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Oxidative insertion into the N–H bond of carbazole, indole and pyrrole with zerovalent metals

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Abstract

The reactions of carbazole ($C_{12}H_8NH$), indole (C_8H_6NH) and pyrrole (C_4H_4NH) with the zerovalent [$Pt(PEt_3)_3$], [$Pd(PEt_3)_3$] and [$Ni(PEt_3)_3$] gave oxidative insertion into the N–H bond, affording the corresponding hydrides of the type *trans*-[$HM(LN)(PEt_3)_2$], LN = de-protonated heterocyclic ligand; the isolated compounds for platinum were *trans*-[$HPt(C_8H_6N)(PEt_3)_2$] (**1**), *trans*-[$HPt(C_4H_4N)(PEt_3)_2$] (**2**), and for nickel *trans*-[$HNi(C_{12}H_8N)(PEt_3)_2$] (**3**), *trans*-[$HNi(C_8H_6N)(PEt_3)_2$] (**4**) and *trans*-[$HNi(C_4H_4N)(PEt_3)_2$] (**5**); on using palladium the corresponding hydrides were also detected in solution, however, after longer reaction time the double substituted compounds: *trans*-[$Pd(C_{12}H_8N)_2(PEt_3)_2$] (**6**), *trans*-[$Pd(C_8H_6N)_2(PEt_3)_2$] (**7**) and *trans*-[$Pd(C_4H_4N)_2(PEt_3)_2$] (**8**) were obtained. A crystal structure is reported for **6**.

Keywords: Carbazole; Indole; Pyrrole; Nickel; Palladium; Platinum

1. Introduction

The hydrotreatment of crude oil reduces the undesired compounds of sulfur, nitrogen, oxygen and metals. Depending on the removed element, the chemical process is known as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) or hydrodemetallation (HDM). The first of them is the one that has received, and is still receiving, the greatest attention; but since a great amount of nitrogen oxides, NO_x, comes from the combustion of N-heterocycles the HDN studies have increased. In the fossil fuels, S- and N-containing compounds are founded as thiols, sulfides, disulfides, thiophenic molecules, amines, pyridines, quinolines and pyrrolic type compounds. Of all of these, the aromatic heterocycles are the hardest to remove, that is one of the reasons to explore the reactivity involved to activate these kind of compounds.

Our group has reported extensive investigations of the chemistry of thiaplatinacycles [1] and recently of thiapalladacycles [2]. These complexes, containing six-membered rings derived from the oxidative addition of platinum(0) or palladium(0) into the C–S bond of a variety of thiophenes, are considered as intermediates in the zerovalent metal promoted hydrodesulfurization process. It was therefore of interest to explore the chemistry involved in the reactions of platinum(0), nickel(0) and palladium(0) with N-heteroaromatic compounds as pyrrole and their annelated analogues, the indole and carbazole. We reported in a previous communication, the oxidative addition of [$Pt(L)_3$] (L = PMe_3 and PEt_3) into the carbazole's N–H bond [3].

Although examples of N–H bond cleavage and formation of $^1\eta$-N coordinated pyrrole, indole or carbazole with transitional metals are known [4,5]; the area remains relatively unexplored. To the best of our knowledge, very few examples of oxidative insertion of Group 10 metals into the N–H bond of these heterocycles have been found. In addition to the one of our group (vide supra), there are few more: Jonas and Wilke [5a] found that a tricyclohexylphosphine complex of

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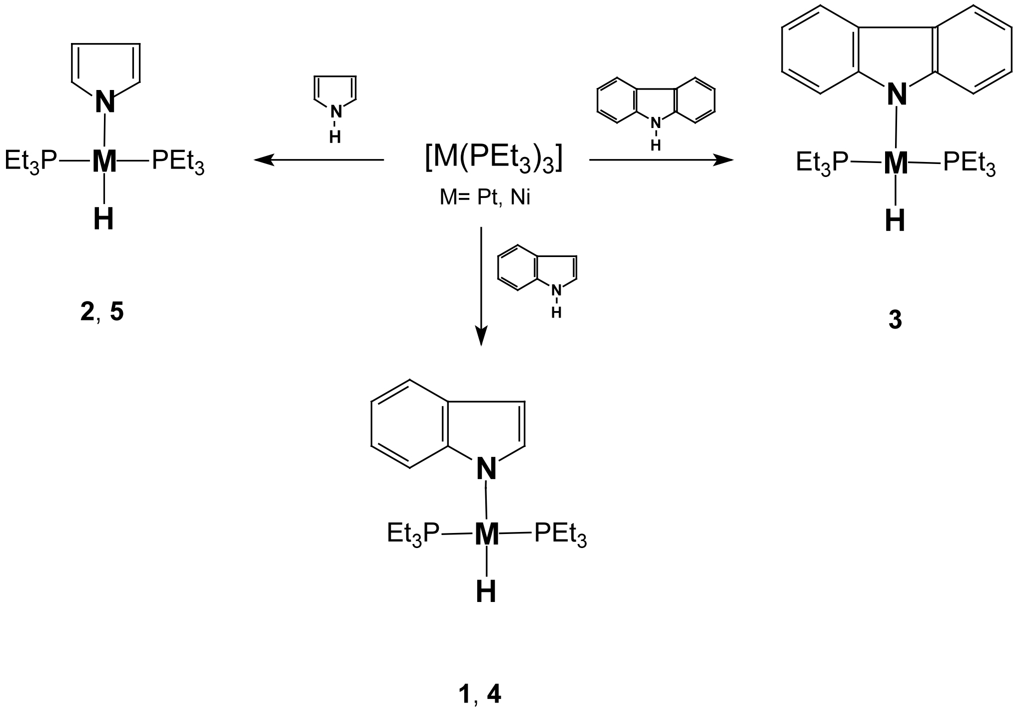
nickel(0) underwent oxidative addition into pyrrole's N–H bond to give *trans*-[HNi{P(C_6H_{11})$_3$}$_2$(C_4H_4N)]; similarly Stone and coworkers [5b] found that a tricyclohexylphosphine complex of platinum(0) underwent, as well an oxidative addition into pyrrole's N–H bond to give *trans*-[HPt{P(C_6H_{11})$_3$}$_2$(C_4H_4N)]; also Hartwig [6], found how a dimeric palladium hydroxide complex gave a proton exchange reaction to cleave the N–H bond of pyrrole to afford *trans*-[(PPh_3)$_2$Pd(Ph)(NC_4H_4)]; also with palladium but using indoles Robson 7a reported the reactions of these substrates to give compounds of the type [$Pd_2L(C_8H_6N)$] (where L is a bidentated ligand); and finally Yamauchi and co-workers [7b] found the reactions of indoles and Na_2PdCl_4 to yield complexes of the type [Pd(C_8H_6N)$_2$$Cl_2$], as a result of hydrogen transfer to the C3 of the indolyl moiety. Finally, there are very few examples with carbazole oxidatively added to transition metals, so far two cases of N–H activation has been found [3,8]. Here we want to report the activation of N–H bonds of heterocycles by zerovalent compounds of platinum, palladium and nickel.

2. Results and discussion

As we observed previously in the reaction of carbazole with [Pt(L)$_n$] (L = PMe_3 and PEt_3) [3] the indole and pyrrole underwent inmediate reaction with [Pt(PEt_3)$_3$], Scheme 1. Here the moiety [Pt(PEt_3)$_2$] oxidatively inserts into the N–H bond. The ^{1}H-NMR spectra of **1** and **2** showed the existence of a hydride coupled to two equivalents of phosphorus nuclei affording a well defined triplet at room temperature, with $^2J_{HP} = 15.8$ and 15.6 Hz, respectively, with the corresponding coupling to ^{195}Pt; this is consistent with a *trans* arrangement of the H and the indolyl or pyrrolyl moiety. As expected, in both cases the ^{31}P{^{1}H}-NMR spectra showed one singlet with satellites due to the coupling to ^{195}Pt, $J = 2723$ and 2748 Hz, respectively, all the above data are consistent with a monomeric nature of these hydridic compounds. The reaction to prepare **1** afforded always a high yield, but the one for pyrrole at room temperature produces two different compounds, **2** in higher amount and other one that could not be isolated, however, on gentle warming for several hours only **2** was produced.

The reactivity found for [Ni(PEt_3)$_3$] with carbazole, indole and pyrrole is rather similar to the one above discussed for [Pt(PEt_3)$_3$], i.e. for all them the corresponding products of N–H oxidative addition **3**, **4** and **5** were isolated; on the ^{1}H-NMR spectra the hydride resonances where observed at δ −21.47; −21.94 and −22.37 respectively, particularly in the case **3** the multiplicity of the hydride signal can be seen at room temperature as a triplet with $^2J_{P-H} = 74.3$ Hz, which as in the case of **1** and **2** is in agreement with the proposed monomeric structure. For carbazole and pyrrole the ^{31}P-NMR spectra shows singlets at δ 19.78 and 9.43, respectively, however in the case of **4** two sharp singlets could be observed at room temperature at δ 10.17 and 10.78 in a ratio (1:1), on warming the sample both



Scheme 1.

singlets began broadening regime unfortunately complete coalescence could not be observed before 80 °C in toluene and warming to higher temperatures some decomposition appeared. On cooling the sample both sharp signals were observed again, this process may be due to a slow rotation of the indole moiety around the Ni–N axis. Compounds **1** to **5** are thermally stable at room temperature and up to 80 °C, however all of them are moderately sensitive to sunlight.

As its platinum(0) analogue [Pd(PEt$_3$)$_3$] activates the N–H bond of an additional nitrogen heterocycle to afford **6**, **7** and **8**, consequently the corresponding hydride was not isolated as the final product, instead we always isolated in pretty good yield the double carbazolyl substituted complex (see Scheme 2). The ^{31}P{^{1}H}-NMR for **6** and **8** consists of a sharp singlet at δ 17.46 and 19.48, respectively, and for **7** a broad singlet centered at δ 18.3. An X-ray determination, Fig. 1, confirm the proposed structure.

This structure shows the *trans* disposition of the two carbazolyl fragments. The Pd, the two P and the two N are all coplanar and the molecule has a plane of symmetry through the nitrogen atoms and the palladium, perpendicular to the Pd1–P1–P2–N1–N2 plane, these symmetry element contains the benzenic rings. The formation of **6**, **7** and **8** can be explained via a hydride intermediate (vide supra), that evolves to the double substituted complex with H$_2$ elimination. Indeed, on carefully following the reaction by ^{1}H-NMR spectroscopy we were able to detect in solution (not isolate) these hydrides, key resonances for the N–H activation of carbazole, indole and pyrrole with [Pd(PEt$_3$)$_3$] are at δ −13.7, −13.8 and −14.0 respectively, attempts to isolate these hydrides by crystallization or chromatography afforded always the hydride free compounds **6**, **7** and **8**. Complex **8** was also sensitive to sunlight.

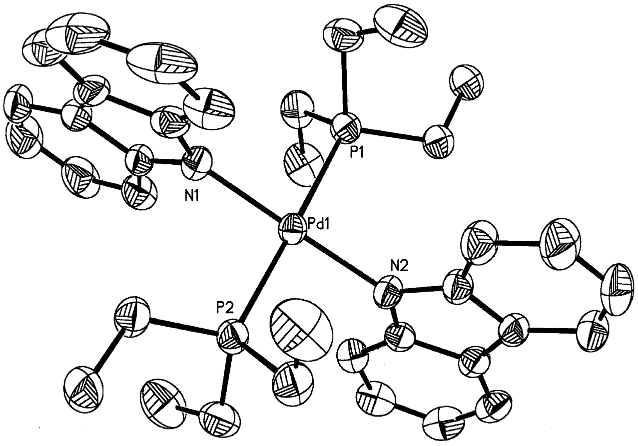
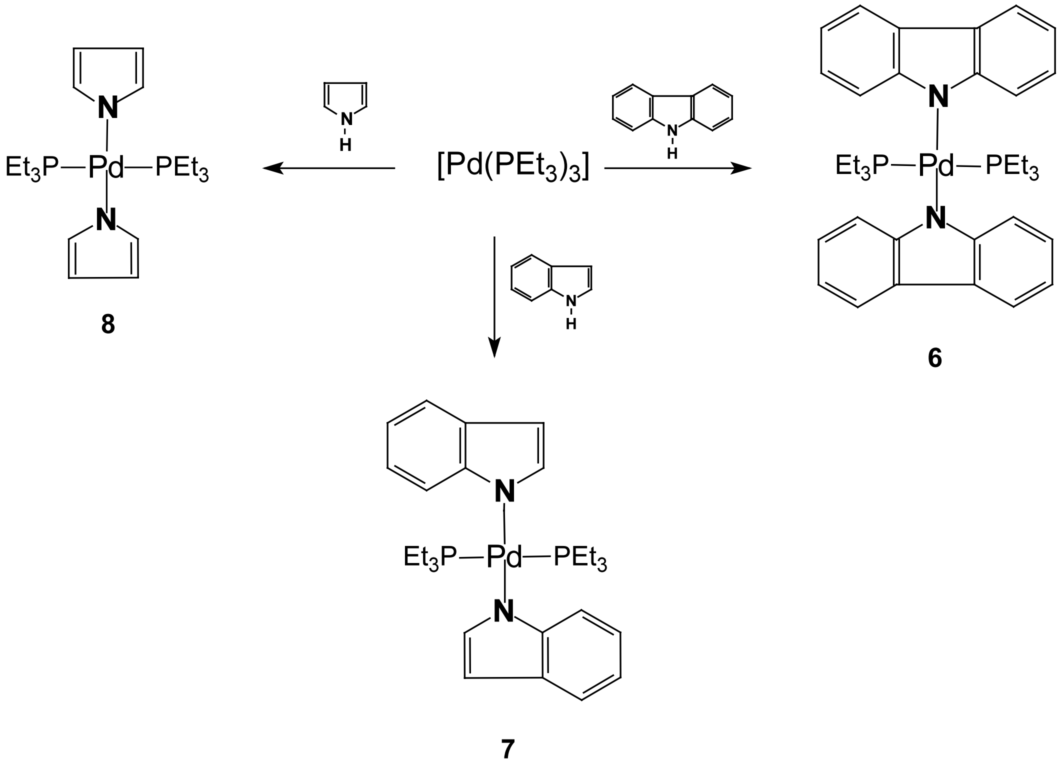


Fig. 1. Molecular structure of complex **6** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd(1)–N(1) 2.025(3), Pd(1)–N(2) 2.026(3), Pd(1)–P(1) 2.3307(9), Pd(1)–P(2) 2.3408(9), N(1)–Pd(1)–N(2) 178.96(11), N(1)–Pd(1)–P(1) 87.27(8), N(2)–Pd(1)–P(1) 91.82(9).



Scheme 2.

3. Conclusions

Here we have demonstrated the achievement of N–H cleavages for a number of aromatic heterocycles under relative mild conditions. This activation gave the formation of the corresponding hydrides and $^1\eta$-N coordination of the heterocycle in the case of platinum and nickel, in a *trans* geometry and thermally stables. For palladium two $^1\eta$-N coordinated heterocycles are observed, the formation of these compounds is probably through the same type of hydrides isolated for platinum and nickel.

4. Experimental

All reactions and purifications were carried out under argon atmosphere using either vacuum line and Schlenk tube techniques and dry box techniques. Solvents were dried and distilled before use. Deuterated solvents (Aldrich) for NMR experiments were dried over molecular sieves. Pyrrole was distilled under reduced pressure, stored under argon and dried over molecular sieves. Carbazole and indole dried in high vacuum for overnight and stored in a dry box. All other chemicals were reagent grade and used as received. ^{1}H-, ^{13}C- and ^{31}P{^{1}H}-NMR spectra were recorded on a Varian VXR-300 spectrometer in toluene-d^8, unless otherwise stated, chemical shifts (δ) are related to deuterated solvent and ^{31}P{^{1}H}-NMR spectra are relative to external H_3PO_4. Infrared spectra were obtained in Perkin–Elmer 1600 FT spectrophotometer and mass determinations in a JEOL SX-102 A using FAB$^+$ as ionization technique. Galbraith Laboratories carried out elemental analysis. The synthesis of [Pt(PEt$_3$)$_3$], [Pd(PEt$_3$)$_3$] and [Ni(PEt$_3$)$_3$] were carried out using the previously reported procedures [9].

4.1. Preparation of *trans*-[HPt(C_8H_6N)(PEt$_3$)$_2$] (**1**)

Indole (0.12 g, 1.01 mmol) was added as a powder to a solution of [Pt(PEt$_3$)$_3$] (0.7 g, 1.25 mmol) in toluene at 20 °C. The color changed immediately from orange to yellow and the resulting mixture was stirred in the darkness for 2 h more. The solvent and excess phosphine were removed in vacuum (20 °C/0.2 mmHg); the remaining solid was warmed 4 h (70 °C) at 0.2 mmHg. The complex was crystallized from hexane. Yield: 65%. Anal. Calc. for $C_{20}H_{37}NP_2Pt$: C, 43.78; H, 6.93; N, 2.55. Found: C, 43.70; H, 6.97; N, 2.52%. IR: ν(Pt–H) 2140 cm^{-1}. m/z: 548 [M$^+$]. NMR spectra are as follows. ^{1}H (acetone-d^6): δ −15.6 (t, HPt, 1H, $^2J_{HP} = 15.8$ Hz; $^1J_{HPt} = 943.8$ Hz), 1.0 (m, from Et–P, 18H), 1.6 (m, from Et–P, 12H), 6.3 (m, CH, 1H), 6.7 (m, CH, 2H), 7.0 (pseudot, 1H, $^3J_{HPt} = 13.2$ Hz), 7.4 (m, CH, 2H). ^{13}C{^{1}H}: δ 8.5 (m, −CH$_3$), 18.0 (m, CH$_2$), 101.0 (pseudot, CH, $^3J_{CPt} = 24.5$ Hz), 114.9 (pseudot, CH, $^3J_{CPt} = 19.6$ Hz), 116.8 (s, CH), 117.9 (s, CH), 120.6 (s, CH), 131.8 (pseudot, C, $^3J_{CPt} = 23.8$ Hz), 136.0 (pseudot, CH, $^2J_{CPt} = 29.8$ Hz) and 146.1 (s, C). ^{31}P{^{1}H}: δ 18.7 (s, $^1J_{PPt} = 2723$ Hz).

4.2. Preparation of *trans*-[HPt(C_4H_4N)(PEt$_3$)$_2$] (**2**)

Pyrrole (0.06 g, 0.88 mmol) was added to a solution of [Pt(PEt$_3$)$_3$] (0.55 g, 1.01 mmol) in toluene. The reaction mixture was stirred, protected from light, for 6 h at 70 °C. The solvent and excess phosphine were distilled out in vacuum (20 °C/0.2 mmHg); the remaining oil was warmed 4 h (70 °C) under reduced pressure. Dried hexane was added (5 ml) to yield a solid at −78 °C, which was washed three times with hexane to afford a yellow liquid at 20 °C. Yield: 40%. Anal. Calc. for $C_{16}H_{35}NP_2Pt$: C, 38.54; H, 7.08; N, 2.81. Found: C, 38.55; H, 7.10; N, 2.79%. IR: ν(Pt–H) 2136 cm^{-1}. m/z: 498 [M$^+$]. NMR spectra are as follows. ^{1}H: δ −15.7 (t, 1H, $^2J_{HP} = 15.6$ Hz, $^1J_{HPt} = 912.6$ Hz), 0.9 (m, from Et–P, 18H), 1.4 (m, from Et–P, 12H), 6.7 (d, 2H, $^3J_{H-H} = 1.8$ Hz), 6.8 (m, 2H). ^{13}C{^{1}H}: δ 8.7 (m, –CH$_3$), 18.0 (m, CH$_2$), 107.6 (pseudot, $^3J_{CPt} = 25.8$ Hz), 127.0 (pseudot, $^2J_{CPt} = 24.3$ Hz). ^{31}P{^{1}H}: δ 27.6 (s, $^1J_{PPt} = 2748$ Hz).

4.3. Preparation of *trans*-[HNi($C_{12}H_8N$)(PEt$_3$)$_2$] (**3**)

Carbazole (71.8 mg, 0.422 mmol) was added to a solution of [Ni(PEt$_3$)$_3$] (174 mg, 0.422 mmol) in toluene at 20 °C. The mixture was stirred for 4 h at 70 °C. The solvent and excess phosphine were removed in vacuum (20 °C/0.2 mmHg); the remaining solid was heated 4 h (70 °C) at 0.2 mmHg, in order to sublime some remaining phosphine oxide, affording a yellow brownish solid unstable to air. Yield: 45%. Anal. Calc. for $C_{24}H_{39}NP_2Ni$: C, 62.36; H, 8.50; N, 3.03. Found: C, 62.40; H, 8.51; N, 3.00%. m/z: 462 [M$^+$]. NMR spectra are as follows: ^{1}H: δ −21.47 (t, 1H, $^2J_{H-P} = 74.3$ Hz), 0.78 (m, CH$_3$ from Et–P, 18H), 1.03 (m, CH$_2$ from Et–P, 12H), 7.7 (m, CH, 1H), 8.15 (m, CH, 1H), 8.31 (m, CH, 1H), 8.90 (m, CH, 1H). ^{31}P{^{1}H}: δ 19.78 (s).

4.4. Preparation of *trans*-[HNi(C_8H_6N)(PEt$_3$)$_2$] (**4**)

Indole (44.2 mg, 0.377 mmol) was added to a solution of [Ni(PEt$_3$)$_3$] (156 mg, 0.773 mmol) in toluene at 20 °C. This mixture was stirred for 9 h at 80 °C. The solvent and excess phosphine were removed in vacuum (20 °C/0.2 mmHg); the remaining solid was warmed 5 h (70 °C) at 0.2 mmHg, to remove any remaining phosphine oxide, affording a dark brown solid air and light sensitive. Yield: 43%. Anal. Calc. for $C_{20}H_{37}NP_2Ni$: C, 58.28; H, 9.04; N, 3.39. Found: C, 58.30; H, 9.09; N, 3.35%. m/z: 412 [M$^+$]. NMR spectra are as follows: ^{1}H: δ −21.94 (m, br, 1H), 0.84 (m, CH$_3$

from Et–P, 18H), 1.09 (m, CH_2 from Et–P, 12H), 7.58 (t, CH, 1H), 7.63 (t, CH, 1H), 8.01 (d, CH, 2H), 8.68 (d, CH, $J_{HH} = 8$ Hz, 1H) and 8.99 (d, CH $J_{HH} = 8$ Hz, 1H). $^{31}P\{^1H\}$: δ 10.17 (s) and 10.78 (s).

4.5. Preparation of *trans*-[HNi(C_4H_4N)(PEt_3)$_2$] (**5**)

Pyrrole (0.05 ml, 0.722 mmol) was added to a solution of [Ni(PEt_3)$_3$] (296 mg, 0.72 mmol) in toluene at 20 °C. This mixture was stirred for 11 h at 80 °C. The solvent and excess of phosphine were removed in vacuum (20 °C/0.2 mmHg); the remaining solid was warmed for 8 h (70 °C) at 0.2 mmHg, in order to remove any phosphine oxide. Fresh distilled toluene was added to re-dissolve the product, the solution was cooled (−78 °C) and filtered off. The filtrate was concentrated to dryness with high vacuum (20 °C/0.2 mmHg), affording a dark brown solid unstable to light and air. Yield: 30%. Anal. Calc. for $C_{16}H_{35}NP_2Ni$: C, 53.06; H, 9.74; N, 3.86. Found: C, 53.01; H, 9.65; N, 3.90%. *m/z*: 362 [M^+]. NMR spectra are as follows: ^1H: δ −22.37 (m, br, 1H), 0.84 (m, CH_3 from Et–P, 18H), 0.99 (m, CH_2 from Et–P, 12H), 7.22 (m, CH, 2H) and 7.31 (m, CH, 2H) $^{31}P\{^1H\}$: δ 9.43 (s).

4.6. Preparation of *trans*-[Pd($C_{12}H_8N$)$_2$(PEt_3)$_2$] (**6**)

Carbazole was added (118.3 mg, 0.693 mmol) to a solution of [Pd(PEt_3)$_3$] (158.4 mg, 0.343 mmol) in toluene at 20 °C. This mixture was stirred for 4 h at 65 °C. The solvent and excess phosphine were removed in vacuum (65 °C/0.2 mmHg). Fresh distilled toluene was added and warmed, time reaction and solvent evaporation were repeated to improve yield. The remaining solid was washed three times with hexane (−78 °C), dried in vacuum (20 °C/0.2 mmHg) and then washed three times with toluene (−78 °C) and dried again in vacuum to afford a yellow solid. The complex was crystallized from toluene–hexane. Yield: 78%. Anal. Calc. for $C_{36}H_{46}N_2P_2Pd$: C, 64.04; H, 6.86; N, 4.14. Found: C, 64.05; H, 6.90; N, 4.11%. *m/z*: 675 [M^+]. NMR spectra are as follows: ^1H: δ 0.90 (m, CH_3 from Et–P, 18H), 1.24 (m, br, CH_2 from Et–P, 12H), 7.2 (t, CH, 4H), 7.6 (m, CH, 4H), 8.19 (d, CH, 4H, $J_{HH} = 7.2$ Hz) and 8.25 (d, CH, 4H). $^{31}P\{^1H\}$: δ 17.46 (s).

4.7. Preparation of *trans*-[Pd(C_8H_6N)$_2$(PEt_3)$_2$] (7)

Indole (100.1 mg, 0.846 mmol) was added to a solution of [Pd(PEt_3)$_3$] (195 mg, 0.423 mmol) in toluene at 20 °C. The mixture was stirred for 3 hours at 65°C. The solvent and excess phosphine were removed in vacuum (65 °C/0.2 mmHg). Dried toluene was added and warmed, time reaction and solvent evaporation were repeated. The remaining solid was dissolved in toluene and filtered off (−78 °C); solvent was then removed in vacuum and the remaining solid washed three times with hexanes (−20 °C), and dried in vacuum (20 °C/0.2 mmHg) to afford a pale yellow solid. Yield: 70%. Anal. Calc. for $C_{28}H_{42}N_2P_2Pd$: C, 58.48; H, 7.36; N, 4.87. Found: C, 58.50; H, 7.34; N, 4.82%. *m/z*: 575 [M^+]. NMR spectra are as follows: ^1H: δ 0.9 (m, CH_3 from Et–P, 18H), 1.26 (m, CH_2 from Et–P, 12H), 7.3 (m, CH, 4H), 7.84 (d, CH, 2H), 7.89 (d, CH, 4H, $J_{HH} = 8$ Hz) and 8.05 (d, CH, 2H). $^{31}P\{^1H\}$: δ 18.3 (s, br).

4.8. Preparation of *trans*-[Pd(C_4H_4N)$_2$(PEt_3)$_2$] (**8**)

Prepared similarly to **7**, from pyrrole (0.058 ml, 0.722 mmol) [Pd(PEt_3)$_3$] (195 mg, 0.423 mmol) in toluene. This sample was highly sensitive to light and air, we failed to obtain reproducible elemental analysis for this complex. Yield: 30%. Anal. Calc. for $C_{20}H_{38}N_2P_2Pd$: C, 50.58; H, 8.06; N, 5.89. Found: C, 50.55; H, 8.02; N, 5.88%. *m/z*: 474 [M^+]. NMR spectra are as follows: ^1H: δ 0.85 (m, CH_3 from Et–P, 18H), 1.13 (m, CH_2 from Et–P, 12H), 6.85 (m, CH, 4H) and 7.23 (m, CH, 4H). $^{31}P\{^1H\}$: δ 19.48 (s).

Table 1
Summary of crystallographic results for **6**

Empirical formula	$C_{36}H_{46}N_2P_2Pd$
Formula weight	675.09
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	$P2_1/c$
Space group	Monoclinic
Unit cell dimensions	
a (Å)	11.7123(11)
b (Å)	19.4935(18)
c (Å)	17.0362(16)
α (°)	90
β (°)	107.072(2)
γ (°)	90
V (Å^3)	3718.2(6)
Z	4
D_{calc} (Mg/m^3)	1.206
Absorption coefficient (mm^{-1})	0.609
F(000)	1408
Crystal size (mm^3)	0.17 × 0.21 × 0.24
θ Range for data collection (°)	1.63–25.00
Index ranges	$-13 \leq h \leq 13$, $-23 \leq k \leq 23$, $-20 \leq l \leq 20$
Reflections collected	35489
Independent reflections	6531 [$R_{int} = 0.0431$]
Completeness to $\theta = 25.00°$	99.8%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6531/0/376
Goodness-of-fit on F^2	0.961
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1311$
R indices (all data)	$R_1 = 0.0536$, $wR_2 = 0.1369$
Largest difference peak and hole (e Å^{-3})	1.577 and −0.427

5. Crystallographic studies

Single crystals suitable for X-ray studies were obtained for compound **6** by slow evaporation of a toluene-hexane solution, at room temperature and were sealed in a thin-walled glass capillary under N_2. Diffraction data were collected at 298 K on a Bruker APEX diffractometer, using a graphite monochromatized Mo–K_α radiation ($\lambda =$ 0.71073 Å. Data were collected using ω scan over the range $1.63 < \theta < 25.00°$. The total number of reflections measured was 35489 of which 6531 were independent. An absorption correction was applied using SADABS. The structure was solved by direct methods. Refinement was carried out by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed into calculated positions and refined using a riding model with a fixed isotropic thermal parameter. The final residuals were $R_1 = 0.0465$, $wR_2 = 0.1311$. A summary of crystallographic results is presented in Table 1. Calculations were carried out with SMART software for data collection and data reduction and SHELXTL for solution and refinement [10].

6. Supplementary material

Tables of complete crystallographic data for **6** and Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 192313 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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