Coordination Chemistry of Inversely Polarized Phosphaalkenes toward Group 10 Metal Centers

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A series of palladium and platinum complexes containing inversely polarized phosphaalkenes $(Me_2N)(R)C=PR'$ (R = H, R' = Mes*, **2**; R = Me, R' = Mes*, **3**; R = H, R' = Mes, **4**), exhibiting different steric and electronic environments, have been synthesized. Ligand **2** coordinates in η^1-P fashion to either palladium $(PdCl_2(\eta^1\text{-}P)_2$, **5**) or platinum $(cis\text{-}Pt(Cl)_2(\eta^1\text{-}P)_2$, **6**; $trans\text{-}Pt(Cl)_2(\eta^1\text{-}P)_2$, **7**). The equimolar reaction of **3** with Pd(COD)Cl$_2$ afforded a mixture in 3/1 ratio of cyclopalladated dimeric complexes $[PdCl(\kappa^2\text{-}P,C-CH_2N(Me)CH=PMes*)]_2$, **9** (cis isomer) and **9'** (trans isomer). The latter was characterized by X-ray diffraction. The less hindered ligand **4** acts as bridging phosphido-like ligand with both palladium $(\mu\text{-}P\text{-}[PdCl_2(MesP=CH(NMe_2))]_2$, **11**) and platinum $(\mu\text{-}P\text{-}[PtCl_2(MesP=CH(NMe_2))]_2$, **12**). In the platinum case, the reaction of two or more equivalents of the ligand **4** gave a mixture of the complex containing 2 ligands/Pt and the cationic complex with 3 ligands/Pt, **13**. This complex was isolated from the reaction of 3.5 equiv of **4** with the Pt precursor.

Introduction

Among low-coordinated phosphorus compounds, phosphaalkenes have been studied in depth and were shown to be versatile ligands in transition metal chemistry. Many modes of coordination are known, involving either the lone pair at phosphorus or the P=C bond, or both. In rare instances, these ligands acted as bridging ligands between two metal centers (Scheme 1).

Once the coordination chemistry was well understood, some applications in catalysis could be envisioned. Recently, Yoshifuji et al. have developed several metal-catalyzed processes with kinetically stabilized bis-phosphaalkenes (mostly with Pd(II) centers) as ligands.[1] In general, phosphaalkenes $R^1P=CR^2R^3$ feature an electron distribution $P^{(\delta+)}=C^{(\delta-)}$ consistent with the difference in electronegativity of the respective elements (P (2.1), C (2.5) according to the Pauling scale). More recently, phosphaalkenes with inverse electron distribution have been synthesized, but their coordination chemistry has been studied only in a few instances so far. In particular, Weber et al. currently are developing the coordination of ferriophosphaalkene ligands.[2] In addition to the coordination modes accessible to phosphaalkenes, these ligands may be viewed as possessing two lone pairs at phosphorus because of the resonance structure in which the doublet at nitrogen participates

Scheme 1

Scheme 2
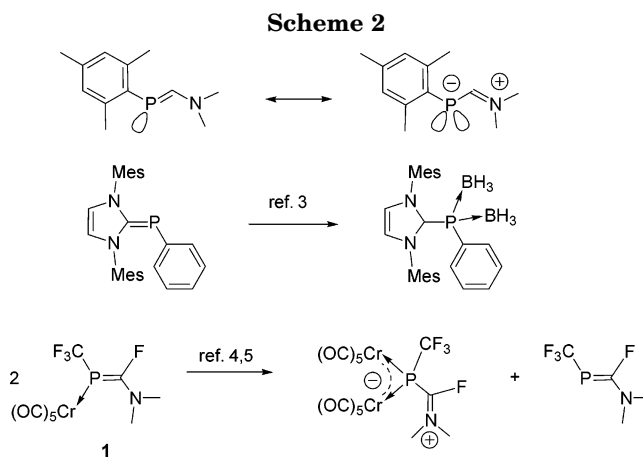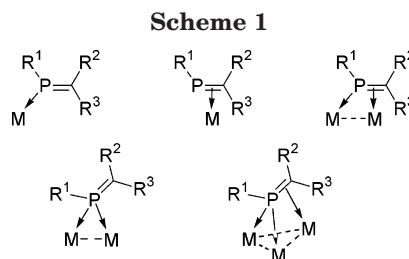
in the delocalization. Accordingly, Cowley, Arduengo, et al. reported the synthesis of a bis-borane adduct in 1997.[3] Also, the η^1-P Cr(0) complexes of derivative **1** dismutate in organic solvents to binuclear species with a bridging phosphorus atom and a free ligand (Scheme 2).[4,5]

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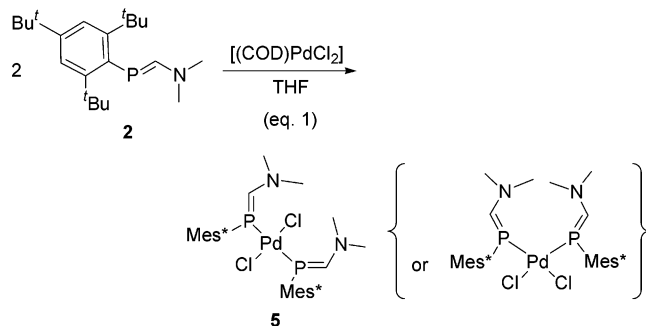

Scheme 3
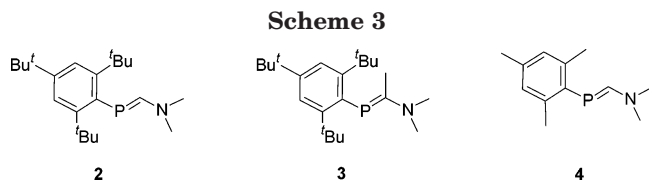
In this instance, inversely polarized phosphaalkenes do resemble phosphido ligands which display richer coordination chemistry. For example, binuclear Ni,[6] Pd,[7,8] and Pt[9] complexes with bis-bridging phosphido ligands have found interesting developments. Both the lack of general knowledge on the coordination chemistry of inversely polarized phosphaalkenes and their potential resemblance to phosphide ligands prompted us to study their behavior toward metal centers with catalytic relevance (Pd(II) and Pt(II)). We wish to present here our first investigations in this area.

Results and Discussion

Three different ligands, **2**−**4**, were selected, allowing the modification of both steric and electronic environment (Scheme 3).

Reactivity of 2. The stoichiometric reaction of ligand **2** with [(COD)PdCl$_2$] in THF led rapidly to the formation of a dark red solution. The ^{31}P NMR spectrum of the crude mixture showed the presence of a single complex, **5**, characterized by a singlet at +32 ppm. The change in the chemical shift by −50 ppm strongly suggested the formation of an η^1 complex. A ^{1}H NMR spectrum recorded from an aliquot of this solution showed that half of the starting [(COD)PdCl$_2$] had not reacted. This was later confirmed by the reaction between 2 equiv of **2** and [(COD)PdCl$_2$] in THF (eq 1). The dark violet crude mixture showed the formation of the same complex, **5**.

This complex was fully characterized by usual NMR techniques, as well as elemental analyses. Unfortunately, X-ray quality crystals of **5** could not be obtained.

The ligand/metal stoichiometry of 2/1 was confirmed by both the elemental analysis and the ^{1}H NMR spectrum. Indeed, the signal of the phosphaolefinic proton is characterized by a deceptively simple virtual triplet (simplified AA′XX′ spin system, ΣJ_{H-P} = 19.5 Hz) at 8.2 ppm. In the ^{13}C NMR spectrum, the signal of the phosphalkene carbon atom (AXX′ spin system) should have allowed us to discriminate between cis and trans geometries. Indeed, the magnitude of the $^2J_{P-P}$ coupling constant is indicative of the geometry. However, it appears as an unresolved broad peak, precluding the extraction of the coupling constants. Complex **5** appeared to be sensitive to hydrolysis. Because of the lack of X-ray structure, the cis or trans geometry, drawn above, could not be ascertained on the basis of NMR spectroscopy alone. To obtain this geometrical information, an IR spectrum in the near-infrared region was recorded. Indeed it is well known that trans complexes give rise to one intense band and cis give two bands in the region between 300 and 350 cm^{-1}.[10] For complex **5**, a broad, intense band was observed at 335 cm^{-1}, clearly proving the trans relation between the two phosphaalkene moieties. The comparison with an analogous Pt center was then envisaged. The same reaction was thus carried out with [(COD)PtCl$_2$] in THF. In this case, an additional piece of information should be accessible because of the existence of a nuclear spin ($I = ^1/_2$) of one of the two Pt isotopes. Indeed, it is well known that the magnitude of the $^1J_{Pt-P}$ coupling constant in [(R$_3$P)$_2$-PtCl$_2$] complexes strongly depends on the cis or trans relation between the two phosphines ligands.[11] Quite surprisingly, **2** did not displace the COD ligand from the Pt center, even under heating conditions in THF. We then turned our attention to a precursor whose ligands would be more easily replaced, such as the propionitrile in [(C$_2$H$_5$CN)$_2$PtCl$_2$], or to a chloro-bridged Pt dimer which is typically cleaved by two electron donors, [PtCl$_2$(PMe$_3$)]$_2$. When the reaction was carried out with the nitrile derivative, the initially pale yellow solution (in CH$_2$Cl$_2$) turned slowly darker, and the formation of the two isomers in a 0.7/1 ratio, **6** and **7**, was observed. The reaction is very slow and requires 48 h to be complete, as indicated by ^{31}P NMR (eq 2).

Complex **6** is characterized by a singlet at −3.6 ppm with Pt satellites ($^1J_{Pt-P}$ = 3888 Hz), and complex **7** is characterized by a singlet at 15.4 ppm with Pt satellites

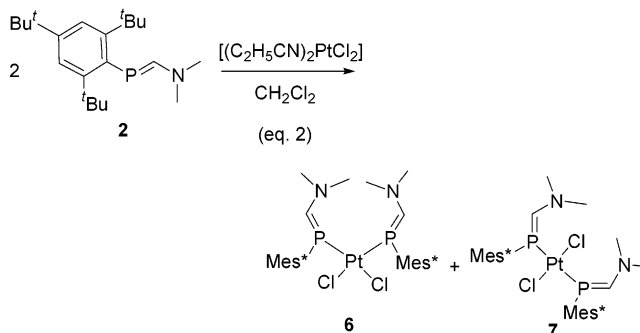(5) Weber, L. *Eur. J. Inorg. Chem.* **2000**, 2425.

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($^1J_{Pt-P}$ = 2855 Hz) in the ^{31}P NMR spectrum. This assignment was done exclusively on the basis of the magnitude of the $^1J_{Pt-P}$ coupling constants, which are not ambiguous in this case (cis having a larger coupling constant than trans), as the mixture of the isomers could not be separated. In the ^{1}H NMR of the mixture, the phosphaolefinic proton appears for **6** as a doublet, with $^2J_{H-P}$ = 14.5 Hz and $^3J_{H-P}$ = 0 Hz at 8.35 ppm, and as a pseudotriplet for **7** (AA′XX′ spin system) with $\sum J_{H-P}$ = 19.5 Hz at 8.22 ppm. These complexes are however sensitive to hydrolysis and partly decomposed during ^{13}C NMR acquisition.

In the case of the Pt dimer precursor, mixing the two reactants in THF or CH_2Cl_2 at room temperature led to a yellow solution. The ^{31}P NMR spectrum of the crude mixture after few minutes showed the formation of a new complex, [**8**], characterized by two sets of doublets centered at 31.0 ppm ($^1J_{Pt-P}$ = 2583 Hz, $^2J_{P-P}$ = 590 Hz, phosphaalkene) and −17.6 ppm ($^1J_{Pt-P}$ = 3026 Hz, $^2J_{P-P}$ = 590 Hz, PMe$_3$) respectively (eq 3).

(eq. 3)

2

[**8**]

Mes* = 2,4,6-tris(^{t}Bu)Ph
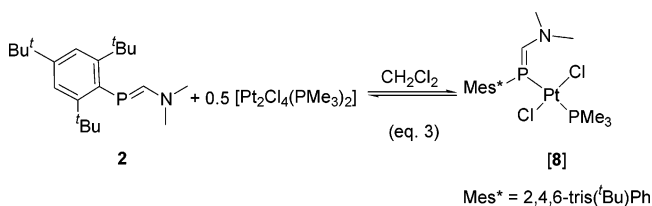
The magnitude of both of these coupling constants, $^1J_{Pt-P}$ and $^2J_{P-P}$, clearly indicate the formation of the trans complex. Unfortunately, an equilibrium is rapidly established as starting ligand **2** and Pt precursor [Pt$_2$Cl$_4$(PMe$_3$)$_2$] remain in the spectrum with constant concentration (even after 24 h), and the complex [**8**] could therefore not be isolated pure from the crude mixture.

Reactivity of 3. We then focused our attention on the closely related, in terms of steric requirements at the phosphorus center, ligand **3**. As expected from the synthesis of the above-mentioned complexes, **3** was reacted with 2 equiv of [(COD)PdCl$_2$]. The solution turned green very fast, then slowly yellow, and a white precipitate appeared overnight. The yellow solution is characterized by two singlets at 70.9 and 71.4 ppm in the ^{31}P NMR spectrum, in a 3/1 ratio. The change in the chemical shift from **3** is only around −22 ppm (compared to −50 ppm from **2** to **5**). Moreover, an aliquot of this yellow solution revealed that only half of the starting [(COD)PdCl$_2$] had been consumed. The reaction was thus carried out with only 1 equiv of palladium precursor and led to the same mixture of complexes, **9** and **9′**. The two complexes possess very similar solubilities and were obtained as a mixture in 68% yield. They are very soluble in THF, less so in acetone, soluble in warm benzene or toluene, and not soluble in hexanes or diethyl ether. The complexes are very robust, as they are not decomposed by either water or air. The elemental analysis was performed on the mixture of the two complexes and confirmed that these are isomers as shown in eq 4. The spectroscopic analysis was also carried out on the mixture of the isomers. ^{1}H NMR spectroscopy verifies the 3/1 ratio observed in the ^{31}P NMR spectrum, which allowed us to clearly assign the various signals. Only two sets of signals are differenti-

ated for the two complexes, at δ 3.05 (major species) and δ 3.08 ppm (minor species) and at δ 7.42 ppm (minor) and δ 7.48 ppm (major), clearly showing the similarity between the complexes **9** and **9′**. The strongest evidence for the formation of a single Pd−CH$_2$ bond is given by a doublet at δ 4.21 ppm, which integrates for two hydrogen atoms. This signal is quite downfield shifted from the N−CH$_3$ signal (broadened doublet at 3.05/3.08 ppm), which integrates as expected for three hydrogens. In the ^{13}C{^{1}H} NMR spectrum, the phosphaalkene carbon resonates at 186.2 ppm, in the usual range for such compounds.[5] As in the ^{1}H spectrum, the signal for the CH$_2$−Pd appears at low field (57.1 ppm) compared to the N−CH$_3$ (40.7 ppm) (eq 4).

(eq. 4)

3

9   **9′**
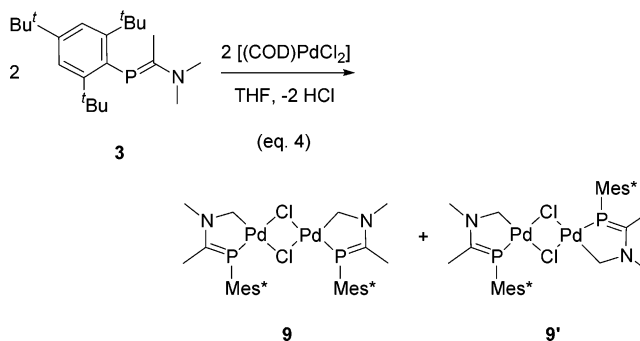
Definitive evidence for the formation of a dimeric species was provided by X-ray crystal analysis. Yellow crystals were obtained by a two-step sequence: first, microcrystals deposited from the C$_6$D$_6$ solution used for NMR characterization. These were then dissolved in acetone, which was allowed to slowly evaporate to yield orange polycrystalline material and dark yellow/orange crystals. The latter were hand picked and the structure was solved. The ORTEP plot is presented in Figure 1 together with significant bond distances and angles. The structure corresponds to isomer **9′**. One clearly sees the formation of a single bond between the Pd center and a former CH$_3$ moiety of the dimethyl-amino group. The bond distances N(1)−C(3) and N(1)−C(2) at 1.486(3) and 1.457(2) Å, respectively, are consistent with single bonds. On the other hand, the N(1)−C(1) bond distance
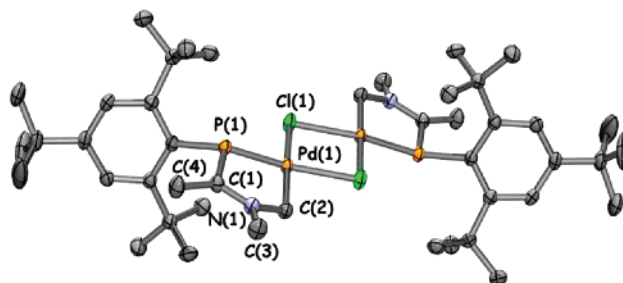

Figure 1. Molecular structure of complex **9′**. Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pd(1)−C(2) 2.018(2); Pd(1)−P(1) 2.2177(5); Pd(1)−Cl(1) 2.4293(5); Pd(1)−Cl(1)# 2.4591(5); C(1)−P(1) 1.746(2); C(5)−P(1) 1.852(2); C(1)−N(1) 1.331(2); N(1)−C(3) 1.486(3); N(1)−C(2) 1.457(2). C(1)−P(1)−C(5) 102.2(1); C(1)−P(1)−Pd(1) 104.07(7); P(1)−C(1)−N(1) 113.9(1); C(1)−N(1)−C(2) 117.8(2); C(1)−N(1)−C(3) 123.7(2); C(2)−N(1)−C(3) 118.4(2); P(1)−C(1)−C(4) 125.6(2); N(1)−C(1)−C(4) 120.1(2).

Scheme 4
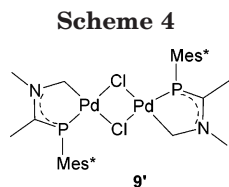
(1.331(2) Å) lies between a single and a double bond. The same situation is found for the P(1)−C(1) bond distance (1.746(2) Å: double bond), which is clearly shorter than the P(1)−C(5) bond to the Mes* group (1.852(2) Å: single bond). The acute C(1)−P(1)−Pd(1) and C(1)−P(1)−C(5) bond angles at 104.07(7)° and 102.2(1)°, respectively, are typical of low-coordinated phosphorus species (weak hybridization at P). However, the geometry at P(1) is strongly pyramidalized ($\sum$angles at P(1) = 320.17°), which suggests a partial loss of the P−C double bond character. Both the C(1) and N(1) are planar (sum of the angles at N(1) = 359.9° and at C(1) = 359.6°), pointing toward a delocalized structure (Scheme 4) en route to the zwitterionic structure. This is corroborated by the dihedral angle C(4)−C(1)−P(1)−C(Ph) of 32.6°.

In this case, the very bulky nature of the phosphorus substituant (Mes*) prevents the formation of bimetallic species with a bridging (phosphido-like) ligand. Diminishing the size of the substituent should favor such a coordination mode (vide supra).

Reactivity of 4. In a last modification of the electronic and steric requirements of the inverse polarized phosphaalkenes, we studied the reactivity of ligand **4** with the same precursors. As in the case of **3**, carrying out the reaction with 1, 2, or more equivalents of **4** with [(COD)PdCl$_2$] led only to the formation of a complex with 1/1 stoichiometry. This complex, **10**, is characterized by a very strong upfield shift from the starting ligand **4** (δ = −115 ppm, $\Delta\delta$ = −170 ppm) in the ^{31}P NMR spectrum. The violet complex was obtained in 90% yield after precipitation with hexanes, filtration, and drying. It was then fully characterized by usual NMR spectroscopy and elemental analysis. Elemental analysis confirmed the stoichiometry but did not allow to differenciate between monomeric and dimeric structure. A first strong indication of the dimeric structure is given by the ^{1}H NMR spectrum, which shows a virtual triplet-like signal for the phosphaalkene hydrogen atom (coupling with two phosphorus atoms, simplified AA′XX′ spin system, $\sum J_{H-P}$ = 13.4 Hz) at 8.95 ppm. The *ortho* (2.90 ppm) and *para* (2.15 ppm) methyl groups of the Mes substituent are quite downfield shifted, clearly indicating a lower electron density. The two methyl groups of the dimethylamino also experience a downfield shift (from 3.0 in **4** to 3.7 and 4.2 in **10**). Altogether, the data points toward the formation of a dimer in which the ligand is bridging (eq 5).
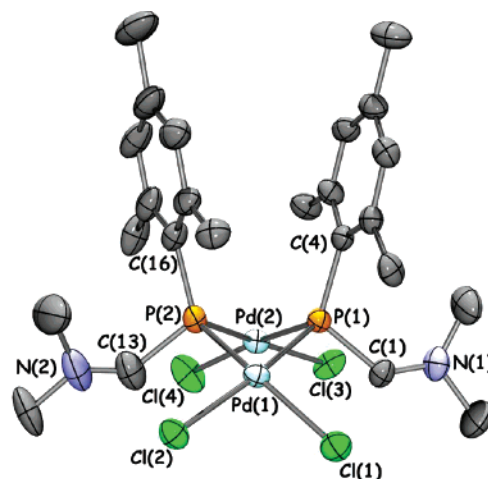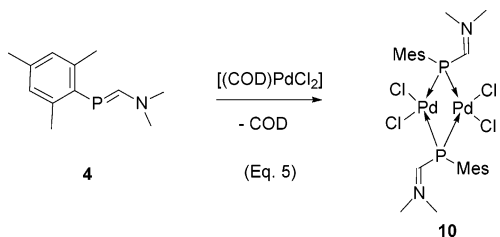

Figure 2. Molecular structure of complex **10**. Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and bond angles (deg): Pd(1)−P(2) 2.251(2); Pd(1)−P(1) 2.279(2); Pd(2)−P(2) 2.272(2); Pd(2)−P(1) 2.246(2); Pd(1)−Cl(1) 2.363(2); Pd(1)−Cl(2) 2.372(2). C(1)−P(1) 1.811(6); C(13)−P(2) 1.804(8); C(1)−N(1) 1.269(8); C(13)−N(2) 1.22(1); C(4)−P(1) 1.823(6); C(16)−P(2) 1.814(6); Pd(2)···Pd(1) 3.1896(6); C(1)−P(1)−Pd(1) 105.6(2); C(13)−P(2)−Pd(1) 104.6(3); C(1)−P(1)−Pd(2) 105.2(2); C(13)−P(2)−Pd(2) 106.1(3); C(1)−P(1)−C(4) 112.5(3); C(13)−P(2)−C(16) 113.1(4); P(1)−C(1)−N(1) 133.6(5); P(2)−C(13)−N(2) 135.7(8); C(1)−N(1)−C(2) 127.8(6); C(1)−N(1)−C(3) 119.5(7).

X-ray quality crystals were obtained by slow diffusion of hexanes into a CH$_2$Cl$_2$ solution of **10**. The ORTEP plot is presented in Figure 2 together with significant bond distances and angles.

The X-ray structure confirmed the formation of a dimer. Most interestingly, the ligand can now be viewed as a pseudozwitterionic moiety (P$^-$∼N$^+$), which is fully consistent with the strong upfield shift observed in the ^{31}P NMR spectrum. Indeed, the nitrogen atom is planar ($\sum$angles = 359.9°) and the C−N bond distance of 1.269(8) Å is consistent with a double bond. On the other hand, the P−C bond distance is now clearly a single bond: 1.811(6) Å (it is similar to the P−C bond distance with the mesityl group: 1.823(6) Å). This indicates a phosphide type structure (R$_2$P$^-$). Overall in this complex, the extreme case of inversely polarized phosphaalkenes is observed. The dimer is slightly disymmetrical, as shown by two "longer" Pd−P at ca. 2.275 Å (average) and two "shorter" Pd−P at ca. 2.248 Å (average). The distance between the two Pd centers is long, 3.1896(6) Å, and clearly shows the absence of a real Pd···Pd bond. The C(1)−P(1)−C(4) bond angle, 112.5°, is much wider than usually observed for free or coordinated phosphaalkene ligands, again showing the phosphido-like structure. The second view of the complex reveals the stacking between the two mesityl moieties (distance C(4)···C(16): 3.72 Å)). Overall this structure is quite similar to the several reported dimers with bridging phosphido ligands.[7,8] Among these, a search in the Cambridge database allowed us to observe two different groups of structures: with or without a Pd−Pd single bond. For the complexes in which there is a metal−metal bond, the distance is short (between

2.57 and 2.62 Å)[12] and the P−Pd−P bond angle is wide (between 112.7° and 113.0°). On the other hand, the distribution of complexes without Pd−Pd single bonds is larger: distance between 3.20 and 3.64 Å, and P−Pd−P bond angle between 68.5° and 81.4°.[7,13] In our complex, the distance between the two Pd centers is marginally shorter (3.1896(6) Å) than the shortest reported structure without a Pd−Pd bond. The P(1)−Pd(1)−P(2) and P(1)−Pd(2)−P(2) bond angles are measured at 75.53° and 75.77°, respectively. Together, these data clearly indicate the absence of a Pd⋯Pd single bond.

The analogous Pt dimeric complex, **11**, was obtained by the stoichiometric reaction between **4** and [(COD)-PtCl$_2$]. Again, the phosphorus chemical shift resonates at high field: −148.9 ppm. Coupling with two equivalent Pt centers is obvious, as the signal appears as a pseudopentet: singlet with satellites of one and/or two ^{195}Pt atoms ($^1J_{Pt-P} = 2600.1$ Hz). Apart from this typical feature, the other ^{1}H and ^{13}C NMR spectra are similar to those of complex **10** (eq 6).
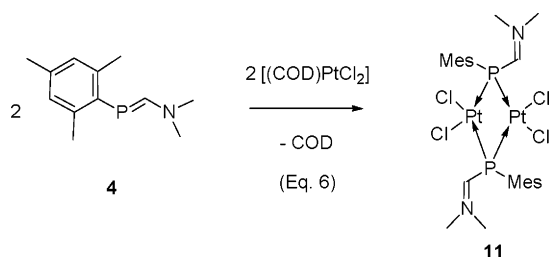
The analogous Pt reactivity of **4** with a platinum center appeared to be richer. Unlike what was observed for the palladium derivatives, variation of the ratio **4**/Pt center from 1/1 to 3.5/1 led to the formation of mixtures of several complexes that are not in equilibrium (eq 7). Indeed, adding 2 equiv of **4** to a CH$_2$Cl$_2$ solution of [(COD)PtCl$_2$] led to a mixture of complex **11** (about 40%), the expected complex [**12**] (about 20%, cis or trans), characterized by a singlet with Pt satellites at −14.3 ppm ($^1J_{Pt-P} = 3037.5$ Hz) and the complex **13** characterized by a doublet and a triplet both with Pt satellites (about 40%). With 3 equiv of **3**, complex **13** becomes the major species (about 90%). The remaining products are the starting material and complex [**12**] (5% according to ^{31}P NMR spectroscopy). With 3.5 equiv, only **4** and **13** are observed by ^{31}P NMR. Thus, complex **13** could be obtained pure in 85% yield (based on the Pt precursor) after extraction of remaining starting material (and COD) in diethyl ether. It was fully characterized by NMR techniques as well as elemental analyses. In the ^{31}P NMR spectrum, complex **13** is characterized by a doublet at −0.4 ppm ($^1J_{Pt-P} = 1780.0$

Hz, $^2J_{P-P} = 25.5$ Hz, 2P) and a triplet at −16.5 ppm ($^1J_{Pt-P} = 3433.6$ Hz, $^2J_{P-P} = 25.5$ Hz, 1P).

x	11	[12]	13	4
1	100	0	0	0
2	40	20	40	0
3	0	5	90	5
3.5	0	0	90	10
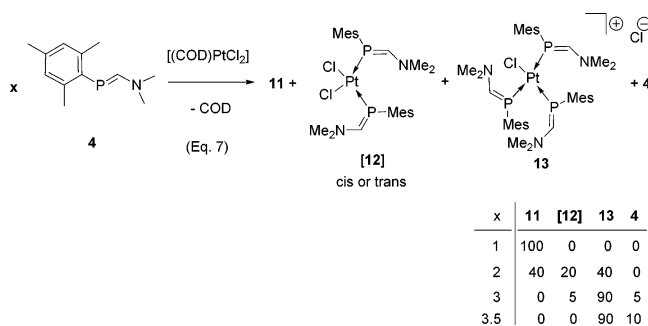
In the ^{1}H NMR spectrum, the signals of the phosphaalkene protons appear at 7.50 ppm as the expected doublet of triplets (1H, AXY$_2$ spin system) and at 8.78 ppm as a second-order virtual triplet (2H, AA′XX′Y spin system). The same type of second-order figure of coupling is observed in the ^{13}C NMR spectrum. Indeed a virtual doublet of triplets is seen at 186 ppm (usual range for inversely polarized phosphaalkene). Finally, adding more starting material did not lead to the formation of the homoleptic dicationic species, most probably for steric reasons.

Conclusion

Through few examples, using three different inversely polarized phosphaalkenes, we have observed several of the possible coordination modes that are accessible to these ligands: (a) η^1 coordination via the lone pair of phosphorus as "regular" phosphaalkenes; (b) bridging phosphido-like ligand, via the two lone pairs of the formally zwitterionic structure; (c) bidentate ligation, via η^1 coordination of the lone pair of phosphorus and Pd−C bond formation via insertion into the C−H bond of the N−CH$_3$ moiety.
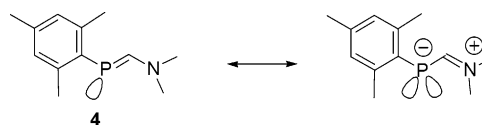
It appeared that ligand **2** is quite a weak ligand of the Pd(II) center (complex **5** was easily hydrolyzed) and Pt(II) center (unable to break quantitatively a chlorobridged dimer). Ligand **3** gave an unprecedented bidentate ligation after a formal Pd insertion into a N−CH$_3$ bond. Finally, ligand **4**, being much less sterically demanding, can either bridge two centers or act as monodentate ligand. We have also observed with these ligands a very significant difference in reactivity toward Pd(II) and analogous Pt(II) centers. In short, the combination of only three ligands with two metal centers led to a very rich coordination chemistry. We are currently studying the mechanism of the formation of complexes **9** and **9′** as well as their use in catalytic processes. Indeed, preliminary experiments show that the bridge is easily cleaved to form monomeric complexes, which are currently under investigation. The behavior of these inversely polarized phosphaalkene ligands toward other metal centers is also being investigated, and results will be presented in due course.

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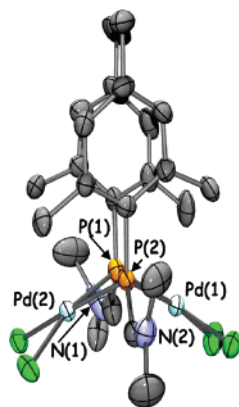
Figure 3. Molecular structure of complex **10**: side view. Thermal ellipsoids are drawn to the 30% probability level. Hydrogen atoms are omitted for clarity.

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and glovebox techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, diethyl ether, hexanes) or from P_2O_5 (dichloromethane, $CDCl_3$). Ligands **2**,[14] **3**,[15] and **4**[16] and complexes [Pd(COD)Cl$_2$],[17] [Pt(COD)Cl$_2$],[18] [Pt(C$_2$H$_5$CN)$_2$Cl$_2$],[19] and [Pt$_2$Cl$_4$(PMe$_3$)$_2$][20] were prepared according to literature procedures.

Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me$_4$Si as external standard. ^{31}P are relative to a 85% H$_3$PO$_4$ external reference. Coupling constants are expressed in hertz. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; v, virtual. Elemental analyses were performed by the "Service d'Analyses du CNRS, Gif/Yvette".

Crystallography. Yellow plates of complex **9′** were obtained by slow evaporation of an acetone/C$_6$D$_6$ solution of the complex at room temperature. Magenta plates of complex **10** were obtained by slow diffusion of hexanes into a solution of the complex in CDCl$_3$ at RT. Data were collected on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71073 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structure was solved using SIR 97 and SHELXL-97. Molecular drawings were made using ORTEP III for Windows, then POV-Ray. CCDC-268892 and 268893 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (international) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Synthesis of Complex 5. 2 (200 mg, 0.6 mmol) and [Pd(COD)Cl$_2$] (85 mg, 0.3 mmol) were weighed in air, then

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Table 1. ^{31}P NMR Data for Complexes 4, 6, 7, 9, 9′, 10, 11, and 13

compound	δ_P in ppm	$^1J_{PPt}$ in Hz	$^2J_{PP}$ in Hz	δ_H in ppm
4	32.0			8.20
6	−3.6	3888		8.35
7	15.4	2855		8.22
9 or 9′	70.9 (major)			
	71.4 (minor)			
10	−114.8			8.85
11	−148.9	2600		9.03
13	−0.4	1780	25.5	7.50

placed under nitrogen. THF (10 mL) was then added and the mixture stirred at room temperature overnight. The volume of the purple solution was reduced to 1/3, and hexanes (7 mL) were added, resulting in the precipitation of a purple solid. It was filtered, washed with diethyl ether, and then dried under vacuum. Yield: 90% (253 mg). ^{31}P{^{1}H} (THF-d_8): δ 31.2. ^{1}H (THF-d_8) δ 1.15 (s, 9H, tBu), 1.75 (s, 18H, 2×tBu), 2.5 (bs, 6H, NMe$_2$), 7.43 (vt, 2H, ΣJ_{HP} = 3.0 Hz, H of Mes*), 8.20 (vt, 1H, ΣJ_{HP} = 19.5 Hz, HC=). ^{13}C{^{1}H} (THF-d_8): δ 31.4 (s, C$_{10}$), 35.7 (s, C$_9$), 35.1 (s, C$_8$), 40.4 (s, C$_2$), 40.6 (s, C$_7$), 123.5 (vt, ΣJ_{C-P} = 8.1 Hz, C$_5$), 125.6 (m, C$_3$), 152.2 (s C$_6$), 157.8 (vt, ΣJ_{C-P} = 5.4 Hz, C$_4$), 165.5 (m, C$_1$). IR (KBr): 335 cm^{-1}, broad, intense. Anal. Calcd for C$_{42}$H$_{72}$Cl$_2$N$_2$P$_2$Pd: C, 59.75; H, 8.60. Found: C, 60.10; H, 8.92.
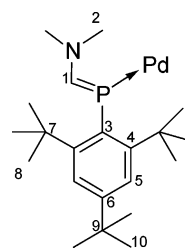
Synthesis of Complexes 6 and 7. 2 (100 mg, 0.3 mmol) and [Pt(C$_2$H$_5$CN)$_2$Cl$_2$] (60 mg, 0.15 mmol) were weighed in air and then placed under nitrogen. CH$_2$Cl$_2$ (7 mL) was then added and the solution stirred at 35 °C overnight. The volume of the orange solution was reduced to 1/3, and hexanes (7 mL) were added, resulting in the precipitation of an orange solid. It was filtered, washed with diethyl ether, and then dried under vacuum. Yield: 89% (124 mg).

6: ^{31}P{^{1}H} (CD$_2$Cl$_2$): δ −3.6 ppm (s, $^1J_{P-Pt}$ = 3888 Hz). ^{1}H (CD$_2$Cl$_2$): δ 1.21 (s, 9H, tBu), 1.80 (s, 18H, 2×tBu), 2.71 (m, 3H, NMe), 3.45 (bs, 3H, NMe), 7.55 (s, 2H, H of Mes*), 8.35 (d, 1H, $^2J_{H-P}$ = 14.5 Hz, HC=).

7: ^{31}P{^{1}H} (CD$_2$Cl$_2$): δ 15.4 ppm (s, $^1J_{P-Pt}$ = 2855 Hz). ^{1}H (CD$_2$Cl$_2$): δ 1.21 (s, 9H, tBu), 1.80 (s, 18H, 2×tBu), 2.65 (bs, 3H, NMe), 3.15 (bs, 3H, NMe), 7.50 (s, 2H, H of Mes*), 8.22 (vt, 1H, ΣJ_{H-P} = 19.5 Hz, HC=). Anal. Calcd for C$_{42}$H$_{72}$Cl$_2$N$_2$P$_2$Pt: C, 54.07; H, 7.78. Found: C, 54.30; H, 7.97.

Synthesis of Complexes 9 and 9′. 3 (300 mg, 0.86 mmol) and [Pd(COD)Cl$_2$] (245 mg, 0.86 mmol) were weighed in air and then placed under nitrogen. THF (20 mL) was then added and the mixture stirred at room temperature overnight, during which time a white precipitate formed. The yellow solution was filtered and reduced to about 3 mL. Hexanes (20 mL) were added, which resulted in the precipitation of a yellow solid, which was filtered. The solid was crystallized from warm benzene. Yield: 68% (287 mg). Anal. Calcd for C$_{44}$H$_{74}$Cl$_2$N$_2$P$_2$Pd$_2$: C, 54.10; H, 7.64. Found: C, 54.00; H, 7.39.

9 or 9′: major species: ^{31}P{^{1}H} (THF-d_8): δ 70.9 ppm (s). ^{1}H (THF-d_8): δ 1.33 (s, 3H, CH$_3$), 1.37 (s, 9H, tBu *para* of Mes*), 1.73 (s, 18H, tBu *ortho* of Mes*), 3.05 (d, $^3J_{HP}$ = 11.8 Hz, 3H, NMe), 4.21 (d, $^3J_{HP}$ = 9.9 Hz, 2H, NCH$_2$Pd), 7.48 (s, 2H, CH arom). ^{13}C{^{1}H} (THF-d_8): δ 17.9 (d, $^2J_{CP}$ = 5.0 Hz, CH$_3$, C$_2$), 31.5 (s, C$_{10}$), 34.2 (d, $^2J_{CP}$ = 5.0 Hz, C$_{12}$), 35.7 (s, C$_9$), 39.5 (s, C$_{11}$), 40.7 (s, CH$_3$−N, C$_4$), 57.1 (m, CH$_2$−N, C$_3$), 122.0

Table 2. Crystal Data and Structural Refinement Details for 9′ and 10

|	9′	10[a]
formula	$C_{44}H_{74}Cl_2N_2P_2Pd_2$,2($C_6D_6$)	$C_{24}H_{36}Cl_4N_2P_2Pd_2$,3.5(CHCl$_3$)
M_r	1144.97	1186.88
T [K]	150.0(1)	150.0(1)
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$
a [Å]	36.0050(10)	12.1510(10)
b [Å]	9.8830(10)	16.8030(10)
c [Å]	17.7840(10)	22.6970(10)
α [deg]	90.00	90.00
β [deg]	117.5200(10)	100.8900(10)
γ [deg]	90.00	90.00
V [Å^3]	5612.2(7)	4550.7(5)
Z	4	4
ρ [g cm^{-3}]	1.355	1.723
μ [cm^{-1}]	0.829	1.736
cryst size [mm]	0.20 × 0.18 × 0.12	0.18 × 0.12 × 0.12
$F(000)$	2368	2348
index ranges	−50 50; −13 13; −25 24	−12 15; −21 19; −29 22
scan type	phi and omega scans	phi and omega scans
$2\theta_{max}$[deg]/criterion	30.03/$I > 2\sigma I$	27.48/$I > 2\sigma I$
no. of params refined;data/param	332; 19	426; 18
no. of reflns collected	15 209	40 629
no. of indep reflns	8167	10 412
no. of reflns used	6368	7767
wR2	0.0912	0.1970
R1	0.0334	0.0650
goodness of fit	1.061	1.070
largest diff peak/hole [e Å^{-3}]	1.018(0.080)/−0.794(0.080)	4.927(0.206)/−1.775(0.206)

[a] Note for structure **10**: Poorly resolved structure due to large mosaicity. Unresolved disorder is apparent. Large unexplained residue near C15. A chloroform molecule located near a symmetry center was incompletely resolved and accounted for using the Platon SQUEEZE function.

(d, $^3J_{CP}$ = 5.0 Hz, C$_7$), 152.1 (s, C$_8$), 159.0 (d, $^2J_{CP}$ = 7.0 Hz, C$_6$), 186.2 (m, P−C−N, C$_1$). Note: C$_5$ is not observed.

9′ or 9: minor species: ^{31}P{^{1}H} (THF-d_8): δ 71.4 ppm (s). ^{1}H (THF-d_8) δ 1.33 (s, 3H, CH$_3$), 1.37 (s, 9H, tBu *para* of Mes*), 1.73 (s, 18H, tBu *ortho* of Mes*), 3.08 (d, $^3J_{HP}$ = 11.8 Hz, 3H, NMe), 4.21 (d, $^3J_{HP}$ = 9.9 Hz, 2H, NCH$_2$Pd), 7.42 (s, 2H, CH *meta*).
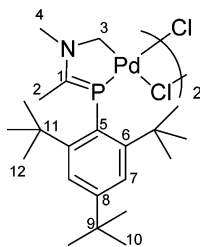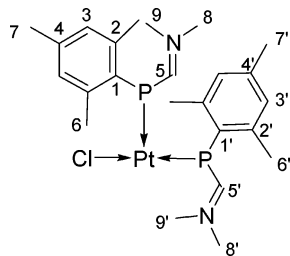

Synthesis of Complex 10. 4 (103 mg, 0.5 mmol) and [Pd(COD)Cl$_2$] (141 mg, 0.5 mmol) were weighed in air and then placed under nitrogen. THF (10 mL) was then added and the mixture stirred at room temperature overnight. The volume of the purple solution was reduced to 1/3, and hexanes (7 mL) were added, resulting in the precipitation of a purple solid. It was filtered, washed with diethyl ether, and then dried under vacuum. The title complex was obtained as a purple solid in 92% yield (176 mg). Anal. Calcd for C$_{24}$H$_{36}$Cl$_4$N$_2$P$_2$Pd$_2$: C, 37.48; H, 4.72. Found: C, 37.16; H, 4.65. ^{31}P{^{1}H} (CDCl$_3$): δ −114.8 ppm (s). ^{1}H (CDCl$_3$): δ 2.18 (s, 3H, H$_5$), 2.90 (s, 6H, 2×H$_6$), 3.70 (s, 3H, H$_8$), 4.15 (bs, 3H, H$_8$), 6.65 (s, 2H, H$_3$), 8.85 (vt, 1H, ΣJ_{H-P} = 13.4 Hz, H$_7$, AA′XX′). ^{13}C{^{1}H} (CDCl$_3$): δ 21.7 (s, C$_5$), 28.1 (s, C$_6$), 33.3 (s, C$_8$), 38.5 (s, C$_8$), 129.3 (s, C$_1$), 130.8 (bs, C$_3$), 143.1 (s, C$_4$), 145.7 (vt, ΣJ_{C-P} = 2.0 Hz, C$_2$), 164.2 (bs, C$_5$).
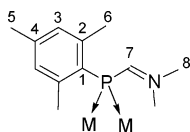
Synthesis of Complex 11. 4 (52 mg, 0.25 mmol) and [Pt(COD)Cl$_2$] (94 mg, 0.25 mmol) were weighed in air and then placed under nitrogen. CH$_2$Cl$_2$ (10 mL) was then added and the mixture stirred at room temperature overnight. The volume of the orange solution was reduced to 1/3, and hexanes (10 mL) were added, resulting in the precipitation of an orange solid. It was filtered, washed with diethyl ether, and then dried under vacuum. The title complex was obtained in 87% yield (103 mg). ^{31}P{^{1}H} (CDCl$_3$): δ −148.9 ppm (s, $^1J_{Pt-P}$ = 2600.1 Hz). ^{1}H (CDCl$_3$): δ 2.25 (s, 3H, H$_5$), 2.90 (s, 6H, 2x H$_6$), 3.85 (s, 3H, H$_8$), 4.40 (bs, 3H, H$_8$), 6.75 (s, 2H, H$_3$), 9.03 (b, 1H, H$_7$, AA′XX′). ^{13}C{^{1}H} (CDCl$_3$): δ 21.7 (s, C$_5$), 27.8 (s, C$_6$), 32.1 (s, C$_8$), 37.4 (s, C$_8$), 129.3 (s, C$_1$), 131.2 (bs, C$_3$), 142.1 (s, C$_4$), 144.7 (m, C$_2$), 163.3 (bs, C$_5$). Anal. Calcd for C$_{24}$H$_{36}$Cl$_4$N$_2$P$_2$Pt$_2$: C, 30.46; H, 3.83. Found: C, 30.76; H, 4.05.

Synthesis of Complex 13. 4 (100 mg, 0.48 mmol) was weighed in a drybox and dissolved in CH$_2$Cl$_2$ (5 mL). [Pt(COD)-Cl$_2$] (52 mg, 0.14 mmol) was added solid to the solution, which turned instantaneously red. The mixture was stirred at room temperature for 2 h, and then the solvent was removed under vacuum, leaving an oily residue. Diethyl ether was added (5 mL) and the mixture stirred for 15 min, which resulted in the precipitation of an orange solid. It was filtrated, washed with diethyl ether (2 × 2 mL), and dried under vacuum to yield the title complex in 85% yield (based on Pt, 105 mg). ^{31}P{^{1}H} (CD$_2$Cl$_2$): δ −0.4 ppm ($^1J_{Pt-P}$ = 1780.0 Hz, $^2J_{P-P}$ = 25.5 Hz, 2P), −16.5 ppm ($^1J_{Pt-P}$ = 3433.6 Hz, $^2J_{P-P}$ = 25.5 Hz, 1P). ^{1}H (CD$_2$Cl$_2$): δ 2.10 (s, 6H, CH$_3$ *para* of Mes), 2.22 (s, 3H, CH$_3$ *para* of Mes), 2.28 (s, 6H, 2×CH$_3$ *ortho* of Mes), 2.48 (s, 6H, 4×CH$_3$ *ortho* of Mes), 2.92 (bs, 12H, NMe$_2$), 3.28 (bs, 6H, NMe$_2$), 6.65 (d, 2H, $^4J_{H-P}$ = 3.0 Hz, H of Mes), 6.85 (s, 4H, H of Mes), 7.50 (dt, 1H, $^2J_{H-P}$ = 16.7 Hz, $^4J_{H-P}$ = 13.6 Hz, HC=, AXY$_2$), 8.78 (vt, 2H, ΣJ_{H-P} = 9.1 Hz, 2×HC=, AA′XX′Y). ^{13}C{^{1}H} (CD$_2$Cl$_2$): δ 20.8 (s, CH$_3$ of Mes), 20.8 (s, C$_6$ of Mes), 20.8 (s, CH$_3$ of Mes), 24.0 (d, ΣJ_{C-P} = 10.8 Hz, C$_7$ of Mes), 25.1 (pt, ΣJ_{C-P} = 11.1 Hz, C$_6$ of Mes), 41.8 (bs, C$_{8\ or\ 9}$), 50.1 (bs, C$_{9\ or\ 8}$), 128.2 (vt, ΣJ_{C-P} = 8.7 Hz, C$_{3'}$), 128.4 (s, C$_3$), 140.2 (s, C$_4$), 140.9 (d, ΣJ_{C-P} = 2.6 Hz, C$_1$), 142.4 (d, J_{C-P} = 7.5 Hz, C$_{1'\ or\ 4'}$), 144.1 (d, $^2J_{C-P}$ = 9.7 Hz, C$_{2'}$), 144.6 (vt, ΣJ_{C-P} = 11.6

Hz, C$_2$), 173.4 (d, C$_{5'}$), 186.4 (vdt, ΣJ_{C-P} = 23.1 Hz, C$_5$). Anal. Calcd for C$_{36}$H$_{54}$Cl$_2$N$_3$P$_3$Pt: C, 48.71; H, 6.13. Found: C, 49.02; H, 6.25.