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Macrocyclic Platinum(II) Complexes with a Bifunctional Diphosphine Ligand

Andrea E. Pascui,[a] Karlotta van Rees,[a] Dirk W. Zant,[a] Daniël L. J. Broere,[a] Maxime A. Siegler,[b] and Jarl Ivar van der Vlugt*[a]

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The preparation and coordination chemistry of a ditopic ligand scaffold ($\mathbf{1^{H2}}$), containing both a phosphorus-donor (*P*) and a nitrogen-donor (*N*) binding pocket, is reported. The ligand was synthesized by reductive amination from 3-(diphenylphosphino)benzaldehyde and *N*-(2-aminophenyl)-*N*-methylbenzene-1,2-diamine. Selective coordination in the *P*-pocket was achieved for Pt^{II}, with careful control over the reaction conditions and precursor materials providing access to either the thermodynamic *cis* isomer, *cis*-$PtCl_2(\mathbf{1^{H2}})$ (**2**), or the kinetic *trans* isomer, *trans*-$PtCl_2(\mathbf{1^{H2}})$ (**3**). Both species have been fully characterized both in the solid state and in solution. Thermodynamic parameters for isomerization processes of **2** and **3** have been determined. Halide abstraction from **2** and **3** led to formation of *cis*-$[Pt(CH_3CN)(Cl)(\mathbf{1^{H2}})]BF_4$ and *trans*-$[Pt(CH_3CN)(Cl)(\mathbf{1^{H2}})]BF_4$.

Introduction

Hybrid ligands bearing both phosphorus (soft) and nitrogen (hard) donors continue to enjoy much attention in areas such as coordination chemistry and catalysis.[1] Recent examples of ditopic phosphine–nitrogen-based ligand structures highlight the potential to selectively metalate one of the two donor groups to access monofunctionalized architectures that are of relevance for the construction of (hetero)bimetallic coordination compounds[2] as well as for applications in supramolecular catalysis, using host-guest or templating principles.[3] C_3-Symmetric building blocks have received much attention for the formation of well-defined (di)metallic complexes, but (*pseudo*-)C_2-symmetric counterparts have also been successfully explored in recent years.[4]

Most of the employed ditopic P,N-ligands feature (semi-)rigid linkers between the two donor sites, which limits the number of possible geometries and hence restricts coordination chemistry. A monoatomic linker or the absence of any linker between P and N units may induce direct metal–metal bonding that could be useful in the context of small-molecule activation.[5] However, straightforward access to more flexible yet site-selective frameworks would facilitate other coordination modes and geometries and allow bimetallic species to be constructed without direct metal–metal interactions, which may be relevant for catalytic activity. Control over metal coordination with flexible ditopic ligands is not trivial, both with respect to selectivity for a specific binding site as well as to the geometry imposed on the metal center. We therefore set out to design a ditopic ligand scaffold featuring two potential binding sites (a *P*- and an *N*-pocket; Figure 1), bridged by a flexible linker, to gain control over the geometry and site selectivity of this framework. We herein discuss the selective metalation of the *P*-pocket toward Pt^{II}, including selective formation of *cis* and *trans* isomers and their interconversion. This research is expected to aid future investigations into the preparation of bimetallic architectures based on flexible scaffolds.

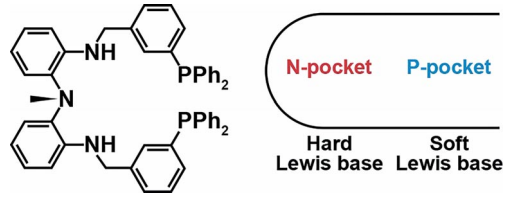

Figure 1. Schematic representation of ditopic ligand $\mathbf{1^{H2}}$.

The use of square-planar Pt^{II} complexes with long-chain chelating (bis)phosphine ligands to generate macrocyclic structures may result in a mixture of *cis* and *trans* isomers and oligomeric species in solution. The choice of the metal precursor, the size and rigidity of the chelate ring, and changes in the reaction conditions (e.g., temperature, reaction time, concentration and solvent) can alter the ratio be-

[a] Homogeneous, Bio-inspired and Supramolecular Catalysis, van't Hoff Institute for Molecular Sciences, University of Amsterdam,
Science Park 904, 1098 XH, Amsterdam, The Netherlands
E-mail: j.i.vandervlugt@uva.nl
www.homkat.nl
[b] Department of Chemistry, John Hopkins University,
3400 N Charles Street, Baltimore, Maryland 21218, USA
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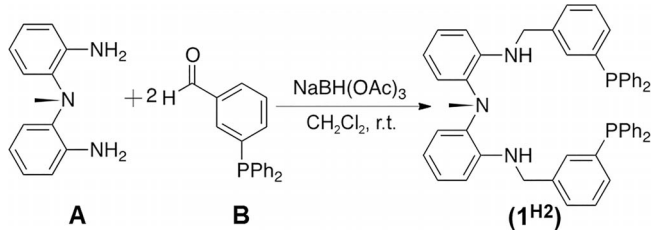
tween the products.[6] The isolation of pure samples of both *cis* and *trans* isomers with the same flexible chelating ligand remains a challenging task. To synthesize the frequently less stable *trans* isomers, the use of *trans*-stabilizing groups in the metal precursors, e.g., Zeise's salt,[7] or an additional chromatographic step to separate the isomers[8] is often necessary, which can increase the time and synthetic cost required to produce such complexes. Taking inspiration from known di- and tripodal P,N ligand systems, we wanted to study what would happen if the distance between both binding pockets was increased. The lack of control over the ratio of *cis*/*trans* isomers and the formation of oligomeric species represent major issues in the development of highly active and selective homogeneous catalysts based on flexible diphosphine ligands.[9] In this paper, we present the successful functionalization of the *P*-pocket to form macrocyclic species, and we discuss selective formation of both isomers in the flexible $PtCl_2(\mathbf{1^{H2}})$ system.

Results and Discussion

Synthesis of Bifunctional Diphosphine Ligand $\mathbf{1^{H2}}$ and X-ray Crystallographic Characterization of Macrocyclic Pt Complexes *cis*-$PtCl_2(\mathbf{1^{H2}})$ (2) and *trans*-$PtCl_2(\mathbf{1^{H2}})$ (3)

Initially, the formation of a tris(*sec*-amine) was targeted, to make use of the reported redox activity of such entities.[10] However, intramolecular cyclization of the peripheral imine and the pivotal secondary amine prevented isolation of the target compound. Hence, this NH group was replaced by an NCH_3 group to avoid this undesirable reactivity.

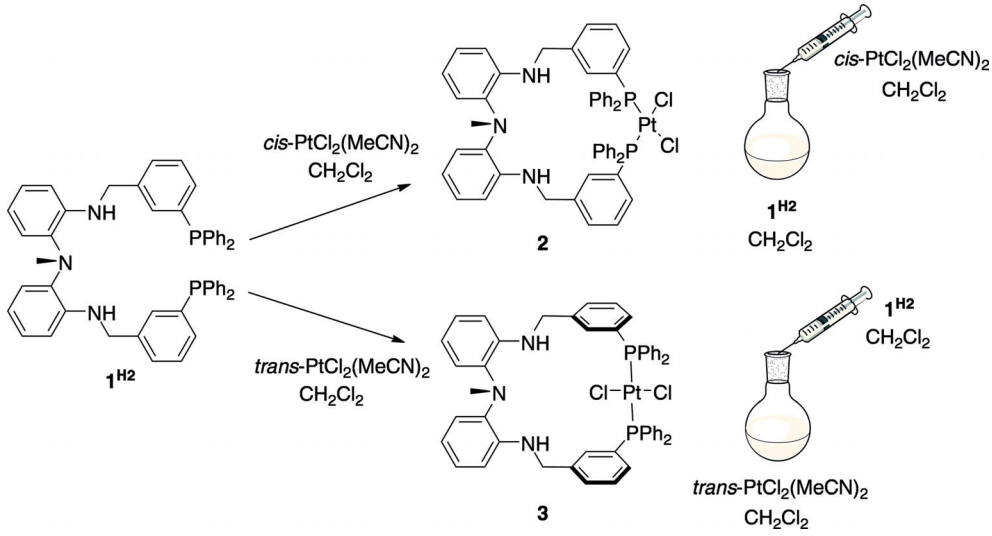
Ligand $\mathbf{1^{H2}}$ was synthesized by a one-pot reductive amination protocol using the readily accessible building blocks *N*-(2-aminophenyl)-*N*-methylbenzene-1,2-diamine (**A**) and 3-(diphenylphosphanyl)benzaldehyde (**B**) (Scheme 1). Given the instability of the intermediate Schiff-base product, the diimine was reduced in situ with the mild reducing agent sodium triacetoxyborohydride (STAB).[11] The ^{31}P NMR spectrum of $\mathbf{1^{H2}}$ displayed a singlet at δ = –5.37 ppm, and the ^1H NMR spectrum showed a broad triplet at δ = 4.53 ppm attributed to the NH protons (^3J = 4.0 Hz). The signals of the *N*-methyl group and the *N*-methylene groups were present at δ = 2.93 and 4.08 ppm, respectively. The ^{13}C (APT) NMR spectrum showed doublets for the resonances of the phenylene and phenyl rings connected to the phosphorus atoms.



Scheme 1. Reaction scheme for the synthesis of ligand $\mathbf{1^{H2}}$.

Initial reaction of ligand $\mathbf{1^{H2}}$ with the commercially available Pt^{II} precursor $PtCl_2(CH_3CN)_2$ (*cis*/*trans* ratio ca. 3:1) led to the formation of both *cis*-$PtCl_2(\mathbf{1^{H2}})$ (**2**) and *trans*-$PtCl_2(\mathbf{1^{H2}})$ (**3**), with no control over the ratio between the two isomers. We therefore screened various preparative methods using *cis*-$PtCl_2(CH_3CN)_2$ and *trans*-$PtCl_2(CH_3CN)_2$ to find the optimal synthetic routes to isolate both **2** and **3** in pure form (Scheme 2).

To suppress the formation of oligomeric species, the reactions were conducted under dilute conditions in CH_2Cl_2. The *cis* isomer **2** could be selectively obtained by addition of either *cis*- or *trans*-$PtCl_2(CH_3CN)_2$ precursor to the ligand. Pure **3** could only be isolated when ligand $\mathbf{1^{H2}}$ was



Scheme 2. Preparative routes for the selective formation of *cis*-$PtCl_2(\mathbf{1^{H2}})$ (**2**) and *trans*-$PtCl_2(\mathbf{1^{H2}})$ (**3**).

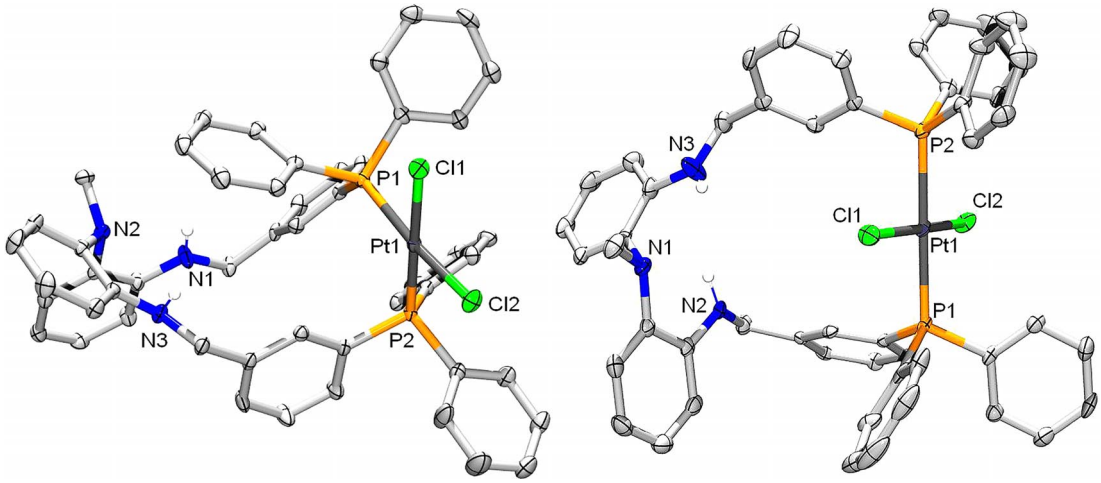


Figure 2. ORTEP plots (50% probability of thermal ellipsoids) of complex *cis*-$PtCl_2(\mathbf{1^{H2}})$ (**2**) (left) and *trans*-$PtCl_2(\mathbf{1^{H2}})$ (**3**) (right). Hydrogen atoms are omitted for clarity, except for NH. Selected bond lengths [Å] and angles [°]. For **2**: Pt(1)–P(1) 2.2599(7), Pt(1)–Cl(1) 2.3568(7), Pt(1)–P(2) 2.2513(8), Pt(1)–Cl(2) 2.3340(7), N(1)···N(3) 3.452, P(1)···P(2) 3.426, C(14)···C(39) 3.516; Cl(1)–Pt(1)–Cl(2) 88.52(3), P(1)–Pt(1)–P(2) 98.63(3), Cl(2)–Pt(1)–P(2) 90.30(3), P(1)–Pt(1)–Cl(1) 82.35(3). For **3**: Pt(1)–P(1) 2.3074(12), Pt(1)–Cl(1) 2.2929(12), Pt(1)–P(2) 2.3106(12), Pt(1)–Cl(2) 2.3087(12), N(2)···N(3) 3.528, P(1)···P(2) 4.618, C(20)···C(27) 5.164; Cl(1)–Pt(1)–Cl(2) 173.16(5), P(1)–Pt(1)–P(2) 178.53(4), P(1)–Pt(1)–Cl(1) 93.25(4), P(1)–Pt(1)–Cl(2) 86.06(4).

added to *trans*-$PtCl_2(CH_3CN)_2$ as the metal precursor. Colorless crystals of **2** and **3** were obtained by diffusion of hexane into CH_2Cl_2 or toluene solutions, respectively. The respective molecular structures are shown in Figure 2.

The geometry around the platinum center in compounds **2** and **3** is slightly distorted square-planar, as indicated by the bond angles around Pt. For species **2**, the Pt–Cl bonds point away from the *P*-pocket as a result of the *cis* orientation of the ligands. The *N*-pocket of $\mathbf{1^{H2}}$ adopts a folded conformation, with intramolecular N(1)···N(3) and C(14)···C(39) distances of 3.542 and 3.516 Å, respectively, whereas the P(1)···P(2) separation is 3.426 Å. Weak π···π stacking interactions are observed between one of the phenylene spacers and the phosphine phenyl ring (centroid···centroid distance 3.62 Å), and a weak intramolecular hydrogen bond between N3 (donor) and N1 (acceptor) is present [H(3A)···N(1) 2.65(4) Å; N(3)–H(3A)···N(1) 156(3)°]. For compound **3**, the ligand backbone (the *N*-pocket) unfolds [N(2)···N(3) 3.528, C(20)···C(27) 5.164 Å] to accommodate the *trans* coordination of both P-arms [P(1)···P(2) 4.618 Å]. A weak intramolecular hydrogen bond is observed between N2 (donor) and N3 (acceptor) [H(2)···N(3) 2.701 Å; N(2)–H(2)···N(3) 160.74°].

NMR Spectroscopic Investigations of *cis*-$PtCl_2(\mathbf{1^{H2}})$ (2) and *trans*-$PtCl_2(\mathbf{1^{H2}})$ (3)

Both **2** and **3** were fully characterized in solution by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The signals of the NCH_3 group show similar chemical shifts in both complexes, but the signals of the NH, CH_2 and some of the aromatic protons are shifted downfield in *trans*-$PtCl_2(\mathbf{1^{H2}})$ (Figure 3, left). The ^{13}C NMR spectrum of **2** contains doublets for the carbon atoms of the phenylene and phenyl rings attached to the phosphorus atoms, similar to that observed for free ligand $\mathbf{1^{H2}}$, whereas for **3**, *pseudo*-triplets are observed for the same fragments, which is in agreement with the respective geometries around Pt^{II} in solution and in the solid state. For **2**, the ^{31}P NMR spectrum shows a singlet with Pt satellites at δ = 14.5 ppm and a $J_{Pt,P}$ coupling constant of 3662 Hz, supporting the coordination of the chloride ion *trans* to the phosphorus atom and thus a mutual *cis* orientation of both phosphines (Figure 3, right).[12,13] For **3**, a singlet at δ = 20.7 ppm with Pt satellites and a $J_{Pt,P}$ coupling of 2614 Hz is observed by ^{31}P NMR spectroscopy, which is in agreement with mutual *trans* coordination of the two phosphine donors.

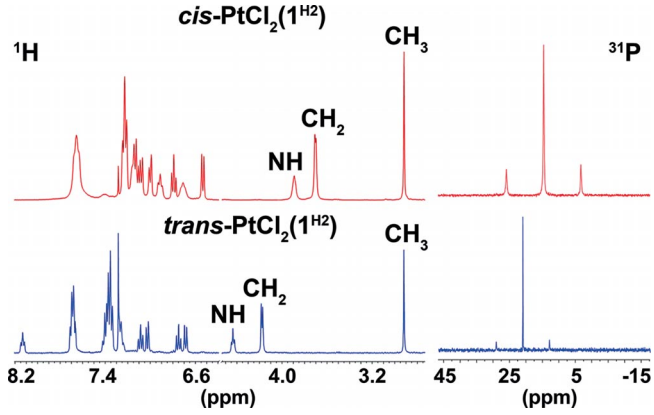


Figure 3. ^1H (left) and ^{31}P (right) NMR spectra of *cis*-$PtCl_2(\mathbf{1^{H2}})$ (**2**) (top) and *trans*-$PtCl_2(\mathbf{1^{H2}})$ (**3**) (bottom).

The spectral features for **2** are broader (for both the ^1H and ^{31}P NMR spectra) than for **3**, except for the methylamine group. We therefore recorded variable-temperature (VT) ^{31}P NMR spectra of both compounds in $CDCl_3$. Upon cooling, no change was observed in the spectrum of *trans*-$PtCl_2(\mathbf{1^{H2}})$. In contrast, the ^{31}P signal for *cis*-

$PtCl_2(\mathbf{1^{H2}})$ broadened at lower temperature, ultimately resulting in two peaks at δ = 17.0 and 10.9 ppm at –60 °C (Figure 4). Both resonances have $J_{P,Pt}$ coupling constants similar to that measured at 20 °C, suggesting the presence of two interconverting *cis* isomers. Reheating the sample to room temperature resulted in the coalescence of these two signals, with no further changes occurring above room temperature. The observed interconversion is probably related to the (substantial) rotational freedom in the flexible ligand backbone. The calculated $\Delta G^{\#}$ value at the coalescence temperature[14] is 10.4 kcal mol^{-1} (±0.2), using Equation (1) (with T_c = 245.15 K, and k_c = 2736 s^{-1}, where $k_c = 2.22\,\Delta\nu$).

$$\Delta G^{\#} = 4.58\,T_c[10.32 + \log(T_c/k_c)] \quad (1)$$

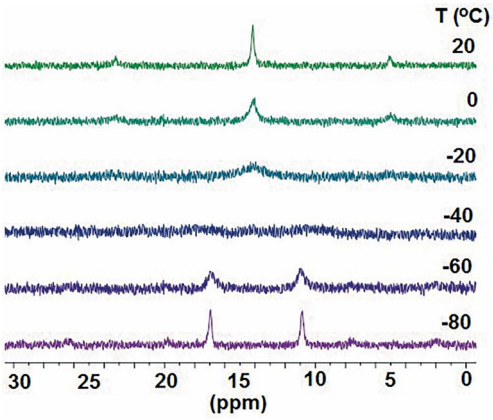


Figure 4. Variable-temperature ^{31}P NMR spectra of *cis*-$PtCl_2(\mathbf{1^{H2}})$ (**2**).

Heating of **3** in [D$_6$]DMSO to 100 °C led to irreversible isomerization to *cis* isomer **2** and to the formation of a second species resonating at δ = 16.18 ppm, which is proposed to be a solvent adduct. Coordination of solvent (either through chloride dissociation or as a five-coordinate intermediate) likely accelerates ligand rearrangement. In [D$_8$]toluene, a solution of *trans*-$PtCl_2(\mathbf{1^{H2}})$ is stable at room temperature and under mild heating (40 °C), with no irreversible isomerization being observed. The irreversible isomerization of **3** in coordinating solvent at elevated temperature suggests that **2** may be the thermodynamic product and that **3** is the kinetic product. To support this, we performed (dispersion-corrected) DFT calculations (BP86-D3/def2-TZVP; see the Supporting Information for the optimized geometries of **2** and **3**). Complex **2** was found to be 11.4 kcal mol^{-1} more stable than the *trans* isomer, partly aided by the presence of an intramolecular hydrogen bond between N(3)–H and N(1), which is also observed in the solid-state structure (Figure 2).

Formation of Cationic Pt^{II} Complexes by Chloride Abstraction

Abstraction of a chloride ligand with $AgPF_6$ led to the formation of the cationic derivatives *cis*-[Pt(CH$_3$CN)Cl($\mathbf{1^{H2}}$)]PF_6 (**4**) and *trans*-[Pt(CH$_3$CN)Cl($\mathbf{1^{H2}}$)]PF_6 (**5**), according to ^{1}H and ^{31}P NMR spectroscopic analysis (Figure 5). Abstraction of one chloride ion from **2** in acetonitrile results in the non-C_2-symmetric NCCH$_3$ adduct **4**. In the ^{31}P NMR spectrum, two doublets are present at δ = 12.32 ppm ($^2J_{P,P}$ = 17.8, $^1J_{P,Pt}$ = 3506 Hz) and 4.52 ppm ($^2J_{P,P}$ = 19.4, $^1J_{Pt,P}$ = 3817 Hz), whereas in the ^{1}H NMR spectrum, two methylene resonances are observed at δ = 3.95 and 3.57 ppm, each corresponding to two protons. A similar reaction with **3** resulted in a signal at δ = 18.0 ppm in the ^{31}P NMR spectrum with Pt satellites ($J_{Pt,P}$ = 2365 Hz) for the symmetric species **5**.

Conclusions

We designed a new ditopic diphosphine ligand bearing a flexible nitrogen-rich backbone and developed synthetic

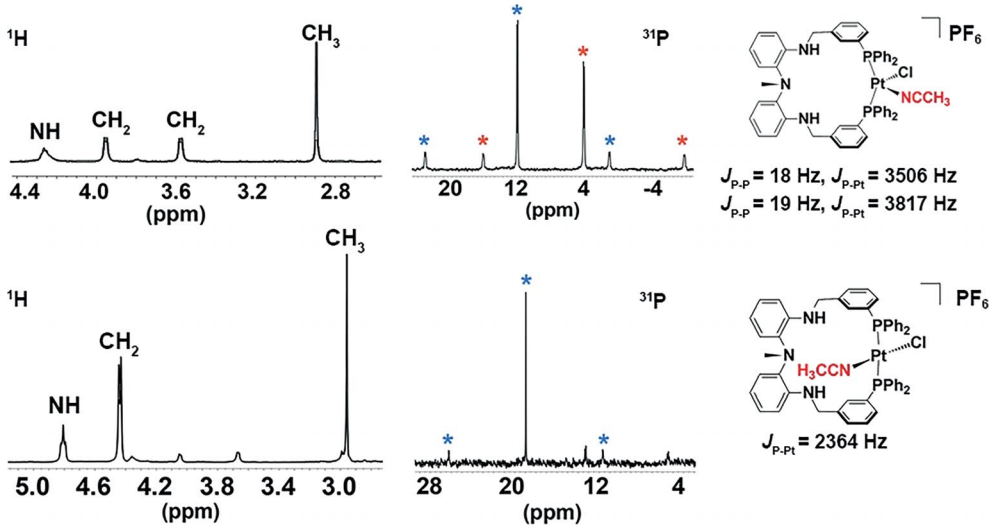


Figure 5. ^{1}H (left) and ^{31}P (right) NMR spectra of *cis*-[Pt(CH$_3$CN)Cl($\mathbf{1^{H2}}$)]PF_6 (**4**) (top) and *trans*-[Pt(CH$_3$CN)Cl($\mathbf{1^{H2}}$)]PF_6 (**5**) (bottom). A small amount of **4** can be observed in the spectra of **5**.

routes to selectively generate 17-membered metallacyclic complexes **2** and **3** by metalation of the *P*-pocket of this ligand. Both isomers could be isolated as spectroscopically and analytically pure species under different reaction conditions, by careful control over the addition protocol. This allows for facile access to both structures and has allowed spectroscopic studies to probe the *cis*/*trans* interconversion. The *cis* isomer appears to be the thermodynamic product, as deduced from spectroscopic and computational data, although the *trans* isomer is stable against isomerization in noncoordinating solvents. These results not only demonstrate the potential to control the geometry around Pt with flexible diphosphine ligands but will also aid future studies to establish the construction of heterodimetallic architectures with both phosphorus and nitrogen coordination. These investigations are ongoing in our laboratories.

Experimental Section

General Methods: All commercial reagents were purchased from Sigma–Aldrich or Strem and were used as received. Syntheses were carried out under N_2 using standard Schlenk techniques and an inert-gas UniLab MBRAUN glovebox. Solvents were distilled from sodium/benzophenone or CaH_2. Glassware was dried at 130 °C unless otherwise stated. Column chromatography was performed on silica gel (400–630 mesh). Analytical thin-layer chromatography (TLC) was performed on precoated gel 60 F_{254} silica plates. The TLC spots were visualized by irradiation with UV light (254 nm). Positive-ion mass spectra were collected with an AccuTOF LC, JMS-T100LP mass spectrometer (JEOL). Infrared spectra (ATR) were recorded with a Bruker Alpha-p FTIR spectrophotometer. NMR (^{1}H, ^{13}C, ^{31}P) spectra were recorded with a Bruker AMX 400 MHz or a Bruker DRX 500 MHz spectrometer. Elemental analysis was performed by the Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany). Precursor **A**, *cis*-$PtCl_2(CH_3CN)_2$ and *trans*-$PtCl_2(CH_3CN)_2$ were prepared according to reported procedures,[15] and the purity of the isomers was checked by TLC (acetone/CH_2Cl_2, 9:1) and by IR spectroscopy.

Synthesis of Precursor A. Step 1:[16] KOH (8.63 g, 153.0 mmol) was added to a stirred solution of *N*-methyl-2-nitroaniline (9.70 g, 63.8 mmol) and 1-fluoro-2-nitrobenzene (8.1 mL, 76.5 mmol) in anhydrous DMSO (170 mL) under atmospheric conditions. The reaction mixture was heated at 120 °C and stirred for 36 h. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 (3× 200 mL). The combined organic extracts were washed with water and brine and dried with $NaSO_4$. All volatiles were removed in vacuo, and the crude product was dry-loaded on silica and purified by column chromatography (hexanes/ethyl acetate, 8:2) to afford *N*-methyl-2-nitro-*N*-(2-nitrophenyl)aniline (7.91 g, 28.9 mmol, 45%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 2 H), 7.53 (ddd, ^3J = 8.5, ^3J = 7.6, ^4J = 1.4 Hz, 2 H), 7.24 (d, ^3J = 8.2 Hz, 2 H), 7.15 (t, ^3J = 7.8 Hz, 2 H), 3.39 (s, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.2 (C), 141.9 (C), 134.0 (CH), 126.4 (CH), 124.9 (CH), 123.8 (CH), 42.6 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 1596, 1515, 1486, 1445, 1363 cm^{-1}. HRMS (ESI$^+$): calcd. for $[C_{13}H_{11}N_3O_4]^+$ 273.0750; found 273.0742. **Step 2:** A mixture of *N*-methyl-2-nitro-*N*-(2-nitrophenyl)-aniline (7.01 g, 25.7 mmol) and Pd/C (508 mg, 10 wt.-%) was suspended in EtOAc (160 mL) and stirred under hydrogen (1 atm) at room temperature. After 24 h, the mixture was filtered through Celite under nitrogen, and the solvent was removed in vacuo to afford **A** (5.45 g, 25.4 mmol, 99%) as a beige solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.02 (dd, ^3J = 7.8, ^4J = 1.4 Hz, 2 H), 6.97 (td, ^3J = 7.7, ^4J = 1.4 Hz, 2 H), 6.77 (dd, ^3J = 7.6, ^4J = 1.4 Hz, 2 H), 6.74 (td, ^3J = 9.5, ^3J = 8.8, ^4J = 1.4 Hz, 2 H), 3.82 (br. s, 4 H), 3.08 (s, 3 H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.7 (C), 136.6 (C), 124.9 (CH), 122.2 (CH), 118.9 (CH), 116.0 (CH), 40.0 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3442, 3349, 1611, 1497, 1453, 1286, 1119 cm^{-1}. HRMS (ESI$^+$): calcd. for $[C_{13}H_{15}N_3]^+$ 213.1266; found 213.11280. ***Note:*** Precursor **A** is very sensitive to oxidation under ambient atmosphere, which limits its shelf-life considerably.

Synthesis of Ligand 1^{H2}: A clear yellow solution of **A** (0.832 g, 2.97 mmol) in CH_2Cl_2 (40 mL) was added dropwise to a brown suspension of **B** (0.305 g, 1.43 mmol) and sodium triacetoxyborohydride (0.852 g, 4.02 mmol) in CH_2Cl_2 (60 mL). The reaction mixture was stirred for 22 h, then saturated $NaHCO_3$ solution (10 mL) and water (10 mL) were added. The yellow suspension was extracted with ethyl acetate (3× 20 mL), and the combined organic layers were washed with water (20 mL) and dried with $MgSO_4$. After filtration, the volatiles were removed, and the resulting crude yellow foam was purified by column chromatography (CH_2Cl_2/hexane, 7:3). Ligand $\mathbf{1^{H2}}$ (75%) was obtained as a white powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.29 (m, 20 H), 7.22–7.13 (m, 6 H), 6.99 (m, 6 H), 6.69 (t, ^3J = 7.5 Hz, 2 H), 6.52 (d, ^3J = 8.0 Hz, 2 H), 4.53 (t, $^3J_{N,H}$ = 4.0 Hz, 2 H, NH), 4.08 (d, ^3J = 8.0 Hz, 4 H, CH_2), 2.93 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.6 (s, C), 139.6 (d, $J_{C,P}$ = 7.5 Hz, C), 137.5 (d, $J_{C,P}$ = 11.3 Hz, C), 137.1 (d, $J_{C,P}$ = 11.3 Hz, C), 136.2 (s, C), 133.7 (d, $J_{C,P}$ = 19 Hz, CH), 132.6 (d, $J_{C,P}$ = 21.3 Hz, CH), 132.3 (d, $J_{C,P}$ = 17.5 Hz, CH), 128.8 (s, CH), 128.7 (s, CH), 128.5 (d, $J_{C,P}$ = 6.3 Hz, CH), 127.7 (s, CH), 125.1 (s, CH), 121.6 (s, CH), 117.3 (s, CH), 110.9 (s, CH), 47.6 (s, CH_2), 40.4 (s, CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –5.37 (s) ppm. HRMS (CSI$^+$): calcd. for $[C_{51}H_{45}N_3P_2 + H]^+$ 762.3089; found 762.3087. $C_{51}H_{45}N_3P_2$ (761.88): calcd. C 80.40, H 5.95, N 5.52; found C 79.96, H 6.37, N 5.35.

Synthesis of *cis*-$PtCl_2(\mathbf{1^{H2}})$ (2): A colorless solution of $\mathbf{1^{H2}}$ (60 mg, 0.08 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of *cis*-$PtCl_2(CH_3CN)_2$ (27 mg, 0.08 mmol) in CH_2Cl_2 (20 mL), and the solution was stirred at room temperature. After 4 h, the solution was concentrated in vacuo, and pentane (10 mL) was added. An off-white precipitate formed that was filtered and dried in vacuo (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.63 (m, 10 H), 7.25–7.21 (m, 8 H), 7.17–7.07 (m, 8 H), 7.01–6.99 (m, 2 H), 6.92 (t, ^3J = 5.6 Hz, 2 H), 6.79 (t, ^3J = 8.0 Hz, 2 H), 6.72 (t, ^3J = 6.4 Hz, 2 H), 6.53 (d, ^3J = 8.0 Hz, 2 H), 3.89 (br. s, 2 H, NH), 3.71 (d, ^3J = 4.0 Hz, 4 H, CH_2), 2.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.1 (s, C), 138.2 (d, $J_{C,P}$ = 11.3 Hz, C), 136.8 (s, C), 134.4 (m, 2CH), 133.4 (d, $J_{C,P}$ = 7.6 Hz, CH), 131.1 (s, CH), 130.8 (s, CH), 130.1 (d, $J_{C,P}$ = 61.3 Hz, C), 129.3 (d, $J_{C,P}$ = 69.3 Hz, C), 129.2 (d, $J_{C,P}$ = 10.0 Hz, CH), 127.9 (d, $J_{C,P}$ = 11.3 Hz, CH), 125.3 (s, CH), 121.6 (s, CH), 117.6 (s, CH), 110.3 (s, CH), 47.5 (s, CH_2), 41.3 (s, CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 14.5 (s, $J_{P,Pt}$ = 3662.3 Hz) ppm. HRMS (CSI$^+$): calcd. for $[C_{51}H_{45}N_3P_2PtCl]^+$ 992.2431; found 992.2356. $C_{51}H_{45}Cl_2N_3P_2Pt$ (1027.88): calcd. C 59.59, H 4.41, N 4.09; found C 59.61, H 4.39, N . 4.06.

Synthesis of *trans*-$PtCl_2(\mathbf{1^{H2}})$ (3): A yellow solution of *trans*-$PtCl_2(CH_3CN)_2$ (73.3 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a colorless solution of $\mathbf{1^{H2}}$ (160 mg, 0.20 mmol) in CH_2Cl_2 (10 mL), and the solution was stirred at room temperature. After 1 h, the solvent was removed in vacuo to give **3** (95%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (t, ^3J = 6.1 Hz, 2 H), 7.78–7.74 (m, 10 H), 7.46–7.32 (m, 16 H), 7.15 (t, ^3J = 7.7 Hz, 2 H), 7.09 (d, ^3J = 7.9 Hz, 2 H), 6.81 (t, ^3J = 7.7 Hz, 2

H), 6.75 (d, ^3J = 7.7 Hz, 2 H), 4.52 (t, ^3J = 2.5 Hz, 2 H, NH), 4.23 (d, ^3J = 1.3 Hz, 4 H, CH_2), 2.98 (s, 3 H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.1 (C), 138.9 (app. t, C), 136.7 (C), 135.7 (app. t, CH), 134.8 (app. t, CH), 132.3 (app. t, CH), 130.6 (CH), 130.4 (CH), 129.4 (app. t, C), 128.9 (app. t, C), 128.5 (app. t, CH), 128.0 (app. t, CH), 125.0 (CH), 121.9 (CH), 117.4 (CH), 111.0 (CH), 48.4 (CH_2), 30.0 (CH_3) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.7 (s, $J_{P,Pt}$ = 2614.2 Hz) ppm. HRMS (CSI$^+$): calcd. for $[C_{51}H_{45}N_3P_2PtCl]^+$ 992.2431; found 992.2398. $C_{51}H_{45}Cl_2N_3P_2Pt$ (1027.88): calcd. C 59.59, H 4.41, N 4.09; found C 59.55, H 4.42, N . 4.05.

Synthesis of *cis*-[Pt(CH$_3$CN)Cl(1^{H2})]PF$_6$ (4): A solution of $AgPF_6$ (17.2 mg, 0.068 mmol) in CH_3CN (5 mL) was added dropwise to a solution of *cis*-$PtCl_2$(**1^{H2}**) (70.0 mg, 0.068 mmol) in CH_3CN (10 mL). After stirring at room temperature for 16 h, the solution was filtered through Celite, and the solvent was removed in vacuo. The resulting solid was washed with pentane (3 × 5 mL) to give **4** (99%) as a white solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.99 (br. s, 1 H), 7.84–7.79 (m, 4 H), 7.60 (br. s, 1 H), 7.46–7.33 (m, 14 H), 7.24–7.00 (m, 7 H), 6.96 (d, ^3J = 7.2 Hz, 1 H), 6.78 (t, J = 14.8 Hz, 1 H), 6.72–6.66 (m, 3 H), 6.52 (m, 2 H), 6.18 (m, 2 H), 4.26 (br. t, 2 H, NH), 3.95 (d, ^3J = 4.0 Hz, 2 H, CH_2), 3.57 (d, ^3J = 4.0 Hz, 2 H, CH_2), 2.89 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 143.1 (s, C), 142.2 (s, C), 140.0 (d, $J_{C,P}$ = 13.3 Hz, C), 138.7 (s, C), 137.8 (s, C), 137.1 (s, C), 135.2 (d, $J_{C,P}$ = 7.5 Hz, CH), 133.2 (m, CH), 132.7 (d, $J_{C,P}$ = 8.7 Hz, CH), 132.2 (s, CH), 132.0 (s, CH), 131.3 (s, CH), 129.1 (m, CH), 128.4 (m, CH), 127.6 (s, C), 126.5 (s, C), 125.9 (s, CH), 124.3 (s, CH), 123.1 (s, CH), 120.6 (s, CH), 117.6 (s, CH), 116.9 (s, CH), 110.6 (s, s, 2 CH), 47.0 (s, CH_2), 46.8 (s, CH_2), 41.3 (s, CH_3) ppm. ^{31}P NMR (162 MHz, CD_3CN): δ = 12.32 (d, J_{P-P} = 19.4, $J_{P,Pt}$ = 3506 Hz), 4.51 (d, J_{P-P} = 17.8, $J_{P,Pt}$ = 3817 Hz), –144.60 (sept, $J_{P,F}$ = 706.32 Hz) ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = –69.32 (d, $J_{P,F}$ = 705.90 Hz) ppm. HRMS (FD$^+$): calcd. for $[C_{53}H_{48}N_4P_2PtCl]^+$ 1033.2640; found 1033.2623.

Synthesis of *trans*-[Pt(CH$_3$CN)Cl(1^{H2})]PF$_6$ (5): A solution of $AgPF_6$ (17.2 mg, 0.068 mmol) in CH_3CN (5 mL) was added dropwise to a solution of *trans*-$PtCl_2$(**1^{H2}**) (70.0 mg, 0.068 mmol) in CH_3CN (40 mL). After stirring at room temperature for 16 h, the solution was filtered through Celite, and the solvent was removed in vacuo. The resulting solid was washed with pentane (3 × 5 mL) to give **5** (99%) as a white solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 8.12 (t, $J_{H,P}$ = 16.0 Hz, 2 H), 7.66–7.46 (m, 24 H), 7.21–7.16 (m, 2 H), 7.03 (t, J = 16 Hz, 2 H), 6.98 (d, ^3J = 4 Hz, 2 H), 6.73–6.70 (m, 2 H), 4.73 (t, 2 H, NH), 4.37 (d, ^3J = 8.0 Hz, 2 H, CH_2), 2.89 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 143.1 (s, C), 140.7 (app. t, $J_{C,P}$ = 10.6 Hz, C), 140.1 (s, C), 139.9 (s, C), 138.6 (s, C), 137.0 (s, C), 134.2 (app. t, $J_{C,P}$ = 12.1 Hz, CH), 133.2 (m, CH), 132.2 (m, CH), 129.2 (m, CH), 127.4 (s, C), 127.1 (s, C), 126.8 (s, C), 126.4 (s, C), 125.2 (s, CH), 122.0 (s, CH), 111.7 (s, CH), 47.3 (s, CH_2), 39.7 (s, CH_3) ppm. ^{31}P NMR (162 MHz, CD_3CN): δ = 18.0 (s, $J_{P,Pt}$ = 2364.9 Hz), –144.63 (sept, $J_{P,F}$ = 705.8 Hz, PF_6^-) ppm. ^{19}F NMR (282 MHz, CD_3CN): δ = –126.89 (d, $J_{F,P}$ = 708.7 Hz, PF_6^-) ppm. HRMS (FD$^+$): calcd. for $[C_{53}H_{48}N_4P_2PtCl]^+$ 1033.2640; found 1033.2611.

DFT Calculations: Geometry optimizations were carried out by using TURBOMOLE[17] coupled with the PQS Baker optimizer[18] with the BOpt package[19] at the DFT level using the bp86 functional and the def2-TZVP basis set. All minima (no imaginary frequencies) were characterized by numerically calculating the Hessian matrix. Grimme's semiempirical DFT-D3 method was employed for a better description of the hydrogen-bonding interactions.[20]

X-ray Crystallography. Data for 2: All reflection intensities were measured at 110(2) K with a SuperNova diffractometer (equipped with Atlas detector) with Cu-K_α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013) was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013[21] and was refined on F^2 with SHELXL-2013.[22] Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro (Version 1.171.36.32, Agilent Technologies, 2013). The temperature of the data collection was controlled with the system Cryojet (manufactured by Oxford Instruments). H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 23, AFIX 43, or AFIX 137, with isotropic displacement parameters having values of 1.2 or 1.5 times U_{eq} of the attached C atoms. The H atoms attached to N1 and N3 were found from difference Fourier maps, and their atomic coordinates were refined freely. **Data for 3:** X-ray intensities were measured with a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator (λ = 0.71073 Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software.[23] Absorption correction and scaling were performed with SADABS.[24] The structures were solved with the program SHELXL.[23] Least-squares refinement was performed with SHELXL-2013[22] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times U_{eq} of the attached C atoms. **Details for *cis*-PtCl$_2$(1^{H2}) (2):** Fw = 1112.75; colorless needle; 0.27 × 0.05 × 0.02 mm; orthorhombic; *Pbcn* (no. 60); a = 19.4701(2), b = 19.2427(2), c = 24.5952(2) Å; V = 9214.77(15) Å^3; Z = 8; D_X = 1.604 g cm^{-3}; μ = 8.798 mm^{-1}; T_{min}–T_{max} = 0.356–0.839. 31918 reflections were measured up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.62 Å^{-1}. 9042 reflections were unique (R_{int} = 0.0382), of which 7579 were observed [$I > 2\sigma(I)$]. 595 parameters were refined using 69 restraints. $R1/wR2$ [$I > 2\sigma(I)$] = 0.0267/0.0572. $R1/wR2$ (all refl.) = 0.0367/0.0612. S = 1.017. Residual electron density found between –0.65 and 0.71 e Å^{-3}. **Details for *trans*-PtCl$_2$(1^{H2}) (3):** Fw = 1112.75; colorless needle; 0.10 × 0.10 × 0.10 mm; monoclinic; $P2_1/n$ (no. 14); a = 10.1748(2), b = 17.4455(4), c = 26.6274(6) Å, β = 94.7410(15)°; V = 4710.31(18) Å^3; Z = 2; D_X = 1.514 g cm^{-3}; μ = 3.201 mm^{-1}; T_{min}–T_{max} = 0.58–0.74. 45484 reflections were measured up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.77 Å^{-1}. 9250 reflections were unique (R_{int} = 0.0670), of which 7491 were observed [$I > 2\sigma(I)$]. 603 parameters were refined using 79 restraints. $R1/wR2$ [$I > 2\sigma(I)$] = 0.0399/0.0717. $R1/wR2$ (all refl.) = 0.0594/0.0767. S = 1.112. Residual electron density found between –2.55 and 1.40 e Å^{-3}. CCDC-1417390 (**2**) and 1416667 (**3**) 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): Computational details with optimized geometries of **2** and **3**, NMR spectra of new compounds.

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