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Pincers and other hemilabile ligands

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PAPER

Pd, Pt, and Ru complexes of a pincer bis(amino)amide ligand†

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An improved synthesis of pincer ligand bis[(2-dimethylamino)phenyl]amine ($^{Me}N_2NH$) was reported. Reaction of the Li complex of $^{Me}N_2N$ with suitable Pd, Pt, and Ru precursors gave the corresponding metal complexes. The structures of the Pd, Pt, and Ru complexes were determined. The Ru complex showed activity in catalytic transfer hydrogenation of aryl and alkyl ketones.

Introduction

Complexes containing pincer-type ligands are now ubiquitous in coordination chemistry and in homogeneous catalysis.[1,2] In recent years, several groups showcased a rich chemistry supported by metal complexes of new pincer PNP ligands (**A**, Fig. 1) in which two phosphine donors are placed on a diarylamido backbone.[3] These PNP pincers are appealing because the rigid biarylamido framework enforces a stable meridional coordination geometry on a metal center. Furthermore, their lack of reactive protons and other sensitive functionalities makes them suitable for stabilizing reactive catalytic intermediates. Thus, shortly after the pioneering work of Liang,[4,5] Kaska,[6] Ozerov,[7,8] and their co-workers, these ligands have been employed by many others for applications in coordination chemistry,[9] group transfer reactions,[10] C–H activation,[11] and catalysis.[12]

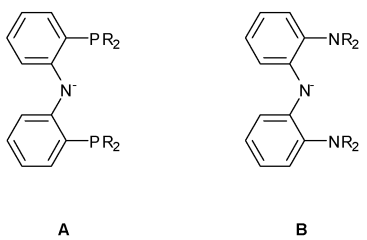

Fig. 1 PNP and N_2N ligands.

Replacing the two phosphine donors of PNP ligands with amines results in bis(amino)amido (N_2N) ligands (**B**, Fig. 1). Phosphines are generally "soft" donors while amines are "hard" donors.[13] Thus, the N_2N ligands shall retain the structural rigidity and stability of PNP ligands, but display drastically different electronic properties. The chemistry of related cyclometallated NCN[2] and bis(quinoline)amido (BQA) ligands[14,15] further inspires us to explore the coordination chemistry and catalytic application of the N_2N ligands.

We initially developed a facile synthesis of the proligand bis[(2-dimethylamino)phenyl]amine ($^{Me}N_2NH$, **1**) and its Ni(II) complexes.[16,17] The complex [($^{Me}N_2N$)Ni(Cl)] (**2**) turned out to be an excellent catalyst for cross coupling of non-activated alkyl halides and direct C–H functionalization.[18] Here we describe an improved synthesis of this ligand and its coordination chemistry with Pd, Pt, and Ru. The application of the Ru complex in catalytic transfer hydrogenation is also reported.

Results and Discussion

1. Ligand synthesis

The protonated ligand, **1**, is now synthesized according to Fig. 2. Several modifications have been made to our original protocol.[16] First, *N*,*N*-dimethyl-2-nitroaniline (**3**) was made by reaction of 1-fluoro-2-nitrobenzene with 1.2 equiv. of dimethylamine at 50 °C. Previously **3** was made by reaction of 1-fluoro-2-nitrobenzene with 6 equiv. of toxic HMPA at 170 °C.[16] Second,

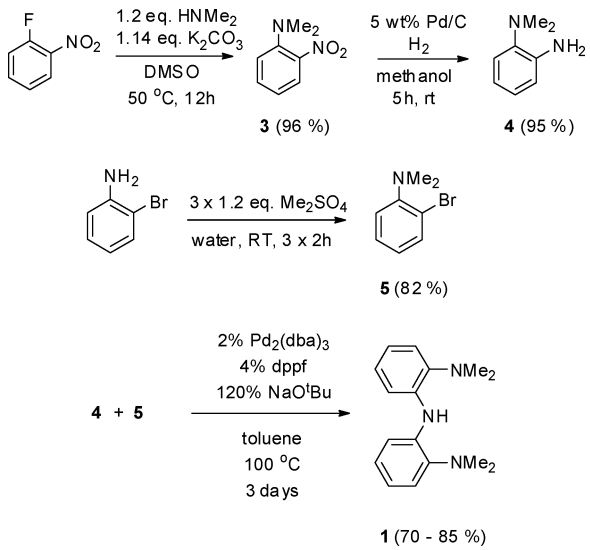

Fig. 2 Optimized synthesis of proligand **1**.

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† CCDC reference numbers 812106–812109. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10195a

the crude, brown 2-amino-*N*,*N*-dimethylaniline (**4**) was purified by vacuum distillation to give a colorless liquid. This additional purification step significantly improved the yields and reproducibility of the following reactions. Third, the final product, $^{Me}N_2NH$ (**1**) was also purified by vacuum distillation to give a slightly yellow liquid which gradually solidifies at room temperature. The yield of the last coupling step ranges from 70 to 85% depending on the batches. Deprotonation of **1** with ^{n}BuLi in toluene gave the dimeric Li complex (**6**) which is an effective transmetallation reagent.[16]

2. Synthesis, structure, and reactivity of Pd–N_2N complexes

The [($^{Me}N_2$N)Pd(Cl)] complex (**7**) was prepared by reaction of Li complex **6** with $Pd(CH_3CN)_2Cl_2$ at room temperature (Fig. 3). The Cl^- anion in **7** could be abstracted by AgOTf to give the triflate complex [($^{Me}N_2$N)Pd(OTf)] (**8**). For both complexes, single crystals suitable for X-ray diffraction analysis were readily obtained. The solid-state molecular structures are depicted in Fig. 4. The Pd ions are in the expected square-planar ligand environment. The pincer $^{Me}N_2N$ ligand coordinates in a meridional fashion, and the anion (Cl^-/TfO^-) occupies the position *trans* to the biaryl amido donor. The Pd–N(amide) bond of 1.960(3) Å in **7** is comparable to that of the analogous [(BQA)PdCl] (BQA = bis(quinoline)amido) complex (1.962(2) Å),[14] but shorter than that of [(PNP)PdCl] (2.0258(19) Å),[7] and [Pd(N($CH_2CH_2P^iPr_2$)$_2$)Cl] (2.033(2) Å).[19] The Pd–N(amide) bond in **8** (1.9344(17) Å) is slightly shorter than in **7**, possibly due to a weaker *trans*-influence of triflate compared to chloride. In both **7** and **8**, the Pd–N(amide) bond is shorter than the averaged Pd–N(amine) bond by about 0.1 Å. The averaged Pd–N(amine) bond distance in **7** (2.065(3) Å) is shorter than that in an analogous Pd–NCN complex (2.1075(15) Å).[20]

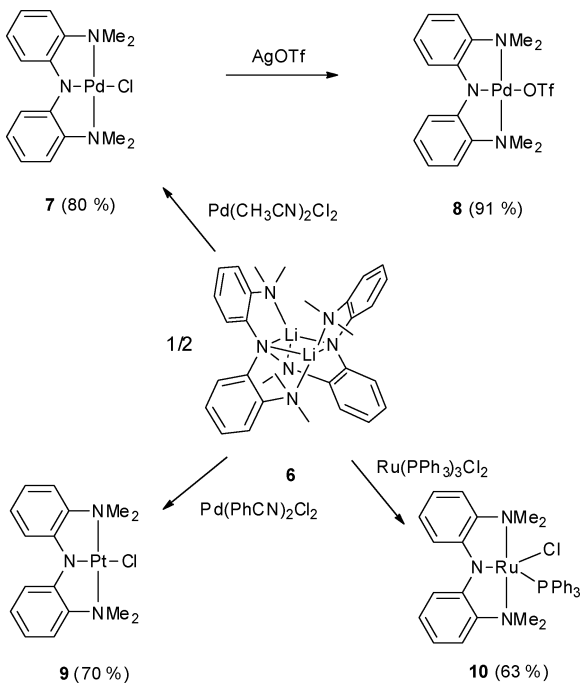


Fig. 3 Synthesis of Pd–, Pt–, and Ru–N_2N pincer complexes.

We showed previously that [($^{Me}N_2$N)Ni(Cl)] complex can be alkylated to form [($^{Me}N_2$N)Ni(alkyl)] species by reaction with an alkyl Grignard reagent.[16,21] That reaction was a key step for

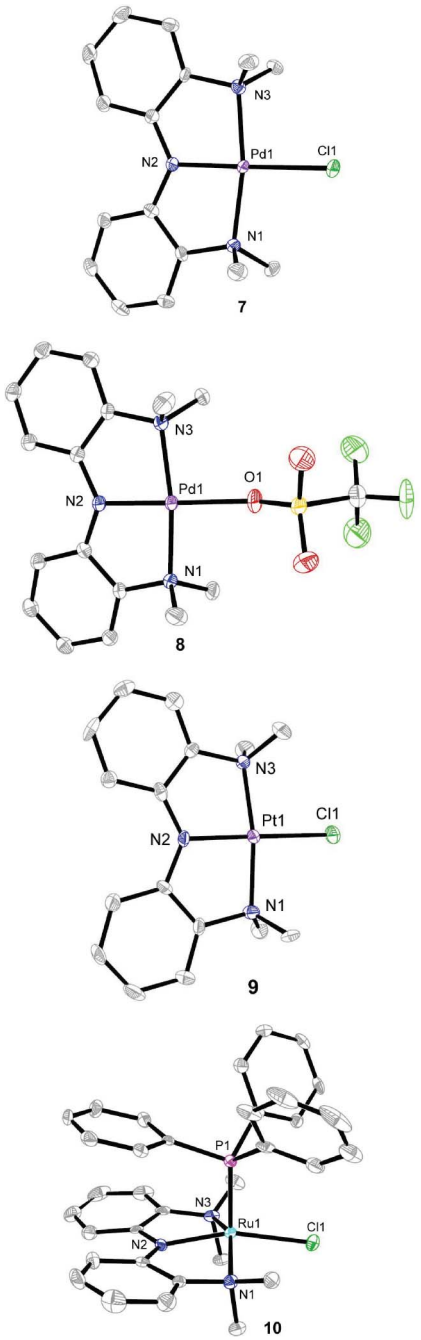


Fig. 4 Solid-state molecular structures of **7**, **8**, **9**, and **10**. The thermal ellipsoids are displayed at a 50% probability. Selected bond lengths (Å) for **7**: Pd1–N1, 2.064(3); Pd1–N2, 1.960(3); Pd1–N3, 2.066(3); Pd1–Cl1, 2.3544(10); for **8**: Pd1–N1, 2.0371(14); Pd1–N2, 1.9344(3); Pd1–N3, 2.0372(14); Pd1–O1, 2.1067(16); for **9**: Pt1–N1, 2.050(3); Pt1–N2, 1.960(3); Pt1–N3, 2.048(3); Pt1–Cl1, 2.3378(10); for **10** (only one of the two independent molecules is displayed): Ru1–N1, 2.136(3); Ru1–N2, 1.991(3); Ru1–N3, 2.124(3); Ru1–Cl1, 2.4191(9); Ru1–P1, 2.1782(9).

Ni-catalyzed alkyl-alkyl coupling.[16,17] When [($^{Me}N_2$N)Pd(Cl)] was reacted with an alkyl Grignard reagent, however, the main isolated product was the known Mg complex [($^{Me}N_2$N)Mg(Cl)(THF)].[17] In addition, black metal particles, presumably Pd(0), were seen in the reaction mixture. It is thus not surprising that Pd complex **7** is inactive in Kumada coupling of non-activated alkyl halides, even

though the Ni complex is an excellent catalyst. Reaction of **7** with H_2 at 50 °C yielded Pd(0) black as well. Reaction of **8** with a base (*e.g.*, Et_3N) in benzene at 80 °C also gave Pd(0) particles.

3. Synthesis, structure, and reactivity of Pt–N_2N complex

The [($^{Me}N_2$N)PtCl] complex (**9**) was prepared by reaction of Li complex **6** with $Pt(PhCN)_2Cl_2$ (Fig. 3). A temperature of 80 °C was required. The use of $Pt(cod)Cl_2$ (cod = cyclo-1,5-octadiene) did not lead to the desired product. The complex has a square-planar structure (Fig. 4). The Pt–N(amide) distance of 1.960(3) Å is similar to that found in the analogous [(BQA)PtCl] complex (1.966(3) Å).[14] It is shorter than that of the [Pt(PNP)Cl] complex (2.024(6) Å).[5] The averaged Pt–N(amine) distance of 2.049(3) Å is slightly shorter than that of an analogous Pt–NCN complex (2.093(5) Å).[20]

Reaction of **9** with MeMgCl led to a mixture of unidentified decomposition products. It is possible that the targeted [($^{Me}N_2$N)Pt(CH_3)] complex is unstable and is subject to several different decomposition pathways such as C–N reductive elimination or alkyl transfer. Reaction of **9** with AgOTf did not give the expected [($^{Me}N_2$N)Pt(OTf)], but rather paramagnetic compounds that could not be purified or isolated. The reactivity of **9** is different from the analogous [Pt(PNP)Cl] complex which undergoes clean transmetallation with alkyl Grignard reagents and halide abstraction with AgOTf.[5]

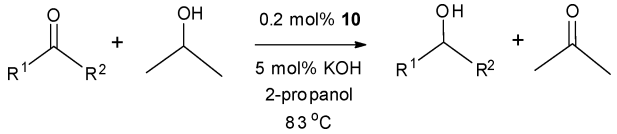
4. Synthesis and structure of Ru–N_2N complex

The [($^{Me}N_2$N)Ru(PPh_3)Cl] complex (**10**) was prepared by reaction of Li complex **6** with $Ru(PPh_3)_3Cl_2$ at room temperature (Fig. 3). The complex is diamagnetic. The Ru center is in a five-coordinate, square-pyramidal ligand environment. The $^{Me}N_2$N ligand and Cl^- anion constitute the plane, and the PPh_3 ligand occupies one axial position (Fig. 4). It was reported earlier that the analogous BQA ligand reacted with $Ru(PPh_3)_3Cl_2$ to give a 6-coordinate, octahedral complex [(BQA)Ru(PPh_3)$_2$Cl].[15] The Ru–N(amide) bond distance of 1.991(3) Å in **10** is slightly shorter than that in [(BQA)Ru(PPh_3)$_2$Cl] (2.048(2) Å).[15]

5. Transfer hydrogenation using Ru–N_2N complex

Ru pincer complexes have been shown to be active catalysts for transfer hydrogenation of ketones.[22,23] We tested complex **10** for its catalytic activity in transfer hydrogenation of ketones using isopropanol as the hydrogen donor, and KOH as the base. Under the standard conditions (5 mol% KOH, 83 °C), hydrogenation of acetophenone was readily achieved using 0.2 mol% of **10**, giving a conversion of 94% in 2 h (Fig. 5 and entry 1, Table 1). Decreasing the Ru loading to 0.1 mol% lowered the conversion to 69%, suggesting that some Ru catalyst might have decomposed during the reaction. The reaction profiles showed no induction period (Fig. 5). The turnover frequencies (TOFs) were modest (in the order of 1000 h^{-1}). Nearly no catalysis was observed without the KOH base (entry 3, Table 1). The same conditions could be applied for transfer hydrogenation of a wide range of other ketones (Table 1). *Ortho*-, *meta*-, and *para*-substituted aryl ketones could be used (entries 4–13, Table 1). Both electron-withdrawing halide groups and electron-donating OMe group were tolerated. The TOFs are slightly higher for *meta*- or *para*-substituted substrates than for *ortho*-substituted substrates, reflecting a steric influence. The TOFs

Table 1 Catalytic transfer hydrogenation of ketones using **10** as the catalyst[a]



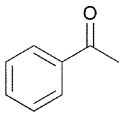
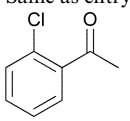
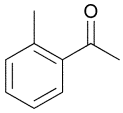
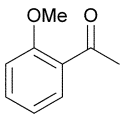
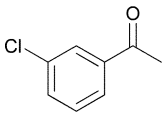
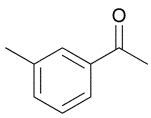
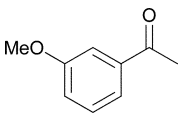
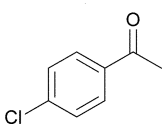
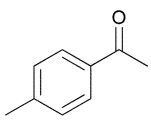
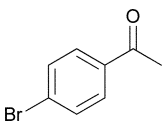
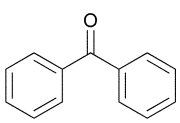
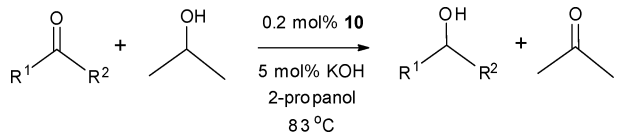
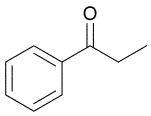
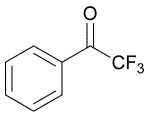
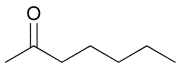
Entry	Substrate	Conversion (%)[b]	TOF (h^{-1})[c]
1		94	2027
2	Same as entry 1	69[d,e]	968
3	Same as entry 1	<2[f]	
4		99	2343
5		82	769
6		89	1500
7		99	2941
8		88	1034
9		97	3061
10		99	2609
11		96	673
13		96	3750
14		82	1546

Table 1 *(Contd.)*



Entry	Substrate	Conversion (%)[b]	TOF (h^{-1})[c]
15		73	361
16		99	833
17		96	536
18		97	1546

[a] Reaction conditions unless otherwise specified: Ketone/KOH/**10** = 1000/50/2.; temperature: 83 °C; reaction time: 2 h. [b] Determined by GC. [c] Turnover frequencies were determined at *ca.* 50% conversion. [d] 0.1 mol % catalyst loading. [e] Reaction time: 4 h. [f] The reaction was performed without KOH.

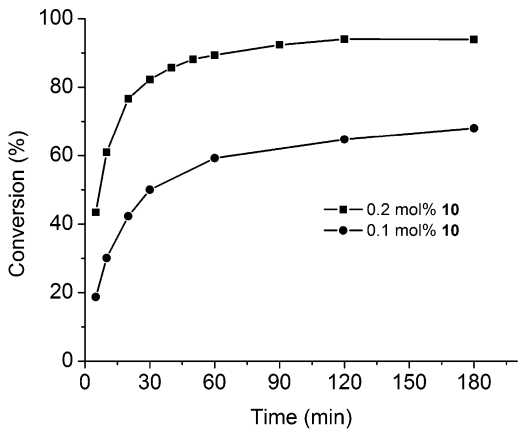


Fig. 5 Time course of transfer hydrogenation of acetophenone using complex **10** as the catalyst. See Table 1 for conditions.

are significantly lower for methyl-substituted aryl ketones than for halide- or methoxide-substituted aryl ketones. Replacing the methyl group by ethyl or CF_3 at the α-position of the aryl alkyl ketones resulted in a decrease in TOF (entries 15 and 16, Table 1). Dialkyl ketones could also be used (entries 17 to 18, Table 1).

The TOFs for transfer hydrogenation of ketones by **10** is lower than some of the fastest Ru(II) pincer catalysts.[23] The difference in reactivity should be due to electronic rather than steric factors, because the latter complexes are 6-coordinate, octahedral.

Conclusions

In summary, we describe here an improved synthesis for pincer ligand bis[(2-dimethylamino)phenyl]amine ($^{Me}N_2N$) and its coordination chemistry with Pd(II), Pt(II), and Ru(II). The ligand adopts the expected meridional geometry. The metal-N distances in these complexes are either shorter than or comparable to those in the analogous PNP and BQA complexes, suggesting that the $^{Me}N_2N$ ligand is a good chelator for 2nd and 3rd row late transition metals. Unlike [($^{Me}N_2N$)Ni(Cl)], the Pd and Pt complexes cannot be cleanly alkylated by Grignard reagents. The Ru complex is five-coordinate, square pyramidal. It is active for catalytic transfer hydrogenation of ketones. A wide range of alkyl and aryl ketones can be reduced.

Experimental

1. General remarks

All manipulations were carried out under an inert N_2(g) atmosphere using standard Schlenk or glovebox techniques. Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 3 Å molecular sieves. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use. $Ru(PPh_3)_3Cl_2$ were prepared according to the literature.[24] The ^1H, ^{31}P and ^{13}C NMR spectra were recorded at 293 K on a Bruker Avance 400 spectrometer. ^1H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si (δ = 0 ppm). The $^{31}P\{1H\}$ chemical shifts were reported in ppm relative to 85% H_3PO_4. The $^{13}C\{^1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm), C_6D_6 (128.0 ppm), THF-d_8 (25.3 ppm). GC-MS measurements were conducted on a Perkin-Elmer Clarus 600 GC equipped with Clarus 600T MS. GC measurement was conducted on a Perkin-Elmer Clarus 400 GC with a FID detector. Elemental analyses were performed on a Carlo Erba EA 1110 CHN instrument at EPFL. X-ray diffraction studies were carried out in the EPFL Crystallographic Facility. Solution, refinement and geometrical calculations for all crystal structures were performed by SHELXTL (Table 2).[25]

2. Synthesis

N,*N*-dimethyl-2-nitroaniline (**3**). 1-fluoro-2-nitrobenzene (2 g, 14 mmol) was dissolved in 20 mL of DMSO and then K_2CO_3 (2.2 g, 16 mmol) was added. A solution of Me_2NH (40% in water. 2 mL) was added slowly under stirring to the above solution. After the addition finished, the solution was heated at 50 °C overnight. Then the reaction mixture was cooled to r.t., and 50 mL of water was added. The organic phase was extracted with ethyl acetate (3 times, 30 mL each), then washed with brine (2 times, 30 mL each). It was then dried over Na_2SO_4, filtered, and evaporated under vacuum to give the product in a pure form. Yield: 2.23 g (96%). ^1H NMR (400.13 MHz, $CDCl_3$): 7.74 (dd, J = 8.2, 1.6 Hz, 1H), 7.38 (td, J = 7.7, 1.6 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.80 (t, 7.7 Hz, 1H), 2.87 (s, 6H). The NMR data are identical to the literature values.[26]

Table 2 Summary of crystallographic data

	7	8	9	10
Chemical Formula	$C_{16}H_{20}ClN_3Pd$	$C_{17}H_{20}F_3N_3O_3PdS$	$C_{16}H_{20}ClN_3Pt$	$C_{34}H_{35}ClN_3PRu$
Formula weight	396.20	509.82	484.89	653.14
T/K	100(2)	140(2)	140(2)	140(2)
Crystal system	Tetragonal	Orthorhombic	Tetragonal	Monoclinic
Space group	$P4_32_12$	*Pnma*	$P4_32_12$	$P2_1/c$
a/Å	9.6434(10)	7.0359(4)	9.63408(10)	18.0619(8)
b/Å	9.6434(10)	14.7010(8)	9.63408(10)	17.4995(5)
c/Å	34.840(5)	19.4779(9)	34.6217(6)	19.9241(8)
α (°)	90.00	90.00	90.00	90.0
β (°)	90.00	90.00	90.00	110.823(5)
γ (°)	90.00	90.00	90.00	90.0
V/Å^3	3239.9(7)	2014.68(17)	3213.43(7)	5886.1(4)
Z	8	4	8	8
D_c/g cm^{-3}	1.624	1.681	2.005	1.474
F(000)	1600	1024	1856	2688
θ range	3.46 to 26.01	3.08 to 26.37	2.99 to 26.37	2.85 to 26.37
Reflections collected	40537	15442	29193	52434
Independent reflections	3140	2143	3261	11960
R(int)	0.0562	0.0200	0.0484	0.0999
R, wR^2 (all)	0.0364, 0.0536	0.0185, 0.0452	0.0222, 0.0318	0.0985, 0.0586
R, wR^2 [$I > 2\sigma(I)$]	0.0313, 0.0523	0.0171, 0.0446	0.0177, 0.0313	0.0394, 0.0513
GOF on F^2	1.281	1.069	0.971	0.813

2-amino-*N*,*N*-dimethylaniline (**4**). *N*,*N*-dimethyl-2-nitroaniline (2 g, 12 mmol) was dissolved in methanol and 100 mg of Pd/C (5% of Pd) was added. The reaction flask was degassed and flushed with hydrogen twice and stirred under hydrogen at r.t. After the orange color of the starting material disappeared, the reaction mixture was stirred 30 additional minutes. The Pd/C catalyst was then filtered off, and the solvent was removed under reduced pressure. The product was purified by vacuum distillation and transferred to a glove box without exposure to oxygen. When contacted with oxygen, the product turns immediately black but it can be purified by distillation. Yield: 1.55 g (95%). ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.05 (d, J = 7.8 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.77 (m, 2H), 4.03 (br, 2H), 2.70 (s, 6H). The NMR data are identical to the literature values.[27]

2-Bromo-*N*,*N*-dimethylaniline (**5**). This compound was synthesized following the literature without modification.[28] In the end the product was purified by vacuum distillation and transferred to a glove box without exposure to oxygen. Yield: 82%. ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.56 (dd, J = 7.9, 1.5 Hz, 1H), 7.26 (td, J = 7.6, 1.5 Hz, 1H), 7.09 (dd, J = 7.9, 1.5 Hz, 1H), 6.89 (td, 7.6, 1.5 Hz, 1H), 2.81 (s, 6H).[28]

Bis[(2-dimethylamino)phenyl]amine ($^{Me}N_2NH$, **1**). A 250 ml reaction vessel was charged with $Pd_2(dba)_3$ (1.36 g, 1.49 mmol), bis(diphenylphosphino)-ferrocene (DPPF) (1.65 g, 2.97 mmol), NaO^tBu (9.84 g, 0.098 mol), and toluene (100 ml) under a dinitrogen atmosphere. 2-Bromo-*N*,*N*-dimethylaniline (14.6 g, 0.073 mol) and 2-amino-*N*,*N*-dimethylaniline (9.95 g, 0.073 mol) were added to the reaction mixture. The resulting brown solution was vigorously stirred for 3 days at 100 °C. The solution was then cooled to room temperature and filtered through Celite. Removal of the solvent yielded a black liquid which was then taken up in dichloromethane and was "flashed" through a silica plug. Removal of the volatiles gave a brown oil which was purified by vacuum distillation. The pure product solidified at room temperature to give a slightly yellow solid. Yield: 13 g (70%). ^{1}H NMR (400.13 MHz, C_6D_6): 7.54 (d, J = 7.8 Hz, 2H), 7.45 (s, 1H), 6.99 (m, 4H), 6.87 (t, J = 7.6 Hz, 2H), 2.43 (s, 12H). ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.40 (dd, J = 8.0, 1.4 Hz, 2H), 7.16 (br, 1H), 7.11 (dd, J = 7.8, 1.4 Hz, 2H), 7.0 (td, J = 7.7, 1.5 Hz, 2H), 6.87 (td, 7.6, 1.5 Hz, 2H), 2.69 (s, 12H). ^{13}C NMR (100.62 MHz, $CDCl_3$): 143.3, 137.5, 123.6, 119. 9, 119.3, 115.4, 43.9. MS: 256.38 [M+H]$^+$. All data are identical to those reported in our earlier paper.[16]

Li complex [($^{Me}N_2N$)$_2$Li$_2$] (**6**). Same as the previous protocol,[16] except that the solvent of reaction was changed from benzene to toluene. ^{n}BuLi (22.3 mmol, 1.6 M in hexane) was slowly added to a toluene solution (60 mL) of **1** (5.43 g, 21.3 mmol) at room temperature. The reaction mixture was stirred for 1 h, and then the solvent was removed under vacuum. Addition of pentane afforded a white precipitate, which was filtered, washed with additional pentane, and dried *in vacuo*. Complex **6** is sensitive to moisture and should be handled under an inert atmosphere. Yield: 4.73 g (85%). ^{1}H NMR (400.13 MHz, C_6D_6): 6.98–7.11 (m, 4H), 6.93 (dd, J = 7.8, 1.3 Hz, 2H), 6.64 (m, 2H), 2.20 (s, 6H), 1.95 (s, 6H). ^{13}C NMR (100.62 MHz, C_6D_6): 157.4, 146.3, 127.6, 122.9, 120.8, 116.1, 48.9, 43.5. All data are identical to those reported in our earlier paper.[16]

Pd complex [($^{Me}N_2N$)PdCl] (**7**). A THF solution (25 mL) of **6** (1.01 g, 1.93 mmol) was added to a THF suspension (15 mL) of $PdCl_2(CH_3CN)_2$ (1 g, 3.86 mmol) under a nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature. After removal of the solvent, the black residue was taken up in toluene and filtered through Celite and then was concentrated to *ca.* 2 mL. Addition of pentane resulted in the formation of red solid, which was filtered, washed with pentane, and dried under vacuum. Crystals suitable for X-ray diffraction analysis were grown by diffusion of pentane to a benzene solution of **7**. Yield 1.22 g (80%). ^{1}H NMR (400.13 MHz, C_6D_6): 7.52 (dd, J = 8.5, 1.2 Hz, 2H), 6.96 (td, J = 7.0, 1.5 Hz, 2H), 6.51 (dd, J = 8.2, 1.5 Hz, 2H), 6.43 (td, J = 7.0, 1.2 Hz, 2H), 2.84 (s, 12H). ^{13}C NMR (100.62 MHz, C_6D_6): 149.2, 147.6, 129.0, 121.8, 116.8, 114.8, 53.2. Anal. Calcd for $C_{16}H_{20}ClN_3Pd$: C, 48.50; H, 5.09; N, 10.61. Found: C, 48.75; H, 5.06; N, 10.62.

Pd complex [($^{Me}N_2N$)Pd(OTf)] (**8**). A solution of AgOTf (65 mg, 0.25 mmol) in THF (1.5 mL) was added to a solution of [($^{Me}N_2N$)PdCl] (100 mg, 0.25 mmol) in THF (2 mL). The resulting solution was stirred for 30 min and then the white precipitate of AgCl was filtered off. The filtrate was evaporated and the rose solid residue was washed with pentane (3 mL) and dried under vacuum (116 mg, 91%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of pentane to a benzene solution of **8**. ^{1}H NMR (400.13 MHz, C_6D_6): 7.36 (d, J = 8.5 Hz, 2H), 6.85 (td, J = 8.5, 1.5 Hz, 2H), 6.37 (m, 4H), 2.66 (s, 12H). ^{13}C NMR (100.62 MHz, C_6D_6): 149.1, 146.3, 129.2, 121.4, 117. 9, 114.8, 52.1. Anal. Calcd for $C_{17}H_{20}F_3N_3O_3PdS$: C, 40.05; H, 3.95; N, 8.24. Found: C, 40.32; H, 4.06; N, 8.15.

Pt complex [($^{Me}N_2N$)Pt(Cl)] (**9**). To a benzene (30 mL) suspension of $Pt(PhCN)_2Cl_2$ (687 mg, 1.46 mmol) was slowly added a benzene (10 mL) solution of **6** (380 mg, 0.73 mmol). The reaction mixture was stirred overnight at 80 °C, and then cooled to room temperature and filtered through Celite. After removal of the solvent, the oily residue was triturated with pentane which afforded the product as an air-stable brown solid. This solid was dried *in vacuo*. Yield: 495 mg (70%). Crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated benzene solution. ^{1}H NMR (400.13 MHz, C_6D_6): 7.59 (dd, J = 8.5, 1.1 Hz, 2H), 6.95 (m, 2H), 6.52 (dd, J = 8.1, 1.4 Hz, 2H), 6.40 (m, 2H), 2.99 (s, 12H). ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.62 (dd, J = 8.2, 0.9 Hz, 2H), 7.15 (dd, J = 8.2, 1.2 Hz, 2H), 7.10 (m, 2H), 6.60 (m, 2H), 3.34 (s, 12H). ^{13}C NMR (100.62 MHz, C_6D_6): 149.55, 149.22, 129.06, 121.81, 116.72, 114.81, 54.75. MALDI-TOF: 485.10 $[M+H]^+$. Anal. Calcd for $C_{16}H_{20}ClN_3Pt$: C, 39.63; H, 4.16; N, 8.67. Found: C, 40.15; H, 4.36; N, 8.23.

Ru complex [($^{Me}N_2N$)Ru(PPh_3)Cl] (**10**). A THF solution (5 mL) of Li complex **6** (200 mg, 0.38 mmol) was added to a THF suspension (10 mL) of $Ru(PPh_3)_3Cl_2$ (729 mg, 0.76 mmol). The reaction mixture was stirred overnight at room temperature. After removal of the solvent, the residue was taken up into dichloromethane and filtered. The filtrate was evaporated, washed with pentane, and dried under vacuum to give a green solid. Yield: 315 mg (63%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of pentane to a THF solution of **10**. ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.47 (d, J = 8.4 Hz, 2H), 7.28–7.38 (m, 6H), 7.12–7.17 (m, 3H), 6.98–7.06 (m, 6H), 6.87–6.95 (m, 4H), 6.54 (t, J = 7.6 Hz, 2H), 3.08 (s, 6H), 2.65 (s, 6H). ^{13}C NMR (100.62 MHz, THF-d_8): 151.04, 138.09, 137.63, 134.32, 134.23, 129.15, 129.12, 127.85, 127.75, 126.55, 118.80, 117.57, 116.26, 51.67, 50.30. ^{31}P NMR (162 MHz): 83.28. Anal. Calcd for $C_{34}H_{35}N_3ClPRu$: C, 62.52; H, 5.40; N, 6.43. Found: C, 62.86; H, 5.69; N, 6.15.

General procedure for transfer hydrogenation catalysis. A freshly prepared dichloromethane solution of **10** (2 μmol, 0.2 mol%) was evaporated under vacuum in a three-necked flask. Next, ketone (1 mmol) was added to the flask under nitrogen, followed by 9.75 mL of 2-propanol. The mixture was heated to 83 °C, and then it was treated with 0.2 M KOH in 2-propanol (0.25 mL), initiating the reaction (t = 0). During the course of the reaction, an aliquot (0.20 mL) solution was removed from the reaction mixture *via* a syringe, diluted with 5 mL of diethyl ether, and cooled to room temperature. The sample was analyzed *via* GC. The products were identified by GC-MS.

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