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New Pyridine ONN-Pincer Gold and Palladium Complexes: Synthesis, Characterization and Catalysis in Hydrogenation, Hydrosilylation and C–C Cross-Coupling Reactions

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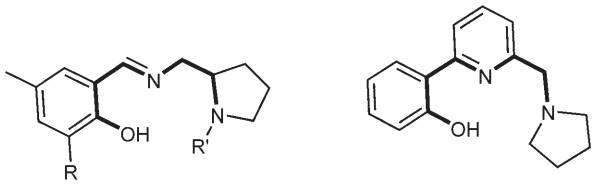
Abstract: The ONN-tridentate unsymmetrical pincer 2-[6-(pyrrolidin-1-ylmethyl)pyridin-2-yl]phenol and *N-tert*-butyl-1-{[6-(2-hydroxyphenyl)pyridin-2-yl]methyl}pyrrolidine-2-carboxamide ligands were synthesized by an easy method in high purity and good yields. All the organic compounds were characterized by elemental analysis, mass spectrometry, IR and ^{1}H and ^{13}C NMR spectroscopy. Palladium(II) and gold(III) complexes have been prepared as air-stable solids, with the ONN-tridentate ligand after deprotonation of the hydroxy group, the coordination of the metal ion is completely stereospecific and gives rise to only one diastereoisomer. These complexes were shown to be very active catalysts in the hydrogenation (80% *ee* was achieved with the chiral gold complex), hydrosilylation and C–C coupling, Suzuki and Heck, reactions, under mild conditions.

Keywords: cross-coupling; gold; hydrogenation; palladium; pincer complexes

Introduction

The use of gold compounds in homogeneous and heterogeneous catalytic organic reactions has been undervalued for many years due to the preconceived idea that gold is chemically inert. However, recent reports have changed this assessment and gold compounds are known to display high catalytic activity.[1] Indeed, Au(III) can act as a Lewis acid catalyst for a large variety of reactions,[2,3] solid gold catalysts on the other hand can be recycled, and when prepared in the form of gold nanoparticles they are highly active and selective for reactions such as hydrogenation,[4] CO oxidation,[5] chemoselective reduction of substituted nitroaromatics by H_2,[6] selective oxidation of alcohols[7] and some C–C bond forming reactions.[8] Moreover, the use of Au complexes in homogeneous catalysis has undergone a renaissance and spectacular achievements have been reported.[9]

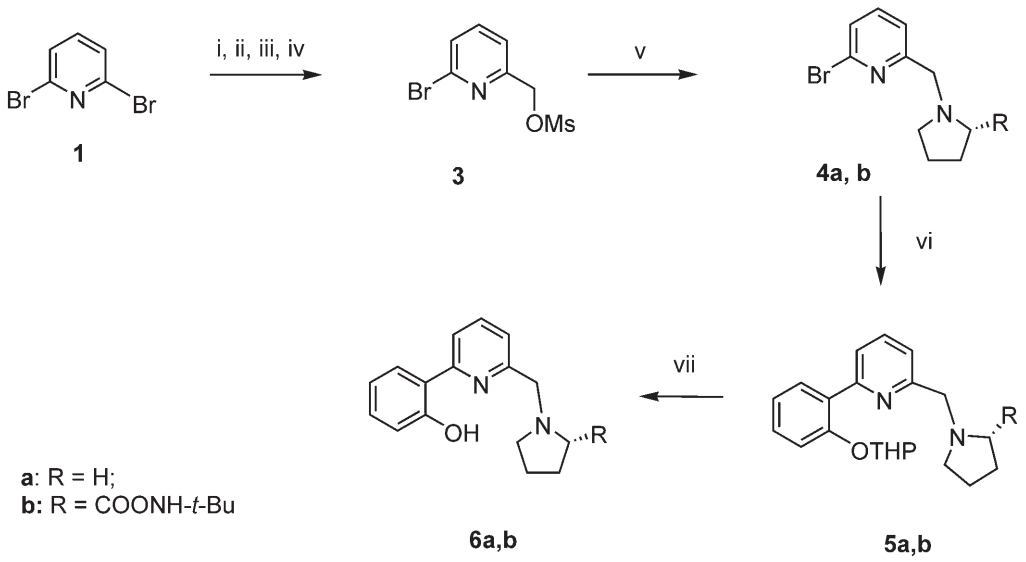
Recently, we have shown that Au(III) complexes with anionic linear Schiff ligands (**a**) exhibit excellent catalytic activity in several reactions.[10] On the other hand, the Pincer-type ligand has become a valuable ligand class and their complexes play crucial roles with respect to unusual conformations, special reactivity, and catalytic applications.[11,12] In the present work, we have developed a series of novel conformationally restricted ONN-pincer-type ligands (**b**) resembling coordination environments present in previously described Schiff base ligands. The respective Au(III) and Pd(II) complexes proved to be active and selective for catalyzing the hydrogenation and hydrosilylation reactions and Suzuki and Heck C–C bond coupling.



(**a**) (**b**)

Results and Discussion

We have developed the synthesis of new ONN-pincer-type ligands (**b**) in several steps starting from 2,6-dibromopyridine as shown in Scheme 1. According to this pathway, mesylation of (6-bromopyridin-2-yl)me-



Scheme 1. Synthesis of the ONN ligand, i) BuLi, ii) DMF, iii) $NaBH_4$, iv) MsCl, Et_3N, v) pyrrolidine, *i*-Pr_2EtN,vi) 2-(tetrahydropyran-2-yloxy)-phenylboronic acid, vii) *p*-TsOH.

thanol (**2**) with methanesulfonyl chloride in the presence of DMAP in CH_2Cl_2 gave the corresponding mesylate **3** in 96% yield. The substitution reactions with pyrrolidine and prolinamide were conducted in acetonitrile in the presence of *N,N*-diisopropylethylamine at 60 °C to afford products **4a** and **4b**, respectively, in 65–70% yield. Suzuki cross-coupling reaction of bromopyridine **4a** or **4b** with 2-(tetrahydropyran-2-yloxy)-phenylboronic acid using $Pd(PPh_3)_4$ as a catalyst in presence of aqueous Na_2CO_3 gave 2-(pyrrolidin-1-ylmethyl)-6-[2-(tetrahydro-2*H*-pyran-2-yloxy)-phenyl]pyridine (**5a**; 80% yield) or (2*S*)-*N*-*tert*-butyl-1-({6-[2-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]pyridin-2-yl}methyl)pyrrolidine-2-carboxamide (**5b**; 75% yield). Finally cleavage of the THP group (using *p*-TsOH in MeOH) went smoothly to furnish **6a** and **6b** with yields of 90–95%. Having succeeded in developing a flexible synthetic scheme for the preparation of a broad variety of new ligands, we were interesting in evaluation their potential (activity and selectivity) in transition metal catalysis.

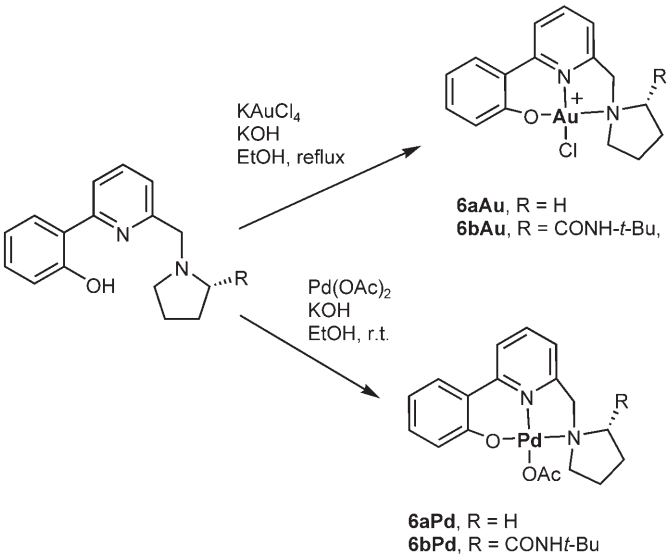
Synthesis of Complexes

For the synthesis of gold and palladium complexes we have followed the route developed for our Schiff base complexes,[13] by addition of the divalent metal salt $Pd(OAc)_2$ or $HAuCl_4$ to an ethanolic solution of ligand; one of the acetate groups or chloride was displaced by the phenolic anion while the amine and pyridine nitrogens were co-ordinated with the metal in a square planar arrangement (Scheme 2). The complexes, which precipitated in EtOH, were obtained as microcrystalline stable solids, soluble in organic solvents, with high purity and in high yields. The structures of all the complexes were confirmed with elemental analysis (C, H, N), IR spectroscopy and ^1H, ^{13}C NMR (data in Experimental Section). All these complexes were characterized by electro-spray mass spectrometry. Thus, the ES-MS of complexes show the ion peaks $[M^+]$ and peaks from the fragments due to elimination of the ion acetate $[M^+-OAc]$ or the molecular ion $[AuLCl]^+$. All assignments were confirmed by good agreement between the observed and calculated isotopic distributions.

The absence of the ν(OH) band (present in the spectra of the free ligands at *ca.* 3430 cm^{-1}) is in accordance with loss of the OH proton. The IR spectra also shows strong bands at 1290 and *ca.* 1500 cm^{-1} assigned to the symmetric and asymmetric ν(COO) vibrations, respectively, in agreement with those expected for monocoordinate acetate ligands.[14] New bands in the 500–600 cm^{-1} region are ascribed to ν(Pd–O) and bands at 320 cm^{-1} were characteristic of ν(Au–Cl).

NMR spectra

Diamagnetic palladium and gold complexes have been characterized by ^1H and ^{13}C NMR spectroscopy. All assignments are based on several correlations in the 2D spectra. They are fully consistent with the structures depicted in Scheme 2. In all cases, the spectra show the simultaneous occurrence of two sets of signals which are attributable on the one hand to the substituted pyridine entity and on the other hand to the aliphatic part of the ligand. In the ^1H NMR spectra all the resonances were high field shifted as com-



Scheme 2.

pared to the uncoordinated ligand and they were in agreement with metallation of the ligand with coordination of the metal atom *via* the pyridine nitrogen atom. The most noticeable shifts concern the CH_2 between the pyridine part and the pyrrolidine part (about 0.5 ppm). Deprotonation of the OH group was confirmed by the absence of OH resonances in the ^1H spectra. The ^1H NMR spectrum shows the signal of the *Me*COO protons as a singlet at $\delta = 2.10$ ppm. The ^{13}C NMR spectra showed the signals assigned to the ligand OAc group for Pd complexes.

Catalytic Activity

In order to evaluate the catalytic performances of these new soluble gold(III) and Pd(II) complexes, we have tested them in hydrogenation, hydrosilylation, Suzuki cross-coupling and Heck reactions as shown in following paragraphs using experimental conditions that could permit us to make a comparative study of different catalysts and substrates, obviously for preparative application a tuning of experimental conditions would have to be done for each case.

Catalytic Hydrogenation of Olefins

The structurally well defined Au(III) and Pd(II) complexes enable us to explore the possibilities of these complexes in hydrogenation. The hydrogenations of diethyl 2-benzylidenesuccinate with Au and Pd complexes were carried out under standard conditions (EtOH as the solvent, 4 atm. hydrogen pressure, 40 °C). Results are summarized in Table 1.

Table 1. Turnover rates[a] for the catalytic hydrogenation of diethyl benzylidenesuccinate with gold and palladium catalysts.[b]

Catalyst	Conversion (%) [h]	TOF[a]	*ee*[c] [%]
(Schiff base)Au	100 (3)	780	15 (*S*)
6aAu	92 (5)	724	-
6bAu	96 (7)	580	80 (*S*)
(Schiff base)Pd	100 (3)	640	<10 (*S*)
6aPd	93(6)	439	-
6bPd	60(7)	565	15 (*S*)

[a] TOF: mmol substrate/mmol catalyst min.
[b] *Conditions:* 4 atm, 40 °C, catalyst: 0.1 mol%.
[c] Average of three values.

The nature of the metal centre has an influence on the catalytic activities. In general, the gold catalyst is more active than the corresponding palladium analogue. The results show that the Pd and Au systems lead to quantitative conversion of olefins, under the hydrogenation conditions. In all cases no gold or palladium black has been formed during the hydrogenation reaction. Low enantiomeric excesses were achieved with the Pd compound (<20%), but **6bAu** shows an *ee* = 80% for the hydrogenation of diethyl 2-benzylidenesuccinate as we could detect from the HPLC analysis of the reaction mixture.

The accumulated evidence concerning the mechanisms of homogeneously catalyzed hydrogenation indicates that three principal modes of hydrogen activation are suitable: oxidative addition, and homolytic or heterolytic hydrogen cleavage. For Au complexes, heterolytic cleavage is preferred to give a hydride intermediate which involves charge separation without any oxidation of the metal. Heterolytic cleavage of hydrogen by Au complexes have been reinforced from our experiments using more polar and protonic acid media which produce a significant increase of reaction rate, probably favouring charge separation in the step of formation of the intermediate.[15]

Catalytic C–C Coupling: Suzuki and Heck Reactions

The gold and palladium complexes were also studied for the Suzuki cross-coupling of PhI with 4-bromophenylboronic acids. The standard reaction conditions were applied to gold and palladium catalysts and the conversions are tabulated in Table 2. In our experiments, we have chosen K_3PO_4 as a mild base because with K_2CO_3 longer reaction times were necessary to obtain reasonable conversions. Excellent yields (calculated with respect to PhI) and 100% selectivity towards the cross-coupling product were found with Pd complexes, gold complexes were inactive for this reaction. For comparison purposes (Schiff base)-Pd com-

Table 2. Influence of ligands on Pd(II) reactivity for Suzuki cross-coupling reactions.[a]

	Catalyst	*t* [min]	Conversion [%][b]
Suzuki reaction	$Pd(PPh_3)_4$	90	71
	(Schiff base)Pd	180	68
	6aPd	180	100
Heck reaction	(Schiff base)Pd	240	75
	6aPd	15	100

[a] Catalyst: 3%, IPh (1 mmol), arylboronic acid (1.5 mmol), K_3PO_4 (2 mmol).

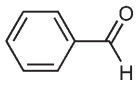
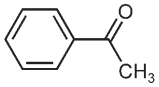
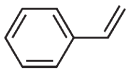
plexes have also been prepared and tested under the same reaction conditions (Table 2). Results show that activity and selectivity are similar.

In this work we have also studied the performance of Pd complexes for Heck reactions of iodobenzene with *n*-butyl acrylate using the biphasic mixture toluene and ethylene glycol as solvent in the presence of potassium acetate under phosphine-free conditions.[16] The complexes are insensitive to oxygen or moisture and no change in their activity was observed when the reaction was carried out in an open system.

Among the various bases examined, 1.14 mmol of NaOAc or KOAc proved to be most suitable in combination with catalyst (<3 mol%), and use of other bases resulted in lower yields: Et_3N (<10%). In the biphasic vinylation system, the toluene phase contains the reactants and products, while metal complex and potassium acetate are in the ethylene glycol phase. The inorganic base added is partly soluble in the ethylene glycol phase. The reaction should occur in the ethylene glycol phase and the ethylene glycol-toluene interface in which the base is partly soluble.

In Table 2, we show the catalytic performance of Pd complexes for the Heck reaction. The reaction was successful using low Pd catalyst loadings (2–5 mol%), but the reactions did not proceed at concentrations below 2 mol%. Analogous gold complexes do not react under the same reaction conditions. When using the palladium complexes, no palladium black was observed after more than 72 h. As shown in Table 2, under the optimized conditions, the Heck-type olefination reactions of iodobenzene were readily achieved with *n*-butyl acrylate. The initial green solution of homogeneous catalysts in *N*-methylpyrrolidone turned to red upon heating after addition of base and particles of palladium black could be seen in the flask. These observations led us to the hypothesis that palladium colloids will be generated upon addition of base to a solution of the homogeneous precursor when heating the reaction mixture.[17] Indeed, upon centrifugation of the reacted mixture we could isolate palladium particles. These isolated particles were used in a new reaction and they were catalytically inactive. The absence of reactivity is presumably due to a significant aggregation of the particles under the reaction conditions. When the filtered solution was used as catalyst, it was observed that the transformation of iodobenzene did not occur.

Table 3. Gold-catalyzed hydrosilylation with Ph_2SiH_2.[a]

Catalyst			
6aAu	90	70	50 (80)[b]
6bAu	80	50	40 (70)[b]

[a] The reactions were carried out with carbonyl compound (1 mmol)/silane (2 mmol), and the gold catalyst (5%) in toluene (1 mL) at 70°C under a nitrogen atmosphere. Yields quoted with respect to carbonyl consumed based on GC-MS. Selectivity >98%.

[b] Gold catalyst 10%.

Catalytic Hydrosilylation

Under a nitrogen atmosphere, in the presence of a catalytic amount of gold compounds (5%), the reaction of the carbonyl compound (1 mmol) with diphenylsilane (2 mmol) in toluene at 70°C for 15 h resulted in the formation of (benzyloxy)(diphenyl)silane in 100% GC yield with >98% selectivity (Table 3).

Conclusions

We have developed a general synthetic scheme which, due to its modularity and efficiency, allows for the synthesis of a broad variety of structurally related ONN-tridentate ligands with low effort. Treatment of these ligands, with $Pd(OAc)_2$ and $K[AuCl_4]$ in EtOH gave air-stable complexes. These complexes were shown to be active catalysts for hydrogenation and hydrosilylation reactions with high reactivity in mild conditions (TOF up to 800 min^{-1}) and $ee = 80\%$ for the Au compound. The palladium complexes are also active for Suzuki and Heck reactions. Studies on the immobilization of these pincer complexes on a support such as silica or MCM-41 and their use as recoverable catalyst are in progress.

Experimental Section

General Remarks

All preparations of metal complexes were carried out under dinitrogen by conventional Schlenk tube techniques. Solvents were carefully degassed before use. Metal contents were analyzed by atomic absorption using a Perkin–Elmer

Analyst 300 atomic absorption apparatus and plasma ICP Perkin–Elmer Optima 2100. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets. ^1H NMR, ^{13}C NMR, spectra were taken on Varian XR300 and Bruker 200 spectrometers. Gas chromatography analyses were performed in a Hewlett–Packard 5890 II with a flame ionization detector or/and in a Hewlett–Packard G1800A with a quadrupole mass detector using a cross-linked methylsilicone column. HPLC analysis were taken in an Agilent 1200 equipped with a chiralcel OD column.

Synthesis of Ligands

General Method for the Substitution Reaction of Mesylate 3 with Pyrrolidines[18]

2-Bromo-6-(pyrrolidin-1-ylmethyl)pyridine (4a): A carefully degassed mixture of (6-bromopyridin-2-yl)methyl methanesulfonate[19] (1 g, 3.8 mmol, 1,0 equiv.), pyrrolidine (373 μL, 4.5 mmol, 1.2 equivs.) and *N*,*N*-diisopropylethylamine (2.6 mL, 15.1 mmol, 4.0 equivs.) in acetonitrile (15 mL) was heated at 50–60 °C under an argon atmosphere. After 4 h, the heating bath was removed and the solvent was evaporated under reduced pressure. Dichloromethane was added and the mixture was washed with a 3% solution of NaOH (20 mL). The organic layer was dried over $MgSO_4$ and condensed. The residual oil was purified by flash column chromatography on silica gel (AcOEt/hexane: 1/1) to give the product as a yellow liquid; yield: 67%; anal. calcd. for $C_{10}H_{13}BrN_2$ (240): C 49.8, H 5.4, N 11.6; found: C 49.9, H 5.2, N 11.5; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.50 (t, ^3J = 7.72 Hz, 1H, *p*-CH), 7.40 (d, ^3J = 7.72 Hz, 1H, *m*-CH), 7.33 (d, ^3J = 7.72 Hz, 1H, *m*-CH), 3.76 (s, 2H, CCH_2N), 2.57 (m, 4H, CH_2CH_2N), 1.79 (m, 4H, CH_2CH_2N); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 161.3 (*C*-Br), 141.1 (*C*-N_{Py}), 138.7 (*p*-CH_{Py}), 126.1 (*m*-CH_{Py}), 121.5 (*m*-CH_{Py}), 61.5 (CCH_2N), 54.2 (CH_2CH_2N), 23.6 (CH_2CH_2N); MS (EI): *m/z* (%) = 171–173; 84; 70.

1-[(6-Bromopyridin-2-yl)methyl]-*N*-*tert*-butylpyrrolidine-2-carboxamide (4b)

Following the general procedure employed for the synthesis of **4a**, the residue was purified by flash column chromatography (AcOEt/hexane: 1/1). The product was obtained as a white solid; yield: 64%; mp 89–93 °C; anal. calcd. for $C_{15}H_{22}BrN_3O$ (339): C 52.9, H 6.5, N 12.3; found: C 52.5, H 6.1, N 12.7; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.50 (t, ^3J = 7.63 Hz, 1H, *p*-CH), 7.43 (br s, 1H, NH), 7.37 (d, ^3J = 7.92 Hz, 1H, CH), 7.19 (d, ^3J = 7.35 Hz, 1H, CH), 3.85 (d, ^2J = 13.38 Hz, 1H, CCH_2), 3.64 (d, ^2J = 13.38 Hz, 1H, CCH_2), 3.09 (m, 2H, CHN, CH_2N), 2.43 (m, 1H, CH_2N), 2.20 (m, 1H, CH_2CHN), 1.86 (m, 1H, CH_2CHN), 1.74 (m, 2H, CH_2CH_2N), 1.30 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 173.4 (*C*=O), 160.1 (*C*Br), 142.1 (CCH_2), 138.8 (*p*-CH), 126.8 (CH), 121.6 (CH), 67.9 (CHN), 60.7 (CCH_2), 54.3 (CH_2N), 50.2 (*C*-*t*-Bu), 30.6 (CH_2CHN), 28.7 (CH_3), 24.1 (CH_2CH_2N); MS (EI): *m/z* (%) = 239–241, 170–172.

2-(Pyrrolidin-1-ylmethyl)-6-[2-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]pyridine[20] (5a)

A 25-mL 2-neck flask equipped with a reflux condenser was charged with 2-(tetrahydropyran-2-yloxy)phenylboronic acid (449 mg, 2.0 mmoles, 1.2 equivs.) and xylene (20 mL) under argon. 2M aqueous Na_2CO_3 solution (2 mL, 2.3 equivs.), EtOH (2 mL), $Pd(PPh_3)_4$ (58 mg, 3 mol%) and the bromopyridine **4a** (406 mg, 1.69 mmol, 1 equiv.) were added. The mixture was stirred for 15 h at 80 °C. The mixture was quenched with 2M sodium carbonate solution and the aqueous phase extracted with toluene. The organic phase was washed with water followed by saturated aqueous NaCl solution. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. Yield: 79%; anal. calcd. for $C_{21}H_{26}N_2O_2$ (338.4): C 74.5, H 7.7, N 8.3; found: C 74.1, H 8.1, N 8.7%; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.55 (m, 3H, CH), 7.23 (m, 3H, CH), 7.05 (td, 1H, CH), 5.39 (br s, 1H, CH_{THP}), 3.76 (m, 1H, CH_{2THP}), 3.47 (m, 1H, CH_{2THP}), 2.58 (m, 5H, CH_{2Pyr}, CH_{2THP}), 2.47 (m, 1H, CH_{2THP}), 1.76 (m, 5H, CH_{2Pirr}, CH_{2THP}), 1.51 (m, 3H, CH_{2THP}); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 161.4 (Cq), 158.8 (Cq) 155.3 (Cq), 135.7 (CH), 131.1 (CH), 130.2 (Cq), 129.6 (CH), 123.2 (CH), 122.2 (CH), 120.6 (CH), 115.5 (CH), 96.7 (CH_{THP}), 62.3 (CH_2N), 61.8 (CH_{2THP}), 54.2 (CH_{2Pyr}, CH_{2THP}), 25.1 (CH_{2THP}), 23.6 (CH_{2Pirr}), 18.6 (CH_{2THP}).

(2*S*)-*N*-*tert*-Butyl-1-({6-[2-(tetrahydro-2*H*-pyran-2-yloxy)phenyl]pyridin-2-yl}methyl)pyrrolidine-2-carboxamide (5b)

Following the general procedure employed for the synthesis of **5a**, starting from **4b** (227 mg, 0.67 mmol), we have obtained **5b**; yield: 116 mg (49%) [two products were obtained, (*RS*, *SS*)]; anal. calcd. for $C_{26}H_{35}N_3O_3$ (437): C 71.4, H 8.1, N 9.6; found: C, 71.0, H 8.1, N 9.7%; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.79 (t, 2H, CH), 7.65 (m, 2H, CH), 7.49 (NH), 7.31 (m, 1H, CH), 7.21 (m, 1H, CH), 7.08 (t, 1H, CH), 5.46 (2 s, 1H, CH_{THP}), 3.98 (2d, ^2J = 13.19 Hz, 1H, CCH_2), 3.84 (m, 1H, CH_2O_{THP}), 3.74 (2d, ^2J = 13.19 Hz, 1H, CCH_2), 3.58 (m, 1H, CH_2O_{THP}), 3.22 (m, 1H, NCHCO), 3.13 (m, 1H, CH_2CH_2N), 2.50 (m, 1H, CH_2CH_2N), 2.22 (m, 1H, CH_2CHN), 1.69 (m, 9H, CH_2CHO_{THP}, $CH_2CH_2CHO_{THP}$, $CH_2CH_2O_{THP}$, CH_2CHN, CH_2CH_2N); 1.23 (2 s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 173.60 (*C*=O), 157.99 (Cq), 155.76 (Cq), 154.32 (Cq), 135.68 (CH), 131.84(CH), 131.21–131.17 (CH), 129.67 (CH), 128.42–128.26 (CH), 123.53–123.49 (CH), 121.71(CH), 120.40–120.36 (CH), 115.25–115.20 (CH), 96.67–96.57 (CHO_{THP}), 67.82–67.76 (NCHCO), 61.77–61.73 (CH_2O_{THP}), 61.43–61.38 (CCH_2N), 54.19–54.09 (CH_2CH_2N), 49.92–49.87 (*C*-*t*-Bu), 30.50–30.45 (CH_2CHN), 30.16 (CH_2CHO_{THP}), 28.55–28.52 (CH_3), 25.01 ($CH_2CH_2O_{THP}$), 23.98–23.95 (CH_2CH_2N), 18.56 ($CH_2CH_2CHO_{THP}$); MS (EI): *m/z* (%) = 437; 337; 253; 185; 85.

2-[6-(Pyrrolidin-1-ylmethyl)pyridin-2-yl]phenol (6a)

To a solution of **5a** (112 mg, 0.26 mmoles, 1 equiv.) in MeOH (5 mL) was added *p*-TsOH (54 mg, 0.28 mmoles, 1.1 equivs.). The mixture was stirred 6 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/*i*-PrOH: 50/

1); yield: 95%; anal. calcd. for $C_{16}H_{18}N_2O$ (254.3): C 75.6, H 7.1, N 11.0; found: C 75.2, H 7.5, N 11.2%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (m, 2H, C*H*), 7.25 (m, 3H, C*H*), 6.93 (d, 1H, C*H*), 6.81 (t, 1H, C*H*), 3.68 (s, 2H, CCH_2N), 2,46 (m, 4H, CH_{2Pyrr}), 1,67 (m, 4H, CH_{2Pyrr}); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 159.9 (*C*q), 156.9 (*C*q), 156.3 (*C*q), 138.2 (*C*H), 131.2 (*C*H), 126.1 (*C*H), 122.3 (*C*q), 121.2 (*C*H), 120.7 (*C*H), 118.6 (*C*H), 117.1 (*C*H), 61.4 (CCH$_2$N), 54.2 (CH$_{2Pyrr}$), 23.8 (CH$_{2Pyrr}$).

N-tert-Butyl-1-{[6-(2-hydroxyphenyl)pyridin-2-yl]methyl}pyrrolidine-2-carboxamide (6b)

Following the general procedure employed for the synthesis of **6a**, the product was obtained with a yield of 80%; anal. calcd. for $C_{21}H_{27}N_3O_2$ (353.5): C 71.4, H 7.7, N 11.9; found: C 71.2, H 7.5, N 11.6%; IR (KBr): ν = 3200 (O–H), 1650, (C=O), 1608 cm^{-1} (C=C); UV-vis: λ = 299, 366 nm; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79 (m, 2H, C*H*, OH), 7.66, 7.47, 7.30 (m, H$_{arom.}$), 7.23 (br, s, 1H, NH), 7.16 (m, H$_{arom.}$), 7.00 (d, 1H, C*H*), 6.90 (t, 1H, C*H*), 3.98 (d, ^2J = 14.04 Hz, 1H, CCH_2), 3.72 (d, ^2J = 14.04 Hz, 1H, CCH_2), 3.16 (m, 2H, NC*H*CO, CH$_2$CH_2N), 2.43 (m, 1H, CH$_2$CH_2N), 2.25 (m, 1H, CH_2CHN), 1.85 (m, 3H, CH_2CHN, CH_2CH$_2$N), 1.23 (s, 9H, CH$_3$); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 173.3 (*C*=O), 159.9 (*C*q), 157.6 (*C*q), 155.2 (*C*q), 138.4 (*C*H), 131.9 (*C*H), 128.3 (*C*H), 121.7 (*C*H), 120.3 (*C*H), 118.7 (*C*H), 118.5 (*C*q), 117.5 (*C*H), 68.5 (N*C*HCO), 60.4 (C*C*H$_2$N), 54.5 (CH$_2$*C*H$_2$N), 50.1 (C-*t*-Bu), 30.7 (*C*H$_2$CHN), 28.5 (*C*H$_3$-*t*-Bu), 24.0 (*C*H$_2$CH$_2$N); MS (EI:) *m/z* (%) = 353, 253, 185.

Preparation of Metal Complexes; General Method

To a solution of ligand (1 equiv.) in EtOH (15 mL), at room temperature, was added 1 equiv. of KOH. The mixture was stirred for 15 min. An ethanolic solution of $Pd(OAc)_2$ or $KAuCl_4$ (0.5 mmol/15 mL) was added. The resulting mixture was stirred overnight at room temperature, and concentrated under vacuum. The residue was washed several times with diethyl ether, dried and filtered to afford the respective complexes in almost quantitative yields.

[Pd(6a)(AcO)] (6aPd): Yield: 93%; anal. calcd. for $C_{18}H_{20}N_2O_3Pd$ (418.8): C 51.6, H 4.8, N 6.7; found: C 51.6, H 4.6, N 6.3%; IR (KBr): ν = 1614–1600 (C=C, C=N), 557 cm^{-1} (Pd–O); UV-vis: λ = 235, 259, 289, 420 nm; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (m, 2H, CH$_{Ph}$), 7.50 (m, 1H, CH_{Py}), 7.07 (m, 3H, CH_{Py}, CH_{Ph}), 6.61 (t, ^3J = 6.53 Hz, 1H, CH_{Py}), 4.16 (s, 2H, CCH_2N), 3.61 (m, 2H, NCH_2CH$_2$), 2.69 (m, 2H, NCH_2CH$_2$), 1.98 (m, 7H, CH_3, NCH$_2$CH_2); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 178.4 (*C*=O), 164.2 (*C*q), 158.3 (*C*q), 152.9 (*C*q), 138.2 (*C*H$_{Ph}$), 131.9 (*C*H$_{Py}$), 128.4 (*C*H$_{Py}$), 122.8 (*C*H$_{Ph}$), 121.6 (*C*q), 120.2 (*C*H$_{Ph}$), 116.3 (*C*H$_{Ph}$), 115.6 (*C*H$_{Py}$), 67.5 (C*C*H$_2$N), 59.9 (N*C*H$_2$CH$_2$), 23.9 (*C*H$_3$), 22.1 (NCH$_2$*C*H$_2$); MS: *m/z* (%) = 419 (M$^+$, for ^{106}Pd), 359 (M$^{+<M}$- > OAc, for ^{106}Pd).

[Pd(6b)(AcO)] (6bPd): Yield: 75%; anal. calcd. for $C_{23}H_{29}N_3O_5Pd$ (534.0): C 51.7, H 5.5, N 7.9; found: C 51.6, H 5.6, N 8.1%; IR (KBr): ν = 1654–1600 (C=C, C=O, C=N), 557 cm^{-1} (Pd–O); UV-vis: λ = 235, 259, 289, 420 nm; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.63 (m, 2H, H$_{arom.}$), 7.47 (m, 1H, H$_{arom.}$), 7.08 (m, 1H, H$_{arom.}$), 6.95 (m, 1H, H$_{arom.}$), 6.82 (m, 1H, H$_{arom.}$), 6.54 (m, 1H, H$_{arom.}$), 4.34 (d, ^2J = 18.2 Hz, 1H, CCH_2N), 3.90 (d, ^2J = 18.2 Hz, 1H, CCH_2N), 3.79 (m, 1H, NC*H*CO), 3.37 (m, 2H, NCH_2CH$_2$), 2.06 (s, 3H, CH$_3$), 1.85 (m, 4H, CH_2), 0.99 (s, 9H, CH$_3$-*t*-Bu); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 179.5 (*C*=O), 165.3 (*C*=O), 163.8 (Cq), 161.0 (Cq), 152.8 (Cq), 138.1 (*C*H), 131.9 (*C*H), 128.5 (*C*H), 122.5 (*C*H), 120.7 (Cq), 119.8 (*C*H), 115.8 (*C*H), 115.7 (*C*H), 70.5 (N*C*HCO), 62.8 (C*C*H$_2$N), 62.7 (N*C*H$_2$CH$_2$), 51.5 (*C*-*t*-Bu), 27.9 (*C*H$_3$-*t*-Bu), 24.1 (*C*H$_3$), 21.7 (*C*H$_2$), 20.4 (*C*H$_2$); MS: *m/z* (%) = 474 (M$^+$–AcO, for ^{106}Pd).

[Au(6a)Cl]Cl (6aAu): Yield: 60%; anal. calcd. for $C_{16}H_{17}N_2AuCl_2O$ (521.2): C 36.8, H 3.3, N 5.4; found: C 36.6, H 3.6, N 5.1%; IR (KBr): ν = 1614–1600 (C=C, C=N), 337 cm^{-1} (Au–Cl); UV-vis: λ = 225, 270, 310, 440 nm; ^{1}H NMR (DMSO, 300 MHz): δ = 8.44 (d, ^3J = 7.9 Hz 1H, H$_{arom}$), 8.21 (m, 1H, H$_{arom}$), 8.06 (d, ^3J = 7.8 Hz, 1H, H$_{arom}$), 7.97 (m, 1H, H$_{arom}$), 7.71 (d, ^3J = 7.8 Hz, 1H, H$_{arom}$), 7.36 (m, 1H, H$_{arom}$), 6.98 (m, 1H, H$_{arom}$), 4.52 (br s, 2H, CCH_2N), 3.41 (m, 1H, CH_2), 3.02 (m, 1H, CH_2), 1.86 (m, 1H, CH_2), 1.07 (m, 1H, CH_2); ^{13}C NMR (DMSO, 300 MHz): δ = 164.0 (*C*q), 158.6 (*C*q), 153.0 (*C*q), 138.0 (*C*H$_{Ph}$), 132.1 (*C*H$_{Py}$), 128.1 (*C*H$_{Py}$), 123.0 (*C*H$_{Ph}$), 121.8 (*C*q), 120.0 (*C*H$_{Ph}$), 116.5 (*C*H$_{Ph}$), 115.3 (*C*H$_{Py}$), 67.1 (C*C*H$_2$N), 60.0 (N*C*H$_2$CH$_2$), 22.0 (NCH$_2$*C*H$_2$); MS: *m/z* (%) = 485 (M$^+$–Cl), 449 ([AuL]).

[Au(6b)Cl]Cl (6bAu): Yield: 65%; anal. calcd. for $C_{21}H_{26}N_3AuCl_2O_2$ (620.3): C 40.7, H 4.2, N 6.8; found: C 40.6, H 4.6, N 7.1%; IR (KBr): ν = 1664–1610 (C=C, C=O, C=N), 335 cm^{-1} (Au–Cl); UV-vis: λ = 240, 265, 310, 450 nm; ^{1}H NMR (DMSO, 300 MHz): δ = 7.60 (m, 2H, H$_{arom.}$), 7.40 (m, 1H, H$_{arom.}$), 7.00 (m, 1H, H$_{arom.}$), 6.93 (m, 1H, H$_{arom.}$), 6.80 (m, 1H, H$_{arom.}$), 6.49 (m, 1H, H$_{arom.}$); 4.390 (d, ^2J = 18.2 Hz, 1H, CCH_2N); 3.96 (d, ^2J = 18.2 Hz, 1H, CCH_2N); 3.82 (m, 1H, N*C*HCO), 3.40 (m, 2H, NCH_2CH$_2$), 2.10 (s, 3H, CH$_3$), 1.95 (m, 4H, CH_2), 1.00 (s, 9H, CH$_3$-*t*-Bu); ^{13}C NMR ($CDCl_3$, 300 MHz): d = 166.0 (*C*=O), 163.7 (Cq), 161.3 (Cq), 153.0 (Cq), 138.4 (*C*H), 132.1 (*C*H), 128.7 (*C*H), 122.8 (*C*H), 120.9 (Cq), 119.6 (*C*H), 115.5 (*C*H), 115.9 (*C*H), 70.2 (N*C*HCO), 62.6 (C*C*H$_2$N), 62.3 (N*C*H$_2$CH$_2$), 51.1 (*C*-*t*-Bu), 27.7 (*C*H$_3$-*t*-Bu), 24.3 (*C*H$_3$), 21.9 (*C*H$_2$), 20.2 (*C*H$_2$); MS: *m/z* (%) = 585 (M$^+$–Cl), 550 ([AuL]).

Catalytic Activity

Hydrogenation of alkenes: The catalytic properties, in the hydrogenation of diethyl benzylidenesuccinate, of the complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 mL capacity at 40 °C temperature, 4 atm dihydrogen pressure and 1/1000 metal/substrate molar ratio. The evolution of the hydrogenated reaction product was monitored by gas chromatography.

Suzuki C–C Coupling: The reaction was carried out in a 25-mL vessel, at 130 °C during a time period time from 20 to 180 min. In a typical run, a mixture of aryl halide (10 mmol), boronic acid (15 mmol), aqueous potassium carbonate or phosphate (20 mmol) and catalyst (3.3%) in 3 mL of *o*-xylene was stirred for the desired time. The solution was allowed to cool, and a 1:1 mixture of ether/water (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL portion of diethyl ether, dried with anhydrous $MgSO_4$ and filtered. The solvent and volatiles were completely removed under vacuum to give the crude product which wassubjected to column chro-

matographic separation, resulting in pure compounds. The reaction was followed by GC-MS.

Heck Reaction: In a typical experiment, catalyst (3–5 mmol%) was suspended in a mixture of ethylene glycol and toluene (1:1, 6 mL). Then iodobenzene (1 mmol), *n*-butyl acrylate (1 mmol) and potassium acetate (1.14 mmol) were added with stirring. The mixture was refluxed and the reaction progress was monitored by gas chromatography.

Catalytic Hydrosilylation: In a 5-mL Schlenk tube, a solution of the catalyst compound in dry toluene (2 mL) was allowed to equilibrate for 5 min with stirring, at which point, styrene (343 μL, 3 mmol), α-methylstyrene (390 μL, 3 mmol), acetophenone (114 μL, 1 mmol), or benzaldehyde (101 μL, 1 mmol) was added. The resultant mixture was stirred for an additional 5–10 min, after which H_2SiPh_2, (1 mmol for styrenes, 2 mmol for benzaldehyde, acetophenone) was added. The reaction mixture was stirred at 70 °C for 1–15 h and the reaction course was monitored by GC-MS analysis. The mixture was filtered through a short column (celite) from which clear, colourless solutions eluted. Products of each reaction were identified by use of GC-MS[21] and ^{1}H NMR.

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