P, 10.93. FAB MS: found, $m/z = 853$ (M, calcd for $\text{C}_{45}\text{H}_{50}\text{ClN}_2\text{P}_3\text{Pd}$, m/z 853.7). ^{13}C NMR (CD_2Cl_2 , 293 K, 75.48 MHz): δ 9.20 (vt, $\text{Pd}-\text{C}$, $^1J(\text{P,C}) = 82$ Hz); δ 8.66 (d, PCH_2CH_3 , $^2J(\text{P,C}) = 3$ Hz); δ 17.24 (d, PCH_2CH_3 , $^1J(\text{P,C}) = 30$ Hz); $\text{C}_6\text{H}_4\text{CH}_3-4$, δ 20.93 (s, CH_3); δ 146.62 (s, C_{ipso}); δ 123.89 (d, C_{ortho} , $^3J(\text{P,C}) = 17$ Hz); δ 129.34 (s, C_{meta}); δ 127.83 (s, C_{para}); phenyls, $\delta(\text{C}_{\text{ipso}})$ obscured; δ 132.7 and 133.6 (d, C_{ortho} , $^2J(\text{P,C}) = 9.8$ Hz); δ 128.8 and 129.3 (d, C_{meta} , $^3J(\text{P,C}) = 12.1$ Hz); δ 132.1 and 132.4 (s, C_{para}).

PdCl(PEt₃) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{OCH}_3-4)_2\}$ (3b**).** FAB MS: found, $m/z = 885$ (M, calcd for $\text{C}_{45}\text{H}_{50}\text{ClN}_2\text{O}_2\text{P}_3\text{Pd}$, m/z 885.7). ^{13}C NMR (CD_2Cl_2 , 293 K, 75.48 MHz): δ 9.01 (vt, $\text{Pd}-\text{C}$, $^1J(\text{P,C}) = 82$ Hz); δ 8.70 (d, PCH_2CH_3 , $^2J(\text{P,C}) = 2$ Hz); δ 17.25 (d, PCH_2CH_3 , $^1J(\text{P,C}) = 30$ Hz); $\text{C}_6\text{H}_4\text{OCH}_3-4$, δ 56.06 (s, OCH_3); δ 142.68 (s, C_{ipso}); δ 124.57 (d, C_{ortho} , $^3J(\text{P,C}) = 16$ Hz); δ 114.27 (s, C_{meta}); δ 153.17 (s, C_{para}); phenyls, $\delta(\text{C}_{\text{ipso}})$ obscured; δ 132.62 and 132.75 (d, C_{ortho} , $^2J(\text{P,C}) = 9.8$ Hz); δ 128.7 and 129.3 (d, C_{meta} , $^3J(\text{P,C}) = 11.5$ Hz); δ 132.1 and 132.3 (s, C_{para}).

PdCl(PMe₂Ph) $\{\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{CH}_3-4)_2\}$ (3c**).** FAB MS: found, $m/z = 873$ (M, calcd for $\text{C}_{47}\text{H}_{46}\text{ClN}_2\text{P}_3\text{Pd}$, m/z

873.7). Further characterization is based on ^1H and ^{31}P NMR spectroscopy.

Synthesis of Orthoplatinated Complexes 4a–d,f, [PtX(PR₃)₂(2-C₆H₄-P(Ph)(NHC₆H₄R'-4)CHPPh₂=N'C₆H₄R'-4)-C,C'] (PR₃ = PET₃, PMe₂Ph; X = Cl, Br; R' = CH₃, OCH₃). To a solution of freshly prepared Na[CR''(PPh₂=NC₆H₄R'-4)₂] (0.32 mmol) in 30 mL of THF was added a solution of Pt₂X₄(PR₃)₂ (0.16 mmol) in 10 mL of THF, and the solution was stirred at 70–80 °C. After 6 h the cloudy yellow solution was filtered through a glass filter (G4) filter, and the residue (precipitated NaX) was washed with 10 mL of THF. The clear yellow filtrate was evaporated to 5 mL. Addition of ether (40 mL) resulted in a white precipitation, which was washed with diethyl ether (20 mL) and pentane (20 mL) and dried in vacuo, yielding a white powder in all cases (39–61%). The washings contained compound **2**, according to ^1H and ^{31}P NMR spectroscopy.

PtCl(PET₃)₂(2-C₆H₄P(Ph)(NHC₆H₄Me-4)CHPPh₂=N'C₆H₄Me-4e) (4a). FAB MS: found, m/z = 943 (M, calcd for C₄₅H₅₀ClN₂P₃Pt, m/z 942.6). Crystals suitable for X-ray diffraction study were obtained by slow diffusion of pentane into a solution of **4a** in toluene at 20 °C for 3 weeks. ^{13}C NMR (CDCl₃, 293 K, 75.48 MHz): δ 13.4 (ddd, Pt–C, $^1J(\text{P},\text{C})$ = 45, 70 Hz, $^2J(\text{P},\text{C})$ = 2 Hz, $^1J(\text{Pt},\text{C})$ \approx 736 Hz); δ 8.15 (vs, PCH₂CH₃); δ 15.0 (d, PCH₂CH₃, $^1J(\text{P},\text{C})$ = 27 Hz); C₆H₄CH₃-4, δ 21.0 and 21.1 (s, CH₃); δ 140.0 and 147.4 (d, C_{ipso}, $^2J(\text{P},\text{C})$ = 5 and 7 Hz, respectively); δ 122.1, 124.3, and 136.1 (d, 2:1:1 C_{ortho}, $^3J(\text{P},\text{C})$ = 17 Hz, 13 Hz, and n.r., respectively); δ (C_{meta} obscured); δ 127.1 and 130.5 (s, C_{para}); phenyls, δ 125.6 (d, 1 C_{ipso}, $^1J(\text{P},\text{C})$ = 91 Hz), remaining δ (C_{ipso}) obscured; δ 120–136 (C_{o,m,p}); δ 167.8 (dd, C_{orthomet}, $^2J(\text{P},\text{C})$ = 36 and 125 Hz, $^1J(\text{Pt},\text{C})$ = n.r.).

PtCl(PET₃)₂(2-C₆H₄P(Ph)(NHC₆H₄OMe-4)CHPPh₂=N'C₆H₄OMe-4) (4b). Anal. Calcd for C₄₅H₅₀ClN₂O₂P₃Pt: C, 55.46; H, 5.17; N, 2.87; P, 9.53. Found: C, 55.38; H, 5.24; N, 2.95; P, 9.39. ^{13}C NMR (CD₂Cl₂, 293 K, 75.48 MHz): δ 13.6 (ddd, Pt–C, $^1J(\text{P},\text{C})$ = 46, 70 Hz, $^2J(\text{P},\text{C})$ = 2 Hz, $^1J(\text{Pt},\text{C})$ = n.r.); δ 8.04 (vs, PCH₂CH₃); δ 15.1 (d, PCH₂CH₃, $^1J(\text{P},\text{C})$ = 27 Hz); C₆H₄OCH₃-4, δ 56.0 and 56.1 (s, OCH₃); δ 136.5 and 143.5 (d, C_{ipso}, $^2J(\text{P},\text{C})$ = 6 and 7 Hz, respectively); δ 122.7, 124.2, and 136.5 (d, 2:1:1 C_{ortho}, $^3J(\text{P},\text{C})$ = 17, 14 Hz and 19 Hz, respectively); δ 114.8 and 115.1 (s, C_{meta}); δ 152.7 and 154.8 (s, C_{para}); phenyls, δ 126.4 (d, 1 C_{ipso}, $^1J(\text{P},\text{C})$ = 94 Hz); remaining δ (C_{ipso}) obscured; δ 120–136 (C_{o,m,p}); δ 168.2 (dd, C_{orthomet}, $^2J(\text{P},\text{C})$ = 37 and 125 Hz, $^1J(\text{Pt},\text{C})$ = n.r.).

PtCl(PMe₂Ph)₂(2-C₆H₄P(Ph)(NHC₆H₄Me-4)CHPPh₂=N'C₆H₄Me-4) (4c). Anal. Calcd for C₄₇H₄₆ClN₂P₃Pt: C, 58.66; H, 4.82; N, 2.91; P, 9.66. Found: C, 58.46; H, 4.90; N, 2.96; P, 9.78. ^{13}C NMR (CDCl₃, 293 K, 100.62 MHz): δ 15.4 (br dd, Pt–C, $^1J(\text{P},\text{C})$ = 47, 67 Hz, $^2J(\text{P},\text{C})$ = n.r., $^1J(\text{Pt},\text{C})$ = n.r.); δ 11.4 (d, PCH₃, $^1J(\text{P},\text{C})$ = 28 Hz); δ 14.0 (d, PCH₃, $^1J(\text{P},\text{C})$ = 33 Hz); C₆H₄CH₃-4, δ 20.4 and 20.6 (s, CH₃); δ 139.5 and 146.4 (d, C_{ipso}, $^2J(\text{P},\text{C})$ = 5 and 6 Hz, respectively); δ 121.7, 124.0, and 135.5 (d, 2:1:1 C_{ortho}, $^3J(\text{P},\text{C})$ = 17, 13 Hz and 19 Hz, respectively); δ (C_{meta}) obscured; δ 126.7 and 130.0 (s, C_{para}); phenyls, δ 126.1 (d, 1 C_{ipso}, $^1J(\text{P},\text{C})$ = 91 Hz); remaining δ (C_{ipso}) obscured; δ 118–135 (C_{o,m,p}); δ 166.2 (dd, C_{orthomet}, $^2J(\text{P},\text{C})$ = 34 and 129 Hz, $^1J(\text{Pt},\text{C})$ = n.r.).

PtCl(PMe₂Ph)₂(2-C₆H₄P(Ph)(NHC₆H₄OMe-4)CHPPh₂=N'C₆H₄OMe-4) (4d). Characterization is based on ^1H and ^{31}P NMR spectroscopy only.

PtBr(PET₃)₂(2-C₆H₄P(Ph)(NHC₆H₄Me-4)CHPPh₂=N'C₆H₄Me-4) (4f). Characterization is based on ^1H and ^{31}P NMR spectroscopy only.

Synthesis of Orthopalladated Compounds 5a,c, [PdCl(PR₃)₂(2-C₆H₄P(Ph)(=NC₆H₄Me-4)CHPPh₂NHC₆H₄Me-4)-C,C'] (PR₃ = PET₃, PMe₂Ph). To a solution of freshly prepared Na[CH(PPh₂=NC₆H₄CH₃-4)₂] (**1a**) (0.48 mmol) in 30 mL of THF was added a solution of Pd₂Cl₄(PR₃)₂ (0.24 mmol) in 10 mL of THF, and the mixture was stirred for 30 min at 20 °C. The cloudy orange solution was then stirred for 7 h at 90 °C, resulting in a color change to yellow. The cloudy yellow

solution was filtered and evaporated to dryness. The residue was washed with pentane (2 \times 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound **3a** or **3c**.

PdCl(PET₃)₂(2-C₆H₄P(Ph)(=NC₆H₄Me-4)CHPPh₂NHC₆H₄Me-4) (5a). Anal. Calcd for C₄₅H₅₀ClN₂P₃Pd: C, 63.31; H, 5.91; N, 3.28; P, 10.88. Found: C, 62.49; H, 5.51; N, 3.53; P, 9.95. FAB MS: found, m/z = 853 (**5a**), 817 (**5a** – Cl) (M, calcd for C₄₅H₅₀ClN₂P₃Pd, m/z 853.7). ^{13}C NMR (C₆D₆, 293 K, 75.48 MHz): δ 35.0 (ddd, Pd–C, $^nJ(\text{P},\text{C})$ = 49, 58, 72 Hz, with n = 1, 2); δ 9.3 (s, PCH₂CH₃); δ 17.0 (d, PCH₂CH₃, $^1J(\text{P},\text{C})$ = 24 Hz); C₆H₄CH₃-4, δ 21.4 (s, CH₃); δ 141.2 and 148.4 (d, C_{ipso}, $^2J(\text{P},\text{C})$ \leq 2 Hz); δ 120.4, 122.9 (d, C_{ortho}, $^3J(\text{P},\text{C})$ = 9.3, 17.1 Hz); δ 129–131 (C_{meta}); δ 126.3 and 130.6 (s, C_{para}); phenyls, δ 126.3 (d, 1 C_{ipso}, $^1J(\text{P},\text{C})$ = 95 Hz); remaining δ (C_{ipso}) obscured; δ 133.4, 134.8 (d, C_{ortho}, $^2J(\text{P},\text{C})$ = 8 and 11 Hz, respectively); δ 129–131 (C_{meta}); δ 131.4, 131.9, 132.0, 132.7 (s, C_{para}); δ 135.7 (dd, C_{ipso}, $^1J(\text{P},\text{C})$ = 83 Hz, $^3J(\text{P},\text{C})$ = 11 Hz); δ 137.5 (dd, C_{ortho}, $^2J(\text{P},\text{C})$ = 18 Hz, $^4J(\text{P},\text{C})$ = 13 Hz); δ 157.9 (dd, C_{orthomet}, $^2J(\text{P},\text{C})$ = 27 and 3 Hz).

PdCl(PMe₂Ph)₂(2-C₆H₄P(Ph)(=NC₆H₄Me-4)CHPPh₂NHC₆H₄Me-4) (5c). FAB MS: found, m/z = 873 (**5c**), 837 (**5c** – Cl) (M, calcd for C₄₇H₄₆ClN₂P₃Pd, m/z 873.7). Further characterization is based on ^1H and ^{31}P NMR spectroscopy.

Following the Reaction Sequence in the Formation of 5c. Compound **3c** was dissolved in 0.5 mL of toluene-*d*₈ in a 5 mm NMR tube, and the reactions were monitored by ^1H and ^{31}P NMR. At 20 °C, the first conversion of **3c** into **5c**ⁱ took place as evidenced by the appearance of three new ^{31}P resonances. The solution was then heated shortly, which resulted in some yellow precipitation. The ^{31}P NMR showed complete conversion of both **3c** and **5c**ⁱ into **5c**.

PdCl(PMe₂Ph)₂(2-C₆H₄P(Ph)(NHC₆H₄Me-4)CHPPh₂=N'C₆H₄Me-4) (5cⁱ). ^{31}P NMR (121.5 MHz; tol-*d*₈): δ –10.0 (d, PMe₂Ph, $^3J(\text{P},\text{P})$ = 36.4 Hz); δ 24.7 (dd, PNH, $^3J(\text{P},\text{P})$ = 36.4 Hz, $^2J(\text{P},\text{P})$ = 19.8 Hz); δ 20.0 (d, P=N, $^2J(\text{P},\text{P})$ = 19.8 Hz).

Reaction of 2a,b with HBF₄ or CF₃COOH. To a solution of 0.10 mmol of PtCl(PET₃)₂(CH(PPh₂=NC₆H₄R'-4)₂) (**2a,b**) in 20 mL of CH₂Cl₂ or toluene was added 14 μL (0.10 mmol) of a 54% (by weight) HBF₄ solution in diethyl ether or 7.6 μL (0.10 mmol) of CF₃COOH. After 5–30 min of stirring, the yellow solution was evaporated to dryness. The solid residue was washed with pentane (2 \times 20 mL) and dried in vacuo, giving [PtCl(PET₃)₂(CH(PPh₂=NC₆H₄R'-4)(PPh₂NHC₆H₄R'-4)-C,N)]⁺Y[–] (**6a**, R' = Me, Y = BF₄; **6b**, R' = OMe, Y = CF₃COO) in quantitative yield. Complexes **6a,b**ⁱ are identical to earlier reported complexes.¹²

Reaction of 4a,b with HBF₄ or CF₃COOH. The reactions were performed similar as described above for the reactions with **2a,b**, giving [PtCl(PET₃)₂(2-C₆H₄P(Ph)(NHC₆H₄R'-4)CHPPh₂(NHC₆H₄R'-4)-C,C')⁺Y[–] (**7a**, R' = Me, Y = BF₄; **7a**ⁱ, R' = Me, Y = CF₃COO; **7b**, R' = OMe, Y = CF₃COO) in almost quantitative amounts. Anal. Calcd for C₄₅H₅₁BClF₄N₂P₃Pt (**7a**): C, 52.64; H, 4.99; N, 2.72; P, 9.02. Found: C, 52.63; H, 5.07; N, 2.67; P, 8.89. FAB MS: found, m/z = 943 (M⁺, calcd for C₄₅H₅₁ClN₂P₃Pt (**7a**), m/z 943.4).

Reaction of 2a,d with CO₂. Dry CO₂ gas, obtained by evaporation of solid CO₂ and led through CaCl₂, was bubbled through a solution of 0.10 mmol of PtCl(PET₃)₂(CH(PPh₂=NC₆H₄R'-4)₂) (**2a,d**) in 10 mL of CH₂Cl₂ (or benzene). After 2.5 h (or 3.5 h) stirring, the solution was evaporated to dryness. The residue contained compound PtCl(PR₃)₂(CH(PPh₂=NC₆H₄R'-4)(PPh₂=O)-C,N) (**8a**, PR₃ = PET₃, R'' = Me; **8d**, PR₃ = PMe₂Ph, R'' = OMe) (99.9%), aryl isocyanate (86%), and bis-(aryl)carbodiimide (14%) according to ^1H and ^{31}P NMR. FAB MS: found for **8a**, m/z = 853 (**8a**) and 817 (**8a** – Cl) (M, calcd for C₃₈H₄₃ClN₂O₂P₃Pt, m/z 853.27).

Reaction of 4c,f with CO₂. Dry CO₂ gas was bubbled through a solution of 0.10 mmol of **4c,f** in 10 mL of benzene. After 3 h the solution was evaporated to 5 mL. The product was precipitated by the addition of 20 mL of cold diethyl ether,

Table 1. Crystallographic Data for 2e and 4a

| | compounds | |
|--|--|---|
| | 2e | 4a |
| Crystal Data | | |
| formula | C ₄₈ H ₄₈ ClN ₂ P ₃ Pt | C ₄₅ H ₅₀ ClN ₂ P ₃ Pt |
| <i>M_r</i> | 976.37 | 942.36 |
| space group | <i>P</i> 1 | <i>P</i> 1 |
| cryst system | triclinic | triclinic |
| <i>Z</i> | 2 | 2 |
| <i>a</i> , Å | 10.1320(10) | 9.4085(8) |
| <i>b</i> , Å | 13.880(2) | 11.050(2) |
| <i>c</i> , Å | 15.456(2) | 19.916(2) |
| α, deg | 103.665(6) | 91.732(11) |
| β, deg | 91.399(7) | 102.509(9) |
| γ, deg | 93.898(7) | 93.374(11) |
| <i>V</i> , Å ³ | 2105.4(5) | 2015.9(5) |
| <i>D</i> _{calcd} , g cm ⁻³ | 1.540 | 1.552 |
| <i>F</i> (000) | 980 | 948 |
| μ _{Mo Kα} , cm ⁻¹ | 35.8 | 37.0 |
| cryst size, mm | 0.13 × 0.20 × 0.26 | 0.12 × 0.12 × 0.25 |
| Data Collection | | |
| <i>T</i> , K | 295 | 150 |
| θ _{min} , θ _{max} , deg | 1.0–23.0 | 1.8, 27.5 |
| λ(Mo Kα), Å | 0.710 69 (mon) | 0.710 73 (graphite monochr) |
| scan type | ω/2θ | ω/2θ |
| Δω, deg | 0.90 + 0.35 tan θ | 0.84 + 0.35 tan θ |
| hor and ver apert, mm | 3.0 + 0.86 tan θ, 4.00 | 3.53, 4.00 |
| X-ray exposure, h | 54 | 46 |
| linear decay, % | 3 | 2 |
| ref reflns | 171, 355, 352 | 230, 332, 223 |
| data set | –11:11, 0:15, –16:16 | –11:12, –14:14, –25:17 |
| tot. data | 6234 | 10862 |
| tot. unique data | 5842 | 9231 |
| <i>R</i> (int) | 0.009 | |
| DIFABS corr range | 0.768–0.999 | 0.951–1.061 |
| Refinement | | |
| no. of refined params | 496 | 474 |
| final <i>R</i> ^a | 0.024 [for 5322, <i>F</i> _o > 4.0σ(<i>F</i> _o)] | 0.059 [for 602, <i>F</i> _o > 4σ(<i>F</i> _o)] |
| final <i>R</i> _w ^b | 0.040 | |
| final <i>wR</i> ^{2c} | | 0.141 (9231 data) |
| <i>S</i> | 1.47 | 1.00 |
| <i>w</i> ^{-1d} | σ ² (<i>F</i> _o) ² + 0.0005(<i>F</i> _o) ² | σ ² (<i>F</i> _o) ² + (0.0824 <i>P</i>) ² |
| (Δ/σ) _{av} , (Δ/σ) _{max} | 0.000, 0.001 | 0.000, 0.003 |
| min and max res density, e Å ⁻³ | –0.28, 0.53 | –4.78, 2.62 (close to Pt) |

^a *R*1 = Σ||*F*_o| – |*F*_c||/Σ|*F*_o|. ^b *R*_w = [Σ|*w*(||*F*_o| – |*F*_c||)|²/Σ|*w*(*F*_o)|²]^{1/2}. ^c *wR*² = [Σ|*w*(*F*_o² – *F*_c²)|²/Σ|*w*(*F*_o²)|²]^{1/2}. ^d *P* = (max(*F*_o², 0) + 2*F*_c²)/3.

washed with diethyl ether (2 × 20 mL), and dried in vacuo, giving the white compound [PtX(PR₃)₂(2-C₆H₄P(Ph)(=O)CHPPh₂-NHC₆H₄CH₃-4)-C-C'] (9c, PR₃ = PMe₂Ph, X = Cl; 9f, PR₃ = PEt₃, X = Br) in 95–99% yield. The washings contained, according to ¹H NMR, *p*-tolyl isocyanate and bis(*p*-tolyl)-carbodiimide. A similar small-scale experiment was performed in CDCl₃ in 5 mm NMR tube and showed a complete conversion within 10 min. FAB MS: found for 9c, *m/z* = 873 (9c), 837 (9c – Cl) (M, calcd for C₄₀H₃₉ClNOP₃Pt, *m/z* 873.3).

X-ray Crystal Structure Determination of 2e. Crystal data and experimental procedures on 2e are collected in Table 1. The X-ray data were collected by using an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation and a graphite monochromator at 22(1) °C. Unit-cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections with the 2θ angle in the range 20.0–30.0°. Absorption corrections were made (μ = 3.58 mm⁻¹); the minimum and maximum transmission factors are 0.767 and 0.998. Structure 2e was solved by direct methods and refined by full-matrix least-squares techniques. The final cycle of the least-squares refinement gave an agreement factor *R* of 0.024, *wR* = 0.040, and *S* = 1.47, for 496 parameters and 5322 reflections with *I*

> 2.0σ(*I*). Hydrogen atoms were introduced in the last step of the refinement procedure on calculated positions. Weights based on counting statistics were used. The weight modifier *K* in *KF*_o² is 0.0005. The final difference Fourier showed no residual density outside –0.28 and 0.53 e Å⁻³, close to Pt. Atom scattering factors, which include anomalous scattering contributions, were taken from ref 18. Positional parameters are listed in Table 2 for 2e. The programs used for the crystallographic computations are listed under ref 19.

X-ray Crystal Structure Determination of 4a. A colorless, transparent crystal (0.12 × 0.12 × 0.25 mm) was mounted on a Lindemann-glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined from the setting angles of 25 reflections (SET4) in the range 11.5° < θ < 14.0°. The unit-cell parameters were checked for the presence of higher lattice symmetry.²¹ Crystal data and details on data collection and refinement are shown in Table 1. Data were corrected for *Lp* effects. An empirical absorption/extinction correction was applied (DIFABS²² as implemented in PLATON²³). The structure was solved by automatic Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).²⁴ Refinement on *F*² was carried out by full-matrix least-squares techniques (SHELXL-93);²⁵ no observance criterion was applied during refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. 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 parameter of the carrier atoms, for the sp³ and sp² hydrogen atoms, respectively. Weights were optimized in the final refinement cycles. Positional parameters are listed in Table 6 for 4a. The structure contains a small void of 13.7 Å³ at 0.425, 0.136, 0.646. However, no residual density was found in that area (PLATON/SQUEEZE).²⁶ Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 27.

Geometrical calculations and illustrations were performed with PLATON;²³ all calculations were performed on a DECstation 5000/125.

Results

Synthesis of Pt- and Pd-Bis(iminophosphoranyl)alkanide Complexes 2 and 3. Reactions of sodium bis(iminophosphoranyl)alkanide, Na[R''C-(PPh₂=NC₆H₄R'-4)₂] (1a, R' = Me, R'' = H; 1b, R' = OMe, R'' = H; 1c, R' = Me, R'' = Me), with the dimeric

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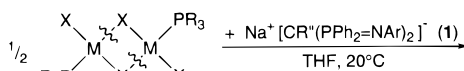
(27) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

Table 2. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms for 2e

| atom | x | y | z | B(eq), Å ² |
|-------|--------------|--------------|--------------|-----------------------|
| Pt | 0.243891(17) | 0.298232(12) | 0.142432(11) | 2.454(9) |
| Cl | 0.43363(14) | 0.40554(11) | 0.14099(10) | 4.41(6) |
| P(1) | −0.00253(11) | 0.34532(9) | 0.19777(8) | 2.36(5) |
| P(2) | 0.07067(12) | 0.15955(9) | 0.25359(8) | 2.78(5) |
| P(3) | 0.33637(14) | 0.18969(10) | 0.03562(9) | 3.08(5) |
| N(1) | 0.1387(4) | 0.4042(3) | 0.23222(24) | 2.29(15) |
| N(2) | −0.0750(4) | 0.1227(3) | 0.2644(3) | 3.99(22) |
| C(1) | 0.0265(4) | 0.2231(3) | 0.1623(3) | 2.42(19) |
| C(2) | 0.1653(5) | 0.5076(3) | 0.2692(3) | 2.58(19) |
| C(3) | 0.0721(5) | 0.5766(4) | 0.2693(3) | 3.19(21) |
| C(4) | 0.1040(6) | 0.6758(4) | 0.3073(4) | 3.9(3) |
| C(5) | 0.2263(7) | 0.7170(4) | 0.3476(3) | 4.1(3) |
| C(6) | 0.3192(6) | 0.6420(4) | 0.3468(3) | 3.81(23) |
| C(7) | 0.2901(5) | 0.5421(4) | 0.3093(3) | 3.13(22) |
| C(8) | 0.2584(9) | 0.8211(5) | 0.3933(5) | 6.7(4) |
| C(9) | −0.0806(5) | 0.3766(3) | 0.1017(3) | 2.57(19) |
| C(10) | −0.0146(5) | 0.3603(3) | 0.0228(3) | 2.87(21) |
| C(11) | −0.0691(6) | 0.3849(4) | −0.0523(3) | 3.60(24) |
| C(12) | −0.1881(6) | 0.4266(4) | −0.0484(4) | 3.9(3) |
| C(13) | −0.2516(5) | 0.4461(4) | 0.0308(4) | 4.2(3) |
| C(14) | −0.1999(5) | 0.4211(4) | 0.1057(4) | 3.68(24) |
| C(15) | −0.1222(4) | 0.3579(4) | 0.2827(3) | 2.79(20) |
| C(16) | −0.0839(5) | 0.4051(4) | 0.3699(3) | 3.31(22) |
| C(17) | −0.1720(6) | −0.4036(4) | 0.4375(4) | 4.1(3) |
| C(18) | −0.2944(6) | 0.3590(6) | 0.4186(4) | 5.1(3) |
| C(19) | −0.3367(6) | 0.3125(6) | 0.3315(4) | 5.6(4) |
| C(20) | −0.2499(5) | 0.3111(5) | 0.2647(4) | 4.5(3) |
| C(21) | 0.1752(5) | 0.0570(4) | 0.2193(3) | 3.15(22) |
| C(22) | 0.3127(6) | 0.0626(4) | 0.2322(4) | 4.0(3) |
| C(23) | 0.3818(7) | −0.0225(5) | 0.2051(4) | 5.3(3) |
| C(24) | 0.3140(9) | −0.1119(5) | 0.1690(4) | 5.9(4) |
| C(25) | 0.1799(8) | −0.1184(4) | 0.1570(4) | 5.5(4) |
| C(26) | 0.1107(6) | −0.0350(4) | 0.1810(4) | 4.3(3) |
| C(27) | 0.1513(5) | 0.2392(3) | 0.3550(3) | 2.80(20) |
| C(28) | 0.2745(5) | 0.2902(4) | 0.3593(3) | 3.20(23) |
| C(29) | 0.3273(6) | 0.3512(4) | 0.4394(4) | 4.3(3) |
| C(30) | 0.2559(8) | 0.3578(5) | 0.5160(4) | 5.0(3) |
| C(31) | 0.1343(8) | 0.3076(5) | 0.5128(4) | 4.9(3) |
| C(32) | 0.0818(6) | 0.2483(4) | 0.4323(4) | 3.85(25) |
| C(33) | −0.1329(5) | 0.0635(4) | 0.3168(4) | 3.78(24) |
| C(34) | −0.0676(5) | 0.0121(4) | 0.3691(4) | 3.7(3) |
| C(35) | −0.1369(6) | −0.0423(4) | 0.4209(4) | 3.9(3) |
| C(36) | −0.2702(5) | −0.0471(4) | 0.4237(4) | 4.0(3) |
| C(37) | −0.3366(6) | 0.0028(5) | 0.3708(5) | 4.8(3) |
| C(38) | −0.2708(6) | 0.0558(5) | 0.3181(4) | 4.8(3) |
| C(39) | −0.3448(7) | −0.1023(5) | 0.4833(5) | 5.3(3) |
| C(40) | 0.3368(5) | 0.2320(4) | −0.0680(3) | 3.37(23) |
| C(41) | 0.4354(7) | 0.2986(5) | −0.0840(4) | 5.2(3) |
| C(42) | 0.4328(9) | 0.3312(5) | −0.1616(5) | 6.6(4) |
| C(43) | 0.3342(10) | 0.2965(7) | −0.2240(5) | 7.0(5) |
| C(44) | 0.2406(10) | 0.2326(9) | −0.2102(5) | 8.6(6) |
| C(45) | 0.2389(7) | 0.1976(6) | −0.1325(4) | 6.5(4) |
| C(46) | 0.2695(7) | 0.0609(4) | −0.0019(4) | 5.0(3) |
| C(47) | 0.5093(6) | 0.1729(5) | −0.0582(4) | 4.6(3) |
| C(48) | −0.0198(5) | 0.1528(4) | 0.0851(3) | 3.38(22) |

platinum and palladium precursors $M_2X_4(PR_3)_2$ ($M = Pt(II), Pd(II)$; $PR_3 = PEt_3, PMe_2Ph$; $X = Cl, Br$) resulted in the formation of new four-membered metallacycles **2** and **3**. The ligand is σ -C, σ -N coordinated to the metal in all cases, leaving one of the $-PPh_2=N$ -aryl entities noncoordinated (eq 1).

The bridge-splitting transmetalation reactions are best performed in THF at 20 °C giving good yields (84–95%); other solvents like toluene or CH_2Cl_2 are unsuitable for this purpose. In toluene no precipitation of NaX occurs, which suggests that the reaction proceeds much slower or stops at an intermediate stage. The transmetalation reaction continues after redissolving the intermediate in THF, as visualized by the precipitation of NaX . In CH_2Cl_2 or $CHCl_3$ decomposition takes place, due to instability of the anionic ligands. The platina-

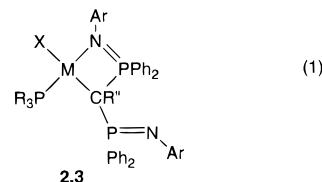


Ligand:

1a: Ar = pTol, R'' = H

1b: Ar = pAn, R'' = H

1c: Ar = pTol, R'' = Me



M = Pt:

2a: $PR_3 = PEt_3$, Ar = pTol, X = Cl, R'' = H

2b: $PR_3 = PEt_3$, Ar = pAn, X = Cl, R'' = H

2c: $PR_3 = PMe_2Ph$, Ar = pTol, X = Cl, R'' = H

2d: $PR_3 = PMe_2Ph$, Ar = pAn, X = Cl, R'' = H

2e: $PR_3 = PMe_2Ph$, Ar = pTol, X = Cl, R'' = Me

2f: $PR_3 = PEt_3$, Ar = pTol, X = Br, R'' = H

M = Pd:

3a: $PR_3 = PEt_3$, Ar = pTol, X = Cl, R'' = H

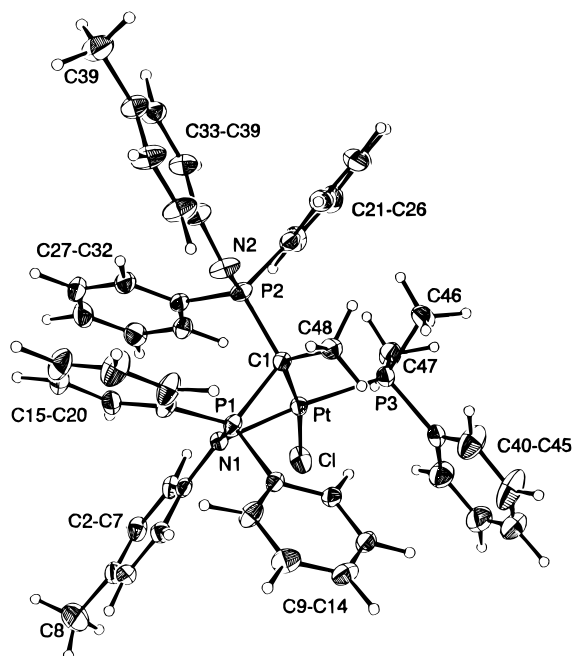
3b: $PR_3 = PEt_3$, Ar = pAn, X = Cl, R'' = H

3c: $PR_3 = PMe_2Ph$, Ar = pTol, X = Cl, R'' = H

cycles **2a–f**, however, are stable in CH_2Cl_2 and $CHCl_3$, whereas the palladium compounds **3a–c** decompose in these solvents after 1 day at 20 °C. The products **2** and **3** are soluble and stable in THF, benzene, and toluene and slightly soluble in Et_2O and pentane. In solution they are unstable in air, due to reactivity with CO_2 (vide infra) and probably also H_2O ; however, they are quite air-stable in the solid state.

The use of $Li^+[HC(PPh_2=NAr)_2]^-$, as reported earlier by Imhoff et al. for the synthesis of related Rh– and Ir–bis(iminophosphoranyl)methanide complexes,⁴ also resulted in the formation of **2** and **3** but proved less suitable for these reactions as a result of LiX formation instead of NaX , due to the fact that LiX is more finely dispersed, which makes filtration difficult. The complexes **2** and **3** are thermally unstable; at higher temperatures (30–80 °C) they undergo orthometalation reactions resulting in the complexes **4** and **5**, respectively (vide infra). The four-membered metallacycles **2** and **3** were analyzed by X-ray crystallography (**2e**), elemental analysis or mass spectroscopy, and 1H NMR (selected data in Table 4 and complete data in Supporting Information), ^{31}P , and ^{13}C NMR spectroscopy (Table 5 and Experimental Section).

X-ray Crystal Structure of $PtCl(PMe_2Ph)\{C(Me)(PPh_2=NC_6H_4Me-4)_2\}$ (2e**).** The molecular structure of **2e** with the adopted atomic labeling scheme is shown in Figure 1. Selected bond distances and bond angles have been compiled in Table 3. Figure 1 shows a distorted monomeric square-planar Pt(II) complex, with N(1) and C(1) of the C,N chelated 1,1-bis(iminophosphoranyl)ethanide ligand, $[CMe(PPh_2=N-p-tolyl)_2]^-$, positioned *trans* to P(3) and Cl, respectively. The resulting small N(1)–Pt–C(1) angle, 73.74(16)°, and folding angle within the four-membered Pt–N(1)–P(1)–C(1) ring around the N(1)⋯C(1) axis, 34.75(19)°, are characteristic features for such metallacyclic systems. For instance, the two related cationic four-membered platynacycles $[PtCl(PMe_2Ph)\{CH(PPh_2=N-p-tolyl)(PPh_2NH-p-tolyl)\}-C,M]^+[Cl]^-$ (**A**)¹² and $[PtCl(PEt_3)\{CH(PPh_2=N-p-tolyl)(PPh_2NH-p-tolyl)\}-C,M]^+[Pt(PEt_3)Cl_3]^-$ (**B**)¹² have similar N–Pt–C angles (73.2(3) and 73.1(4)°) and are folded by 32.7(4) and 36.4(4)°. Other C,N-chelated

**Figure 1.** ORTEP plot of **2e** at the 30% probability level.**Table 3.** Selected Interatomic Distances (Å) and Angles (deg) for **2e**

| Distances around Pt | | | |
|----------------------------|------------|------------------|------------|
| Pt–P(3) | 2.2283(13) | Pt–C(1) | 2.116(4) |
| Pt–Cl | 2.3544(13) | Pt–N(1) | 2.132(4) |
| Distances within Phosphine | | | |
| P(3)–C(40) | 1.831(5) | P(3)–C(47) | 1.819(6) |
| P(3)–C(46) | 1.821(6) | | |
| Distances within Ligand | | | |
| P(1)–N(1) | 1.612(4) | P(2)–N(2) | 1.555(4) |
| N(1)–C(2) | 1.418(6) | N(2)–C(33) | 1.396(7) |
| P(1)–C(1) | 1.829(5) | P(2)–C(1) | 1.834(5) |
| P(1)–C(9) | 1.820(5) | P(2)–C(21) | 1.818(5) |
| P(1)–C(15) | 1.795(5) | P(2)–C(27) | 1.828(5) |
| Angles around Pt | | | |
| Cl–Pt–P(3) | 86.20(5) | N(1)–Pt–C(1) | 73.74(16) |
| Cl–Pt–C(1) | 169.58(13) | P(3)–Pt–N(1) | 172.98(10) |
| Cl–Pt–N(1) | 95.93(10) | P(3)–Pt–C(1) | 104.22(13) |
| Angles within Ligand | | | |
| Pt–N(1)–P(1) | 92.58(17) | P(1)–N(1)–C(2) | 127.6(3) |
| Pt–N(1)–C(2) | 132.2(3) | P(2)–N(2)–C(33) | 133.0(4) |
| N(1)–P(1)–C(1) | 95.41(20) | N(2)–P(2)–C(1) | 104.91(22) |
| N(1)–P(1)–C(9) | 115.69(20) | N(2)–P(2)–C(21) | 112.07(25) |
| N(1)–P(1)–C(15) | 113.39(21) | N(2)–P(2)–C(27) | 114.3(3) |
| C(1)–P(1)–C(9) | 108.96(21) | C(1)–P(2)–C(21) | 107.37(22) |
| C(1)–P(1)–C(15) | 116.22(22) | C(1)–P(2)–C(27) | 112.31(21) |
| C(9)–P(1)–C(15) | 107.10(21) | C(21)–P(2)–C(27) | 105.78(22) |
| Pt–C(1)–P(1) | 87.26(18) | Pt–C(1)–C(48) | 122.2(3) |
| Pt–C(1)–P(2) | 113.89(22) | P(1)–C(1)–C(48) | 113.2(3) |
| P(1)–C(1)–P(2) | 112.01(24) | P(2)–C(1)–C(48) | 107.1(3) |

(iminophosphoranyl)methanides show comparable N–M–C angles and ring puckering, i.e. for [Ir{CH(PPh₂=N-*p*-tolyl)₂}COD] a N–Ir–C angle of 73.4(4)° and folding of 35.1°,^{4,28} for [Rh(COD){CH₂PPh₂=N-*p*-tolyl}] a N–Rh–C angle of 74.2(2)° and folding of 30.4°,²⁹ and for [Rh(COD){CH(PPh₂=N-*p*-tolyl)(PPh₂-NH-*p*-tolyl)}]⁺ values of 73.1(1) and 33.6°,^{28,30} respectively.

The Pt–N(1) distance of 2.132(4) Å for complex **2e** is somewhat longer than the corresponding Pt–N bonds in the cations **A** and **B**, i.e. 2.099(6) and 2.124(8) Å,¹²

respectively. Although **2e** contains an C,N-coordinated 1,1-bis(iminophosphoranyl)ethanide ligand, having a methyl group instead of an hydrogen atom on the coordinating C(1), the Pt–C(1) bond length of 2.116(4) Å is within the range found for other related compounds containing a Pt–C(sp³) bond in a four-membered ring.^{3a,12,32}

Comparison of the phosphinimine bond lengths within the complex **2e** clearly shows that the P(1)–N(1) bond, 1.612(4) Å, is significantly elongated due to coordination to Pt. A value between 1.60 and 1.64 Å is normal for this type of coordinated phosphinimine.^{4,7,8f,12,13,29–31,33} The much shorter P(2)–N(2) distance in **2e**, 1.555(4) Å, is indicative for a P–N double bond, since it is comparable to the P=N bonds in the free 1,1-bis(iminophosphoranyl)ethanide ligand (1,1-BIPE) (*d*(P–N) = 1.559(3) and 1.553(3) Å).¹³

One striking difference between the crystal structures of the neutral complex **2e** and its closely related Ir–bis(iminophosphoranyl)methanide complex⁴ is the orientation of the noncoordinated PPh₂=N-*p*-tolyl entity. In **2e**, it is pointed away from the platinum center (torsion angles P(1)–C(1)–P(2)–N(2) = 75.4(2)° and Pt–C(1)–P(2)–N(2) = 172.5(3)°), whereas in the Ir complex this group is directed toward the Ir center (torsion angles P–C–P–N = –42.9(9)° and Ir–C–P–N = 55.4(8)°).⁴ A similar phenomenon has also been found for the related complex [PtCl(PET₃){CH(PPh₂=S)₂}], wherein the noncoordinated P=S group of the C,S-coordinated ligand is pointed toward the Pt center.^{3a} Probably, the steric influence of the methyl group on C(1) is responsible for the unusual orientation of the noncoordinated P=N group in complex **2e**.

Spectroscopic Characterization of the Four-Membered Metallacycles 2 and 3. The ¹H and ³¹P-{¹H} NMR data for the four-membered metallacycles **2** and **3** are listed in Tables 4 and 5. ¹³C-{¹H} NMR data (only for **2a,b,c,e** and **3a,b**) are given in the Experimental Section. The ¹H NMR spectra of Pt–bis(iminophosphoranyl)methanides **2a–d** and **2f** show the CH resonance in the region 2.44–2.64 ppm as a broad multiplet due to coupling with three different phosphorus atoms and ²*J*(Pt,H) of about 60 Hz,³⁴ which establishes the presence of a Pt–C linkage, and agrees with earlier reported NMR data for compound **2a** obtained from a reaction of Pt₂Cl₄(PET₃)₂ with 4 equimolar amounts of CH₂(PPh₂=NC₆H₄Me-4)₂.¹² The ¹³C NMR spectra of **2a–c** show methine carbon resonances between 1.5 and 2.0 ppm (dd, ¹*J*(P,C) = 58–95 Hz; ¹*J*(Pt,C) was not observed). The corresponding ¹³C resonance for **2e** lies somewhat higher, 4.82 ppm (dd), whereas the Me group on this coordinated C atom is found at 15.27 ppm. The Pt–bis(iminophosphoranyl)ethanide complex **2e** has a characteristic doublet of doublet resonance in

(28) Folding angles are unpublished results by P. Imhoff.

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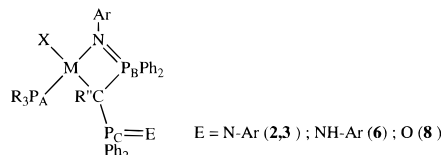
(33) Imhoff, P.; van Asselt, R.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chim. Acta* **1991**, 184, 73.

(34) ²*J*(Pt,H) is determined by ¹H{³¹P} NMR spectroscopy in all cases. A coupling between 40 and 80 Hz is normal of Pt–CH *σ*-bond interactions. See e.g.: Henderson, W.; Kemmitt, R. D. W.; Prouse, L. J. S.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1990**, 1853 and ref 12.

Table 4. Selected ^1H NMR Data (ppm) for the Complexes **2**–**9**^a

| | type ^b | solvent/ <i>T</i> (K) | P–alkyl ^c | $\delta(\text{M–CH})^d$ | $^2J(\text{Pt,H})$, Hz | $\delta(\text{NH})^d$ |
|-------------------------|-------------------|------------------------------|-------------------------------|-----------------------------|-------------------------|-------------------------|
| 2a | FMP | CD_2Cl_2 | 0.99 (dt), 1.66 (m), 1.93 (m) | 2.47 (m) | 59 | |
| 2b | FMP | $\text{CD}_2\text{Cl}_2/233$ | 1.05 (dt), 1.65 (m), 2.01 (m) | 2.44 (m) | 58 | |
| 2c | FMP | $\text{CDCl}_3/253$ | 1.35 (d), 1.49 (d) | 2.52 (m; 2.5, nr, 12.8) | 67 | |
| 2d | FMP | $\text{C}_6\text{D}_6/283$ | 1.16 (d), 1.41 (d) | 2.64 (m) | nr | |
| 2e ^e | FMP | CDCl_3 | 0.73 (d), 1.65 (d) | <i>f</i> | | |
| 2f | FMP | CDCl_3 | 0.95 (dt), 1.6–1.9 (m) | 2.6 (m) | nr | |
| 3a | FMP | CD_2Cl_2 | 1.03 (dt), 1.9 (m) | obs | | |
| 3b | FMP | C_6D_6 | 0.92 (dt), 1.93 (m) | 2.02 (dt; 1.9, 7.7) | | |
| 3c | FMP | tol- <i>d</i> ₈ | 1.3 (br) | obs | | |
| 4a | OM | CDCl_3 | 0.61 (dt), 1.14 (m) | 3.25 (dt; 6.9, 16.6) | 86 | nr |
| 4b ^g | OM | C_6D_6 | 0.56 (dt), 1.11 (m) | nr | nr | 11.2 (br) |
| 4c | OM | CDCl_3 | 1.12 (d), 1.22 (d) | 2.88 (dt; 7.5, 15.0) | 86 | 10.7 (br) |
| 4d ^g | OM | tol- <i>d</i> ₈ | 1.11 (d), 1.19 (d) | 2.84 (m) | 75 | 11.2 (br) |
| 4f ^g | OM | CDCl_3 | 0.56 (dt), 1.17 (m) | 3.35 (dt; 6.8, 15.7) | nr | nr |
| 5a | OM | C_6D_6 | 0.75 (dt), 1.49 (m) | 4.24 (ddd; 7.0, 11.2, 16.0) | | 10.2 (br) |
| 5c | OM | tol- <i>d</i> ₈ | 0.93 (d), 1.42 (d) | 4.09 (ddd; 7.4, 11.7, 15.4) | | nr |
| 6a | FMP | CD_2Cl_2 | 0.86 (dt), 1.12 (m), 1.39 (m) | 3.37 (m) | 60 | obs ^h |
| 6b | FMP | CD_2Cl_2 | 0.91 (dt), 1.12 (m), 1.40 (m) | 3.88 (m) | 63 | 10.5 (br d; 7) |
| 7a ^g | OM | C_6D_6 | 0.56 (dt), 1.11 (m) | 4.51 (m) | 70 | nr |
| 7a' | OM | C_6D_6 | 0.61 (dt), 1.15 (m) | 4.98 (ddd; 6.8, 12.2, 13.9) | 94 | 9.4 (br), 11.7 (d; 8.3) |
| 7b' ^g | OM | C_6D_6 | 0.63 (dt), 1.15 (m) | 4.96 (dt; 6.6, ~14) | nr | 9.2 (br), 11.5 (d; 7.9) |
| 8a | FMP | CDCl_3 | 0.99 (dt), 1.68 (m), 1.95 (m) | ~2.3 (obs) ⁱ | nr | nr |
| 8d | FMP | C_6D_6 | 1.32 (d), 1.48 (d) | 2.31 (m) | nr | nr |
| 9c | OM | CDCl_3 | 1.24 (d), 1.34 (d) | 2.61 (dt; 7.4, 13.0) | 91 | 8.9 (d; 6.3) |
| 9f ^g | OM | CDCl_3 | 0.64 (dt), 1.22 (m) | 3.22 (dt; 6.7, 13.3) | 88 | 10.0 (d; 7.2) |

^a Recorded at 300.13 MHz at 293 K, unless noted otherwise. Complete ^1H NMR data are listed in the Supporting Information. Multiplets and abbreviations: d = doublet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of triplet, m = multiplet, br = broad; nr = not resolved, obs = obscured. ^b FMP = four-membered platina- or palladacycle, OM = orthometalated compound. ^c For Et_3P : $\delta(\text{P–CH}_2\text{–CH}_3)$ (dt) and $\delta(\text{P–CH}_2\text{–CH}_3)$ (m) are given successively, with coupling constants $^3J(\text{H,H}) = 7.5$ Hz, $^3J(\text{P,H}) = 15.0$ Hz, and $^2J(\text{P,H}) = \text{n.r.}$ For Me_2PhP : $\delta(\text{P–CH}_3)$ (d) with $^2J(\text{P,H}) \approx 8.7\text{--}9.0$ Hz. ^d Multiplicity and $^nJ(\text{P,H})$ (with $n = 2$ or 3) are given successively. ^e Measured at 500 MHz. ^f $\delta(\text{Pt–CMe}) = 1.68$ ppm (dd, $^3J(\text{P,H}) = 19.1$, 17.9 Hz). ^g Measured at 100.13 MHz. ^h $\delta(\text{NH})$ is obscured by phenyl proton resonances. ⁱ $\delta(\text{CH})$ is obscured by the methyl resonance of the *p*-tolyl group on N.

Table 5. ^{31}P NMR Data for the Four-Membered Metallacycles **2**, **3**, **6** and **8**^a

| | solvent/ <i>T</i> (K) | $\delta(\text{P}_\text{A})$ | $\delta(\text{P}_\text{B})$ | $\delta(\text{P}_\text{C})$ | $^1J(\text{Pt,P}_\text{A})$ | $^2J(\text{Pt,P}_\text{B})$ | $^2J(\text{Pt,P}_\text{C})$ | $^2J(\text{P}_\text{B,P}_\text{C})$ |
|------------------------|---------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-------------------------------------|
| 2a | $\text{CD}_2\text{Cl}_2/253$ | 0.7 (s) | 32.5 (d) | 8.0 (d) | 3740 | 426 | 114 | 3.9 |
| 2b | $\text{CD}_2\text{Cl}_2/253$ | 0.8 (s) | 32.1 (d) | 7.0 (d) | 3735 | 413 | 108 | 3.6 |
| 2c | $\text{CDCl}_3/253$ | –21.4 (s) | 35.2 (d) | 3.2 (d) | 3784 | 424 | 87 | 6.5 |
| 2d | tol- <i>d</i> ₈ /293 | –21.6 (s) | 29.8 (br) | –1.6 (br) | 3840 | 427 | 91 | nr |
| 2e | $\text{CDCl}_3/293$ | –22.6 (s) | 45.0 (br) | 7.8 (br) | 3913 | 427 | 89 | nr |
| 2f | $\text{CDCl}_3/293$ | –0.7 (s) | 30.5 (br) | 5.5 (br) | 3713 | 427 | 96 | nr |
| 3a | $\text{CD}_2\text{Cl}_2/293$ | 29.1 (br) | 15.7 (br) ^c | 15.7 (br) ^c | | | | |
| | $\text{CD}_2\text{Cl}_2/183$ | 29.9 (s) | 25.8 (d) | 12.1 (d) | | | | 13.9 |
| 3b | $\text{CDCl}_3/293$ | 28.7 (br) | 15.5 (br) ^c | 15.5 (br) ^c | | | | |
| <i>b</i> | $\text{CD}_2\text{Cl}_2/190$ | 29.7 (s) | 25.0 (d) | 11.1 (d) | | | | 11.8 |
| 3c | tol- <i>d</i> ₈ /293 | 3.5 (br) | 12.8 (br) ^c | 12.8 (br) ^c | | | | |
| <i>b</i> | <i>d</i> /184 | 5.0 (s) | 27.6 (br) | 7.5 (br) | | | | nr |
| 6a | $\text{CD}_2\text{Cl}_2/293$ | –0.3 (s) | 27.2 (d) | 29.9 (d) | 3576 | 400 | 117 | 10.2 |
| 6b | tol- <i>d</i> ₈ /293 | 0.3 (s) | 28.5 (s) ^e | 28.5 (s) ^e | 3616 | 402 | 103 | 9.4 |
| 8a | $\text{CDCl}_3/293$ | 1.0 (s) | 30.3 (s) | 30.3 (s) | 3733 | 425 | 129 | nr |
| 8d ^b | $\text{C}_6\text{D}_6/293$ | –21.8 (s) | 30.2 (d) | 25.0 (d) | 3821 | 429 | 110 | 3.9 |

^a Recorded at 40.53 MHz, unless noted otherwise. *J* values in Hz. Multiplicity labels and abbreviations: br = broad, s = singlet, d = doublet, dd = doublet of doublet, nr = not resolved. ^b Recorded at 121.48 MHz. ^c Italicized values are averages by exchange. ^d CD_2Cl_2 mixed with CDCl_3 . ^e $\delta(\text{P}_\text{B}) = \delta(\text{P}_\text{C})$. In CD_2Cl_2 two separate signals at $\delta(\text{P}_\text{B}) = 32.1$ (d) and $\delta(\text{P}_\text{C}) = 29.5$ (d) are found.¹²

the ^1H NMR at 1.68 ppm ($^3J(\text{P,H}) = 19.1$ and 17.9 Hz) belonging to the methyl group on the coordinated C. This signal is slightly shifted to lower frequency, when compared to $\text{Na}^+[\text{MeC}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{Me-4})_2]^-$ (**1c**) (see Experimental Section). Support for the C,N coordination of the ligand to Pt and Pd was also provided by **2c,d**, containing a prochiral phosphine PMe_2Ph . As C,N coordination induces chirality on the coordinated sp^3 -carbon atom, two sets of signals are observed for the diastereotopic PMe groups in the ^1H and ^{13}C NMR. All data indicate that the molecular structure of the Pt

complexes in solution is similar to the solid-state structure, which has been established for **2e** (Figure 1).

As reported earlier for complex **2a**,¹² the platina- and palladacycles **2a–f** show broadening of most ^1H , ^{31}P , and ^{13}C signals at 293 K, which has been attributed to a dynamic process involving slow N,N' exchange of the C,N-coordinated ligand at 293 K. For **2a–f** broad resonances are found in ^{31}P NMR at 293 K for P_B (29.8–45.0 ppm) and P_C (–1.6 to 8.0 ppm), whereas the peak due to $\text{P}_\text{A}\text{R}_3$ is hardly broadened and shows characteristic $^1J(\text{Pt,P}_\text{A})$ coupling of 3713–3913 Hz for *trans* P–Pt–N com-

plexes.^{12,35} The $^2J(\text{Pt}, \text{P}_\text{B})$ value, ranging from 413 to 427 Hz, is characteristic for these types of four-membered platinacycles.¹² Similar two-bond Pt,P couplings have been reported for related C,X-coordinated Pt compounds, i.e. $\text{PtCl}(\text{PR}_3)\{\text{CH}(\text{PPh}_2=\text{X})(\text{PPh}_2=\text{Y})\}$ (X, Y = S, O, Se).³ Cooling the solution to 253 K (**2a–c**) resulted in sharpening of the P_B and P_C signals into doublets ($^2J(\text{P}_\text{B}, \text{P}_\text{C}) = 3.6\text{--}6.5$ Hz).

For the palladium complexes **3a–c** the CH resonance is found at about 2 ppm, although it is obscured for **3a,c** by the 4- $\text{CH}_3\text{C}_6\text{H}_4$ signal, and is evident from the ^{13}C NMR CH signal at 9.01 ppm (vt, $^1J(\text{P}, \text{C}) = 82$ Hz). The Pd complexes **3a–c**, in contrast to their Pt analogues, are in the fast exchange mode relative to the NMR time scale. In the ^1H NMR and ^{13}C NMR at ambient temperature only a single set of resonances is found for the $\text{NC}_6\text{H}_4\text{R}'$ -4 groups, whereas the Pt complexes show two sets of resonances for each group. For compound **3c**, containing a prochiral PMe_2Ph ligand, only one broad PMe signal at 1.3 ppm is observed at 293 K, which resolves into two broad signals ("doublets") at 185 K,³⁶ similar to what has been observed for the Pt complexes **2c,d**. Evidently, the exchange process results in inversion of configuration at the sp^3 -carbon.

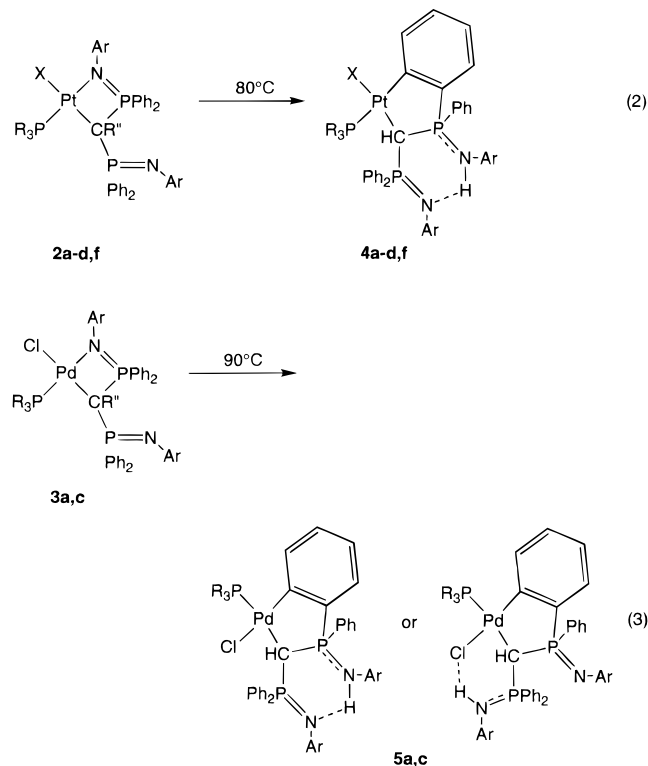
The same phenomenon is found in the ^{31}P NMR for the signals of the two $\text{P}=\text{N}$ -aryl groups of the coordinated ligand, implying equivalence of these groups on the NMR time scale at 293 K. At 183–190 K the slow-exchange regime is reached for **3a,b**.^{36a} The initially broad ^{31}P resonance at approximately 12.8–15.7 ppm splits into two doublets, one in the region 25.0–27.6 ppm and the other around 7.5–12.1 ppm, with mutual $\text{P}_\text{B}, \text{P}_\text{C}$ coupling of 11.8–13.9 Hz. The latter is assigned to the noncoordinated $\text{P}_\text{C}=\text{N}$ function, since it shows the strongest resemblance with the frequency of a free $\text{R}_3\text{P}=\text{NR}'$ ligand.^{13,17}

From the fact that the palladium complexes **3** show similar fluxional behavior as observed for their platinum analogues **2**, like in $\text{PtCl}(\text{PET}_3)\{\text{CH}(\text{PPh}_2=\text{S})_2\}$ ³ and $\text{PtCl}(\text{PET}_3)\{\text{C}(\text{PPh}_2=\text{S})_3\}$ ³⁷ with S *trans* to PET_3 , it is deduced that the complexes **3** have N *trans* to the phosphine, i.e. the *trans* influence of the phosphine is causing the relative weakness of the M–N (M = Pt, Pd) and Pt–S bonds. A complex with the opposite geometry would not show such dynamic behavior, which has been established for the "rigid" complex $\text{PtCl}(\text{PET}_3)\{\text{CH}(\text{PPh}_2=\text{S})_2\}$ with S *trans* to Cl.³

For both **2** as **3**, the broadness of the ^1H and ^{31}P signals at room temperature does not change significantly upon variation of the complex concentration, which means that the N,N' exchange takes place via an intramolecular process.

Synthesis of Orthometalated Platinum and Palladium Complexes 4 and 5. New orthometalated platinum(II) and palladium(II) complexes **4** and **5** containing the bis(iminophosphoranyl)methanide ligand $[\text{HC}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2]^-$ (**1a**, $\text{R}' = \text{Me}$; **1b**, $\text{R}' = \text{OMe}$)

were synthesized in fairly good yield (39–80%) by reaction of $\text{M}_2\text{X}_4(\text{PR}_3)_2$ (M = Pt(II), Pd(II); $\text{PR}_3 = \text{PET}_3$, PMe_2Ph ; X = Cl, Br) with 2 equiv of $\text{Na}[\text{HC}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2]$ at elevated temperatures (70–90 °C). Also, when the neutral C,N-coordinated four-membered metallacycles **2** and **3** were heated in THF or toluene solution, orthometalation of one of the phenyl groups of the $\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'-4)_2^-$ ligand took place (eqs 2 and 3). Unfortunately, **2e** could not be converted into an orthometalated product due to decomposition during prolonged stirring or heating, visible by the formation of Pt(0).



The ligand in **4** is σ -C, σ -C' coordinated to the platinum center by the methanide-C, bridging the two phosphinimine functions of the ligand, and by the ortho-C of the metalated phenyl group on P, resulting in a five-membered ring. The sp^3 -carbon atom is still coordinated *trans* to the Pt–X bond, as in the neutral four-membered platinacycles **2**. The original ortho-H of the phenyl group has shifted to the noncoordinated N atoms forming a H-bridge between them. Its exact position has been determined by means of a crystal structure determination of **4a** and has been corroborated by ^1H and ^{31}P NMR spectroscopy (Tables 4 and 8). The orthometalated Pd complex **5** shows much resemblance to its Pt analogue but has the opposite geometry; i.e. the sp^3 -carbon atom is coordinated *trans* to the Pd– PR_3 bond. In eq 3 two structural proposals are given for **5**, either of which is consistent with the data (see spectroscopic characterization). Complexes **4** and **5** represent rare examples of orthometalated complexes with a C,C'-coordinating ligand.^{14,38a,39}

For the $(\text{PMe}_2\text{Ph})\text{--Pt}$ and --Pd complexes **2c,d** and **3c**, the reaction to **4c,d** and **5c** already proceeds at room

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(36) (a) The slow-exchange limit for **3c**, which lies just below 185 K, was not reached. (b) Recording of ^{13}C NMR was impossible due to the low solubility of the complexes at low temperatures.

(37) Browning, J.; Beveridge, K. A.; Bushnell, G. W.; Dixon, K. R. *Inorg. Chem.* **1986**, *25*, 1987.

(38) (a) Liu, C.-H.; Li, C.-L.; Cheng, C.-H. *Organometallics* **1994**, *13*, 18. (b) Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3619.

(39) Avis, M. W.; van der Boom, M. E.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. To be published.

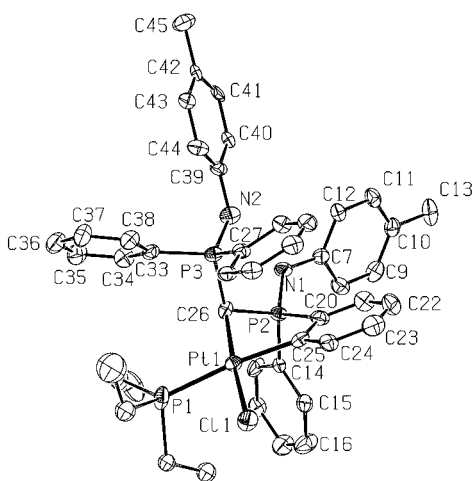


Figure 2. ORTEP²³ plot of **4a** at 50% probability level. Hydrogen atoms were left out for clarity. Only the major disorder from the triethylphosphine is shown.

temperature, which contrasts with their PEt_3 analogues. For the $(\text{PMe}_2\text{Ph})\text{Pd}$ compound **3c**, the reaction to **5c** is completed within 24 h at 20 °C, whereas for Pt compounds **2c,d** it takes about 3–7 days to convert into **4c,d** at 20 °C.

The reason for the moderate yield of **4** is not clear. When a small-scale reaction is carried out in toluene- d_8 in a NMR tube, 100% conversion of **2** into **4** is observed. At larger scale a significant amount of the neutral C,N-coordinated complex **2** is still present, which is washed out with Et_2O or pentane. The platinum compounds **4** are highly soluble in CH_2Cl_2 , CHCl_3 , and THF, are less soluble in toluene or benzene, and are insoluble in Et_2O or pentane, whereas the palladium compounds **5** are more soluble in toluene and are slightly soluble in pentane also. In solution they are unstable in air, due to the aza-Wittig reactivity with CO_2 (vide infra). However when pure oxygen was bubbled through a CH_2Cl_2 solution of **4b**, or H_2O was added, no reaction took place. An attempt to increase the rate of the reaction or the conversion by further increase of the temperature (120 °C in toluene) or longer reaction time (10 h) failed. Blackening of the solution occurs as a result of decomposition into Pt(0) and Pd(0), which lowers the yield.

X-ray Crystal Structure of $[\text{PtCl}(\text{PEt}_3)\{\text{2-C}_6\text{H}_4\text{P}(\text{Ph})(\text{NHC}_6\text{H}_4\text{CH}_3\text{-4})\text{CHPh}_2=\text{NC}_6\text{H}_4\text{CH}_3\text{-4}\}\text{-C,C'}]$ (4a**).** The molecular structure of **4a** with the adopted atomic labeling scheme is shown in Figure 2. Selected bond distances and angles have been compiled in Table 7. The structure of **4a** shows a monomeric neutral complex in which the Pt(II) center is square-planar-surrounded by P(1), Cl(1), C(25), and C(26); the latter carbons belong to the orthometalated bis(iminophosphoranyl)methanide ligand. Complex **4a** represents one of the few examples of orthometalated complexes of Pt and Pd, containing C,C'-chelated ligands, that have been characterized crystallographically.^{14b,e,39}

An isotropic refinement has been carried out for the Et_3P ligand, since it is considerably distorted. The relatively long Pt–P(1) bond (2.315(2) Å) directly reflects

Table 6. Final Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms for **4a**

| atom ^a | x | y | z | $U(\text{eq}), \text{\AA}^2$ |
|-------------------|-------------|-------------|-------------|------------------------------|
| Pt(1) | −0.10216(3) | 0.24179(3) | 0.24718(2) | 0.0214(1) |
| Cl(1) | −0.3286(2) | 0.1294(2) | 0.22929(11) | 0.0358(6) |
| P(1) | −0.0137(2) | 0.0656(2) | 0.21123(12) | 0.0343(7) |
| P(2) | 0.0893(2) | 0.4242(2) | 0.34300(10) | 0.0207(5) |
| P(3) | 0.0903(2) | 0.4586(2) | 0.19278(10) | 0.0224(6) |
| N(1) | 0.2194(7) | 0.5332(6) | 0.3609(3) | 0.0260(17) |
| N(2) | 0.1996(7) | 0.5722(6) | 0.2243(3) | 0.029(2) |
| C(1) | 0.1771(9) | 0.0535(9) | 0.2084(5) | 0.040(3) |
| C(2) | 0.2821(11) | 0.0616(10) | 0.2782(6) | 0.057(4) |
| *C(3A) | −0.1053(16) | −0.0196(14) | 0.1337(7) | 0.036(4) |
| *C(3B) | −0.093(2) | 0.064(2) | 0.1159(12) | 0.033(6) |
| *C(4A) | −0.103(3) | 0.053(2) | 0.0738(14) | 0.078(7) |
| *C(4B) | −0.070(3) | −0.050(2) | 0.0773(13) | 0.042(7) |
| *C(5A) | −0.0355(18) | −0.0668(14) | 0.2707(9) | 0.025(4) |
| *C(5B) | −0.081(2) | −0.0613(16) | 0.2374(11) | 0.030(5) |
| *C(6A) | −0.0142(19) | −0.0289(16) | 0.3459(9) | 0.032(5) |
| *C(6B) | −0.077(3) | −0.060(2) | 0.3147(12) | 0.048(6) |
| C(7) | 0.2561(8) | 0.6185(7) | 0.4178(4) | 0.025(2) |
| C(8) | 0.2849(8) | 0.5836(7) | 0.4859(4) | 0.030(2) |
| C(9) | 0.3265(8) | 0.6684(8) | 0.5394(4) | 0.030(3) |
| C(10) | 0.3397(8) | 0.7908(7) | 0.5279(4) | 0.026(2) |
| C(11) | 0.3099(8) | 0.8255(7) | 0.4595(4) | 0.028(2) |
| C(12) | 0.2682(8) | 0.7408(7) | 0.4059(4) | 0.024(2) |
| C(13) | 0.3870(10) | 0.8817(9) | 0.5878(5) | 0.042(3) |
| C(14) | 0.1272(7) | 0.3151(6) | 0.4086(4) | 0.020(2) |
| C(15) | 0.0142(8) | 0.2650(7) | 0.4351(4) | 0.027(2) |
| C(16) | 0.0425(9) | 0.1812(9) | 0.4863(5) | 0.043(3) |
| C(17) | 0.1814(9) | 0.1509(9) | 0.5111(5) | 0.039(3) |
| C(18) | 0.2947(8) | 0.2003(8) | 0.4839(4) | 0.029(3) |
| C(19) | 0.2671(8) | 0.2827(8) | 0.4333(4) | 0.028(2) |
| C(20) | −0.0926(8) | 0.4678(7) | 0.3331(4) | 0.027(2) |
| C(21) | −0.1350(9) | 0.5677(8) | 0.3646(4) | 0.034(3) |
| C(22) | −0.2830(10) | 0.5937(9) | 0.3468(5) | 0.040(3) |
| C(23) | −0.3800(9) | 0.5170(9) | 0.3014(5) | 0.042(3) |
| C(24) | −0.3348(8) | 0.4161(7) | 0.2709(4) | 0.028(2) |
| C(25) | −0.1885(8) | 0.3876(7) | 0.2860(4) | 0.026(2) |
| C(26) | 0.0868(7) | 0.3545(7) | 0.2618(3) | 0.0213(19) |
| C(27) | −0.0934(7) | 0.4985(7) | 0.1556(4) | 0.023(2) |
| C(28) | −0.1287(8) | 0.6144(7) | 0.1741(4) | 0.026(2) |
| C(29) | −0.2695(9) | 0.6488(8) | 0.1524(5) | 0.036(3) |
| C(30) | −0.3737(8) | 0.5744(8) | 0.1096(4) | 0.034(3) |
| C(31) | −0.3380(8) | 0.4606(7) | 0.0897(4) | 0.028(2) |
| C(32) | −0.1988(8) | 0.4236(7) | 0.1139(4) | 0.027(2) |
| C(33) | 0.1582(8) | 0.3744(7) | 0.1272(4) | 0.024(2) |
| C(34) | 0.2929(8) | 0.3286(8) | 0.1487(4) | 0.032(3) |
| C(35) | 0.3595(9) | 0.2705(9) | 0.1031(5) | 0.038(3) |
| C(36) | 0.2931(9) | 0.2606(9) | 0.0346(5) | 0.039(3) |
| C(37) | 0.1590(10) | 0.3102(9) | 0.0124(5) | 0.038(3) |
| C(38) | 0.0904(8) | 0.3667(8) | 0.0577(4) | 0.029(3) |
| C(39) | 0.2546(8) | 0.6597(7) | 0.1852(4) | 0.024(2) |
| C(40) | 0.3690(8) | 0.7417(7) | 0.2186(4) | 0.025(2) |
| C(41) | 0.4284(9) | 0.8286(7) | 0.1835(5) | 0.030(3) |
| C(42) | 0.3806(9) | 0.8393(7) | 0.1130(4) | 0.028(3) |
| C(43) | 0.2666(9) | 0.7606(7) | 0.0801(4) | 0.031(3) |
| C(44) | 0.2043(8) | 0.6724(7) | 0.1153(4) | 0.029(2) |
| C(45) | 0.4474(12) | 0.9336(9) | 0.0743(5) | 0.052(4) |

^a The asterisks indicate disordered atoms.

the strong *trans* influence caused by $\text{sp}^2\text{-C}(25)$, when compared to the Pt–P bond in **2e** (2.2283(13) Å) *trans* to N or $d(\text{Pt}–\text{P})$ of 2.245(4) Å *trans* to S in $[\text{PtCl}(\text{PEt}_3)\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$.^{3a}

The *ortho* sp^2 -carbon atom, C(25), of the orthometalated phenyl group on P(2), is directly attached to the Pt center, resulting in a Pt–C(25) distance of 2.050(8) Å, which is in the range of $d(\text{Pt}–\text{C})$ values (1.975–2.051 Å) found for other orthometalated Pt complexes.^{14b,40} The five-membered metallacycle in **4a** also strongly resembles the C,C'-chelate ring in $[\text{PdCl}_2\{2\text{-(4-Me-C}_6\text{H}_3\text{)P(pTol)}_2\text{CHPy}\}\text{-C,C'}]_2$ ^{14e} and $[\text{PdCl}_2\{2\text{-C}_6\text{H}_4\text{PPh}(\text{NHpTol})\text{CHPh}_2\text{NHpTol}\}\text{-C,C'}]$.³⁹ The H atom that originated from the *ortho* position of the phenyl group

(40) (a) Stoccoro, S.; Cinellu, M. A.; Zucca, A.; Minghetti, G.; Demartin, F. *Inorg. Chim. Acta* **1994**, 215, 17. (b) Crespo, M.; Solans, X.; Font-Bardia, M. *Organometallics* **1995**, 14, 355. (c) Mdleleni, M. M.; Bridgewater, J. S.; Watts, R. J.; Ford, P. C. *Inorg. Chem.* **1995**, 34, 2334.

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for Compound 4a

| Distances around Pt(1) | | | |
|-------------------------|-----------|-------------------|-----------|
| Pt(1)–P(1) | 2.315(2) | Pt(1)–C(25) | 2.050(8) |
| Pt(1)–Cl(1) | 2.354(2) | Pt(1)–C(26) | 2.071(7) |
| Distances within Ligand | | | |
| P(2)–N(1) | 1.639(7) | P(3)–N(2) | 1.596(7) |
| N(1)–C(7) | 1.421(10) | N(2)–C(39) | 1.404(10) |
| P(2)–C(26) | 1.765(7) | P(3)–C(26) | 1.823(7) |
| P(2)–C(14) | 1.798(8) | P(3)–C(27) | 1.812(7) |
| P(2)–C(20) | 1.777(8) | P(3)–C(33) | 1.827(8) |
| Angles around Pt(1) | | | |
| Cl(1)–Pt(1)–P(1) | 85.76(7) | C(25)–Pt(1)–C(26) | 84.7(3) |
| Cl(1)–Pt(1)–C(25) | 90.7(2) | P(1)–Pt(1)–C(25) | 174.3(2) |
| Cl(1)–Pt(1)–C(26) | 174.9(2) | P(1)–Pt(1)–C(26) | 98.9(2) |
| Angles within Ligand | | | |
| Pt–C(25)–C(20) | 117.4(6) | Pt–C(26)–P(2) | 101.0(3) |
| Pt–C(25)–C(24) | 126.9(6) | Pt–C(26)–P(3) | 114.0(3) |
| P(2)–C(26)–P(3) | 115.2(4) | | |
| P(2)–N(1)–C(7) | 129.8(5) | P(3)–N(2)–C(39) | 124.7(5) |
| N(1)–P(2)–C(26) | 109.8(3) | N(2)–P(3)–C(26) | 107.5(3) |
| N(1)–P(2)–C(14) | 107.7(3) | N(2)–P(3)–C(27) | 113.8(4) |
| N(1)–P(2)–C(20) | 116.8(4) | N(2)–P(3)–C(33) | 111.1(4) |
| C(14)–P(2)–C(26) | 109.8(4) | C(26)–P(3)–C(27) | 109.8(3) |
| C(20)–P(2)–C(26) | 102.3(3) | C(26)–P(3)–C(33) | 105.9(3) |
| C(14)–P(2)–C(20) | 110.3(3) | C(27)–P(3)–C(33) | 108.5(4) |
| P(2)–C(20)–C(21) | 125.7(6) | P(2)–C(20)–C(25) | 110.2(6) |
| C(20)–C(21)–C(22) | 118.1(8) | C(20)–C(25)–C(24) | 115.7(7) |
| C(21)–C(22)–C(23) | 119.5(9) | C(23)–C(24)–C(25) | 121.4(7) |
| C(22)–C(23)–C(24) | 121.3(8) | | |

concerned is shifted to N(1) and forms an intramolecular hydrogen bridge with N(2), resulting in a N–H···N angle of 125.3(7)°. The coordination position of the sp³-carbon atom C(26), bridging the two P–N entities of the ligand, is still *trans* to the Pt–Cl bond, similar to **2e**. The Pt–C(26) bond (2.071(7) Å), however, is significantly shorter than the Pt–C bond in **2e** (2.116(4) Å) or in other four-membered platinacycles with a similar *trans* Cl–Pt–C geometry (*d*(Pt–C) of ca. 2.10 Å).^{3a,12} This is probably due to the diminished constraints in the five-membered ring as comparison to four-membered rings. As can be seen in Figure 2, the five-membered platinacycle is puckered. A least-squares plane analysis of the ring defined by Pt(1), C(25), C(20), P(2), and C(26) shows deviations of 0.283(1), –0.160(8), –0.067(8), 0.335(2), and –0.390(7) Å, respectively.

In general, the P–C bond distances around P(2) (average P–C = 1.780(8) Å) are shorter than around P(3) (P–C_{av} = 1.821(8) Å), which is presumably the result of a positive charge on P(2), being part of the protonated P(2)–N(1) function. The differences in character of the two P atoms of the ligand is supported by the P(2)–N(1) and P(3)–N(2) distances of 1.639(7) and 1.596(7) Å, respectively. The *p*-tolyl group on N(2) is, in contrast to the one on N(1), practically in plane with its P=N bond (torsion angles P(3)–N(2)–C(39)–C(40) = 168.7(6)°, whereas P(2)–N(1)–C(7)–C(12) = –127.1(7)°). The planarity could be explained by electron delocalization which occurs as a result of the interactions of the 2p_π-orbitals of the sp²-N with the 3d_π-orbitals of P, which is extended to the π-system of the aryl group on N, as evidenced by the widening of the P–N–C angle (>120°).¹⁷

Spectroscopic Characterization of Orthometalated Complexes 4 and 5. Selected ¹H NMR data are compiled in Table 4. Complete ¹H NMR data are available from the Supporting Information. ³¹P{¹H}

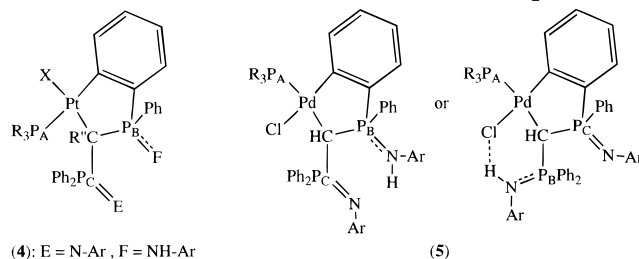
and ¹³C{¹H} NMR data of the orthometalated complexes **4** and **5** are listed in Table 8 and the Experimental Section, respectively. Direct evidence for orthometalation in **4** was obtained from the ¹³C NMR spectra of **4a–c**, showing a characteristic sp²-C resonance at ca. 167 ppm, a doublet of doublets as a consequence of coupling with P_AR₃ *trans* to it (²*J*(P_A,C_{om}) = 125–129 Hz) and P_B (²*J*(P_B,C_{om}) = 34–36 Hz). This corresponds well with the values reported for other orthometalated Pt and Pd complexes of the same geometry, with δ(C_{om}) ranging from 155 to 164 ppm and ²*J*(P_{trans},C) values of 112–115 Hz, respectively.³⁸ Unfortunately, ¹*J*(Pt,C_{om}) could not be resolved. The methine-C resonance is found between 13.4 and 15.4 ppm (ddd, ¹*J*(P,C) ≈ 46 and 70 Hz, ¹*J*(Pt,C) ≈ 736 Hz (**4a**)). Due to the multiplicity and resulting low intensity of the signals it was impossible to obtain all ¹*J*(Pt,C) values.

The ¹H NMR of the orthometalated Pt complexes **4a–d,f** (Table 4) show characteristic multiplets for the CH resonance in the range 2.84–3.57 ppm, resulting from coupling with three different P atoms (*J*(P,H) is approximately 7, 15, and 16 Hz). Its coupling with ¹⁹⁵Pt (86 Hz) is larger than that of the four-membered platinacycle **2** (60 Hz), which agrees with the crystallographically observed shorter Pt–C bond of **4a** compared to **2e** (vide supra). The H atom, originating from the orthometalated C_{om}, is positioned between the two P=N groups as evidenced by X-ray structure determination of **4a** (vide supra) and by the extremely broad NH resonance for **4b–d** between 10.7 and 11.2 ppm (*σ*_{1/2} > 200 Hz in the case of **4c**), which resembles the NH frequency found in the cationic four-membered platinacycle [PtCl(PET₃){CH(PPh₂=N-*p*An)(PPh₂NH-*p*An)-C,N}]⁺(CF₃CO₂)[–] (**6b'**) (vide infra) and analogous complexes.^{12,33}

The ³¹P NMR spectra for **4a–d,f** (Table 8) show three signals. The doublet resonance with the largest ¹⁹⁵Pt coupling is assigned to P_AR₃; the ¹*J*(Pt,P_A) value (1913–1941 Hz) proves that P_A is *trans* to C,⁴¹ instead of N, and confirms that the structure in solution is similar to that in the solid state. The remaining two ³¹P signals, a doublet of doublet at about 30 ppm (P_B, ³*J*(P_A,P_B) = 34.3–36.3 Hz and ²*J*(P_B,P_C) = 14.8–15.8 Hz) and a doublet at 17 ppm (P_C), are assigned to the aminophosphonium entity and the remote phosphiminine group in **4**, respectively, since they resemble the frequencies of the corresponding groups in other complexes^{12,33} (see also **2** and **3**). The coupling patterns for P_B (dd) and P_C (d) might be explained by the dihedral angles P_A–Pt–C–P_B (–133.54°) and P_A–Pt–C–P_C (102.39°) obtained from the X-ray crystal structure determination of **4a**, which indicates that ³*J*(P_A,P_C) coupling will, according to the Karplus relations, indeed be small or zero, since the dihedral angle is approaching 90°.

Comparison of the NMR data of **4** and **5** (Tables 4 and 8 and Experimental Section) indicate that the molecular structure of the palladium complexes **5a,c** differs from the platinum complexes **4a–d,f**. First of all, in the ¹³C NMR of **5a** the signal belonging to the orthometalated carbon atom (C_{om}) is found at 157.9 ppm (dd), with rather small ²*J*(P,C) values of 27 and 3 Hz,

(41) (a) Allen, F. H.; Pidcock, A. *J. Chem. Soc.* **1968**, 2700. (b) Lukehart, C. M.; McPhail, A. T.; McPhail, D. R.; Meyers, J. B., Jr.; Soni, H. K. *Organometallics* **1989**, *8*, 1007. (c) Dema, A. C.; Li, X.; Lukehart, C. M.; Owen, M. D. *Organometallics* **1991**, *10*, 1197. (d) Romeo, R.; Arena, G.; Scolaro, L. M. *Inorg. Chem.* **1992**, *31*, 4879.

Table 8. ^{31}P NMR Data for the Orthometalated Complexes **4**, **5**, **7**, and **9**^a

| | $\delta(\text{P}_A)$ | $\delta(\text{P}_B)$ | $\delta(\text{P}_C)$ | $^1J(\text{Pt}, \text{P}_A)$ | $^2J(\text{Pt}, \text{P}_B)$ | $^2J(\text{Pt}, \text{P}_C)$ | $^3J(\text{P}_A, \text{P}_B)$ | $^2J(\text{P}_B, \text{P}_C)$ |
|--------------------------|------------------------|----------------------|-----------------------|------------------------------|------------------------------|------------------------------|-------------------------------|-------------------------------|
| 4a | 5.5 (d) | 30.8 (dd) | 17.9 (d) | 1941 | nr | 80 | 34.5 | 15.0 |
| 4b ^b | 5.5 (d) | 31.1 (dd) | 17.9 (d) | 1939 | 20 | 80 | 34.3 | 14.8 |
| 4c | -7.8 (d) | 30.2 (dd) | 16.1 (d) | 1914 | nr | 88 | 35.5 | 15.5 |
| 4d ^{c,d} | -8.3 (d) | 30.0 (dd) | 15.6 (d) | 1913 | 16 | 86 | 36.3 | 15.8 |
| 4f | 2.8 (d) | 29.5 (dd) | 17.6 (d) | 1929 | 20 | 73 | 33.4 | 15.5 |
| 5a ^b | 22.3 (dd) ^e | 34.0 (d) | 11.0 (d) ^e | | | | 12.0 | |
| 5c ^c | -1.6 (dd) ^f | 33.7 (d) | 11.6 (d) ^f | | | | 12.1 | |
| 7a ^b | 5.5 (d) | 23.0 (dd) | 24.9 (d) | 1988 | nr | 137 | 30.5 | 12.2 |
| 7a' ^b | 3.6 (d) | 23.2 (dd) | 21.0 (d) | 1973 | 63 | 140 | 30.9 | 12.4 |
| 7b' ^b | 3.6 (d) | 23.9 (dd) | 21.0 (d) | 1972 | 62 | 140 | 30.6 | 12.8 |
| 9c | -6.5 (d) | 45.0 (dd) | 29.9 (d) | 1870 | nr | 120 | 34.0 | 10.7 |
| 9f | 3.8 (d) | 45.6 (dd) | 29.8 (d) | 1884 | 18 | 99 | 31.8 | 10.2 |

^a Recorded at 40.53 MHz in CDCl_3 at 293 K, unless stated otherwise. J values in Hz. Multiplicity labels and abbreviations: s = singlet, d = doublet, dd = doublet of doublet, nr = not resolved. ^b In C_6D_6 . ^c In toluene- d_8 . ^d Recorded at 121.48 MHz. ^e $^3J(\text{P}_A, \text{P}_C) = 16.0$ Hz. ^f $^3J(\text{P}_A, \text{P}_C) = 17.0$ Hz.

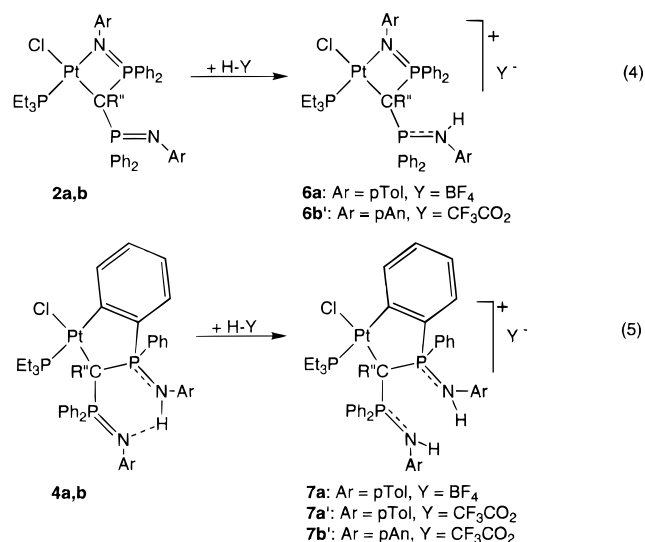
which indicates that C_{om} is *cis* to P_AR_3 ,³⁸ instead of *trans* as in **4**. Second, the methine-carbon resonance lies at a much higher frequency (35.0 ppm) and shows spin-spin coupling with all three phosphorus atoms, which implies that CH is coordinated *trans* to P_AR_3 . The CH group is probably more weakly coordinated due to the *trans* influence of the phosphine as compared to CH in the complexes **2**, **3**, or **4**, and its chemical shift resembles the frequency for ylide carbon atoms.^{14b,c} In the ^1H NMR of **5**, a CH resonance is found at about 4.1 ppm (ddd, $J(\text{P}, \text{H}) \approx 7, 12$, and 15 Hz), also at a higher frequency than their Pt analogues **4**. Furthermore, a broad signal is observed for **5a** at approximately 10 ppm, characteristic for a NH group.^{12,33}

A comparison of the ^{31}P NMR data of **5a** with **5c** with the results described above shows that the doublet resonance at about 34 ppm should be assigned to an aminophosphonium entity. The doublet at ca. 11 ppm agrees well with the value found in **3** for a noncoordinated $\text{P}=\text{N}$ group. The remaining signal, a doublet of doublet, belongs to P_AR_3 (**5a**, PEt_3 ; **5c**, PMe_2Ph), as confirmed for **5c** by selective irradiation in the $^{31}\text{P}_A$ resonance frequency at -1.6 ppm resulting in a collapse of the doublet PMe resonances into singlets in the ^1H NMR. These data are consistent with either of the two structural proposals for **5** given at the top of Table 8 and in eq 3.

An in situ ^{31}P NMR experiment, following the reaction sequence of **3c** into **5c**, revealed an intermediate **5c**ⁱ, which shows striking resemblance to the ^{31}P NMR data for **4c,d**, a doublet at -10 ppm ($\delta(\text{P}_A)$, $^3J(\text{P}_A, \text{P}_B) = 36.4$ Hz), a doublet of doublet at 24.7 ppm ($\delta(\text{P}_B)$, $^3J(\text{P}_A, \text{P}_B) = 36.4$ Hz, $^2J(\text{P}_B, \text{P}_C) = 19.8$ Hz), and the $^{31}\text{P}_C$ resonance at 20.0 ppm (d). The last two resonance relate to the remote $\text{P}=\text{N}$ groups, which are presumably connected via an H-bridge, similar to **4**. The coupling pattern suggests that **5c**ⁱ has a *trans* $\text{P}_A\text{--Pd--C}(\text{sp}^2)$ geometry, like in **4**, since the multiplicity of the ^{31}P signals changes drastically upon isomerization of **5c**ⁱ into **5c**. The

signals belonging to the intermediate **5c**ⁱ disappear when the three ^{31}P resonance signals of complex **5c** show up. The sequence of formation of **5c** is shown in Scheme 3 and will be discussed at the end of this paper.

Reactivity of the Platinacycles **2 and **4** with HY ($\text{Y} = \text{BF}_4, \text{CF}_3\text{COO}$).** The cationic platinacycles **6a,b'** and **7a,a',b** were readily obtained by quantitative protonation of the noncoordinated $\text{P}=\text{N}$ groups in **2a,b** and **4a,b**, respectively, with 1 molar equiv of HBF_4 or CF_3COOH (eqs 4 and 5), at 20 °C in CH_2Cl_2 , benzene, or toluene, analogous to the earlier reported protonation reactions of Rh- and Ir-bis(iminophosphoranyl)methanide complexes.⁴

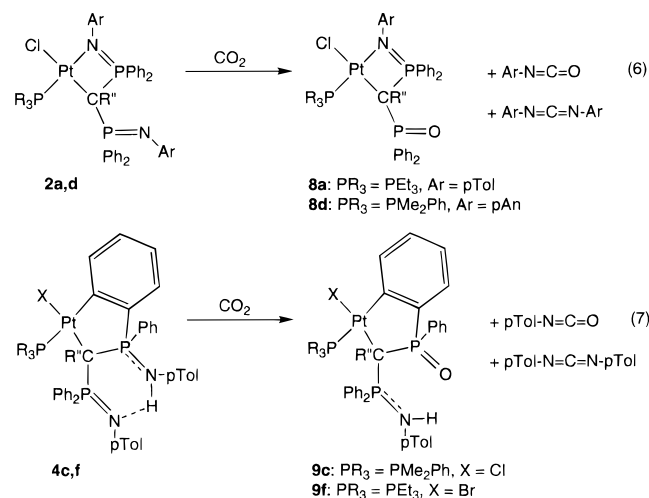


The new cationic orthometalated compounds **7** are fairly stable in solution when stored under nitrogen; however, decomposition is observed when they are held in solution for 2–3 weeks. In general, the solubility of the cationic complexes **7**, in for instance benzene, is better than its neutral counterparts (**4**).

The NMR spectroscopic data for the cationic four-membered platinacycles **6**, which show a characteristic NH resonance in the ^1H NMR (Table 4) and a high-frequency shift for P_C (Table 5), are identical to the data that have been reported previously for the products obtained from the bridge-splitting reactions of neutral bis(iminophosphoranyl)methanes $\text{CH}_2(\text{PPh}_2=\text{NAr})_2$ (Ar = *p*-tolyl, *p*-anisyl) with $\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2$ in the presence of NaY.¹² The protonation reaction is reversible as the neutral complexes **2a,b**, are regenerated upon reaction of the cationic complexes **6a,b** with an appropriate base (LDA, NaH, DBU, or 1 equiv of BIPM¹²).

The NMR data for **4** and **7** (see Tables 4 and 8) are quite similar, except for the occurrence of two NH resonances in the ^1H NMR for **7** and shifts due to the ionic character of **7**, which indicates that the basic structure of the orthoplatinated complexes hardly changes upon protonation of **4**.

Reactivity of the Platinacycles 2 and 4 with CO_2 . The complexes **2a,d** and **4c,f** reacted with 1 molar equiv of CO_2 to give the new platinum complexes **8a,d** and **9c,f**, respectively, in high yields (95–100%) together with aryl isocyanate and bis(aryl)carbodiimide in an approximate 6:1 ratio (eqs 6 and 7).



Complexes **8a,d** could not be separated from the organic byproducts, since they are all soluble in diethyl ether or petroleum ether (40/60). Other apolar solvents (pentane, hexane) were unsuitable for washing out the byproducts. The reactions proceeded much faster in CH_2Cl_2 (2.5 h for **2**, 15 min for **4**) than in benzene or toluene (3.5 h for **2**, 3 h for **4**). Continued stirring under an atmosphere of CO_2 for another 20 h did not lead to reaction with the second PN group; decomposition was observed instead, presumably due to traces of H_2O .

The structure of the complexes **8** is directly deduced from the characteristic high-frequency shift of the P_C resonance (Table 5), which establishes the conversion of the remote $\text{P}=\text{N}$ group in **2** into a $\text{P}=\text{O}$ function,⁴² similar to the earlier reported reactions of analogous Rh- and Ir-bis(iminophosphoranyl)methanide complexes,⁴ the BIPM ligand,¹⁷ and other phosphinimines with CO_2 .⁴³ The sharp doublets in the ^{31}P NMR indicate that complexes **8a,d** have a rigid structure on the NMR

time scale in solution at room temperature, in contrast to the fluxional complexes **2** and **3**.

The identification of the aza-Wittig products **9c,f** was more complicated, since the ^{31}P NMR (Table 8) shows that both P_B and P_C have shifted to higher frequencies when compared to the corresponding signals of **4c,f**, which indicates that both PN functions have changed in character. The signal at 45.3 ppm resembles the $\text{P}=\text{O}$ resonance frequency as reported for the four-membered platinacycles $[\text{Pt}(\text{L}_2)\{\text{NPhP}(\text{=O})\text{PhNPh}\}]$, $\delta(\text{P}=\text{O}) = 38.9\text{--}46.5$ ppm,⁴⁴ and is therefore assigned to a $\text{P}_\text{B}=\text{O}$ moiety contained in a five-membered ring in our case. The ^{31}P signal at 29.9 ppm is characteristic for a PPh_2NH -aryl moiety,^{12,33} like in **6**, which is in agreement with the observation of NH and $\text{C}_6\text{H}_4\text{R}'$ -4 resonances in the ^1H NMR (Table 4 and Supporting Information) and confirms that only one $\text{P}=\text{N}$ group has reacted with CO_2 . Comparison of these data with the structure analysis of **4c,f**, shows that an H-shift from the original $\text{P}_\text{B}\text{NHAr}$ group to the previous $\text{P}_\text{C}=\text{NAr}$ group must have taken place upon reaction with CO_2 (eq 7).

Discussion

Formation of the Four-Membered Metallacycles 2 and 3. In principle there are two possible reaction pathways (Scheme 1, routes a and b) in which the anionic ligand $[\text{CR}(\text{PPh}_2=\text{NAr})_2]^-$ (**1**) might attack the precursor $\text{M}_2\text{X}_4(\text{PR}_3)_2$ (M = Pt, Pd): (a) nucleophilic attack by one of the nitrogen atoms; (b) nucleophilic attack by the methine carbon atom. Considering what is known about these types of bridge-splitting reactions by σ -donor ligands,^{3,12,13,45} a preliminary conclusion can be drawn that the N atoms of the $[\text{CR}'(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R}'')_2]^-$ ligand have the strongest σ -donor capacity, since the products **2** and **3** both have a *trans* N-M- PR_3 geometry. For instance, the recently investigated bridge-splitting reaction of $\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2$ by the neutral BIPM ligand $\text{CH}_2(\text{PPh}_2=\text{N-}i\text{pTol})_2$ gave a cationic four-membered platinacycle of similar geometry, which was formed via initial nucleophilic attack by N as evidenced by the observation of the monodentate intermediate *trans*- $\text{PtCl}_2(\text{PEt}_3)\{\text{N}(i\text{pTol})=\text{PPh}_2\text{CH}_2\text{PPh}_2=\text{N-}i\text{pTol}\}$.¹² We therefore assume that a similar reaction path (route a) also accounts for the reactions with the anionic derivative. If the methine-C would have initiated the bridge-splitting reaction (route b), the other geometric isomer with C *trans* to PR_3 would have been formed, which is never observed (Scheme 1).

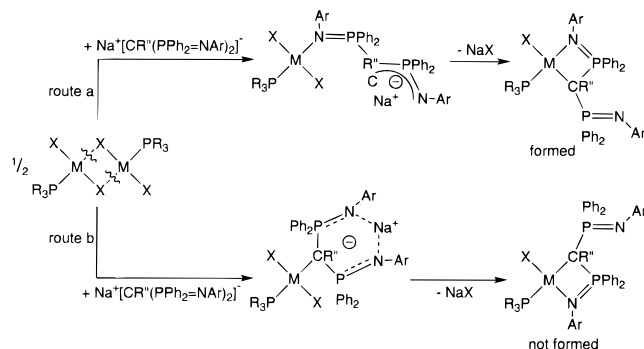
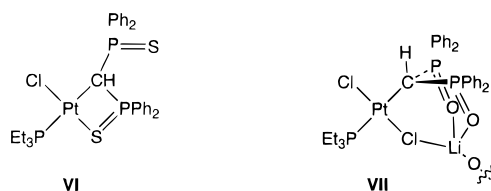
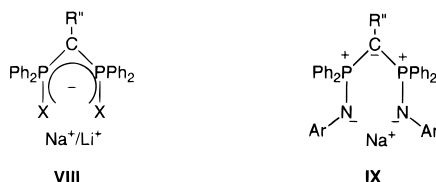
The preference for nucleophilic attack by N (route a) instead of C (route b) of the anionic ligand (**1**) is supported by earlier reported reactions of $\text{Li}[\text{CH}_2\text{-PPh}_2=\text{NC}_6\text{H}_4\text{R-4}]^{29}$ and $\text{Li}[\text{CH}(\text{PPh}_2=\text{NC}_6\text{H}_4\text{R-4})_2]^{14}$ with $[\text{ML}_2\text{Cl}]_2$ (M = Rh, Ir; $\text{L}_2 = \text{COD}$, NBD, $(\text{CO})_2$). For these ligands a strong dependence of the product formation on the nucleophilicity of the nitrogen atom, as a

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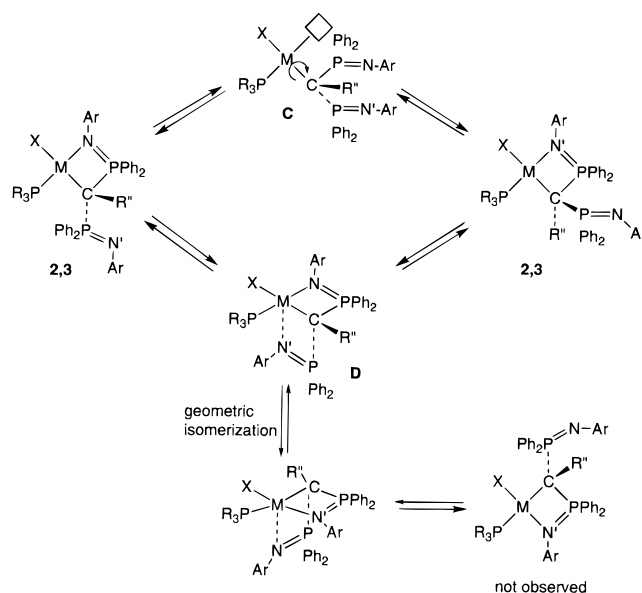
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Scheme 1. Different Routes for the Bridge-Splitting Reaction with Bis(iminophosphoranyl)methanide**Chart 4****Chart 5**

function of the substituent 4-RC₆H₄, has been observed; e.g. for R = NO₂, no reaction or decomposition took place.^{4,29} These findings differ considerably with the results reported by Dixon and co-workers, wherein bridge-splitting reactions of Pt₂Cl₄(PEt₃)₂ by the ligands Li[CH(PPh₂=S)₂]³ and Li[CH(PPh₂=O)₂]⁴⁶ have led to the formation of the initial products **VI** and **VII**, respectively (Chart 4), by nucleophilic attack of the carbanion on the Pt–Cl bond *trans* to the stabilizing phosphine,^{3b} as demonstrated by route b in Scheme 1.

The overall conclusion that can be drawn from this comparison is that the nucleophilicity of the σ -donor atoms play a significant role in the initial product formation in case of these multifunctional ligands and determines the preference for the initial attack of N > C > S > O of the [CH(PPh₂=X)₂][–] ligands (with X = NAr, S, O) to Pt₂X₄(PR₃)₂. Whether or not ring closure takes place is strongly dependent on the nucleophilicity of the remaining two potential σ -donor atoms.

The differences in product formation could also depend on the structural differences within the ligand itself (in solution), e.g. bonding of M⁺ to the anion [CR'(PPh₂=N-aryl)₂][–] (M = Na, Li), in comparison to [CH(PPh₂=X)₂][–] (with X = S, O). For the [CH(PPh₂=X)₂][–] ligands (X = CR₂, S, O) it is generally accepted that the negative charge is completely delocalized over the π -system and that M⁺ is situated between the two X functions (**VIII**)^{1c,3b,47} (Chart 5), which probably makes these σ -donor atoms less nucleophilic than the methine carbon.

Scheme 2. N,N' Exchange in 2 and 3

For several related compounds a N–M linkage has been established,⁴⁸ and from the high-frequency shift in the ³¹P NMR and the Me group in the ¹H NMR for Na[CMc(PPh₂=N-*p*-tolyl)₂] (**1c**) in comparison to the neutral ligand, 1,1-BIPE,¹³ it is also deduced that Na⁺ is probably strongly coordinated to both N atoms, as strong polarization of the P=N bonds has occurred (**IX**). So, as compared to other ligands (with X = S, O) the electron density in [CR'(PPh₂=NR-aryl)₂][–] is expected to be localized on the N atoms instead of being delocalized.

Fluxionality of 2 and 3. Variable-temperature NMR spectroscopy of the neutral four-membered metallacycles [MX(PR₃)₂{CR'(PPh₂=N-aryl)₂–C,M}] (**2**, M = Pt, X = Cl, Br; **3**, M = Pd, X = Cl) has established that an intermediate (for **2**) or fast (for **3**) N,N' exchange process occurs on the NMR time scale at 293 K, which can be brought into slow exchange by cooling to 253 K (**2**) or 183–190 K (**3**). In view of the structural similarities between the Pt complexes **2** and the Pd complexes **3** we gather that their fluxional processes probably follow the same exchange mechanism, which will be elaborated only for the four-membered palladacycles **3**.

We have shown that the two halves of the bis(iminophosphoranyl)methanide ligand in **3a–c** become magnetically equivalent on the NMR time scale (¹H, 300 MHz) at 293 K. For complex **3c** we have also found that the diastereotopic PMe groups become equivalent, indicating that inversion of configuration at the methine carbon atom occurs. Since the bis(iminophosphoranyl)methanide ligands in the complexes **2** and **3** are coordinated by a strong M–C bond, as evidenced by ¹H and ¹³C NMR, the dynamic process must involve a net rotation of the [CH(PPh₂=N-aryl)₂][–] ligand around the M–C axis, whereby P=N and P=N' exchange positions as indicated in Scheme 2. As the fluxional processes are concentration independent, they must proceed intramolecularly.

Two possible mechanisms could account for the N,N' exchange processes in **2** and **3**, an associative mecha-

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nism, involving five-coordinated intermediates, or a dissociative mechanism, in which the M–N bond is broken and a T-shaped intermediate is formed. Earlier investigations in our laboratory concerning the fluxional processes of analogous complexes $[\text{ML}_2\{\text{CH}(\text{PPh}_2=\text{N-aryl})_2\}\text{-C,N}]$ (with $\text{M} = \text{Rh, Ir}$; $\text{L}_2 = \text{COD, NBD, (CO)}_2$) pointed to an associative N,N' exchange process in which geometric isomerizations via five-coordinated intermediates are involved.⁴ Only such an isomerization step could account for the equivalence of the two halves of the bis(iminophosphoranyl)methanide ligand as well as for the coligands (L_2) in the Rh and Ir complexes.⁴

Clearly, such an associative mechanism is not operating for the Pt– and Pd–bis(iminophosphoranyl)methanide complexes **2** and **3**, since this would have led to geometric isomerization around the metal center, resulting in a C,N-coordinated species with opposite *trans* ligands, which is not observed. An associative mechanism involving only exchange of the pendant and bound σ -donor groups via **D** (Scheme 2) explains the observed phenomena for the metallacycles **2** and **3**. However, a dissociative route through **C** cannot be excluded. One may argue that an associative process is favored over a dissociative one, since (i) N' is a good nucleophile and (ii) the X-ray crystal structures of the $[\text{Ir}(\text{COD})\{\text{CH}(\text{PPh}_2=\text{N-}i\text{-pTol})_2\}\text{-C,N}]$ complex⁴ and $[\text{PtCl}(\text{PET}_3)\{\text{CH}(\text{PPh}_2=\text{S})_2\}\text{-C,S}]$ ³ have shown that the noncoordinated $\text{P}=\text{X}$ functions ($\text{X} = \text{N}$ or S) are already in close proximity of the metal centers. The fact that the X-ray crystal structure of complex **2e** (Figure 1) shows a different picture, i.e. the noncoordinated $\text{P}=\text{N}$ group pointing away from the metal, is probably an exception caused by the steric effect of the Me group on the coordinated methine carbon.

Also, for several other d⁸-transition metal complexes, i.e. $[\text{Pt}(\text{PET}_3)\text{Cl}\{\text{CH}(\text{PPh}_2=\text{S})_2\}]$,³ $[\text{Pt}(\text{PET}_3)\text{Cl}\{\text{C}(\text{PPh}_2=\text{S})_3\}]$,³⁷ $[\text{M}\{\text{PPh}(\text{C}_6\text{H}_4\text{SMe-}o)_2\}_2\text{X}_2]$, and $[\text{M}\{\text{P}(\text{C}_6\text{H}_4\text{SMe-}o)_3\}_2][\text{ClO}_4]_2$ ($\text{M} = \text{Pt, Pd, X} = \text{halide}$),⁴⁸ the observed S,S'-exchange processes within the bidentate ligands are assumed to operate via associative mechanisms, involving short-lived 18-electron five-coordinated intermediates.^{3,37,49} Other closely related complexes, i.e. $[\text{Rh}(\text{COD})\{(\text{O}=\text{PPh}_2)_2\text{C}(\text{PPh}_2=\text{S})\}]$,^{42b} $[\text{Ir}(\text{COD})\{(\text{S}=\text{PPh}_2)_3\text{-C}\}]$,^{50a} and $[\text{M}(\text{COD})\{(\text{O}=\text{PPh}_2)_3\text{C}\}]$ ($\text{M} = \text{Rh, Ir}$),^{50bc} exhibit similar fluxional behavior of the tris(phosphine–chalcogenide) ligand.

Reactivity of the Platinacycles **2 and **4**.** The reactions with 1 equiv of CF_3COOH and HBF_4 , giving the cationic complexes **6a,b'** (eq 4)¹² and **7a,a',b'** (eq 5), have most likely proceeded via direct protonation of the noncoordinated nitrogen atom. The same type of reactivity has been proposed for the reactions of Rh– and Ir–bis(iminophosphoranyl)methanide complexes with

CF_3COOH .⁴ The stability of the orthometalated platinum complexes **4a,b** toward protonation is remarkable. Protonation of the orthometalated aryl group does not occur, whereas this type of reactivity has been observed for other orthometalated compounds.^{38a,51a}

The aza-Wittig product **8**, obtained from the reaction of **2** with CO_2 , has proved that this type of reaction is a suitable method to investigate the reactivity or kinetic stability of coordinated phosphiminines.^{8b,c} We found that CO_2 only reacts with the pendant iminophosphoranyl group of the complexes **2a,d** (eq 6), which means that one $\text{P}=\text{N}$ function is kinetically stabilized within the metallacycle by coordination to platinum. A similar nonreactivity toward CO_2 has been reported earlier for Rh and Ir complexes containing a single C,N-coordinated iminophosphoranylmethanide moiety, e.g. $\text{RhL}_2\{\text{N}(\text{Ar})=\text{PPh}_2\text{CH}_2\}$.^{4,29} The rigidity of the product **8**, $\text{PtCl}(\text{PR}_3)\{\text{CH}(\text{PPh}_2=\text{NAr})(\text{PPh}_2=\text{O})\}$, in contrast to the fluxionality of the complexes **2**, is a direct consequence of the weak σ -donor capacity of the noncoordinated $\text{P}=\text{O}$ group and is in agreement with the nonfluxional behavior of analogous Rh and Ir complexes.⁴

The orthometalated complexes **4c,f** also react with only 1 equiv of CO_2 , but this reaction is not as straightforward as described above for the complexes **2**. The structure of the products **9c,f** (eq 7) points to the fact that $\text{P}_\text{B}=\text{NAr}$ attacks CO_2 and becomes $\text{P}_\text{B}=\text{O}$, concomitant with or after a shift of H to $\text{P}_\text{C}=\text{NAr}$ to become $\text{P}_\text{C}-\text{NHAr}$. The latter is not nucleophilic enough to undergo another aza-Wittig reaction with excess CO_2 , which explains why only one $\text{P}=\text{O}$ moiety is formed. The preference for reaction of CO_2 with $\text{P}_\text{B}=\text{NAr}$ stems from the fact that this group is more polarized than $\text{P}_\text{C}=\text{NAr}$ because of the stabilizing effect of the formally anionic orthometalated aryl group on the developing positive charge on phosphorus during an aza-Wittig reaction.

Formation of the Orthometalated Complexes **4 and **5**.** Factors that contribute to orthometalation have been summarized in several reviews^{51,52} and generally imply the following: (a) Metalation requires a certain flexibility of the ligand. (b) The presence of bulky groups on the donor group (the methine carbon atom in our case) is of importance. Bulky groups have less rotational entropy than smaller ones, and the internal entropy loss on cyclization will therefore be correspondingly lower. (c) Where four-membered rings are involved, orthometalation could occur, since their internal entropy is already small and also greater ring strain exists. These factors will promote orthometalation to energetically more favorable five-membered rings.

The most important driving force for orthometalation of the four-membered metallacycles **2** and **3** is probably the ring strain. The bulky phenyl groups on both P atoms of the C,N-coordinated bis(iminophosphoranyl)methanide ligands also supply a significant contribution to the promotion of orthometalation, which is clearly evident by looking at the X-ray crystal structure of **2e**. Figure 1 shows that the ortho H atom of the Ph group on the P within the four-membered platinacycle is in close proximity of the Pt center and is most likely to orthometalate.

There are two generally accepted mechanisms for CH bond cleavage by Pt and Pd: an oxidative addition by nucleophilic attack of the metal center on the aromatic

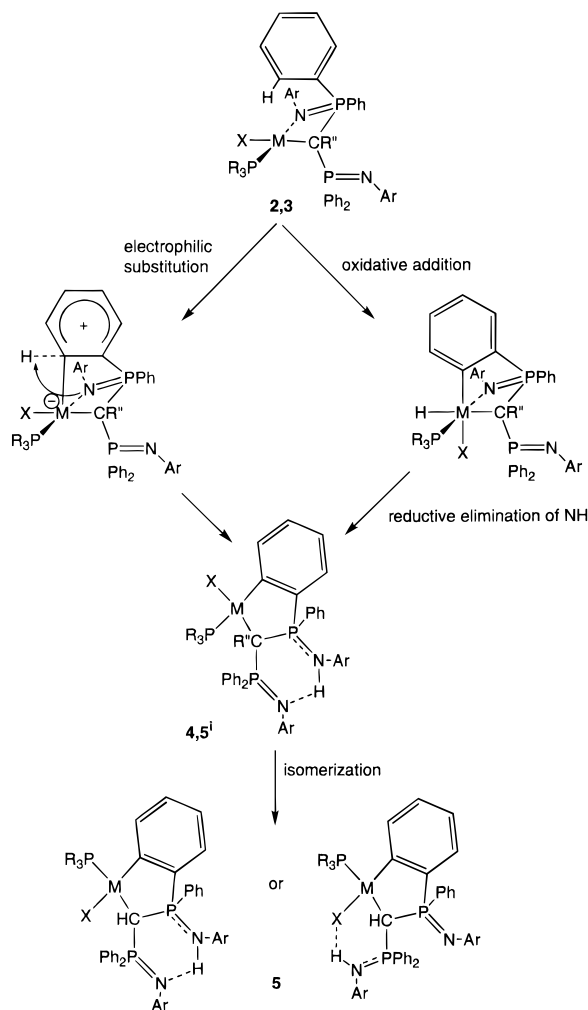
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Scheme 3. Proposed Reaction Mechanism for Orthometalation



Compound **4**: M = Pt; X = Cl, Br, I; PR₃ = PEt₃, PMe₂Ph; R' = H.
Compound **5**ⁱ and **5**: M = Pd; X = Cl; PR₃ = PEt₃, PMe₂Ph; R' = H.

ring or by an electrophilic substitution reaction.⁵² Distinction between the two mechanisms is rather complicated, especially when the H atom is eliminated in the process, as is the case for **2** and **3** where it is abstracted by N. Usually the observation of metal-hydride species provides sufficient evidence for a nucleophilic pathway. Altering the electron density on the aromatic ring or the metal center, introducing electron-donating or -withdrawing substituents, has in many cases revealed the mechanism of orthometalation.⁵²

In our case, the rates of orthometalation seem to be largely dependent on the phosphine bound to the metal. For both the Pt as the Pd complexes, the PMe₂Ph derivatives (**2c,d** and **3c**) orthometalated much faster than their PEt₃ analogues (**2a,b** and **3a,b**), whereas no significant difference is observed for the rate of N,N' exchange in the Pt complexes (**2a–f**) or the Pd complexes (**3a–c**). We have therefore eliminated the possibility that this effect is caused by the difference in cone angles of the phosphines and have attributed it to the difference in electron-donating capacity, PEt₃ > PMe₂Ph, which indicates that a diminished electron density is favorable for orthometalation, supporting an electrophilic substitution mechanism (Scheme 3).

Others have already established in a similar way that orthometalation reactions usually occur via electrophilic

aromatic substitutions for Pd in particular⁵³ but also for Pt.^{53b} These electrophilic substitutions are also often nucleophilically assisted by coordinated or free bases (e.g. base catalyzed), which certainly could account for the orthometalation reactions of **2** and **3**, where the C–H bond cleavage probably proceeds easily because an internal base is present in the form of two N atoms of the coordinated ligand, which entrap the proton. Similar features have been reported for other orthometalation reactions involving nitrogen-donor ligands, where pendant N atoms act as intramolecular proton acceptors and thus lead to acceleration of orthometalation reactions.⁵⁴ This also explains why for the PtCl(PEt₃){CH(PPh₂=S)₂} complex, which closely resembles **2** and **3**, orthometalation has not been found even at higher temperatures.^{3b}

The fact that for analogous Rh- and Ir{CH(PPh₂=N-aryl)₂} complexes no orthometalation reactions have been found, but show extreme thermal stability instead,⁴ indicates that an electrophilic mechanism is indeed favored over an nucleophilic pathway, as Rh(I) and Ir(I) are less electrophilic in nature than Pt(II) and Pd(II). It must be noted that for the earlier reported cationic four-membered platinacycles (identical to **6**) orthometalation has not been observed either (at higher temperatures), but decomposition is observed instead.^{12,55}

As shown by the X-ray crystal structure of **2e**, one of the phenyl groups on P is in close proximity of the metal center, which is most favorable for an electrophilic attack of the metal on the phenyl. Possibly, the flexibility of the C,N-coordinated bis(iminophosphorayl)methanide ligand in the complexes **2** and **3**, involved in an N,N' exchange process, facilitates the approach of the metal.

In contrast to the orthometalation reactions involving platinum, the conversion of the four-membered palladacycles **3a,c** into the orthopalladated complexes **5a,c** requires an isomerization step (Scheme 3). Fortunately, the conversion of the PMe₂Ph derivative **3c** already takes place at room temperature, which made it possible to observe an initial product **5c**ⁱ which has the same *trans* R₃P_A–Pd–C(sp²) geometry as found for the final orthopalladated products **4**. In keeping with recent results by Vicente and co-workers,^{14d} where the PR₃ ligand in orthopalladated compounds [PdCl(PR₃){2-C₆H₃RP(Ar)₂C'HR''}-C,C'] is positioned *trans* to the Pd–C(sp³) bond instead of *trans* to Pd–C(sp²), the isomerization of complex **5c**ⁱ is probably driven by the fact that the *trans* influence of sp²-C > sp³-C, giving the thermodynamically more stable *trans* R₃P–Pd–C(sp³) isomer **5c**. No geometric isomerization has been observed for the platinum complexes **4**, probably due to the

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(55) One would expect that if orthometalation takes place via an electrophilic pathway, the reaction should proceed more readily for these cationic derivatives in view of the more positive character of the metal center. The fact that this is not the case is probably due to the relatively strong Pt–N bonds in the cationic complexes as compared to the relatively weak M–N bonds in **2** and **3**.

overall higher thermal stability of the platinum complexes as compared to their palladium analogues **5ⁱ**.

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Supporting Information Available: Two ¹H NMR tables, containing the complete data for the four-membered metallacycles **2**, **3**, **6**, and **8** and the orthometalated compounds **4**, **5**, **7**, and **9**, respectively, and further details of the structure determinations, including tables of hydrogen coordinates and *U* values, bond lengths and angles, and anisotropic thermal parameters for **2e** and **4a** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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