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Exceptional Coordination Mode of Unsaturated PNP Ligands $(Me_3Si)_2C{=}PN(R)PPh_2$ with Palladium and Platinum Dichlorides: Insertion of Phosphaalkene Phosphorus Atoms into Metal–Chlorine Bonds

Daniela Lungu,[a] Constantin Daniliuc,[a] Peter G. Jones,[a] László Nyulászi,[b]
Zoltán Benkõ,[b] Rainer Bartsch,[a] and Wolf-W. du Mont*[a]

Dedicated to Professor Reinhard Schmutzler on the occasion of his 75th birthday

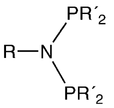
Keywords: Palladium / Platinum / Insertion / *P*-Chloroylides / Phosphaalkenes / Density functional calculations

Unique molecular bis-chelate complexes $M[(Me_3Si)_2C{=}P(Cl)N(1\text{-}Ada)PPh_2]_2$ (1-Ada = 1-adamantyl; **3**: M = Pt; **4**: M = Pd) were isolated as crystalline solids from solutions that contain mixtures of products from reactions of the metal dichlorides with the *P*-phosphanylaminophosphaalkene $(Me_3Si)_2C{=}PN(1\text{-}Ada)PPh_2$ (**1**). Attachment of chloride ions to Pd^{II}- and Pt^{II}-coordinated **1** leads to the novel anionic (alkylidene)(chlorido)(phosphanylamino)phosphanido ligand $[(Me_3Si)_2C{=}P(Cl)N(1\text{-}Ada)PPh_2]^-$, which contains a stereogenic phosphorus atom. With $PdCl_2(COD)$, only the centrosymmetric (*R*,*S*) isomer **4a** was isolated, whereas three of the four possible isomeric platinum complexes $Pt[(Me_3Si)_2C{=}P(Cl)N(1\text{-}Ada)PPh_2]_2$ (**3a**–**3c**) were investigated crystallographically. DFT calculations on model compounds indicate that the enhanced electrophilicity of the chelating phosphaalkene ligand **1** leads to chlorine migration from the metals to the phosphaalkene phosphorus atom.

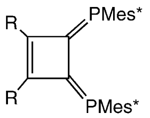
Introduction

We are currently exploring properties of "hybrid" *P*-phosphanylaminophosphaalkene ligands $(Me_3Si)_2C{=}PN(R)PR'_2$ (**C**) with the intention of combining features of catalytically significant, small-bite-angle iminobis(phosphane) "PNP" ligands $RN(PR'_2)_2$ (**A**)[1] with those of more recently developed bidentate phosphaalkenes such as Yoshifuji's strongly π-accepting 1,2-diaryl-3,4-diphosphanylidene-cyclobutene ligands DCPB-Y (**B**).[2,3] The electronegative nitrogen substituent is expected to enhance the π-acceptor properties of the P=C bond in type **C** ligands.[4–6]

On subjecting this concept to experimental investigation by reacting type **C** ligands with halides of nickel(II), palladium(II) and platinum(II), in the case of Pd^{II} and Pt^{II} we unexpectedly observed the crystallisation of 2:1 chelate complexes of the composition $MCl_2[(Me_3Si)_2C{=}PN(R)PPh_2]_2$, which proved to contain chlorine atoms covalently bonded to phosphorus and not to palladium or platinum.[7] In this paper, we report initial results of the characterisation of the novel complexes $M[(Me_3Si)_2C{=}P(Cl)N(1\text{-}Ada)PPh_2]_2$ (1-Ada = 1-adamantyl; **3**: M = Pt; **4**: M = Pd), which are unprecedented in phosphaalkene coordination chemistry.[5,6]



A



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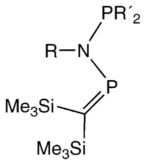

C

Results and Discussion

Synthetic experiments on type **C** ligands showed that $(Me_3Si)_2C{=}PCl$ fortuitously reacted with lithium iminophosphanides $Li[Ph_2PNR]$,[8] prepared in situ by the reaction of the aminophosphanes $Ph_2PN(H)(1\text{-}Ada)$[7] and $Ph_2PN(H)tBu$ with LDA,[9] to give the type **C** *P*-(phosphanylamino)phosphaalkenes $(Me_3Si)_2C{=}PN(1\text{-}Ada)PPh_2$ (**1**) and $(Me_3Si)_2C{=}PN(tBu)PPh_2$ (**2**),[7] whereas the reaction of the 1-aza-2-phosphaallyl anion $[(Me_3Si)_2C{=}PNtBu]^-$[10,11] with R_2PCl led preferentially via P–P bond formation to the undesired phosphanylphosphorane iso-

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[a] Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig,
Hagenring 30, 38106, Braunschweig, Germany
[b] Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics,
Szt Gellert ter 4, 1521, Budapest, Hungary

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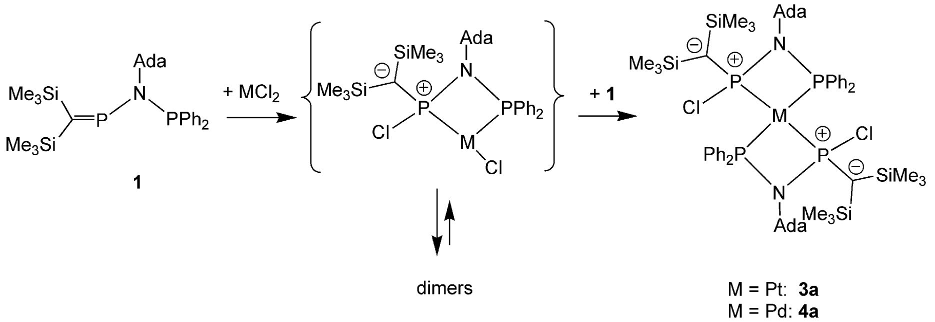


Scheme 1.

mers $(Me_3Si)_2C{=}P({=}NtBu)PR_2$.[10b,11,12] The molecular structure of solid **1** was determined by X-ray crystallography.

After adding a solution of ligand **1** in an aprotic solvent to an equimolar amount of the $PtCl_2$ cyclooctadiene (COD) complex suspended in dichloromethane, ^{31}P NMR spectra of the orange solution indicate the complete consumption of **1** [AX-pattern, δ = +373.5, +37.7 ppm, ^2J(P,P) = ±12 Hz] and the formation, depending on the reaction conditions, of up to three new species exhibiting AX-patterns that all appear in the chemical shift range +60 to +15 ppm [initially an AX pattern with $\delta(^{31}P)$ = 60.5 and 21.8 ppm, J = ±45 Hz, predominates], showing couplings ^2J(P,P) and ^1J(PtP). Free COD was detected by ^1H NMR spectroscopy. Sets of further weak ^{31}P NMR signals are assigned to an A_2M_2 pattern [δ = +71, +42; ^2J(P,P) = ±21 Hz], and tentatively to higher-order multiplets, partially hidden by platinum satellites of the stronger signals. The signals do not appear in the "P=C" range, but rather in a shift range typical of tetracoordinated phosphorus, suggesting an unusual bonding mode of the P=C function of **1** with $PtCl_2$. Further characterisation of the species giving rise to AX-patterns, which we tentatively assign to isomers of di-μ-Cl-bridged 1:1 complexes (Scheme 1), has not yet been achieved. Crystallisation from pentane/dichloromethane provided a very small amount of single crystals of **3a**, but the major part of the reaction products remained in the mother liquor, exhibiting the above-mentioned AX-patterns in the ^{31}P NMR spectrum. Redissolved crystals of **3a**, however, exhibited in their ^{31}P NMR spectra the above-mentioned A_2M_2 pattern with platinum satellites. This pattern is in accordance with a *trans*-configured bis-chelate moiety $[Pt(PP')_2]$, as in a 1:2 chelate complex of $PtCl_2$ with ligand **1**. When two equivalents of ligand **1** were used to favour the formation of the 1:2 complex, ligand **1** and the coordinated species giving rise to AX-patterns were consumed within several days according to ^{31}P NMR spectra, which showed, inter alia, overlapping signals of multiplets including the A_2M_2 pattern of **3a** as a major product.

The X-ray crystallographic structure determination confirmed that the solid **3a** is a complex of the composition $[PtCl_2(\mathbf{1})_2]$ (as a 1:1 pentane solvate) with tetracoordinated platinum surrounded by two *trans*-oriented *P,P'*-chelating ligands in a square-planar fashion, but is uniquely different from usual cationic platinum bis-chelates of the type $\{[PtL_4]^{2+}(X^-)_2\}$: there are covalent bonds between the phosphorus atoms of the hypothetical cationic moiety $[Pt(\mathbf{1})_2]^{2+}$ and the two chlorine atoms. The molecular structure of **3a** is shown in Figure 1. The related 1:1 reaction of ligand **1** with $PdCl_2(COD)$ provided a solution exhibiting two AX patterns in its ^{31}P NMR spectrum [δ = 86 and 35 ppm, J(P,P) = ±28 Hz; δ = 76 and 32 ppm, J(P,P) = ±38 Hz] and a few crystals of the solid pentane-solvated palladium complex **4a**. Complexes **4a** and **3a** are isotypic.

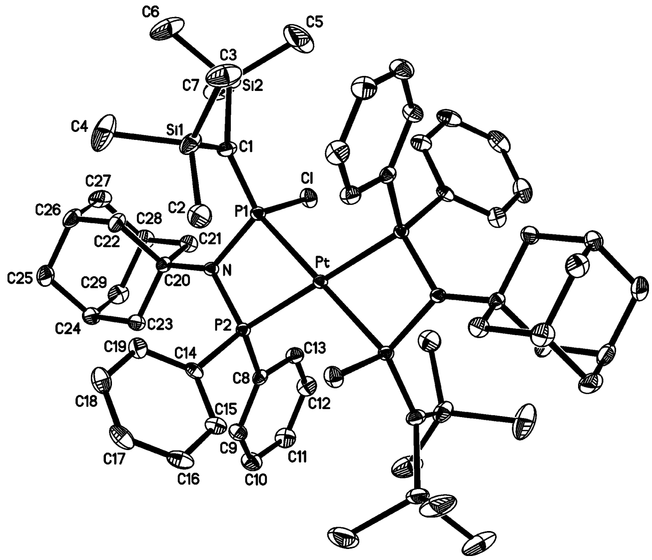
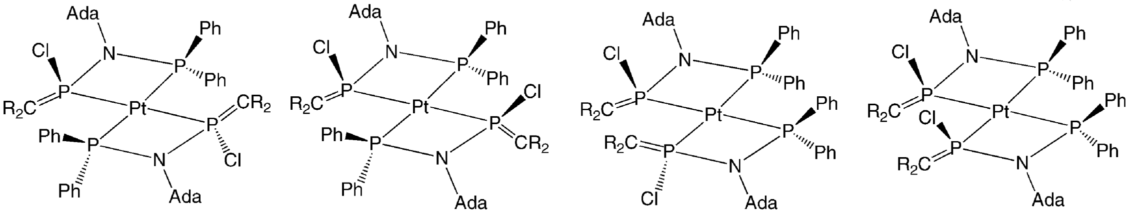


Figure 1. Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): P1–Pt 2.3411(5), P2–Pt 2.2900(5), P1–C1 1.673(2), P1–N 1.7617(17), P2–N 1.6945(16), P1–Cl 2.1107(7), P1–N–P2 100.96(9). Hydrogen atoms are omitted for clarity. Atoms are drawn as 50% thermal ellipsoids.

The addition of two chloride ions to the phosphaalkene phosphorus atoms of the hypothetical cationic moiety *trans*-$[M(\mathbf{1})_2]^{2+}$ (M = Pd, Pt) leads formally to two four-coordinate stereogenic phosphorus atoms P(C)(N)(Cl)(M) in the resulting molecular complexes. Complexes **3a** and **4a** consist of centrosymmetric molecules with *trans* orientation of the two types of phosphorus atoms around palladium and platinum; the chlorine atoms are *anti* oriented, one



vv **3a** **3b** **3c** **3d**

E_{rel}: 0.4 / **1.7** 0.0 /**0.0** 7.2 / **4.3** 7.5 / **4.1**

Scheme 2. Relative energies of complexes related to isomers **3a**–**3d** (R = Me_3Si) for ligand **1′** and for **1′′** (in boldface) $[(H_3Si)_2C{=}PN(Me)\text{-}PR'_2$, R′: Me (**1′**), Ph (**1′′**)] in kcal mol^{-1} at the B3LYP/*B*//B3LYP/*A* level of theory (see ref.[15]).

above and one below the square plane (*R*,*S*). The alternative (*R*)- or (*S*) configurations at the phosphorus atom, together with the intrinsic possibility of *cis*- or *trans*-P,P′-chelate ligand orientations around square-planar platinum or palladium, mean that up to four stereoisomers **3a**–**3d** (or **4a**–**4d**) are possible (Scheme 2).

Variation of the reaction conditions and of the solvent mixtures for crystallisation allowed us to isolate a few single crystals of two further isomers, **3b** and **3c** (Scheme 2), of the platinum complex **3**. Complex **3b** (from CH_2Cl_2/CH_3CN) is another *trans* complex, but with *syn* orientation of the Cl atoms, which leads to a chiral molecule that has no imposed symmetry. The insertion of the carbenoid phosphorus atom into the Pt–Cl bonds must have involved an attack of the two chlorine nucleophiles at the two electrophilic phosphorus atoms from the same side of the square plane. Complex **3c** (from THF/pentane) contains the chelate ligands with a *cis* arrangement of the PPh_2 groups and of the P=C functions; one of its chlorine atoms is above and the other is below the square plane (*anti*), i.e. the complex displays approximate C_2-symmetry. Solid **3b** and **3c** exist as racemic mixtures of (*R*,*R*) and (*S*,*S*) enantiomers.

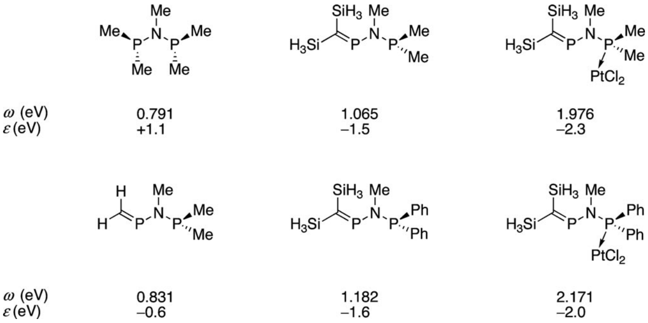
Bond lengths and angles of **3b** and **3c** show no significant differences from those of **3a**. In all three isomers, each bidentate ligand **1** unit has acquired one chlorine atom bonded to a (formerly) phosphaalkene phosphorus atom. This phosphorus atom acts as a σ-donor towards platinum and as a σ-acceptor towards the chlorine atom, i.e. the phosphaalkene phosphorus atom has *inserted* in a carbene-like fashion into the Pt–Cl bond. Carbene-like behaviour of uncharged two-coordinate phosphorus is common in the chemistry of iminophosphanes RP=NR′, but it is unusual in phosphaalkene chemistry.[6] The 1,1-addition of M–Cl units to an uncharged two-coordinate phosphorus atom is without precedence. The formation of tetracoordinated phosphonium centres as parts of *P*-chloro-*P*-metallaylide functions $(N)(Cl)(M)P^{(+)}\text{–}C^{(-)}(SiMe_3)_2$ in **3a**–**3c** and **4a** by M–Cl addition to two-coordinate phosphorus can be considered as the reverse reaction of 1,1-eliminations on organic *P*-chloroylides $R_2P(Cl){=}CHR'$ leading to phosphaalkenes RP=CHR′. Lewis acids are known to catalyse such eliminations by the formation of cationic species $[R_2P{=}CHR']^+$.[13,14]

Under the criterion of bond lengths, the $P{=}C(SiMe_3)$ groups of **1** remain unaffected upon coordination [ligand **1**: P=C 1.665(1) Å; complex **3a**: $P^+\text{–}C^-$ 1.673(2) Å; complex **4a**: $P^+\text{–}C^-$ 1.667(3) Å]. The bond from the ylide phosphorus to nitrogen, however, is lengthened to 1.7618(17) Å (**3a**) and 1.7618(17) Å (**4a**), relative to 1.746(1) Å in ligand **1**, concomitant with a shortening of the other P–N bond lengths [Ph_2P–N; **1**: 1.724(1); **3a**: 1.6942(16) Å; **4a**: 1.695(2) Å] upon coordination. The strong coordination of the Ph_2P group to the metals [Pt–P 2.2900(5) Å; Pd–P 2.2996(8) Å] will enhance the electron-withdrawing capacity of nitrogen towards the adjacent P=C moiety, which thereby becomes so Lewis acidic that phosphorus "satisfies its needs" by coordination with the chloride ion as a Lewis base. This occurs at the expense of P(ylide)–N and M–P(ylide) bond strengths [**3a**: *d*(Pt–P) = 2.3410(5) Å; **4a**: *d*(Pd–P) = 2.3460(8) Å].

In order to understand the remarkable electrophilicity of type **C** PNP ligands, model calculations based on density functional theory have been performed: the electrophilicity index (*ω*) was obtained from vertical ionisation energies and electron affinities calculated at the (U)B3LYP/6-311+G**//B3LYP/6-31+G* level of theory[15b] by using the original definition reported by Parr et al.[16] The electrophilicity indices (*ω*) and the energies of the π*(C=P) antibonding orbitals (*ε*, these are the LUMOs, except for the Pt complexes, where they are the LUMO+1s) of some compounds are shown in Scheme 3.

On the basis of these results, the known strong electron-acceptor behaviour of the π*(C=P) unit[4] is remarkably increased by the silyl groups (the LUMO energy drops). The effect is enhanced by attaching phenyl groups on the σ^3,λ^3-P instead of methyl groups. Further remarkable enhancement of the electrophilicity is achieved for the entire ligand by the metal complexation. It is interesting to note that the electrophilicity of the Pt-complexed ligands surpasses that of some typical electrophiles such as formaldehyde [H_2CO, ω = 1.127 eV, (U)B3LYP/6-311+G**], borane [BH_3, ω = 1.693 eV, (U)B3LYP/6-311+G**] and boron trifluoride [BF_3, ω = 1.654 eV, (U)B3LYP/6-311+G**].[17]

In addition to the electrophilicity indices, the Fukui functions[18] can be applied[19] to understand the site reactivity of molecules. The Fukui function for nucleophilic attack



Scheme 3. Electrophilicity indices (ω, in eV, B3LYP/6-311+G**//B3LYP/6-31+G*[15b]) and the $\pi^*_{C=P}$ Kohn–Sham orbital energies (ε, in eV, B3LYP/6-31G*//B3LYP/6-31+G*) for various PNP model compounds.

[$f^+(\boldsymbol{r})$, $\boldsymbol{r}$ is the vector of the point of interest] was calculated as the electron density difference between the anion formed by the addition of an electron to the ligand and the neutral molecule. This density distribution for a model ligand is shown in Figure 2, and as can be seen, the nucleophilic attack occurs at the P=C bond, especially at the dicoordinated phosphorus.

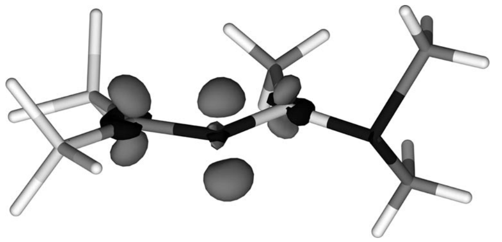


Figure 2. Representation of the Fukui function for nucleophilic attack [$f^+(\boldsymbol{r})$] in the case of $(H_3Si)_2C{=}PN(Me)PMe_2$ calculated at the (U)B3LYP/6-311+G**//B3LYP/6-31+G* level of theory.

We are currently investigating whether the AX patterns in the ^{31}P NMR spectra of solutions delivering solid **3a**–**3c** and **4a** are attributable to mixtures of diastereomers of the chloride-bridged dimers, and further DFT calculations are being carried out in order to comprehend the mechanism of the P atom insertion and the formation of complexes.

To understand and to control the migration of anionic ligands from the metal to unsaturated PNP ligands ("anionotropy"), we are presently engaged in tuning type **C** ligands. Current experiments show that ligand **2** behaves just like ligand **1**, but, by using the *N*-supermesityl-bridged ligand $(Me_3Si)_2C{=}PN(2,4,6\text{-}t\mathrm{Bu}_3C_6H_2)PPh_2$, ^{31}P NMR spectroscopic data of the $PtCl_2$ complex are in agreement with a "normal" 1:1 chelate.[7] When anion migration in 1:1 complexes of type **C** ligands with d^8 metal ions can be made reversible by appropriate choice of metal salts and ligands, chelating unsaturated type **C** PNP ligands may create vacant coordination sites for coordination of substrates by reversibly hosting the neighbouring anions (such as chloride), i.e. anionotropy offers an alternative to the concept of hemilabile ligands. Anionotropic σ-acceptor mechanisms involving metallaylides with reactive P–Cl bonds should also be taken into consideration for explaining some peculiar observations in the coordination chemistry of low-coordinated phosphorus ligands,[5b,20–23] which have hitherto been ascribed to their excellent π-accepting capacity.

Experimental Section

1: Lithium diisopropylamide (1.65 mL 2 M in THF, 3.3 mmol) was added dropwise at –40 °C to (1-adamantylamino)diphenylphosphane (1.1 g, 3.3 mmol) dissolved in dry THF (30 mL). The reaction mixture was allowed to reach room temperature and stirred for about 2 h. After removal of all volatiles in vacuo, the residue was dissolved in THF (30 mL), and this solution was added dropwise to a stirred solution of $(Me_3Si)_2C{=}PCl$ (1.07 g, 3.3 mmol) in THF (30 mL) at –40 °C. The mixture was warmed slowly to room temperature and stirred for 2 h, the solvent was pumped off, and the residue was redissolved in pentane. After removal of LiCl by filtration, pentane was evaporated to leave behind a brown oil. Crystallisation from THF/pentane (at room temp.) afforded **1** as pale yellow crystals. Yield: 95% (1.6 g); m.p. 105 °C. $C_{29}H_{43}NP_2Si_2$ (523.78): calcd. C 66.5, H 8.27, N 2.67; found C 65.8, H 8.33, N 2.85. MS (EI): *m*/*z* (%) = 523 (4) $[M]^+$, 450 (100) $[M - SiMe_3]^+$, 335 (15) $[M - C{=}P(SiMe_3)_2]^+$, 135 (16) $[M - (SiMe_3)_2C{=}PN\text{-}PPh_2]^+$. ^{1}H NMR (200.1 MHz, C_6D_6): δ = 7.7–7.6 (m, CH, Ph), 7.08–6.9 (m, CH, Ph), 2.3 (br. s, 6 H, 3 CH_2, Ada), 1.9 (br. s, 3 H, 3 CH, Ada), 1.5 (br. s, 6 H, 3 CH_2, Ada), 0.2 (d, $^4J_{H,P}$ = 3 Hz, $SiMe_3$), 0.0 (s, $SiMe_3$) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 190.5 [d, ^1J(C,P) = 98.8 Hz, C=P], 139.7 (d, $^1J_{C,P}$ = 17.7 Hz, C-P), 135.0 (m, CH, Ph), 128.6 (s, CH, Ph), 128.1 (d, $^3J_{C,P}$ = 6.5 Hz, CH, Ph), 60.6 (d, $^2J_{C,P}$ = 22.7 Hz, C-P, Ada), 46.2 (d, $^3J_{C,P}$ = 11.5 Hz, 3 CH_2, Ada), 36.6 (s, 3 CH_2, Ada), 31 (s, 3 CH, Ada), 3.6 (d, $^3J_{C,P}$ = 17.18 Hz, $SiMe_3$), 2.9 (d, $^3J_{C,P}$ = 3.5 Hz, $SiMe_3$) ppm. ^{31}P NMR (80.1 MHz, C_6D_6): δ = 373.5 (d, $^2J_{P,P}$ = 12 Hz, P=C), 37.7 (d, $^2J_{P,P}$ = 12 Hz, PPh_2) ppm.

3a: A solution of **1** (0.77 g, 1.47 mmol) in dichloromethane (20 mL) was added dropwise (2 hours) to a solution of $Pt(COD)Cl_2$ (0.275 g, 0.73 mmol) in dichloromethane (20 mL). The red solution was stirred for a further 5 d. The solution was concentrated to about 20 mL under reduced pressure, and the product was precipitated as an orange solid by addition of pentane (40 mL). After washing with pentane (40 mL) and drying in vacuo, an orange powder was obtained. Crystallisation from dichloromethane/pentane at room temperature provided a small crop of orange single crystals of **3a**. $C_{58}H_{86}Cl_2N_2P_4PtSi_4$ (1313.57): calcd. C 53.03, H 6.60, N 2.13; found C 51.48, H 6.99, N 2.04. ^{31}P NMR (80.1 MHz, CD_2Cl_2) (*trans*/*anti* isomer **3a**): δ = 71.3 (t, $^2J_{P,P}$ = 21, $^1J_{P,Pt}$ = 2112 Hz), 41.9 (t, $^2J_{P,P}$ = 21, $^1J_{P,Pt}$ = 2940 Hz) ppm.

CCDC-731434 (**1**), -731435 (**3a**), -731436 (**3b**), -731437 (**3c**) and -731438 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Total energies (in hartrees) and geometrical parameters in Cartesian coordinates (in Å) calculated at the B3LYP/6-31+G* level of theory for selected compounds.

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