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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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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Received August 10, 1995

Reaction of the sodium bis(iminophosphoranyl)alkanide compounds Na[CR”’(PPh2=NC6H4R’-4)2] (1a, R”’ = H, R’ = CH3; 1b, R”’ = H, R’ = OCH3; 1c, R”’ = CH3, R’ = CH3) with PtCl3(PR3)2 (M = Pt, Pd; X = Cl, Br; PR3 = PEt3, PMe2Ph) yields the four-membered metallacycles MX(PR3)3CR”’(PPh2=NC6H4R’-4)2 (2a–f, M = Pt; 3a–c, M = Pd), containing the bis(iminophosphoranyl)alkanide ligand coordinated in a ω-C,ω-N chelating fashion. The molecular structure of 2e (X = Cl, PR3 = PMe2Ph, R”’ = CH3, R’ = CH3) has been determined by X-ray crystallography. The 1,1-bis(iminophosphoranyl)ethanide ligand (1c) in 2e is ω-C,ω-N-chelated toward the square-planar-surrounded Pt, with N coordinated to Cl (Pt−C = 2.116(4) Å), resulting in a puckered M−N−P−C metallacycle and one noncoordinated phosphinimino 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 orthometallated complexes PtX(PR3)2[2-C6H4PPh(NHC6H4R'-4)CHPPh2=NC6H4R'-4] (4a–d,f) and PdCl(PR3)2[2-C6H4PPh(NHC6H4Me-4)CHPPh2=NC6H4Me-4] (5a,c). The X-ray crystal structure of 4a (X = Cl, PR3 = PEt3, R”’ = CH3) has been determined. The new mononuclear orthometallated Pt complexes 4 contain a ω-C,ω-C’ coordinated [2-C6H4-PPh(NHC6H4R'-4)CR”’(PPh2=NC6H4R’-4)4]− ligand, in which the ortho-H (Ph) has shifted to a bridge position between the two noncoordinating nitrogen atoms. The four-membered platinnacycles 2a,b and the orthometallated platinnacycles 4a,b react with 1 equiv of HBF4 or CF3COOH to give 6a,b and 7a,b, respectively, by protonation of the noncoordinated P=N=NC6H4R’-4 groups only. Addition of CO2 to 2a,d and 4c,f results in an aza-Wittig reaction, giving PtCl(PR3)(CH(PPh2=NC6H4R’-4)(PPh2=O)) (8a,d) and PtX(PR3)(2-C6H4(PPh=O)-CHPPh2=NC6H4R’-4) (9c,f), respectively, together with aryl isocyanate and bis(aryl)carbodiimide.

Introduction

The coordination chemistry of phosphorus-containing monoanions 1 (Chart 1), that are structurally related to acetylacetone (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 [CH2-(PR2=CR’)]2 by LDA, NaH, BuLi, or other strong bases, are convenient precursors for transmetalation reactions.

References


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

Such a coordination mode was rather peculiar since the closely related bis(chalcogenophosphoranyl)methanide ligands \( \text{CH}([\text{PR}_2=\text{X})(\text{PR}_2=\text{Y})]) \) (\( X = O, S, Se \), coordinate exclusively as \( X \), chelates to Rh and Ir,\(^{1,2}\) but C, X and Y coordination was observed for these ligands with Pt\(^{3,4}\) and Au.\(^5\) Furthermore, an entirely different reactivity has been observed for the related N-SiMe\(_2\)-substituted bis(chalcogenophosphoranyl)methanide ligand \( \text{CH}([\text{PR}_2=\text{NSiMe}_2])_2 \), forming planar six-membered metallacycles with WCl\(_6\) under elimination of Me\(_3\)Si-halide.\(^6\)

It was therefore interesting to examine whether the bis(N-arylaminophosphoranyl)methanide ligands would coordinate to Pt and Pd similarly as found for Rh and Ir,\(^4\) especially since only a few phosphinimine complexes of Pt\(^7\) and Pd\(^8\) 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]methanide)phosphorus ylides, \( \text{CH}_2([\text{PR}_2=\text{N}-\text{aryl}])_2 \), react with \( \text{PtCl}_2(\text{PR}_3)_2 \) to give cationic or neutral four-membered platinacycles (IV) (Chart 3), depending on the metal-to-ligand ratio, in which the ligand is \( \sigma\)-N,\(\sigma\)-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-BIP), which has a 1,1-ethanediyl bridge instead of a methylene bridge between the two P--N moieties, resulted in the formation of \( \sigma\)-N,\(\sigma\)-N'-coordinated Pt(II) complexes (V).\(^13\)

In view of the ring strain in the above mentioned four-membered \( M--X--P--C \) metallacycles (\( M = \text{Rh}, \text{Ir}, \text{Pt} \); \( X = S, \text{Se} \) ), analogous palladium complexes could not be obtained due to instability.\(^12\) Similar reactions with the modified ligand 1,1-bis([iminophosphoranyl])ethane (1,1-BIP), which has a 1,1-ethanediyl bridge instead of a methylene bridge between the two P--N moieties, resulted in the formation of \( \sigma\)-N,\(\sigma\)-N'-coordinated Pt(II) complexes (V).\(^13\)

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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. \(^{1}H\) and \(^{31}P\)\((1H)\) 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 SiMe\(_4\) and 85% H\(_3\)PO\(_4\) as the

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(e) Vicente, J.; Chicote, M. T.; Laguna, M.-C.; Jones, P. G.; Bembenek, E. Organometallics 1993, 13, 1243.
external standards, respectively, positive shifts to high frequency of the standard in all cases. 11C NMR data were obtained from Bruker AMX 300 and ARX 400 spectrometers (operating at 75.48 MHz). Using SiMe3 as the external standard. Elemental analyses were carried out by Donnis and Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. PtX4(PR3)2, PdCl2(PR3)2 (with PR3 = PEt3, PMe2Ph; X = Cl, Br), the bis(iminophosphoranylmethanes) (BIPM) CH3(PPh2=NC6H4R=4)4, R = Me, OMe)15 and 1,1-bis(iminophosphoranylmethane) (1,1-BIPE) CH3- (PPh2=NC6H4R=4)4,15 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 NaNH (washed with ether, dried in vacuo, and stored under nitrogen). After 2 h, during which H2 gas evolved, the light yellow solution was filtered and the residue washed with THF (2 × 5 mL). The clear filtrate, containing only the bis(iminophosphoranylmethane) Na[CH3(PPh2=NC6H4R=4)]4 (1a), R = Me; 1b, R = OMe)15 in quantitative amount, was used directly for the preparations described below. For deprotonated 1,1-BIPE, Na[CCH3(PPh2=NC6H4R=4)]4 (1c), a different procedure was used; NaNH 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 NaNH, was directly used for reaction with PtCl2(PMe4)2 (see 2e), as removal of NaNH by filtration resulted in back-reaction into the neutral ligand.

Na[CMe(PPh2=NC6H4Me=4)]4 (1d). 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 C6H6, since traces of H2O result in the formation of 1,1-BIPE.-4 H NMR (C6D6): phenyl rings, δ 8.0–7.1 (m, 20H); NC6H4CH3, δ 6.50, 6.63 (d, 8H, J2,3 = 8.7 Hz, J5,6 = 15.5 Hz); C6H4CH3, δ 2.20 (s, 6H). 31P NMR (C6D6): δ(P) = 23.4 ppm (s). 13C NMR (C6D6, 75.48 MHz, 293 K): CCH3, δ 16.97 (t, 3J(C,P) = 8.8 Hz); CCH3 not resolved; C6H4CH3δ 21.23 (dd, 11C2(Pd, C) = 19.7 Hz); 130.48 (s, Cmeta); 125.14 (s, Cpara); 153.99 (vs, Cipso); phenyls, δ 138.4 (dd, Cipso) J2,3(Pd, C) = 105.7 Hz, J5,6(Pd, C) = 11.6 Hz); 133.88 (vs, Cmeta) J2,3(Pd, C) = 128.56 (observed by C6D6, Cpara); 130.61 (s, Cpara).

Synthesis of 2a–f, PtX2(PR3)2CR2(PPh2=NC6H4(R)=4)2-CN (PR3 = PPh3, PMe2Ph; X = Cl, Br, R = CH3, OCH3, R′ = H, Me). To a stirred solution of freshly prepared Na[CR2(PPh2=NC6H4(R)=4)]4 (0.45 mmol) in 30 mL of THF was added a solution of PtX2(PR3)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 THF. The combined yellow 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%).

PdCl2(PeMe3)(PHP2=NC6H4OCH3-4)(2a). Anal. Calcd for C36H35ClNO2Pd: C, 43.9; H, 4.1; N, 2.1; P, 6.8. Found: C, 43.7; H, 4.1; N, 2.7; P, 6.7.

PdCl2(PeMe3)(PHP2=NC6H4CH3-4)(2a). Anal. Calcd for C36H35ClNO2Pd: C, 43.9; H, 4.1; N, 2.1; P, 6.8. Found: C, 43.7; H, 4.1; N, 2.7; P, 6.7.

PdCl2(PeMe3)(PHP2=NC6H4OCH3-4)(2a). Anal. Calcd for C36H35ClNO2Pd: C, 43.9; H, 4.1; N, 2.1; P, 6.8. Found: C, 43.7; H, 4.1; N, 2.7; P, 6.7.

PdCl2(PeMe3)(PHP2=NC6H4CH3-4)(2a). Anal. Calcd for C36H35ClNO2Pd: C, 43.9; H, 4.1; N, 2.1; P, 6.8. Found: C, 43.7; H, 4.1; N, 2.7; P, 6.7.
C₄₅H₅₀ClN₂P₃Pt, diethylether (20 mL) and pentane (20 mL) and dried in vacuo, (precipitated NaX) was washed with 10 mL of THF. The clear solution was filtered and evaporated to dryness. The residue was washed with pentane (2 x 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound 3a or 3c.

PdCl(PPh₃)₂·2C₂H₅OH(PH)(NC₄H₄Me-4)CHPPPh₂-N(C₆H₄R-4)Me-4 (5a). Anal. Calc for C₃₈H₴₃ClNOP₃Pt: C, 63.61; 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, calc for C₃₉H₴₂ClNP₃Pt, m/z 853.7). ¹³C NMR (CD₂Cl₂, 293 K, 75.48 MHz): δ 35.0 (dd, Pd – C, δ (P) = 49, 58, 72 Hz, with n = 1, 2); δ 9.3 (s, PCH₂CH₃); δ 17.0 (d, PCH₂CH₃). (J) (P) = 24 Hz); C₆H₄CH₃-4, δ 21.4 (s, CH₃); δ 141.2 and 148.4 (d, (Cipso) (P), (J) (P) ≤ 2 Hz); δ 120.4, 122.9 (d, (Cortho, (J) (P) = 9.3, 17.1 Hz); δ 129 – 131 (Cmeta); δ 126.3 and 130.6 (s, (Cpara); phenyls, δ 126.3 (d, 1(Cipso, (J) (P) = 95 Hz); remaining (δ(Cipso) obscured; δ 133.4, 134.8 (d, (Cortho, (J) (P) = 8 and 11 Hz, respectively); δ 129 – 131 (Cmeta); 131.4, 131.9, 132.0, 132.7 (s, (Cpara); δ 135.7 (dd, (Cipso, (J) (P) = 18 Hz, (J) (P) = 13 Hz); δ 157.9 (dd, (Cortho, (J) (P) = 27 and 3 Hz).

PdCl(PMe₂Ph)₂·2C₂H₅OH(PH)(NC₄H₄Me-4)CHPPPh₂-N(C₆H₄R-4)Me-4 (5c). FAB MS: found, m/z = 873 (5c), 837 (5c – Cl) (M, calc for C₃₉H₴₂ClNP₃Pd, m/z 873.7). Further characterization is based on ¹H and ³¹P NMR spectroscopy.

Following the Reaction Sequence in the Formation of 5c. Compound 3c was dissolved in 0.5 mL of toluene-d₈ in a 5 mm NMR tube, and the reactions were monitored by ¹H and ³¹P NMR. At 20 °C, the first conversion of 3c into 5c took place as evidenced by the appearance of three new ³¹P resonances. The solution was then heated shortly, which resulted in some yellow precipitation. The ³¹P NMR showed complete conversion of both 3c and 5c into 5c.

Reaction of 2a,b with HBF₄ or CF₃COOH. To a solution of freshly prepared [PtCl(PMe₂Ph)₂] (0.10 mmol) in 30 mL of THF, 0.32 mmol of CF₃COOH was added in a solution of PtCl₂X₄-(PR₃)₂ (0.16 mmol) in 10 mL of THF, and the mixture was stirred for 30 min at 20 °C. The cloudy solution was filtered and evaporated to dryness. The residue was washed with pentane (2 x 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound 3a or 3c.

PdCl(PPh₃)₂·2C₂H₅OH(PH)(NC₄H₄Me-4)CHPPPh₂-N(C₆H₄R-4)Me-4 (2a,b). Reaction of 2a,b with HBF₄ or CF₃COOH. To a solution of freshly prepared [PtCl(PPh₃)(PEt₃)] (0.10 mmol) in 30 mL of THF, 0.32 mmol of CF₃COOH was added in a solution of PtCl₂X₄-(PR₃)₂ (0.16 mmol) in 10 mL of THF, and the mixture was stirred for 30 min at 20 °C. The cloudy solution was filtered and evaporated to dryness. The residue was washed with pentane (2 x 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound 3a or 3c.

Reaction of 2a,b with HBF₄ or CF₃COOH. The reactions were performed similar as described above for the reactions with 3a,b giving [PtCl(PPh₃)₂·2C₂H₅OH(PH)(NC₄H₄R-4)](2a,b). The solution was filtered and evaporated to dryness. The residue was washed with pentane (2 x 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound 3a or 3c.

PdCl(PPh₃)₂·2C₂H₅OH(PH)(NC₄H₄Me-4)CHPPPh₂-N(C₆H₄R-4)Me-4 (2a,b). Reaction of 2a,b with HBF₄ or CF₃COOH. The reactions were performed similar as described above for the reactions with 3a,b giving [PtCl(PPh₃)₂·2C₂H₅OH(PH)(NC₄H₄R-4)](2a,b). The solution was filtered and evaporated to dryness. The residue was washed with pentane (2 x 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound 3a or 3c.

PdCl(PMe₂Ph)₂·2C₂H₅OH(PH)(NC₄H₄Me-4)CHPPPh₂-N(C₆H₄R-4)Me-4 (2c,d). Reaction of 2a,b with HBF₄ or CF₃COOH. The reactions were performed similar as described above for the reactions with 3a,b giving [PtCl(PMe₂Ph)₂·2C₂H₅OH(PH)(NC₄H₄R-4)](2c,d). The solution was filtered and evaporated to dryness. The residue was washed with pentane (2 x 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound 3a or 3c.

**Experimental Section**

**Synthesis of Orthopalladated Compounds 4a-d, f, [PdCl(PPh₃)]·2C₂H₅OH(PH)(NC₄H₄R-4)CHPPPh₂-N(C₆H₄R-4)C-C(1PR₃)·(PMe₂Ph). A solution of freshly prepared Na[PtCl₂(PPh₃)(PEt₃)] (3a) (0.48 mmol) in the cloudy solution was filtered and evaporated to dryness. The residue was washed with pentane (2 x 20 mL) and dried in vacuo, giving a yellow solid in 76–80% yield. The washings contained compound 3a or 3c.
Table 1. Crystallographic Data for 2e and 4a compounds

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<th>2e</th>
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<tr>
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<td>C₆H₄H₂CIN₃P₂Pt</td>
</tr>
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<td>9.4085(8)</td>
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<tr>
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<td>11.050(2)</td>
</tr>
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<td>c, Å</td>
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<td>19.916(2)</td>
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<td>1.552</td>
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<td>0.12 × 0.12 × 0.25</td>
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<table>
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<tr>
<td>σ(Cl)</td>
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</table>

washed with diethyl ether (2 × 20 mL), and dried in vacuo, giving the white compound [PX(PR₃)₂(C₆H₄)]₂(μ-O)(μ-O)(μ-O)CPPPh₃-SiPh₃, which was recrystallized from CHCl₃ in 5 mm NMR tube and showed a complete conversion within 10 min. FAB MS: found for [C₆H₄]⁺ m/z = 873 (9c), 837 (9c - Cl) (M, calc for C₆H₄H₂CIN₃P₂Pt, 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 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 0.990. Structure 2e was solved by direct methods and refined by full-matrix least-squares techniques. The final cycle of 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 > 2σ(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 KF² is 0.0005. The final difference Fourier showed no residual density outside −0.28 and 0.53 eÅ⁻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 (Σ4) in the range 11.5° < 2θ < 14.0°. The unit-cell parameters were checked for the presence of higher lattice symmetry. 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 (DMFABS23 as implemented in PLATON23). The structure was solved by automatic Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).24 Refinement on F² 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 DEC-station 5000/125.

Results

Synthesis of Pt− and Pd−Bis(iminophosphoranyl)alkanide Complexes 2 and 3. Reactions of sodium bis(iminophosphoranyl)alkanide, Na[R−C(PP₂)(CH₃CH₂)₁₄]₂, and tolyl isocyanate and bis(20 mL), and dried in vacuo, giving the white compound [PX(PR₃)₂(C₆H₄)]₂(μ-O)(μ-O)(μ-O)CPPPh₃-SiPh₃, which was recrystallized from CHCl₃ in 5 mm NMR tube and showed a complete conversion within 10 min. FAB MS: found for [C₆H₄]⁺ m/z = 873 (9c), 837 (9c - Cl) (M, calc for C₆H₄H₂CIN₃P₂Pt, m/z 873.3).


platinum and palladium precursors $\text{M}_2\text{X}_4(\text{PR}_3)_2$ (M = Pt(II), Pd(II); $\text{PR}_3 = \text{PET}_{3}, \text{PMe}_2\text{Ph}; \text{X} = \text{Cl}, \text{Br}$) resulted in the formation of new four-membered metallacycles 2 and 3. The ligand is $\sigma$-$\pi$-$\pi$ coordinated to the metal in all cases, leaving one of the $-\text{PH}_2-$aryl entities noncoordinated (eq 1).

The bridge-splitting transmetallation reactions are best performed in THF at 20 °C giving good yields (84–95%); other solvents like toluene or CHCl$_3$ 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 transmetallation reaction continues after redissolving the intermediate in THF, as visualized by the precipitation of NaX. In CH$_2$Cl$_2$ or CHCl$_3$ decomposition takes place, due to instability of the anionic ligands. The platinum and palladium precursors $\text{M}_2\text{X}_4(\text{PR}_3)_2$ (M = Pt(II), Pd(II); $\text{PR}_3 = \text{PET}_{3}, \text{PMe}_2\text{Ph}; \text{X} = \text{Cl}, \text{Br}$) resulted in the formation of new four-membered metallacycles 2 and 3. The ligand is $\sigma$-$\pi$-$\pi$ coordinated to the metal in all cases, leaving one of the $-\text{PH}_2-$aryl entities noncoordinated (eq 1).
(iminophosphoranyl)methanides show comparable N−M−C angles and ring puckering, i.e., for [Ir(CH2PPh2=CH2)2]COD] a N−Ir−C angle of 73.4(4)° and folding of 35.1°,4,28 for [Rh(COD)(CH2PPh2=CH2)2] a N−Rh−C angle of 74.2(2)° and folding of 30.4° and for [Rh(COD)(CH(PPh2=CH2)2)2(COD)] 13C values of 73.1(1) and 33.6° respectively. Although 2e contains an C,N-coordinated 1,1-bis(iminophosphoranyl)ethane 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(sp2) bond in a four-membered ring.3a,12.32

Comparison of the phosphinimine bond lengths within the complex 2e clearly shows that the P1−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 P2−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(iminophosphoryl)ethane 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−IPhenyl moiety. In 2e, it is pointed away from the platinum center (torsion angles P1−C(1)−P2−N(2)=75.4(2)° and Pt−C(1)−P2−N(2)=172.5(3)°), whereas in the Ir complex this 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 [Pt(Cl2)(CH(PPh2=CH2)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 unususal orientation of the noncoordinated P=S 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, and the 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(iminophosphoryl)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 2f (Pt,H) of about 60 Hz, 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=CH2)2.12 The 13C NMR spectra of 2a−c show methine carbon resonances between 1.5 and 2.0 ppm (dd, 2f (P,C)=58−95 Hz; 2e (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(iminophosphoryl)methanide complex 2e has a characteristic doublet of doublet resonance in
the $^1$H NMR at 1.68 ppm ($\delta$ (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 Na$^+$[MeC(PPh$_2$)$_2$NC$_6$H$_4$Me-4)]$^+$ (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$_2$Ph. As C,N coordination induces chirality on the coordinated sp$^3$-carbon atom, two sets of signals are observed for the diastereotopic PMe$_2$Ph groups in the $^1$H 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, the platinacycles 2a–f show broadening of most $^1$H, $^{31}$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$_A$ (29.8–45.0 ppm) and P$_C$ (−1.6 to 8.0 ppm), whereas the peak due to P$_A$R$_3$ is hardly broadened and shows characteristic $^3$(Pt,P$_A$) coupling of 3713–3913 Hz for trans P$_A$–Pt–N com-
plexes.\textsuperscript{12,35} The $\text{J}(\text{Pt}, \text{P})$ value, ranging from 413 to 427 Hz, is characteristic for these types of four-membered platinacycles.\textsuperscript{12} Similar two-bond Pt-P couplings have been reported for related C,X-coordinated Pt compounds, i.e. PtCl(PR$_3$)($\text{CH(PPPh}_{2}={\text{X}}=\text{X}(\text{PPPh}_{2}={\text{Y}})$) ($\text{X} = \text{S, O, Se}$).\textsuperscript{3} Cooling the solution to 253 K (2a–c) resulted in sharpening of the P$_6$ and P$_C$ signals into doublets ($\text{J}(\text{P}_6, \text{P}_C) = 3.6–6.5$ 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-CH$_3$C$_6$H$_4$ signal, and is evident from the $^{13}$C NMR CH signal at 9.01 ppm (vt, $\text{J}(\text{P}, \text{C}) = 82$ 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 $^1$H NMR and $^{13}$C NMR at ambient temperature only a single set of resonances is found for the NC$_6$H$_4$R$^{-4}$-groups, whereas the Pt complexes show two sets of resonances for each group. For compound 3c, containing a prochiral PM$_2$Ph ligand, only one broad PM signal at 1.3 ppm is observed at 293 K, which resolves into two broad signals (“doublets”) at 185 K, 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 P=N-aryl groups of the coordinated ligand, implying equivalence of these groups on the NMR time scale. At 183–190 K the slow-exchange regime is reached for 3a,b.\textsuperscript{36} 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 P$_6$,P$_C$ coupling of 11.8–13.9 Hz. The latter is assigned to the noncoordinated P=N function, since it shows the strongest resemblance with the frequency of a free R$_3$P=NR$^-$ ligand.\textsuperscript{13,17}

From the fact that the palladium complexes 3 show similar fluxional behavior as observed for their platinum analogues 2, like in PtCl(P(PEt$_3$)$_2$($\text{CH(PPPh}_{2}={\text{S}}$)$_2$)\textsuperscript{3} and PtCl(P(PEt$_3$)$_2$($\text{C(PPPh}_{2}={\text{S}}$)$_2$)\textsuperscript{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 PtCl(P(PEt$_3$)$_2$($\text{CH(PPPh}_{2}={\text{S}}$)$_2$) with S trans to Cl.\textsuperscript{3}

For both 2 as 3, the broadness of the $^1$H 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(I) and palladium(II) complexes 4 and 5 containing the bis(iminophosphoryl)methanide ligand [HC(PPPh$_2$=NC$_6$H$_4$($\text{R}^{-4}$)$_2$)] (1a, R$^-$ = Me; 1b, R$^-$ = OMe)

were synthesized in fairly good yield (39–80%) by reaction of M$_2$X$_4$(PR$_3$)$_2$ (M = Pt(II), Pd(II); PR$_3$ = PET$_3$, PMe$_2$Ph; X = Cl, Br) with 2 equiv of Na[HC-(PPPh$_2$=NC$_6$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 CH(PPPh$_2$=NC$_6$H$_4$($\text{R}^{-4}$)$_2$)-ligand took place (eqs 2 and 3). Unfortunately, 2c 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 $\sigma$-C,\$\sigma$-C$'$-coordinated to the platinum center by the methanide-C, bridging the two phosphine-imine functions of the ligand, and by the ortho-C of the metalated phenyl group on P, resulting in a five-membered ring. The sp$^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 $^1$H 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.\textsuperscript{14,38a,39}

For the (PMe$_2$Ph)$^-$Pt and –Pd complexes 2c,d and 3c, the reaction to 4c,d and 5c already proceeds at room
temperature, which contrasts with their PEt₃ analogues. For the (PMe₂Ph)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-d₈ 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 Et₂O or pentane. The platinum compounds 4 are highly soluble in CH₂Cl₂, CHCl₃, and THF, are less soluble in toluene or benzene, and are insoluble in Et₂O 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 CO₂ (vide infra). However when pure oxygen was bubbled through a CH₂Cl₂ solution of 4b, or H₂O 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 [PtCl₂(PMe₂Ph)₂(C₆H₄CH₂CH₂CH₃)₂CHPy₂=NC₆H₄CH₂CH₃-C₆C₃] (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-saturated by P(1), Cl(1), C(25), and C(26); the latter carbons belong to the orthometalated bis(aminophosphonyl)methane 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.

An isotropic refinement has been carried out for the Et₃P ligand, since it is considerably distorted. The relatively long Pt–P(1) bond (2.315(2) Å) directly reflects the strong trans influence caused by sp²-C(25), when compared to the Pt–P bond in 2e (2.228(3) Å) trans to N or d(Pt–P) of 2.245(4) Å trans to S in [PtCl₂(PMe₂Ph)₂(CH₂PPh₂=NC₆H₄CH₂CH₃)]₃.

The ortho sp²-carbon atom, C(25), of the orthometallated phenyl group on P(2), is directly attached to the Pt center, resulting in a Pt–C(25) distance of 2.058(9) Å, which is in the range of d(Pt–C) values (1.975–2.051 Å) found for other orthometallated Pt complexes. The five-membered metallacycle in 4a also strongly resembles the C,C'-chelate ring in [PdCl₂(2-(4-MeC₆H₄)P(Tol)₂CHPy=)C₆C₃]₁₆ and [PdCl₂(2-(4-MeC₆H₄)P(NH(Tol)₂)CHPPh₂NH(Tol)₂)C₆C₃]₁₉. The H atom that originated from the ortho position of the phenyl group...
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 sp²-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).21,32 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), 0.335(2), and −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–Caw = 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 aligned 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 2pπ-orbitals of the sp²-N with the 3dπ-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 ¹²C{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 PA/Pr; 3 = (PA, Com) = 125–129 Hz and 6 (Pb, Cm) = 34–36 Hz. This corresponds well with the values reported for other orthometalated Pt and Pd complexes of the same geometry, with δ(Com) ranging from 155 to 164 ppm and ³¹P (trans,C) values of 112–115 Hz, respectively.38 Unfortunately, ³¹P (Cm) could not be resolved. The methine-C resonance is found between 13.4 and 15.4 ppm (dd, ³¹P, C ≈ 46 and 70 Hz, ³¹P (Cm) ≈ 736 Hz (4a)). Due to the multiplicity and resulting low intensity of the signals it was impossible to obtain all ³¹P (Cm) values.

The ¹H NMR of the orthometalated Pt complexes 4a–d, f (Table 4) show characteristic multiplets for the CH resonances 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 ¹⁹⁹Pt (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 Cm, 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 (ω/2 > 200 Hz in the case of 4c), which resembles the NH frequency found in the cationic four-membered platinacycle [PtCl(PPEt3)(C(PPh3=N−P−an)(PPh2NH−an)-C=N)]⁺ (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 ³¹P coupling is assigned to PA/Pr; the ³¹P (Pt, Pr) value (1913–1941 Hz) proves that PA 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 (PA, ³¹P, Pb = 34.3–36.3 Hz and ³¹P (Pt, Pb) = 14.8–15.8 Hz) and a doublet at 17 ppm (Pc), are assigned to the aminophosphinonyl entity and the remote phosphine 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 Pb (dd) and Pc (d) might be explained by the dihedral angles PA−Pt−C−Pb (−133.54°) and PA−Pt−C−Pc (102.39°) obtained from the X-ray crystal structure determination of 4a, which indicates that ³¹P (PA, Pb) 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 (Com) is found at 157.9 ppm (dd), with rather small ³¹P (Cm) values of 27 and 3 Hz,

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

<table>
<thead>
<tr>
<th>Distances around Pt(1)</th>
<th>Distances within Ligand</th>
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<tbody>
<tr>
<td>Pt(1)–P(1) 2.315(2)</td>
<td>P(2)–N(1) 1.639(7)</td>
</tr>
<tr>
<td>Pt(1)–C(1) 2.354(2)</td>
<td>N(1)–C(7) 1.421(10)</td>
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<tr>
<td>Pt(1)–C(2) 2.050(8)</td>
<td>P(2)–C(26) 1.765(7)</td>
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<td>P(2)–C(14) 1.798(8)</td>
</tr>
<tr>
<td></td>
<td>P(2)–C(20) 1.777(8)</td>
</tr>
</tbody>
</table>

Angles around Pt(1)

| Cl(1)–Pt(1)–Cl(1) 85.76(7) | C(25)–Pt(1)–C(26) 84.7(3) |
| Cl(1)–Pt(1)–C(25) 90.7(2)  | C(2)–Pt(1)–C(26) 174.3(2) |
| Cl(1)–Pt(1)–C(26) 174.9(2) | C(1)–Pt(1)–C(26) 98.9(2)  |

Angles within Ligand

| Pt–C(25)–C(20) 117.46(6) | Pt–C(26)–P(2) 101.0(3)   |
| Pt–C(25)–C(24) 126.96(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(14)–P(2)–C(20) 102.3(3) | C(26)–P(3)–C(33) 105.9(1) |
| C(14)–P(2)–C(20) 110.3(3) | C(27)–P(3)–C(33) 108.5(4) |
| P(2)–C(2)–C(21) 125.7(6) | P(2)–C(20)–C(21) 125.0(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) |
which indicates that C_Metallacycles Organometallics, Vol. 15, No. 9, 1996 2387

which indicates that C on is cis to P_A in 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 to P_X. 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.14d,c In the 31P NMR of 5, a CH resonance is found at about 4.1 ppm (dd, J (P, H) ≈ 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 31P 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 P-N group. The remaining signal, a doublet of doublet, belongs to 5a, PEt3, 5c, PMe2Ph, as confirmed for 5c by selective irradiation in the 31P 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 31P NMR experiment, following the reaction sequence of 3c into 5c, revealed an intermediate 5c', which shows striking resemblance to the 31P NMR data for 4c,d, a doublet at -10 ppm (δ(5c') = 36.4 Hz), a doublet of doublet at 24.7 ppm (δ(P) = 36.4 Hz, J(P, C) = 19.8 Hz), and the 31P resonance at 20.0 ppm (d). The last two resonances to the remote P=N groups, which are presumably connected via an H-bridge, similar to 4. The coupling pattern suggests that 5c' has a trans P_A-Pd-C(sp2) geometry, like in 4, since the multiplicity of the 31P signals changes drastically upon isomerization of 5c' into 5c. The signals belonging to the intermediate 5c' disappear when the three 31P 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 Platinum cycles 2 and 4 with HY (Y = BF4, CF3COO).** The cationic platinum complexes 6a,b,c and 7a,b,c, respectively, with 1 molar equiv of HBF4 or CF3COO as in benzene, tolune, analogous to the earlier reported protonation reactions of Rh and Ir-bis(iminophosphanyl)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. 7a, b is better than its neutral counterparts (4).

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

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>4a</td>
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<td>17.9 (d)</td>
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<td>29.8 (d)</td>
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a Recorded at 40.53 MHz in CDCl3 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 C6D6. c In toluene-d8. d Recorded at 121.48 MHz. e (PB, PA) = 16.0 Hz. f (PA, PC) = 17.0 Hz.
The NMR spectroscopic data for the cationic four-membered platinate complexes 6, which show a characteristic NH resonance in the $^1$H 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(iminophosphoranylmethane) $CH_2(PPh_2=NAr)_2$ ($Ar = \text{p-tolyl}, \text{p-anisyl}$) with $Pt_2Cl_2(PET_3)_2$ 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 BIPM$^{2d}$).

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 $^1$H NMR for 7 and shifts due to the ionic character of 7, which indicates that the basic structure of the orthoplatinate complexes hardly changes upon protonation of 4.

**Reactivity of the Platinate Complexes 2 and 4 with CO$_2$.**

The complexes 2a,d and 4c,f reacted with 1 mol 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).

![Diagram of complexes 2a,d and 4c,f reacting with CO$_2$](image)

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 pentane (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$_2$O.

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 $P=N$ group in 2 into a $P=O$ function,$^{42}$ similar to the earlier reported reactions of analogous Rh– and Ir–bis(iminophosphoranylmethane) complexes,$^4$ the BIPM ligand,$^{17}$ and other phosphinimines with CO$_2$. The sharp doublings of the $^3$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 azaphosphetane 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 $P=O$ resonance frequency as reported for the four-membered platinate complexes $[PtL_2](NPh(=O)PhNPh)$, $\delta$ ($P=O$) = 38.9–46.5 ppm,$^{44}$ and is therefore assigned to a $P=O$ moiety contained in a five-membered ring in our case. The $^{31}$P signal at 29.9 ppm is characteristic for a PPh$_2$NH-aryl moiety,$^{12,33}$ like in 6, which is in agreement with the observation of NH and C$_6$H$_4$R$^\prime$-4 resonances in the $^1$H NMR (Table 4 and Supporting Information) and confirms that only one $P=N$ 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 P$_B$NHAr group to the previous PC 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 [CR(PPh$_2$=NAr)$_2$]$_2$ (1) might attack the precursor $M_2X_4(PR_3)_2$ ($M = Pt, Pd$): (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 $\sigma$-donor ligands,$^{3,12,13,45}$ a preliminary conclusion can be drawn that the N atoms of the [CR(PPh$_2$=NC$_6$H$_4$R′-4)$_2$]$_2$ ligand have the strongest $\sigma$-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 Pt$_2Cl_2(PET_3)_2$ by the neutral BIPM ligand CH$_2(PPh_2=NPtO)$ gave a cationic four-membered platinate of similar geometry, which was formed via initial nucleophilic attack by N as evidenced by the observation of the monodentate intermediate trans-PtCl$_2$(PET$_3$)$_2[N(p Tol)=PPh_2(CH$_2$PPh$_2=NPtO)].$^{12}$ 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).

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(PR₃)₂ by the ligands Li[CH(PPh₂=CH)₂]⁵ and Li[CH(PPh₂=CH)O₂]⁶ 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 labilizing phosphine,³⁰ 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=NR₂)]⁻ 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 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=NR₂)]⁻ (M = Na, Li), in comparison to [CH(PPh₂=XR₂)]⁻ (with X = S, O). For the [CH(PPh₂=XR₂)]⁻ 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)¹⁰,¹³,⁴⁷ (Chart 5), which probably makes these σ-donor atoms less nucleophilic than the methine carbon.

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[CM(η⁶-C₅H₅)₂N-P-2-tol] (IX) in comparison to the neutral ligand, 1,1-BIPEN,¹¹ it is also deduced that Na⁺ is probably strongly coordinated to both N atoms, as strong polarization of the P=N bond has occurred (IX). So, as compared to other ligands (with X = S, O) the electron density in [CR⁺(PPh₂=NR-aryl)]⁻ 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}₂]⁻, C₇N (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 [CR⁺(PPh₂=NR₂)]⁻ 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-
Ryabov, A. D.

mayarguethatanassociativeprocessisfavoredoveraphenomenaforthemetallacycles
σligands, which is not observed. An associative mechanism, resulting in a C,N-coordinated species with opposite geometric isomerization around the metal center, re-

sultion step could account for the equivalence of the two aza-Wittig reactions. Other closely related complexes, i.e. [Rh(COD)(PR3)2](eq 4)12 and [Ir(COD)(CR2)(PPh2(CO)2)](eq 5), points to the fact
9c,f that P9=NAr st"ems from the presence of bulky groups as donor groups in the donor group (the methane 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 four-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(iminophosphoryl) 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 metallacycle 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: (a) oxidative addition by nucleophilic attack of the metal center on the aromatic

CF3COOH.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.30a,51a

The aza-Wittig product 8, obtained from the reaction of 2 with CO2, has proved that this type of reaction is a suitable method to investigate the reactivity or kinetic stability of coordinated phosphinimines.30c We found that CO2 only reacts with the pendant iminophosphoryl group of the complexes 2a,d (eq 6), which means that one P=N function is kinetically stabilized within the metallacycle by coordination to platinum. A similar nonreactivity toward CO2 has been reported earlier for Rh and Ir complexes containing a single C,N-coordinat-
ed iminophosphorylmethanide moiety, e.g. Rh2{(Ar)(N(Ph2CH2))2}2,4,20 The rigidity of the product 8, PtCl{(PPh2(S)3}{CH(PPh2=NAr)(PPh2=O)}, in contrast to the fluxionality of the complexes 2, is a direct consequence of the weak σ-donor capacity of the noncoordinated P=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 CO2, but this reaction is not as straightforward as described above for the complexes 2. The structure of the products 4c,f (eq 7) points to the fact that P9=NAr attacks CO2 and becomes P9=O, concomitantly with or after a shift of H to P9=NAr to become P9=NHAr. The latter is not nucleophilic enough to undergo another aza-Wittig reaction with excess CO2, which explains why only one P=O moiety is formed. The preference for reaction of CO2 with P9=NAr stems from the fact that this group is more polarized than P9=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 reviews51,52 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 methane 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 four-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(iminophosphoryl)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 metallacycle 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: (a) oxidative addition by nucleophilic attack of the metal center on the aromatic

Scheme 3. Proposed Reaction Mechanism for Orthometalation

orthometalation seems 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 particular but also for Pt. 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 entraps 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. This also explains why for the PtCl2(PEt3)(CH2Ph2=S)2 complex, which closely resembles 2 and 3, orthometalation has not been found even at higher temperatures.

The fact that for analogous Rh- and Ir(CH2Ph2=N-) complexes no orthometalation reactions have been found, but show extreme thermal stability instead, 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.

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(iminophosphoryl)-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 which has the same trans R3P-Ar-Pd-C(sp3) geometry as found for the final orthopalladated products 4. In keeping with recent results by Vicente and co-workers, where the Pr3 ligand in orthopalladated compounds [PdCl(Pr3)]2[C6H4R(Pr3)(Cp*H)] is positioned trans to the Pd-C(sp3) bond instead of trans to Pd-C(sp3), the isomerization of complex 5c 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

(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 P−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.

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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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