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Journal Name

ARTICLE

1,4-Dihydrophosphinolines and Their Complexes with Group 10 Metals

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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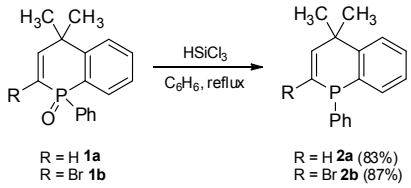
Syntheses and characterizations of novel phosphaheterocycles, 1-phenyl-4,4-dimethyl-1,4-dihydrophosphinoline (**2a**) and 1-phenyl-2-bromo-4,4-dimethyl-1,4-dihydrophosphinoline (**2b**), and their complexes with Pd(II) and Pt(II) are described. Reduction of 1-phenyl-4,4-dimethyl-1,4-dihydrophosphinoline 1-oxide (**1a**) and 1-phenyl-2-bromo-4,4-dimethyl-1,4-dihydrophosphinoline 1-oxide (**1b**) using trichlorosilane in refluxing benzene gave the target phosphines in a yield of 83–87%. Reactions of phosphines with acetonitrile complexes of Pd(II) (**3**) *и* Pt(II) (**4**) yielded *bis*(phosphine) species $[MCl_2L_2]$ (**5**–**8**). Complexes **5**–**8** were characterized by ^{1}H, ^{13}C, ^{31}P, ^{195}Pt NMR and HRMS. The structures of all these new complexes were determined with single crystal X-ray diffraction. The configuration of the complexes in a $CDCl_3$ solution was investigated via comparing of ^{31}P NMR data in solution and solid state.

Introduction

Complexes of group 10 metals (especially palladium) with phosphine ligands have long been attracting the attention of researchers as objects for theoretical study and as homogeneous metal-complex catalysts.[1] They were one of the first catalysts of the most famous cross-coupling reactions (such as Suzuki,[2] Sonogashira,[3] and Heck[4]), which became a powerful tool of organic synthesis.[5] And, despite the fact that now some other types of ligands (for instance, diaminocarbenes) have forced phosphines to make room,[6] phosphine complexes of palladium continue to figure prominently in the field of catalysis.[7] They gained a new impulse thanks to works of several researchers who have developed obtaining new phosphine ligands (such as, tri-*tert*-butylphosphine,[8] Buchwald's biarylphosphines,[9] Hartwig's Q-Phos,[10] 2-phosphino-substituted 1-arylpyrroles (PAPs),[11] and 2-arylindoles[12]) and showed interesting properties of various metal complexes with these ligands. This shows that synthesis of new phosphines and complexes of group 10 metals with these ligands is still important research thrust.

Results and Discussion

We recently obtained novel 1,4-dihydrophosphinoline 1-oxides **1a, 1b** (Scheme 1).[13] The main goals of this work were the synthesis a new class of phosphine ligands, 1,4-dihydrophosphinolines **2a, 2b** (Scheme 1), preparation of their complexes with Pd(II) and Pt(II), and study the structures and conformational behaviour of these complexes.



Scheme 1. Synthesis of 1,4-dihydrophosphinolines **2a, 2b** from 1,4-dihydrophosphinoline 1-oxides **1a, 1b**.

We used $HSiCl_3$ in a benzene solution to reduce the P=O group in **1a, 1b** (analogous to the known phosphine oxides reduction[14]) that afforded the desired phosphines in good yields (83–87%). Compounds **2a**,**b** were also obtained by the other method[15] using PPh_3 as the reducing agent. However, in this case yields of the reaction products were lower (49–56%), due to difficulties in chromatographic separation of **2a, 2b**, which have very close retention parameters R_f with triphenylphosphine. Apart from that, elution of **2a, 2b** on silica-gel for long time led to partial back oxidation of these compounds. Structures of compounds **2a, 2b** were determined by ^{1}H, ^{13}C, ^{31}P NMR and HRMS (see Experimental and Supplementary Information). Additionally the structure of phosphine **2b** was confirmed by X-ray analysis (Figure 1).

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Electronic Supplementary Information (ESI) available: ^{1}H, ^{13}C, ^{31}P, ^{195}Pt NMR spectra, X-ray data. See DOI: 10.1039/x0xx00000x

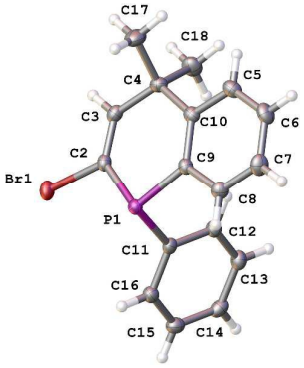


Figure 1. View of **2b** with the atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

More rigid structure of phosphine **2b** decreases the C–P–C angles (98.3 °, 100.6 °, and 101.3 °) compared to PPh3 (102.1 °, 103.6 °.[16] Lower magnitudes of the valence angles indicate increased s-character of the lone pair orbital of the phosphorus (by which it can be coordinated to the metal centers) and thereby arisen electronegativity of the phosphorus atom.

The reaction of phosphines **2a, 2b** and nitrile complexes of Pd(II) **3** and Pt(II) **4** proceeded at room temperature for *ca* 24 h and resulted in the formation of phosphine complexes $[MCl_2L_2]$ **5–8** (Scheme 2). After recrystallization from the mixture of CH_2Cl_2/Et_2O these compounds were isolated as *trans*-$[PdCl_2L^1_2]$ (***trans*-5**, yield of 82 %), *cis*-$[PtCl_2L^1_2]$ (***cis*-6**, yield of 87 %), *trans*-$[PdCl_2L^2_2]$ (***trans*-7**, yield of 86 %), trans-$[PtCl_2L^2_2]$ (***trans*-8**, yield of 94 %). The latter was quantitatively isomerized into ***cis*-8**.

$$[MCl_2(NCR)_2] \;+\; 2\,L \xrightarrow[-2\,NCR]{} [MCl_2(L)_2]$$

3, **4** **2a**, **b** **5–8** (82–94%)

3: M = Pd, R = CH_3
4: M = Pt, R = C_2H_5

5: M = Pd, L^1 = **2a**
6: M = Pt, L^1 = **2a**
7: M = Pd, L^2 = **2b**
8: M = Pt, L^2 = **2b**

Scheme 2. Synthesis and numbering of $[MCl_2L_2]$.

The composition and the structures of compounds **5–8** were determined by means of high-resolution mass spectrometry (HRMS), ^1H, ^{13}C, ^{31}P, ^{195}Pt, solid state ^{31}P NMR spectroscopy (see Experimental and Supplementary Information), and X-ray analysis (Figures 2−6).

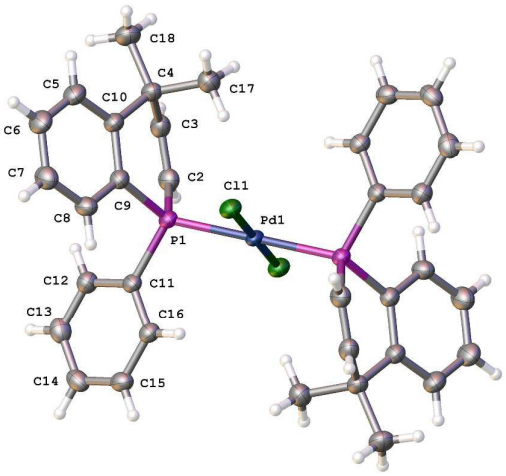


Figure 2. View of ***trans*-5** with the atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

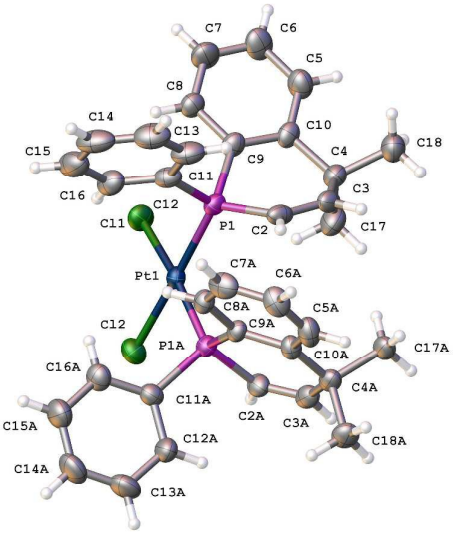


Figure 3. View of ***cis*-6** with the atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

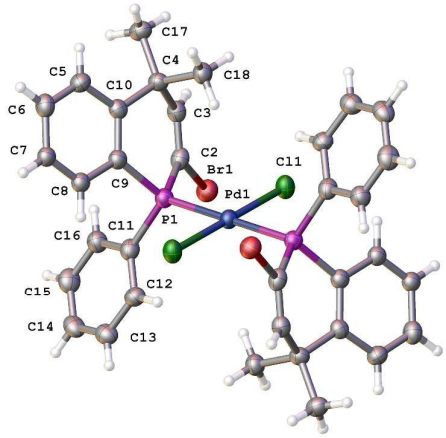


Figure 4. View of ***trans*-7** with the atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

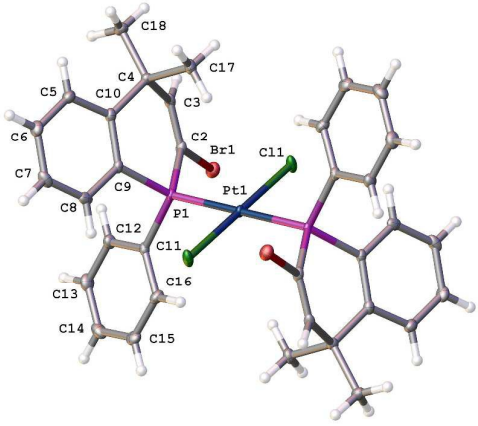


Figure 5. View of ***trans*-8** with the atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

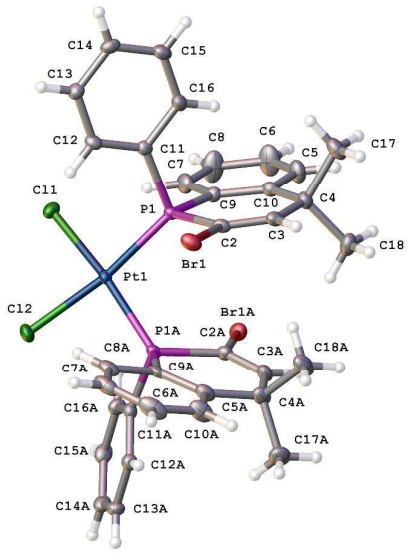


Figure 6. View of ***cis*-8** with the atomic numbering schemes. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for ***trans*-5**, ***cis*-6**, ***trans*-7**, ***trans*-8** and ***cis*-8**.

	***trans*-5**	***cis*-6**	***trans*-7**	***trans*-8**	***cis*-8**
M−P	2.3150(8)	2.244(2) 2.258(2)	2.3281(12)	2.3131(7)	2.2501(8) 2.2552(8)
M−Cl	2.3093(9)	2.350(2) 2.342(2)	2.2916(12)	2.3047(7)	2.3518(8) 2.3518(8)
P1−M1−P1A	180.0	98.90(7)	180.0	180.0	98.79(3)
Cl1−M1−Cl1A	180.0	88.06(8)	180.00	180.0	87.31(3)
P1−M1−Cl1	86.48(3)	90.08(8)	91.06(4)	89.02(2)	168.48(3)
P1−M1−Cl1A	93.52(3)	178.01(8)	88.94(4)	89.02(2)	88.77(3)
P1A−M1−Cl1	93.52(3)	170.71(8)	88.94(4)	90.98(2)	87.31(3)
P1A−M1−Cl1A	86.48(3)	82.99(8)	91.06(4)	90.98(2)	166.33(3)

Table 2. ^{31}P and ^{195}Pt NMR data for ***trans*-5**, ***cis*-5**, ***cis*-6**, ***trans*-7**, ***trans*-8** and ***cis*-8**.

	***trans*-5**	***cis*-5**	***cis*-6**	***trans*-7**	***trans*-8**	***cis*-8**

δ_P, $CDCl_3$	−9.7, −6.9	−14.3, −13.8	−27.1	4.1, 4.3	1.9	−7.9, −6.9
δ_P, solid state	−5.2	–	−27.4, −23.7	3.9, 5.9	1.9	−9.2, −5.6
δ_{Pt}, $CDCl_3$	–	–	−4380, −4365	–	−4028	−4401, −4398
$^1J_{P,Pt}$, Hz	–	–	3635, 3638	–	2782	3840, 3880

The X-ray data gave us possibility to calculate cone angles for new phosphine ligands **2a** and **2b** and to compare their steric features with PPh_3.[1b] These phosphines are bulkier than PPh_3 (**2a** Θ = 152 °, **2b** Θ = 158 °, PPh_3 Θ = 145 °) but their volumes are not very large. We synthesised bromo-substituted phosphine **2b** due to the high volume of the Br atom (**1b** was the most bulky substituted 1,4-dihydrophosphinoline 1-oxide among all available starting compounds for our studying). Really, the cone angle of **2b** is 6 ° more than the one of **2a**.

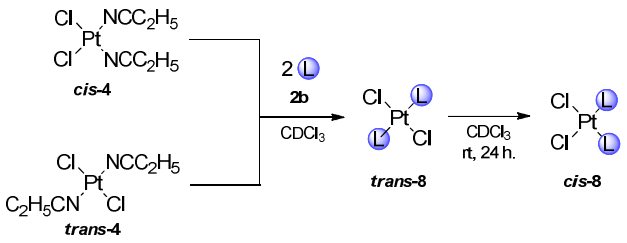
Complexes ***trans*-5**, ***trans*-7**, and ***trans*-8** have almost undistorted square-planar structure of the metal centers and C_2 rotation axis while the structures of ***cis*-6** and ***cis*-8** are some distorted squares due to the bulkier phosphines ligands in comparison with the Cl atoms (Figures 2–6, Table 1). The enhanced cone angle of phosphine **2b** comparing **2a** results the small distortion of the square plane in complex ***cis*-8** (Table S2). Lengths of M–P bonds are typical for Pd–P and Pt–P bonds in other phosphine complexes.[17] The lengths of M–P bonds in the *trans*-complexes are slightly higher than in the *cis*-species (***trans*-5** Pd1–P1 2.3150(8) Å, ***trans*-7** Pd1–P1 2.3281(12) Å, ***trans*-8** Pt1–P1 2.3131(7) Å, ***cis*-6** Pt1–P1 2.258(2) Å and Pt1–P1A 2.244(2) Å, ***cis*-8** Pt1–P1 2.2552 (8) Å and Pt1–P1A 2.2501(8) Å). It can be discussed in relation to the *trans*-influence.[18] In the case of *trans*-$[PtCl_2L_2]$ the phosphorus ligand is *trans*-oriented to an identical ligand, which exerts a large *trans*-influence, thereby weakening the Pt–P bond. In *cis*-$[PtCl_2L_2]$ the phosphorus ligand is *trans*-located to Cl which has a small *trans*-influence and, therefore, does not greatly elongate the *trans* Pt–P bond.

It is worth noting, that the crystals of ***trans*-7** and ***trans*-8** are isomorphic. Such isomorphism of Pd and Pt species was reported early for some other phosphine complexes (e.g. *trans*-$[MCl_2(PPh_3)_2]\cdot CH_2Cl_2$ M = Pd,[19] Pt[20] or *trans*-$[MCl_2(PPh_2t\text{-}Bu)_2]\cdot CH_2Cl_2$ M = Pd,[21] Pt[21]).

The homogeneity of the reaction products ***trans*-5**, ***cis*-6**, ***trans*-7**, and ***trans*-8** was proven by the solid state ^{31}P NMR spectra of these complexes, which contained one broad signal or two close overlapping signals corresponding to one geometric isomer in each compound.

To determine the geometry of complexes in solution we used ^{31}P NMR spectroscopy. It should be noted that, at the coordination of phosphine **2a, 2b** to metal, a stereogenic center appears on the phosphorus atom, resulting in each of geometric isomers of complexes **5–8** (bearing two stereogenic centres) can exist as a racemate or a *meso*- form. Therefore, "paired" signals with comparable intensity were observed in the ^{31}P NMR spectra of complexes **5–8** in solution.

Two sets of signals (δ_P = −14.3, −13.8 and −9.7, −6.9 ppm) were detected in ^{31}P NMR spectrum of Pd complex **5** in $CDCl_3$ that indicated the existence of both *cis*-and *trans*-isomers in solution. It is known that phosphorus atoms in complexes $[MX_2L_2]$ (M = Pd, Pt; X = Cl, Br; L = phosphine) in *trans*-isomers resonate at higher frequencies than phosphorus atoms in *cis*-isomers.[17b, 22] Thus, the signals at δ_P = −14.3 and −13.8 ppm correspond to *cis*-isomers, but signals at δ_P = −9.7 and −6.9 ppm belong to *trans*-ones. This conclusion is also confirmed by the fact that in solid state ^{31}P NMR spectrum of ***trans*-5** a signal at −5.2 ppm was observed. Based on ^{31}P NMR data we found that *cis*- and *trans*- isomers of complex **5** were in equilibrium in a $CDCl_3$ solution. At 20 °C the equilibrium mixture consisted of 45% of ***trans*-5** and 55% of ***cis*-5,** upon heating to 50 °C the content of ***cis*-5** was increased up to 73%, but then subsequent cooling to 20 °C led to the initial ratio of isomers. The other Pd complex **7** in solution in $CDCl_3$ existed as the *trans*-isomer only (δ_P = 4.1 and 4.3 ppm). Presumably, this is due to the larger spatial volume of bromo-substituted phosphine **2b** compared to **2a**. Pt complex **6** in solution in $CDCl_3$ was present only in a single geometrical isomer with *cis*-configuration (at the synthesis from both ***cis*-4** and from ***trans*-4**) that followed from the close values of chemical shifts of the phosphorus in ^{31}P NMR spectra registered in solution and in solid state. Complex **8** was initially formed only in the *trans*-form, which in the presence of small amounts of phosphine **2b** (10% mol, accordingly to the procedure that reported for phosphine catalysed *trans*-, *cis*- isomerization[23]) was completely transformed into ***cis*-8** at room temperature for 24 h (Scheme 3) and crystallized in this form. The signals of phosphorus atoms in ^{31}P NMR spectrum of ***trans*-8** were at δ_P = 1.9 ppm, whereas the signals of phosphorus atoms in ^{31}P NMR spectrum of ***cis*-8** were located at lower frequencies δ_P = −7.9 and −6.9 ppm. It was also found that at room temperature for solution of complex ***trans*-8** in $CDCl_3$, even in the absence of phosphine, isomerization slowly occurred leading to ***cis*-8**, the content of the latter reached 66% after 6 months keeping. This revealed that the *trans*-isomer **8** was a kinetically controlled reaction product, while its *cis*-isomer was thermodynamically controlled one, i.e. more stable in solution.



Scheme 3. Formation of complex **8** from ***cis*-4** and ***trans*-4**.

It was found that the geometric structure of the complexes with phosphine **2b** can also be determined by ^1H NMR spectroscopy. The ligands in the *trans*-complexes are magnetically inequivalent and the signal of the hydrogen atom at the double bond has the structure of a triplet, while in the *cis*-complexes it is a doublet[24]. That allows figuring out the geometry for complexes **7** and **8**. Such determination of structure for complexes **5** and **6** is difficult due to signal overlapping in their ^1H NMR spectra.

The geometric configuration for platinum complexes **6** and **8** can also be determined from analysis of the P,Pt-coupling constants: for *cis*-$[PtCl_2(PR_3)_2]$ $^1J_{P,Pt}$ > 3000 Hz,[17b,22a,25] and for *trans*-$[PtCl_2(PR_3)_2]$ $^1J_{P,Pt}$ < 2800 Hz.[17b,22c,26,] Analysis of values of $^1J_{P,Pt}$ constants confirmed the above conclusion on the structure of complexes **6** and **8** in the $CDCl_3$ solution.

Usually it is assumed that these coupling constants are dominated by the Fermi contact interaction of nuclei with *s*-orbital electrons[27] and are taken as an estimation of bond strength, provided such bonds involves hybrid orbitals with some *s* character. As the magnitude of $^1J_{P,Pt}$ coupling constants is related to the *s*-character of the Pt–P bond they give information on the geometry of the complexes.[27-28] For the *cis*-geometry the displacement of the π-acceptor orbitals on phosphorus is such that they overlap with the d_{xy}, d_{zy}, and d_{xz} orbitals of platinum. The geometry of the phosphorus π-orbitals in the *trans*-configuration means that only two metal *d*-orbitals are available for π-bonding.[29] The increased π-bonding in the *cis*-isomers leads to a synergic increase in the *s*-character of the Pt–P bond and, hence, to a larger $^1J_{P,Pt}$ coupling constant relative to the *trans*-isomer.

Conclusions

In conclusion, we have synthesized a new type of phosphine ligands, 1,4-dihydrophosphinolines. They exhibit properties of typical phosphine ligands forming complexes with Pd(II) and Pt(II). Both 1-phenyl-4,4-dimethyl-1,4-dihydrophosphinoline **2a,** 1-phenyl-2-bromo-4,4-dimethyl-1,4-dihydrophosphinoline **2b** and their complexes with Pd(II), Pt(II) **5–8** have been fully characterized by means of ^{1}H, ^{13}C, ^{31}P, and ^{195}Pt (for the Pt species) NMR and HRMS. Structures of **2b** and complexes **5–8** and have been confirmed by X-ray analysis. Both in palladium and platinum complexes, the phosphine ligands are coordinated through phosphorus atoms, the C=C double bonds of phosphines are not involved in the coordination. Due to the presence of prochiral phosphorus atom in the ligands, the complexes have formed mixtures of racemate and *meso*-form in comparable ratios. Palladium complexes are more stable in *trans*-form, although the complex with ligand **2a** (having a smaller spatial volume) exists as a mixture of the *cis*-/*trans*-isomers. Larger metal center and, consequently, less stringent sterical demands, allow the platinum complexes to exist in *cis*-form, which is more favorable from the point of view of differences in the *trans*-influence of phosphine and chloride ligands.

Experimental Section

Materials and Instrumentation. Solvents, $PdCl_2$, $PtCl_2$, PPh_3, and $HSiCl_3$ were obtained from commercial sources and used as received, apart from CH_2Cl_2, which was purified by the conventional distillation over K_2CO_3. Complexes $PdCl_2(CH_3CN)_2$ (**3**)[30] and $PtCl_2(C_2H_5CN)_2$ (**4**)[31] were synthesised by the known procedure. C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNS/O analyzer. The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker AVANCE III 400 spectrometers at 25 °C (at 400, 100, 162, and 86 MHz for ^{1}H, ^{13}C, ^{31}P, and ^{195}Pt NMR spectra, respectively). Chemical shifts are given in δ-values [ppm] referenced to the residual signals of non-deuterated solvent ($CHCl_3$): δ 7.26 (^{1}H), 77.2 (^{13}C), or to the signal of 85% H_3PO_4 δ 0.0 ppm (^{31}P) and 1.2 M Na_2PtCl_6 in D_2O. Solid-state NMR experiments were performed on a Bruker Avance III NMR spectrometer operating at 9.4 T. ^{31}P CP/MAS NMR spectra were acquired using a double-resonance 4 mm MAS Bruker probe at a resonance frequency of 162 MHz under 12 kHz MAS. The CP contact time in all experiments was 2 ms with a delay between acquisitions of 20 seconds. SPINAL-64 proton decoupling was used during spectra acquisition. 256 scans were collected. ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4. Mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source; MeOH was used as the solvent. The instrument was operated both at positive and negative ion modes using *m/z* range of 50–3000. The capillary voltage of the ion source was set at –4500 V (ESI^+) or 3500 V (ESI^-) and the capillary exit at ±(70–150) V. The nebulizer gas pressure was 0.4 bar and drying gas flow 4.0 L/min.

Synthesis of phosphines 2. A solution of phosphinoline oxides **1** (1.49 mmol for **1a**; 1.15 mmol for **1b**) in 5 ml of benzene was placed into a 20 ml pressure tube followed by addition of $HSiCl_3$ (3 mL, 30 mmol) under argon. The reaction mixture was heated at 100 °C for 5 h, cooled with ice bath, and quenched by dropwise addition of 25% aq. NaOH (30 mL) at cooling. The organic layer was separated; the aqueous solution was extracted with Et_2O (30 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, and the solvent was removed to give yellow oil. The product was isolated by flash chromatography with petroleum ether as eluent.

1-Phenyl-4,4-dimethyl-1,4-dihydrophosphinoline (***2a***). Yield 0.31 g (83%), colorless oil. ^{1}H NMR ($CDCl_3$, δ): 1.36 s (3H, CH_3), 1.68 s (3H, CH_3), 6.22 dd (1H, C^3H, $^3J_{HH}$ 12.0 Hz, $^3J_{HP}$ 28.0 Hz), 6.37 dd (1H, C^2H, $^3J_{HH}$ 12.0 Hz, $^2J_{HP}$ 16.0 Hz), 7.08–7.16 m (2H, $H_{arom.}$), 7.27–7.31 m (1H, $H_{arom.}$), 7.36–7.39 m (3H, $H_{arom.}$), 7.51–7.58 m (3H, $H_{arom.}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 30.6 d (CH_3, $^4J_{CP}$ 2.0 Hz), 31.7 d (CH_3, $^4J_{CP}$ 2.0 Hz), 38.3 s (C^4), 123.3 d (C^3, $^2J_{CP}$ 9.0 Hz), 125.2 d (C^5, $^3J_{CP}$ 1.0 Hz), 125.5 d (C^7, $^3J_{CP}$ 8.0 Hz), 128.1 s ($C^{4'}$), 128.5 d ($C^{3'}$,$C^{5'}$, $^3J_{CP}$ 8.0 Hz), 129.4 s (C^6), 132.2 d (C^8, $^2J_{CP}$ 24.0 Hz), 134.0 d (C^9, $^1J_{CP}$ 9.0 Hz), 134.7 d ($C^{2'}$,$C^{6'}$, $^2J_{CP}$ 21.0 Hz), 138.4 d (C^{10}, $^2J_{CP}$ 17.0 Hz), 144.2 d (C^2, $^1J_{CP}$ 3.0 Hz), 145.4 d ($C^{1'}$, $^1J_{CP}$ 5.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –39.3. ESI^+-MS, *m/z*: calcd. for $C_{17}H_{17}PH^+$ 253.1141, found 253.1156 $[M+H]^+$; calcd. for $C_{17}H_{17}PNa^+$ 275.0955, found 275.0979 $[M+Na]^+$.

1-Phenyl-2-bromo-4,4-dimethyl-1,4-dihydrophosphinoline (***2b***). Yield 0.33 g (87%), m.p. 185−187 °C. ^{1}H NMR ($CDCl_3$, δ): 1.46 s (3H, CH_3), 1.66 s (3H, CH_3), 6.70 d (1H, C^3H, $^3J_{HP}$ 8.0 Hz), 7.10–7.15 m (2H, $H_{arom.}$), 7.30–7.42 m (4H, $H_{arom.}$), 7.49–7.56 m (3H, $H_{arom.}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 31.6 d (CH_3, $^4J_{CP}$ 2.0 Hz), 32.7 d (CH_3, $^4J_{CP}$ 2.0 Hz), 42.4 (C^4, $^3J_{CP}$ 2.0 Hz), 118.4 d (C^2, $^1J_{CP}$ 25.0 Hz), 126.2 d (C^5, C^7, $^3J_{CP}$ 7.0 Hz), 128.5 d ($C^{3'}$,$C^{5'}$, $^3J_{CP}$ 8.0 Hz), 128.8 s ($C^{4'}$), 129.9 s (C^6), 132.7 d (C^8, $^2J_{CP}$ 29.0 Hz), 133.0 d (C^9, $^1J_{CP}$ 10.0 Hz), 134.7 d ($C^{2'}$,$C^{6'}$, $^2J_{CP}$ 21.0 Hz), 137.1 d (C^{10}, $^2J_{CP}$ 18.0 Hz), 144.2 d ($C^{1'}$, $^1J_{CP}$ 2.0 Hz), 145.8 d (C^3, $^2J_{CP}$ 4.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –22.1. ESI^+-MS, *m/z*: calcd. for $C_{17}H_{16}BrPH^+$ 331.0246, found 331.0258 $[M+H]^+$; calcd. for $C_{17}H_{16}BrPNa^+$ 353.0060, found 353.0081 $[M+Na]^+$.

Synthesis of complexes 5–8

Complex 5. A solution of **2a** (0.30 mmol) in CH_2Cl_2 (1 mL) was rapidly added to a suspension of nitrile complex **3** (0.15 mmol) in CH_2Cl_2 (2 mL) at room temperature. The slurry was stirred under argon for 15 min. The solvent was removed and the oily residue treated with diethyl ether. Complex **5** was isolated as a yellow solid and dried at the air. Yield of 82 % (mixture of *cis-, trans-* isomers with two diastereomers for each), m.p. 230 °C (dec.). Anal. Calcd. for $C_{34}H_{34}Cl_2P_2Pd$: C, 59.89; H, 5.03. Found: C, 59.94; H, 5.07. ^{1}H

NMR ($CDCl_3$, δ): 1.30 (s, CH_3), 1.46 (s, CH_3), 1.56 (s, CH_3), 1.58 (s, CH_3), 1.59 (s, CH_3), 1.62 (s, CH_3), 1.63 (s, CH_3), 5.55–5.63 (m, =CH), 6.11–6.88 (m, =CH), 7.10–7.18 (m, H_{arom}), 7.29–7.93 (m, H_{arom}), 8.23–8.25 (m, H_{arom}). $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$, δ): 30.4 (CH_3), 30.6 (CH_3), 30.8 (CH_3), 31.0 (CH_3), 31.6 (CH_3), 31.8 (CH_3), 38.7 (C^4), 38.8 (C^4), 115.3, 115.7, 116.2, 124.0, 125.4, 125.6, 125.7, 125.8, 125.9, 126.4, 128.3, 128.4, 128.5, 130.2, 130.6, 130.8, 131.2, 131.4, 132.0, 132.3, 132.4, 134.7, 135.1, 135.6, 135.7, 136.3, 148.0, 148.3, 151.8, 151.9, 154.2, 155.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −14.3 (***cis*-5**), −13.8 (***cis*-5**), −9.7 (***trans*-5**), −6.9 (***trans*-5**). ^{31}P MAS NMR (δ): −5.2 (***trans*-5**). HRMS(ESI^+), *m/z*: calcd. for $C_{34}H_{34}P_2PdCl^+$ 645.0859, found 645.0905 $[M–Cl]^+$, calcd. for $C_{34}H_{34}P_2PdCl_2Na^+$ 703.0445, found 703.0473 $[M+Na]^+$.

Complex *cis*-6. A solution of **2a** (0.30 mmol) in CH_2Cl_2 (2 mL) was rapidly added to a solution of nitrile complex **4** (0.15 mmol) in CH_2Cl_2 (3 mL) and the reaction mixture was stirred overnight at room temperature under argon. The solvent was removed and the colorless residue was washed with diethyl ether and dried at the air. Yield of 87 % (mixture of two diastereomers), m.p. 300 °C (dec.). Anal. Calcd. for $C_{34}H_{34}Cl_2P_2Pt$: C, 52.99; H, 4.45. Found: C, 53.07; H, 4.47. ^1H NMR ($CDCl_3$, δ): 1.22 (s, CH_3), 1.45 (s, CH_3), 1.51 (s, CH_3), 1.57 (s, CH_3), 5.49–5.57 (m, =CH), 6.11–6.55 (m, =CH), 6.85–7.15 (m, H_{arom}), 7.30–7.56 (m, H_{arom}), 7.79–7.90 (m, H_{arom}). $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$, δ): 30.7 (CH_3), 30.9 (CH_3), 31.2 (CH_3), 31.4 (CH_3), 38.6 (C^4), 114.7, 115.1, 125.6, 125.7, 125.9, 126.2, 128.1, 128.3, 128.4, 130.4, 130.7, 131.1, 131.2, 131.4, 131.6, 132.6, 133.7, 133.9, 134.3, 134.9, 135.3, 136.1, 148.0, 153.5, 155.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −27.1 (s + d, $^1J_{P,Pt}$ = 3635 Hz), −25.3 (s + d, $^1J_{P,Pt}$ = 3638 Hz). ^{195}Pt NMR ($CDCl_3$, δ): −4380 (t, $^1J_{Pt,P}$ = 3635 Hz), −4365 (t, $^1J_{Pt,P}$ = 3638 Hz). ^{31}P MAS NMR (δ): −27.4, −23.7. HRMS(ESI^+), *m/z*: calcd. for $C_{34}H_{34}P_2PtCl^+$ 734.1472, found 734.1497 $[M–Cl]^+$, calcd. for $C_{34}H_{34}P_2PtCl_2Na^+$ 792.1058, found 792.1087 $[M+Na]^+$.

Complex *trans*-7. A solution of **2b** (0.30 mmol) in CH_2Cl_2 (2 mL) was rapidly added to a suspension of nitrile complex **3** (0.15 mmol) in CH_2Cl_2 (3 mL) at room temperature. The slurry was stirred overnight under argon, then the bright yellow solid was filtered, washed with diethyl ether and dried at the air. Yield of 86 % (mixture of two diastereomers), m.p. 257 °C (dec.). Anal. Calcd. for $C_{34}H_{32}Br_2Cl_2P_2Pd$: C, 48.63; H, 3.84. Found: C, 48.50; H, 3.80. ^1H NMR ($CDCl_3$, δ): 1.55 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 6.85 (t, $^3J_{P,H}$ = 10.5 Hz, 2H, C^3H), 7.25–7.55 (m, 12H, $H_{arom.}$), 7.68–7.71 (m, 4H, $H_{arom.}$), 7.86–7.95 (m, 2H, $H_{arom.}$). $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$, δ): 31.2 ($2CH_3$), 32.1 (CH_3), 32.2 (CH_3), 42.6 ($2C^4$), 110.0 (C^3H), 110.1(C^3H), 124.2, 124.3, 126.5, 126.7, 127.9, 128.0, 128.2, 129.1, 129.2, 130.9, 131.0, 131.03, 131.06, 134.7, 135.0, 135.1, 147.0, 147.1, 151.3, 151.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 4.1, 4.3. ^{31}P MAS NMR (δ): 3.9, 5.9. HRMS(ESI^+), *m/z*: calcd. for $C_{34}H_{32}P_2Br_2PdCl^+$ 802.9049, found 802.9066 $[M–Cl]^+$, calcd. for $C_{34}H_{32}P_2Br_2PdCl_2Na^+$ 862.8639, found 862.8647 $[M+Na]^+$.

Complex *trans*-8. Complex was prepared as described for ***trans*-7** starting from **2b** (0.30 mmol) and nitrile complex **4** (0.15 mmol) in CH_2Cl_2 (5 mL) to give pale yellow solid. Yield of 94 %, m.p. 265 °C (dec.). Anal. Calcd. for $C_{34}H_{32}Br_2Cl_2P_2Pt$: C, 43.99; H, 3.47. Found: C, 43.92; H, 3.43. ^1H NMR ($CDCl_3$, δ): 1.56 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 6.86 (t, $^3J_{P,H}$ = 10.5 Hz, 1H, C^3H), 7.30–7.57 (m, 6H, $H_{arom.}$), 7.69–7.74 (m, 2H, $H_{arom.}$), 7.96 (ddd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 6.9 Hz, 1H, $H_{arom.}$). $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$, δ): 31.1 (CH_3), 32.3 (CH_3), 42.6 (C^4), 109.1, 123.9, 126.4, 126.6, 127.9, 128.6, 130.9, 131.0, 134.7, 134.9, 147.1, 151.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 1.9 (s + d, $^1J_{P,Pt}$ = 2782 Hz). ^{195}Pt NMR ($CDCl_3$, δ): −4028 (t, $^1J_{Pt,P}$ = 2782 Hz). ^{31}P MAS NMR (δ): 1.9. HRMS(ESI^+), *m/z*: calcd. for $C_{34}H_{32}P_2Br_2PtCl_2Na^+$ 949.9248, found 949.9254 $[M+Na]^+$.

Complex *cis*-8. A solution of **2b** (0.002 mmol, 10 mol%) in $CDCl_3$ (0.05 mL) was rapidly added to a solution of complex ***trans*-8** (0.02 mmol) in $CDCl_3$ (0.5 mL) at room temperature. The slurry was kept under argon for 24 h. The solvent was rapidly removed and the solid residue treated with diethyl ether. Yield of 98% (mixture of two diastereomers), m.p. > 300 °C (dec.). Anal. Calcd. for $C_{34}H_{32}Br_2Cl_2P_2Pt$: C, 43.99; H, 3.47. Found: C, 43.90; H, 3.42. ^1H NMR ($CDCl_3$, δ): 0.78, 1.30, 1.36, 1.64 (s, 12H, CH_3), 6.36–6.54, 7.07–7.24, 7.28–7.30, 7.37–7.42, 7.47–7.63 8.79–8.89 (m, 20H). $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$, δ): 30.3, 30.5, 30.6, 32.4, 42.6, 42.8, 108.8, 108.9, 123.9, 126.3, 126.8, 126.9, 127.4, 127.5, 127.6, 130.4, 131.7, 132.2, 132.3, 132.8, 136.3, 146.6, 152.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −7.9 (s + d, $^1J_{P,Pt}$ = 3880 Hz), −6.9 (s + d, $^1J_{P,Pt}$ = 3840 Hz). ^{195}Pt NMR ($CDCl_3$, δ): −4401 (t, $^1J_{Pt,P}$ = 3840 Hz), −4398 (t, $^1J_{Pt,P}$ = 3880 Hz). ^{31}P MAS NMR (δ): −9.2, −5.6. HRMS(ESI^+), *m/z*: calcd. for $C_{34}H_{32}P_2Br_2PtCl_2Na^+$ 949.9248, found 949.9254 $[M+Na]^+$.

X-ray Structure Determination. Crystals of **2b**, ***trans*-5, *cis*-6, *trans*-7, *trans*-8**, and ***cis*-8** suitable for X-ray diffraction were obtained upon slow evaporation of a solution of respective compounds in CH_2Cl_2/Et_2O mixture in air at room temperature. Single-crystal X-ray diffraction experiments were carried out with Agilent Technologies Excalibur Eos and Agilent Technologies SuperNova Atlas diffractometers (monochromated Mo *Kα* and Cu *Kα* radiations). The unit cell parameters and refinement characteristics for the crystal structures are given in **Table S1**. The structures had been solved by the direct methods and refined by means of the SHELXL-97 program[32] incorporated in the OLEX2 program package.[33] Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCD 1426280, 1432267-1432271) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Synthesis of phosphine ligands was supported by Saint Petersburg State University (grants no. 12.50.2525.2013 and 12.38.195.2014). The complexes study was supported by RFBR (grants no. 14-03-00297 and no. 16-33-60123). Spectral studies were performed at the Center for Magnetic Resonance, the Center for Chemical Analysis and Materials Research, and the Research Center for X-ray Diffraction Studies of Saint Petersburg State University.

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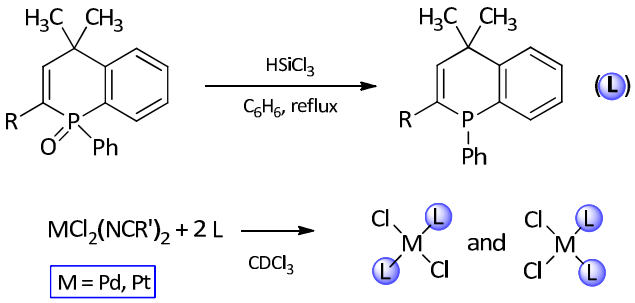

Syntheses and characterizations of novel 1,4-dihydrophosphinolines and their complexes with Pd(II) and Pt(II) are described.