Complexation of an Indole-based α-Aminoimine Ligand to Pd(II)

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Abstract

The indole-based α-aminoimine ligand 6-Me-4-^{i}Pr-6-{(2,6-^{i}Pr$_2$-C$_6$H$_3$)N=CMe}-6,11-dihydro-5*H*-indolo[3,2-*c*]quinoline (**6**) was synthesized by condensation of (2,6-^{i}Pr$_2$-C$_6$H$_3$)N=C(Me)C(=O)Me (**5**) and 2-(indol-2-yl)-6-^{i}Pr-C$_6$H$_3$NH$_2$ (**4**). Ligand **6** coordinates in a κ^2-C=*N*,*N*H fashion in the square planar complex (**6**)PdCl$_2$.

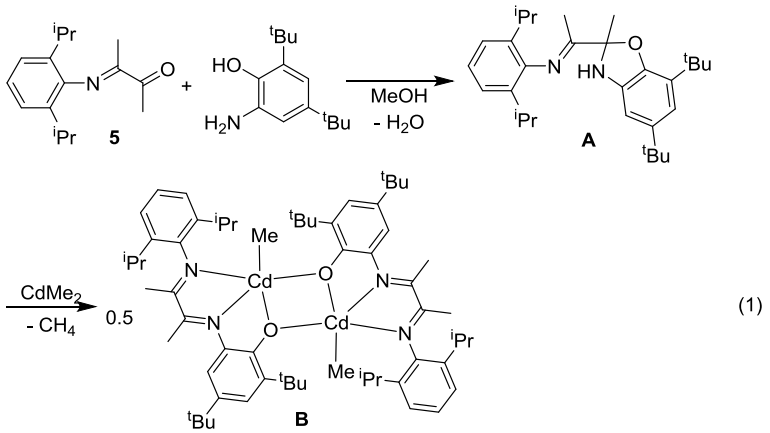
Keywords

α-Aminoimine ligand; Indole; Cyclization; Palladium compounds

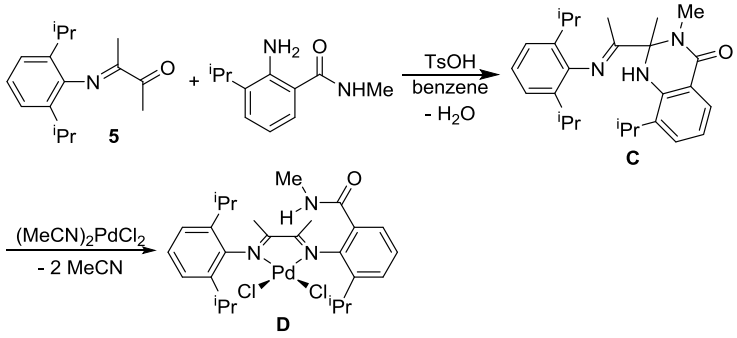
Introduction

N,N'-Diaryl α-diimines comprise an important family of structurally tunable ancillary ligands in transition metal catalysis.[1,2,3,4] The most general method for the synthesis of α-diimines is the acid-catalyzed condensation of vicinal diketones (or glyoxal) with anilines. However, when the aniline contains nucleophilic groups close to the amino group, such as –OH (eq 1),[5,6] or –C(=O)NMe$_2$ (eq 2)[7] groups, the initially formed α-diimine can undergo cyclization to yield a heterocyclic product. Similarly, Friedel–Crafts cyclization may occur after condensation when the aniline contains activating substituents such as *meta*-OMe groups (eq 3).[8]

The heterocyclic products in eqs 1–3 may be considered as cyclic forms of the corresponding open-chain α-diimine ligands, and in some cases do in fact react with metal reagents with ring opening to afford α-diimine complexes.[6,7] For example, **A** reacts with $CdMe_2$ to form dimeric (κ^3-diimine-phenolate)CdMe complex **B** via ring opening assisted by deprotonation (eq 1).[6] Similarly, **C** reacts with $(MeCN)_2PdCl_2$ to yield (α-diimine)$PdCl_2$ complex **D** through ring opening of the dihydroquinazolinone system (eq 2).[7] Ring opening of **C** is triggered by coordination of the amine N (and perhaps the imine N) to Pd, which significantly decreases the pK_a of the amine N*H* and drives the elimination of the amide unit. Metal-coordination-triggered ring opening reactions of other aminal-type heterocycles, including imidazolidines,[9,10] dihydrobenzimidazoles,[11] tetrahydropyrimidines,[12] and tetrahydroquinazolines,[13] to form complexes that contain multidentate imine ligands have been reported.



(1)



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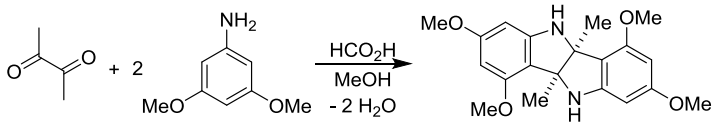


(3)

As part of an investigation of α-diimine ligands that contain hydrogen bonding groups, which are of interest for advanced group 10-metal catalysts for the copolymerization of ethylene with polar vinyl monomers,[7,14] we identified the indolyl-substituted (α-diimine)$PdCl_2$ complex (**6'**)$PdCl_2$ (Fig. 1) as a potential synthetic target. However, the indolyl-α-diimine ligand **6'** undergoes rapid cyclization to form the 6-iminoyl-dihydroindolo[3,2-*c*]quinoline compound **6**, which reacts with $(CH_3CN)_2PdCl_2$ *without* ring-opening to afford (**6**)$PdCl_2$. Here we describe the synthesis of **6** and (**6**)$PdCl_2$ and the single crystal structure of the latter compound.

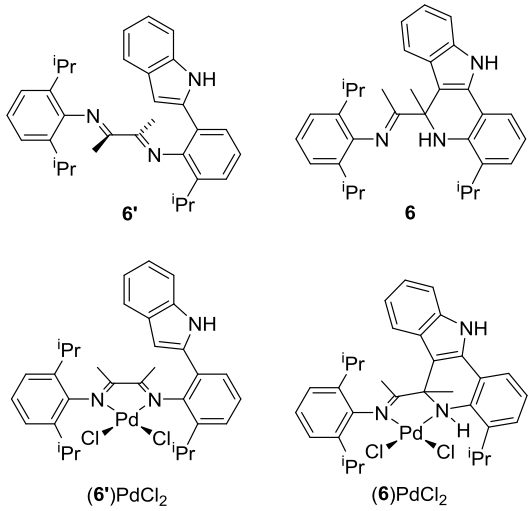
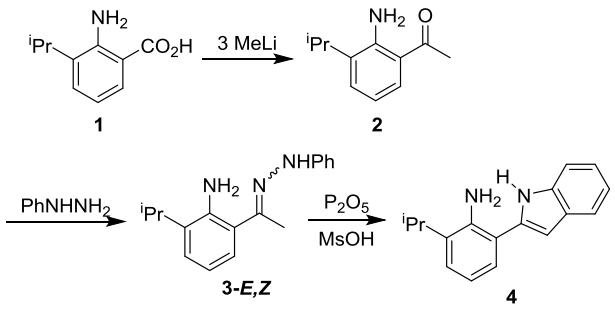


Fig. 1. Structures of targeted compounds.

Results and Discussion

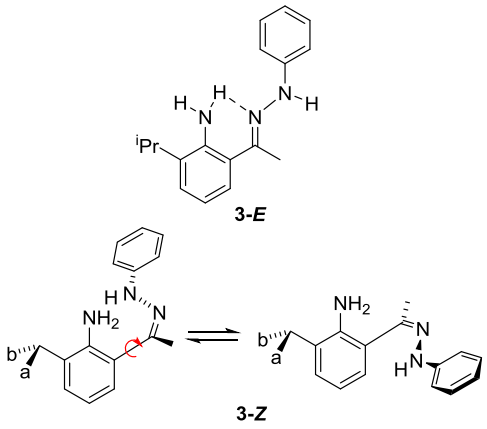
Indolylaniline **4** was prepared by the Fischer indole synthesis shown in Scheme 1. The reaction of anthranilic acid **1** with 3 equiv of MeLi afforded *o*-aminoacetophenone **2**.[15,16] Condensation of **2** with phenylhydrazine produced the corresponding phenylhydrazone as a mixture of *E,Z* isomers (**3-*E*,*Z***), which was converted to indole **4** under acidic conditions.



Scheme 1. Synthesis of indolylaniline **4**.

While **3-*E*** and **3-*Z*** were not separated, samples enriched in either isomer were obtained during crystallization experiments and enabled NMR assignments. Intramolecular H-bonding

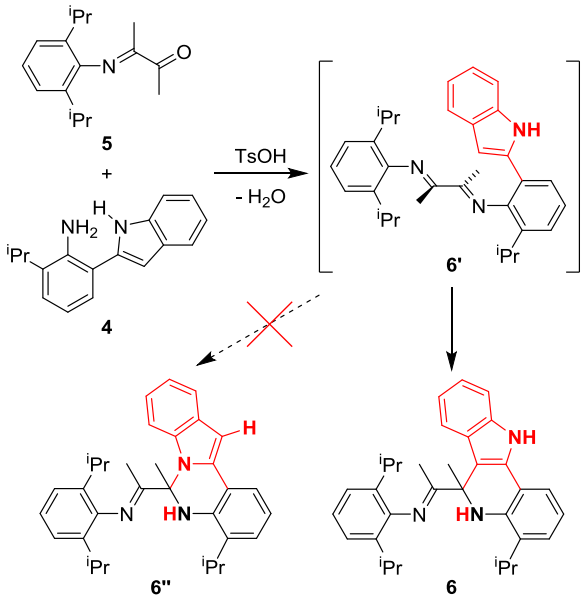
between the amino group and the hydrazone N-atom is possible for **3-*E*** but not **3-*Z*** (Scheme 2), and as a result, the ^{1}H NMR resonance for the amino group in **3-*E*** (δ 6.00) is 2.22 ppm downfield from that for **3-*Z*** (δ 3.78) in $CDCl_3$ solution. The room-temperature ^{1}H and ^{13}C NMR spectra of **3-*E*** each contain a single sharp resonance for the isopropyl Me groups as expected for the planar H-bonded structure. In contrast, the NMR spectra of **3-*Z*** each contain two broad resonances for the two isopropyl Me groups (a and b, Scheme 2), consistent with a sterically induced non-planar conformation and restricted rotation around the C_{aryl}–C(=N) bond. Similar conformational differences between the *E* and *Z* isomers of *ortho*-aminophenyl ketone hydrazones have been observed in the solid state.[17,18]



Scheme 2. Conformations and dynamic behavior of **3-*E*** and **3-*Z***.

The condensation reaction between **4** and α-iminoketone **5** afforded the dihydroindolo[3,2-*c*]quinoline product **6** by initial generation of diimine **6'** followed by nucleophilic attack of the indole-C^3 carbon on the adjacent imine carbon and a subsequent 1,3-H shift (Scheme 3). Nucleophilic attack of the indole nitrogen N^1 on the imine carbon, analogous to the cyclization reaction in eq 2 that generates **C**, would generate **6''**, which was not observed. Compound **6** was isolated in low (9%) yield due to low conversion. The ^{1}H NMR spectrum of **6**

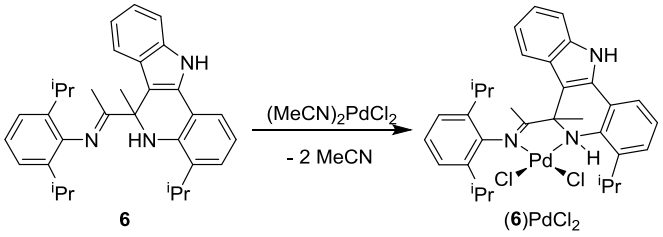
exhibits a broad signal at δ 8.42 for the indole N–H, and the ^{13}C NMR spectrum contains a signal at δ 63.0 for the spiro C atom, both consistent with the assignment of structure **6** rather than **6''** or the open-chain form **6'**. While condensation reactions between 2-(indol-2-yl)aniline and carbonyl compounds have been reported to yield products of both N-attack[19] and C^3-attack[20], the N-attack product can rearrange to the C^3-attack product through an open-chain intermediate under acidic conditions.[21,22] Thus, any **6"** that is formed in Scheme 3 would be expected to rearrange to **6** under the acidic conditions used.



Scheme 3. Formation of **6** via cyclization.

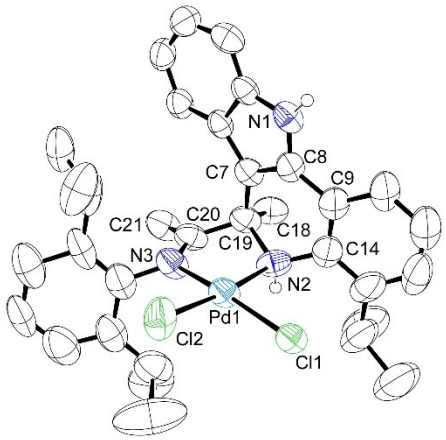
Compound **6** reacts with $(MeCN)_2PdCl_2$ without ring opening to yield the square planar complex (**6**)$PdCl_2$ through κ^2-C=*N*,*N*H coordination (Scheme 4). The solid-state structure of (**6**)$PdCl_2$ is shown in Fig. 2a. The Pd–N3 bond (2.008(6) Å) is ca. 0.07 Å shorter than the Pd–N2 bond (2.084(7) Å). This difference reflects the stronger donor ability of the imine N atom versus the amine N atom and is consistent with previous reports.[23,24,25] The 5-membered chelate ring is

puckered due to the presence of the sp^3-carbon C19, and the indole unit and the C18 methyl group occupy axial and equatorial positions, respectively. The $PdCl_2$ unit occupies an axial position on the puckered 6-membered N2–C19–C7–C8–C9–C14 ring, which minimizes steric crowding with the isopropyl group on adjacent fused 6-membered ring. The (**6**)$PdCl_2$ molecules are arranged in the crystal in pairs that are linked by intermolecular H-bonds between the indole NH unit on one molecule and a Cl ligand of the other (Fig. 2b), constructing 16-membered rings. Similar intermolecular indole N–H···Cl–M H-bonding was observed in the solid state structures of several Cu[26,27] and Pd[28] complexes.



Scheme 4. Synthesis of (**6**)$PdCl_2$.

(a)



(b)

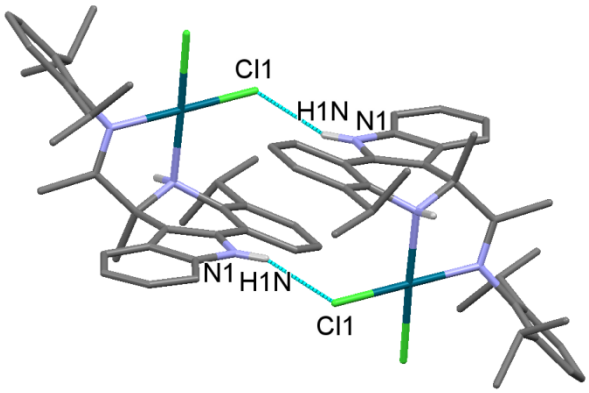
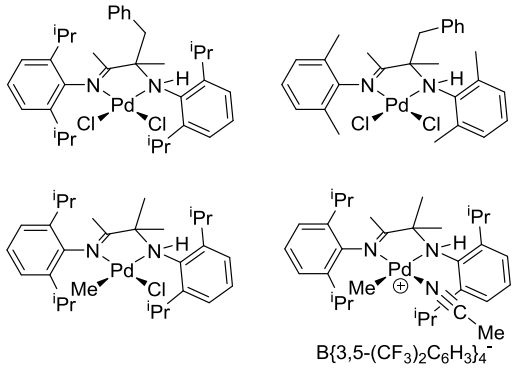


Fig. 2. (a) Molecular structure of (**6**)$PdCl_2$. Hydrogen atoms are omitted except for the H-atoms on N1 and N2. Selected bond lengths (Å) and angles (deg): Pd1–N2, 2.084(7); Pd1–N3, 2.008(6); C20–N3, 1.281(10); C19–N2, 1.533(9); C19–C20, 1.510(11); N3–Pd1–N2, 80.3(3); N2–Pd1–Cl1, 94.7(2); N3–Pd1–Cl2, 95.8(2); Cl1–Pd1–Cl2, 89.89(7). (b) Intermolecular H-bonding of (**6**)$PdCl_2$ in the solid state. Selected distances (Å) and angles (°): N1···Cl1, 3.183(6); H1N···Cl1, 2.35(4); N1–H1N···Cl1, 158(7).

Several Pd complexes that contain *N,N*-diaryl-α-aminoimine ligands and are structurally similar to (**6**)$PdCl_2$ have been reported (Chart 1).[23,24] These compounds have been exploited as catalysts for Suzuki–Miyaura coupling reactions of aryl bromides and chlorides,[23] living polymerization of ethylene, and the copolymerization of methyl acrylate (MA) and ethylene to form copolymers with in-chain MA units.[24] (α-aminoimine)Pd complexes also exhibit interesting isomerism phenomena and orthometalation reactivity.[29,30]

Chart 1. Crystallographically Characterized Square Planar (α-Aminoimine)Pd Complexes



(**6**)$PdCl_2$ is stable for at least 1 h at 95 °C but decomposes at 125 °C in a few hours to form a black precipitate and unidentified soluble products in $C_2D_2Cl_4$ solution. (**6**)$PdCl_2$ is also stable for at least 20 h at 90 °C in CD_2Cl_2/CD_3CO_2D (10/1 by volume, sealed NMR tube under N_2), showing that acid does not promote ring opening. Ring opening of (**6**)$PdCl_2$ to form (**6'**)$PdCl_2$ is thus highly disfavored relative to ring opening of aminal-type complexes such as (**C**)$PdCl_2$, the presumed intermediate in the formation of **D** in eq 2. As these ring opening reactions require net proton transfer from the Pd-bound amine to the indolyl-C^3 carbon (C7 in Figure 7) of (**6**)$PdCl_2$ or the amide nitrogen in (**C**)$PdCl_2$, the difference in reactivity likely reflects the low basicity of the indolyl-C^3 carbon of (**6**)$PdCl_2$.

Conclusion

Condensation of (2,6-^{i}Pr$_2$-C_6H_3)N=C(Me)C(=O)Me (**5**) and 2-(indol-2-yl)-6-^{i}Pr-$C_6H_3NH_2$ (**4**) affords the indole-based α-aminoimine ligand 6-Me-4-^{i}Pr-6-{(2,6-^{i}Pr$_2$-C_6H_3)N=CMe}-6,11-dihydro-5*H*-indolo[3,2-*c*]quinoline (**6**). Ligand **6** coordinates in a κ^2-C=*N*,*N*H fashion in the square planar complex (**6**)$PdCl_2$ without ring opening to the diimine form.

Experimental

1. General procedures

All experiments were performed under nitrogen using drybox or Schlenk techniques unless otherwise noted. Nitrogen was purified by passage through activated molecular sieves and Q-5 oxygen scavenger. Solvents for manipulations under N_2 were purified as follows. Benzene was purified by passage through activated alumina and BASF R3-11 oxygen scavenger, and CH_2Cl_2 was purified by passage through activated alumina. 1,2-Dimethoxyethane (anhydrous, Aldrich) was used as received. All workup and purification procedures for organic compounds were carried out with reagent grade solvents in air. 2-Amino-3-isopropylbenzoic acid (**1**)[31] and 3-(2,6-diisopropylphenylimino)butan-2-one (**5**)[32] were synthesized by reported procedures.

NMR spectra were recorded on a Bruker DRX-500 spectrometer at ambient temperature unless otherwise indicated. ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent resonances. Coupling constants are given in hertz (Hz). Infrared spectra were recorded on thin-film samples on NaCl plates using a Nicolet NEXUS 470 FT-IR spectrometer. Mass spectrometry was performed on Agilent 6130 LCMS (low resolution) or Agilent 6224 Tof-MS (high resolution) instruments. The listed *m*/*z* value corresponds to the most intense peak in the isotope pattern. Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ).

2. Synthesis of 2'-amino-3'-isopropylacetophenone (**2**)

A Schlenk flask was charged with **1** (2.00 g, 11.2 mmol) and anhydrous 1,2-dimethoxyethane (100 mL). The mixture was cooled to 0 °C, and MeLi (1.6 M in Et_2O, 23.0 mL,

36.8 mmol, 3.3 equiv) was added dropwise by syringe at 0 °C to yield an orange solution. The mixture was stirred at 0 °C for 2 h and quenched with aqueous saturated NH_4Cl. The 1,2-dimethoxyethane was removed on a rotovap. The remaining aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was washed with brine, dried with Na_2SO_4, filtered, and taken to dryness under vacuum to give a yellow oil. The residue was purified by flash column chromatography (silica, hexane/EtOAc = 4/1 by volume) and dried under vacuum to yield a yellow oil. Yield: 1.35 g (68%). ^{1}H NMR ($CDCl_3$): δ 7.64 (dd, J = 8.1, 1.5, 1H), 7.29 (dd, J = 7.4, 1.5, 1H), 6.67 (t, J = 7.8, 1H), 6.62 (br s, 2H), 2.89 (septet, J = 6.8, 1H), 2.60 (s, 3H), 1.27 (d, J = 6.8, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 201.4, 147.9, 133.4, 130.4, 130.0, 118.0, 115.4, 28.5, 27.0, 22.1. IR (cm^{-1}): ν_{N-H} 3483, 3323; $\nu_{C=O}$ 1645. HRMS (ESI-TOF, positive ion, m/z): Calc. 178.1232 ($[M + H]^+$), found 178.1238.

3. Synthesis of 2'-amino-3'-isopropylacetophenone phenylhydrazone (**3**)

A flask was charged with **2** (1.35 g, 7.62 mmol), phenylhydrazine (1.2 mL, 12 mmol, 1.6 equiv), anhydrous EtOH (10 mL) and AcOH (0.5 mL). The mixture was refluxed for 24 h under air and cooled to room temperature. The mixture was maintained at –30 °C for 3 d, resulting in the formation of yellow crystals. The crystals were collected by vacuum filtration, rinsed with EtOH, and dried under vacuum. Yield: 1.69 g (83%, sum of 4 crops). The isolated product comprised a mixture of **3-*E*** and **3-*Z***. The isomers was not separated, however, samples enriched in either **3-*E*** and **3-*Z*** were obtained during crystallization experiments and enabled NMR assignments. Data for **3-*E***: ^{1}H NMR ($CDCl_3$): δ 7.32–7.28 (m, 2H), 7.26 (dd, J = 7.8, 1.5, 1H), 7.23 (br s, 1H, NH), 7.14 (dd, J = 7.8, 1.4, 1H), 7.10–7.07 (m, 2H), 6.90 (tt, J = 7.3, 1.0, 1H), 6.77 (t, J = 7.8, 1H), 6.00 (br s, 2H, NH_2), 3.00 (septet, J = 6.8, 1H), 2.34 (s, 3H), 1.32 (d, J =

6.8, 6H, ^{i}Pr). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 145.9, 145.2, 142.8, 133.1, 129.5, 126.3, 125.1, 121.3, 120.3, 116.7, 113.1, 27.7, 22.4, 14.3 (^{i}Pr). Data for **3-*Z***: ^{1}H NMR ($CDCl_3$): δ 7.24–7.20 (m, 4H, 3 ArH + NH), 7.01–6.98 (m, 2H), 6.94 (dd, *J* = 7.6, 1.6, 1H), 6.87 (t, *J* = 7.5, 1H), 6.82 (tt, *J* = 7.3, 1.0, 1H), 3.78 (br s, 2H, NH_2), 2.93 (septet, *J* = 6.8, 1H), 2.30 (s, 3H), 1.33 (br d, *J* = 6.8, 3H, ^{i}Pr), 1.30 (br d, *J* = 6.8, 3H, ^{i}Pr). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 145.5, 144.1, 139.4, 133.3, 129.3, 126.2, 125.7, 120.7, 119.8, 119.0, 112.9, 28.0, 24.4, 22.4 (br, ^{i}Pr), 22.3 (br, ^{i}Pr). IR (cm^{-1}, isomer mixture): 3452, 3328, 3266, 1602. HRMS (ESI-TOF, positive ion, *m*/*z*): Calc. 268.1814 ($[M + H]^{+}$), found 268.1823.

4. Synthesis of 2-(indol-2-yl)-6-isopropylaniline (**4**)

$MeSO_3H$ (12 mL) was added to a flask and heated to 80 °C. P_2O_5 (1.65 g) was added in one portion, and the mixture was stirred at 80 °C under air for 15 min until all of the solid dissolved. Hydrazone **3** (*E*,*Z* isomer mixture, 1.36 g, 5.09 mmol) was added in one portion. The mixture was stirred at 80 °C for 30 min and poured over a mixture of ice and NaOH (8 g) to precipitate a white solid. The solid was collected by vacuum filtration, washed with water, and dissolved in CH_2Cl_2 (20 mL). The solution was washed with brine in a separatory funnel, dried with $MgSO_4$, filtered, and taken to dryness under vacuum to yield a red oil, which slowly solidified at –30 °C to form a white solid. Yield: 0.990 g (78%). Prolonged exposure to air leads to a color change to brown, and thus quick manipulation is required. The product should be stored under N_2 to minimize oxidation. ^{1}H NMR ($CDCl_3$): δ 8.37 (br s, 1H, NH), 7.65 (dd, *J* = 7.8, 1.0, 1H), 7.42–7.40 (m, 1H), 7.24 (dd, *J* = 7.6, 1.6, 1H), 7.23–7.20 (m, 2H), 7.16–7.13 (m, 1H), 6.89 (t, *J* = 7.6, 1H), 6.72 (dd, *J* = 2.2, 0.8, 1H), 4.38 (br s, 2H, NH_2), 2.98 (septet, *J* = 6.8, 1H), 1.33 (d, *J* = 6.8, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 141.4, 136.4, 136.3, 133.4, 129.0, 127.3,

125.6, 122.2, 120.5, 120.2, 119.2, 118.8, 110.9, 102.1, 28.1, 22.5. IR (cm^{-1}): ν_{N-H}, 3397, 3232. HRMS (ESI-TOF, positive ion, *m*/*z*): Calc. 251.1548 ($[M + H]^+$), found 251.1551.

5. Synthesis of 6-{1-(2,6-diisopropylphenylimino)ethyl}-6,11-dihydro-4-isopropyl-6-methyl-5*H*-indolo[3,2-*c*]quinoline (**6**).

A Schlenk flask was charged with **5** (246 mg, 1.00 mmol), **4** (250 mg, 1.00 mmol), $TsOH \cdot H_2O$ (20 mg) and benzene (50 mL). The flask was equipped with a Dean-Stark trap containing 4 Å molecular sieves and a water condenser. The mixture was refluxed under nitrogen for 2 d. The mixture was cooled to room temperature and quenched with Et_3N (1 mL). The volatiles were removed under vacuum to give a yellow oil. The oil was purified by flash column chromatography (silica, hexane/EtOAc/Et_3N = 80/10/1 by volume) and taken to dryness under vacuum to yield a white solid. This material was recrystallized by diffusion of pentane into a CH_2Cl_2 solution at room temperature, yielding analytically pure **6** as white needles (42 mg, 9%). The low isolated yield is likely due to overall low conversion. ^1H NMR (CD_2Cl_2): δ 8.42 (br s, 1H, indole NH), 7.71 (d, *J* = 7.9, 1H), 7.43 (d, *J* = 7.9, 1H), 7.20–7.06 (m, 5H), 6.99–6.93 (m, 2H), 6.78 (t, *J* = 7.6, 1H), 4.94 (br s, 1H, amine NH), 3.04 (septet, *J* = 6.8, 1H), 2.76 (septet, *J* = 6.8, 1H), 2.20 (septet, *J* = 6.8, 1H), 2.17 (s, 3H), 1.57 (s, 3H), 1.30 (d, *J* = 6.8, 3H), 1.29 (d, *J* = 6.8, 3H), 1.18 (d, *J* = 6.8, 3H), 1.12 (d, *J* = 6.8, 3H), 0.83 (d, *J* = 6.8, 3H), 0.75 (d, *J* = 6.8, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 174.5, 146.3, 141.4, 137.8, 136.6, 136.2, 132.7, 132.4, 126.7, 125.6, 123.4, 123.1, 123.0, 122.2, 120.6, 119.8, 118.4, 118.1, 114.2, 111.6, 110.3, 63.0, 28.3, 28.0, 27.8, 26.9, 23.5, 23.1, 23.0, 22.8, 22.5, 22.3, 16.8. HRMS (ESI-TOF, positive ion, *m*/*z*): Calc. 478.3222 ($[M + H]^+$), found 478.3219.

6. Synthesis of (**6**)$PdCl_2$

A Schlenk flask was charged with **6** (179 mg, 0.375 mmol), $(MeCN)_2PdCl_2$ (96 mg, 0.37 mmol) and CH_2Cl_2 (35 mL). The mixture was refluxed for 22 h and cooled to room temperature. The mixture was concentrated under vacuum to ca. 10 mL, and the yellow precipitate was collected by vacuum filtration. The solid was dissolved in CH_2Cl_2 (160 mL) upon gentle heating. The solution was filtered through Celite to remove trace solid particles, and the filtrate was taken to dryness to yield (**6**)$PdCl_2$ as a yellow powder (168 mg, 69%). The solid contains 0.16 equiv CH_2Cl_2 and 0.10 equiv hexane as determined by ^{1}H NMR. ^{1}H NMR (CD_2Cl_2): δ 9.30 (br s, 1H, indole NH), 7.57 (d, *J* = 8.2, 1H), 7.49 (d, *J* = 7.8, 1H), 7.40 (t, *J* = 7.6, 1H), 7.34–7.19 (m, 6H), 7.15 (t, *J* = 7.5, 1H), 5.77 (br s, 1H, amine NH), 3.61 (septet, *J* = 6.8, 1H), 3.28 (septet, *J* = 6.8, 1H), 2.70 (septet, *J* = 6.8, 1H), 2.44 (s, 3H), 1.89 (d, *J* = 6.8, 3H), 1.68 (s, 3H), 1.63 (d, *J* = 6.8, 3H), 1.43 (d, *J* = 6.8, 3H), 1.42 (d, *J* = 6.8, 3H), 1.31 (d, *J* = 6.8, 3H), 1.18 (d, *J* = 6.8, 3H). ^{13}C NMR analysis was precluded by the low solubility of (**6**)$PdCl_2$ in common NMR solvents. ESI-MS (1:1 MeOH:H_2O, positive ion scan, *m*/*z*): 582.3 ($[M - Cl - HCl]^+$). Anal. Calcd. for $C_{33}H_{39}Cl_2N_3Pd \cdot 0.16(CH_2Cl_2) \cdot 0.10(C_6H_{14})$, %: C, 59.88; H, 6.06; N, 6.20. Found: C, 59.65; H, 5.75; N, 6.30.

7. Details of crystallographic analysis for (**6**)$PdCl_2$

Diffraction data were measured on a Bruker D8 VENTURE with a PHOTON 100 CMOS detector system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). Data reduction and integration were performed with the Bruker APEX2 software package. Data were corrected for absorption effects using empirical methods as implemented in SADABS. The structure was solved and refined by full-matrix least-squares procedures using the Bruker SHELXTL software

package.

Crystals were grown by diffusion of hexane into a CH_2Cl_2 solution of (**6**)$PdCl_2$ at 0 °C. Crystallographic data and details of the data collection and structure refinement are listed in Table 1. All non-H atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions for structure factor calculations except those bound to nitrogen atoms N1 and N2. These hydrogen atoms (H1N and H2N) were found on the difference Fourier map and allowed to be refined at 0.88 Å within a default 0.02 Å standard deviation with their thermal parameters being constrained to be 1.2 times of the U_{eq} value of the N atoms. (**6**)$PdCl_2$ crystallized in a large unit cell with a volume of 16484(2) $Å^3$. Disordered solvent molecules were treated by application of the program SQUEEZE[33,34] as implemented in Platon[35] using the "fab" file construct and ABIN command in XL. The SQUEEZE algorithm located a void, centered at (0, 0, 0), with a large volume of 3916 $Å^3$ (ca. 22% of the unit cell volume) and an electron count of 537.

CCDC 1552623 contains the supplementary crystallographic data for complex (**6**)$PdCl_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 1. Crystallographic data for compound (**6**)$PdCl_2$

Empirical formula	$C_{33}H_{39}N_3PdCl_2$
Formula weight	654.97
T (K)	120(2)
Crystal system	Trigonal
Space group	*R*-3
a (Å)	28.4722(19)
b (Å)	28.4722(19)

c (Å)	23.4797(16)
α (°)	90
β (°)	90
γ (°)	120
Volume (Å^3)	16484(2)
Z	18
Density (calc.) (g cm^{-3})	1.188
Absorption coefficient (mm^{-1})	0.675
F(000)	6084
Crystal size (mm^3)	0.140 × 0.130 × 0.080
2Θ range for data collection (°)	2.351 to 25.167
Index ranges	–33 ≤ h ≤ 33, –33 ≤ k ≤ 33, –28 ≤ l ≤ 28
Reflections collected	84533
Independent reflections (R_{int})	6532 (0.0480)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6532/2/366
Goodness-of-fit (GOF) on F^2	1.033
Final R indexes [I >= 2σ (I)]	R_1 = 0.0812, wR_2 = 0.2020
Final R indexes (all data)	R_1 = 0.1121, wR_2 = 0.2278
Largest diff. peak/hole (e Å^{-3})	3.161/–2.133

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/.

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