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Catalytic Reduction of Nitroarenes by Dipalladium Complexes: Synergistic Effect

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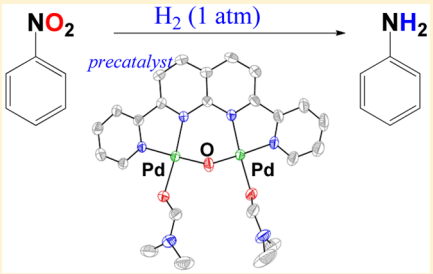
Supporting Information

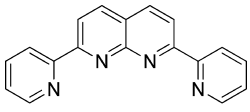
ABSTRACT: The direct reaction between 2,7-bis(2-pyridinyl)-1,8-naphthyridine (**bpnp**) and $Pd(CH_3COO)_2$ in CF_3COOH yields the new dinuclear palladium(II) complex $[Pd_2(\mathbf{bpnp})(\mu\text{-}OH)(CF_3CO_2)_2](CF_3CO_2)$ (**1**). Similarly, substitution of $Pd(CH_3CN)_4(BF_4)_2$ with **bpnp** in DMF gives $[Pd_2(\mathbf{bpnp})(\mu\text{-}OH)(DMF)_2](BF_4)_3$ (**2**). Treatment of **1** or **2** with Cl^- readily provide the chloro-substituted species $[Pd(\mathbf{bpnp})(\mu\text{-}OH)(Cl)_2]^+$. All complexes were characterized by spectroscopic methods, and the structure of **2** was further confirmed by X-ray crystallography. Complex **1** is an efficient catalyst for the reduction of aromatic nitro compounds leading to the corresponding aniline derivatives under atmospheric pressure of hydrogen at 50 °C. The mechanistic pathway of the catalysis is investigated. From the reaction pathway, it is suggested that a facile condensation of nitroso and hydroxylamine intermediates is enabled by the dipalladium system and the desired transformation proceeds smoothly under mild reaction conditions to yield the reduced product.



INTRODUCTION

2,7-Bis(2-pyridinyl)-1,8-naphthyridine (**bpnp**; Chart 1) has already been shown to act as a relatively rigid tetradentate ligand for accommodation of dimetallic systems in several examples involving copper,[1,2] rhenium,[3] ruthenium,[4] rhodium,[5] and palladium.[6] The corresponding dinuclear species exhibit specific properties and reactivity, particularly in homogeneous catalysis, due to the synergistic effect.[1−6] Typically, dicopper complexes with **bpnp** were shown to catalyze the oxidative coupling reaction of 2,6-disubstituted phenols into diphenoquinones in high conversions and a catalytic cycle involving the synergistic effect was illustrated through a mechanistic study.[1b] Here we continue to exploit the preparation of dipalladium complexes with **bpnp** and their catalytic activity in particular to study the possible synergistic effect due to the short distance between two metal ions.

Chart 1. Structure of bpnp



bpnp

RESULTS AND DISCUSSION

Preparation and Characterization of Metal Complexes. The desired ligand **bpnp** was prepared by a previously reported method.[7] Complexation of **bpnp** with an equimolar amount of $Pd(CH_3COO)_2$ in trifluoroacetic acid/MeOH at 50 °C provided the dipalladium complex **1** as yellow solids in 98% yield (Scheme 1). The solubility of **1** in most organic solvents is poor; **1** is slightly soluble in dimethyl sulfoxide (dmso) and nitromethane. The ^1H NMR spectrum of **1** in dmso-d_6 shows six signals in the aromatic region, indicating a symmetrical environment of the molecule: i.e., two palladium ions are coordinating toward **bpnp**. It is noticed that complex **1** shows only one broad shift in the ^{19}F NMR spectrum, suggesting an exchange phenomenon among trifluoroactates in solution. The ESI-HRMS spectrum of **1** shows a peak at m/z at 738.8892, which is consistent with the formula of $[Pd_2(\mathbf{bpnp})(\mu\text{-}OH)(CF_3COO)_2]^+$. Conductivity measurements of **1** at 4×10^{-3} M in dmso and nitromethane were obtained. The molar conductivities of **1** in dmso and nitromethane are 54 and 81 Ω^{-1} cm^2 mol^{-1}, respectively, which are in agreement with the proposed 1:1 electrolyte.[8]

On the other hand, the dipalladium framework with **bpnp** can be also prepared from substitution of $[Pd(CH_3CN)_4](BF_4)_2$ with **bpnp** in DMF at ambient temperature (Scheme 1). In this case, a dipalladium complex with coordinating DMF ligands, $[Pd_2(\mathbf{bpnp})(\mu\text{-}OH)(DMF)_2](BF_4)_3$ (**2**), was obtained. In addition to the spectroscopic characterization, the detailed structural formulation of complex **2** was confirmed by a single-crystal X-ray study. The ORTEP plot (Figure 1) of the cationic portion of **2** shows a pair of palladium atoms bridged by **bpnp** and a −OH group. Each metal ion is in a square-planar environment, as expected, with the coordination sphere formed by the bridging ligands and a DMF molecule. The average of Pd−N bond distances is 2.00 Å, which is in the normal range of such bonds (Table 1). The Pd(1)−O(2) (2.023(4) Å) and Pd(2)−O(3) distances (2.000(5) Å) are in the typical bonding

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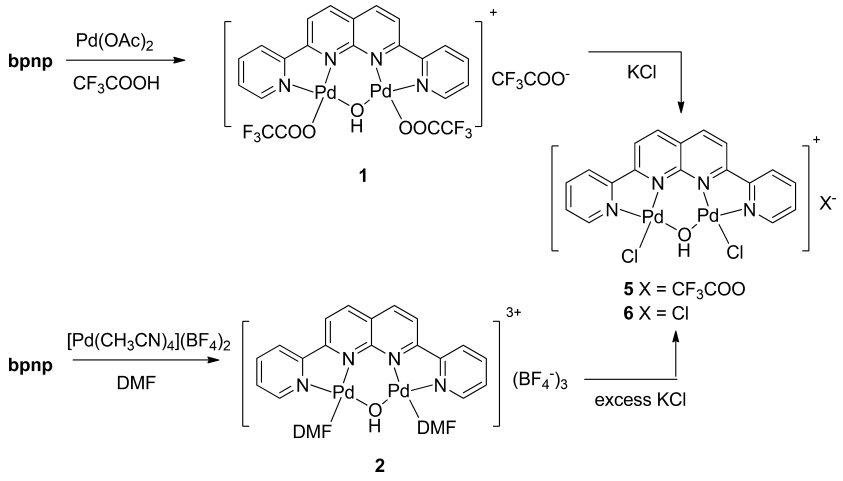
Scheme 1. Preparation of Dipalladium Complexes



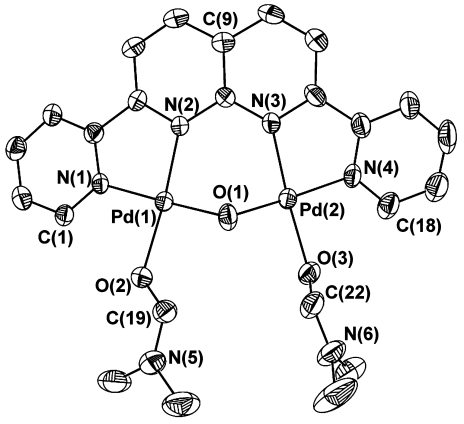


Figure 1. ORTEP plot of the cationic portion of **2** (30% probability level; labels of aromatic carbons are omitted for clarity).

range, clearly indicating the coordination of the DMF molecule toward the metal center. The bite angles N(1)−Pd(1)−N(2) and N(3)−Pd(2)−N(4) are 82.6(2) and 82.3(2)°, respectively, which are typical in bipyridine complexes. The Pd−(μ-OH)−Pd linkage is quite similar to those in the structures of $[Pd(phen)(\mu\text{-}OH)]_2[CF_3SO_3]_2$ (**3**; phen = 1,10-phenanthroline) and $[Pd(bpy)(\mu\text{-}OH)]_2[CF_3SO_3]_2$ (**4**; bpy = bipyridine).[9] The two palladium atoms are separated by 3.1696(7) Å in **2**, indicating no bonding interaction between metal ions, which is similar to those in **3** and **4**: 3.0001(11) and 3.0834 (3) Å, resepectively. The Pd(1)−O(1)−Pd(2) angle in **2** is 107.2(2)°, which is significantly larger than those of **3** (96.2(1)°) and **4** (99.28(8)°). This difference is attributed to the rigid chelation of the **bpnp** ligand. No significant discrepancies in other bond lengths and angles are noticed in complex **2**.

Treatment of **1** with 2 equiv of potassium chloride yielded the chloride-substituted complex **5**. The ^{1}H NMR spectrum of **5** in dmso-d_6 shows five sets of signals in the aromatic region due to the overlap of two sets of protons. However, the ESI-HRMS spectrum clearly verifies the coordination of chlorides. A peak at m/z 584.8532 is in agreement with the formula $[Pd_2(\mathbf{bpnp})(\mu\text{-}OH)Cl_2]^+$ (calcd 584.8597). Conductivity measurements of **5** in dmso and nitromethane show its molar conductivities to be 54 and 100 Ω^{-1} cm^2 mol^{-1}, respectively, implying the 1:1 electrolyte nature.[8] Substitution of DMF in **2** by chlorides took place similarly to give **6** quantitatively.

Reduction of Nitro Compounds. It is well-documented that palladium complexes can frequently be used as catalysts for the reduction of nitroarenes.[10] Thus, the activity of these dipalladium complexes toward the reduction of $ArNO_2$ under a hydrogen atmosphere was investigated. We chose the reduction of *p*-nitrotoluene as the model reaction with the use of **1** as the precatalyst. At the beginning, we ran a series of trial experiments in the presence of reducing agents for the reduction of Pd(II) to a lower oxidation state, but only a trace amount of toluidine was detected in these catalytic reactions. Investigation was then moved to the reaction without using any reducing agent. We were pleased to discover that *p*-nitrotoluene could be reduced to toluidine quantitatively in MeOH under an atmospheric pressure of hydrogen without any other additive (Table 2, entry 1). Encouraged by this promising result, adjustment of reaction parameters including catalyst loading, temperature, and solvents was examined (Table 2).

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) of 2

Pd(1)−O(1)	1.969(5)	Pd(2)−O(1)	1.969(5)
Pd(1)−N(1)	1.993(6)	Pd(2)−N(3)	2.002(5)
Pd(1)−N(2)	2.025(5)	Pd(2)−N(4)	1.983(6)
Pd(1)−O(2)	2.023(4)	Pd(2)−O(3)	2.000(5)
Pd(1)···Pd(2)	3.1696(7)		
N(1)−Pd(1)−N(2)	82.6(2)	N(3)−Pd(2)−N(4)	82.3(2)
N(1)−Pd(1)−O(1)	174.4(2)	N(4)−Pd(2)−O(1)	167.5(2)
N(2)−Pd(1)−O(2)	173.7(2)	N(3)−Pd(2)−O(3)	173.8(2)
O(1)−Pd(1)−O(2)	88.98(19)	O(1)−Pd(2)−O(3)	89.9(2)
Pd(1)−O(1)−Pd(2)	107.2(2)		

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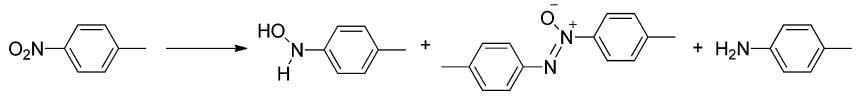
Table 2. Optimization for the Reduction of 4-Nitrotoluene[a]



7 8 9

entry	temp (°C)	solvent	cat. loading (mol %)	conversn (%)[b]	yield (%)[b] 7	8	9
1	50	MeOH	0.5	100	0	0	100
2	5	MeOH	0.5	<5	0	0	0
3	25	MeOH	0.5	25	17	0	8
4	40	MeOH	0.5	76	0	0	68
5	65	MeOH	0.5	87	0	0	87
6	50	H_2O	0.5	45	trace	<5	32
7	50	CH_3CN	0.5	100	trace	<5	87
8	50	acetone	0.5	75	trace	7	41
9	40	CH_2Cl_2	0.5	32	5	<5	23
10	50	THF	0.5	41	10	<5	0
11	50	toluene	0.5	17	Trace	<5	8
12	50	MeOH	0.1	59	0	<5	37
13	50	MeOH	0.2	95	0	0	89
14	50	MeOH	1.0	100	0	0	100

[a]Reaction conditions: a mixture of *p*-nitrotoluene (0.5 mmol) and **1** in solvent (0.5 mL) was stirred under an H_2 atmosphere (1 atm) for 6 h. [b]Based on NMR integration.

Screening revealed that running the reaction at 50 °C achieved the best yield. At a higher temperature, the yield dropped due to the decomposition of the catalysts, as evidenced by the precipitation of palladium black. At ambient temperature, the reaction proceeded very slowly accompanied by the formation of **7** (Table 2, entry 3), an intermediate of the reduction (see below). For solvent effects, a full conversion of substrate was observed in both MeOH and acetonitrile, but a 100% yield of *p*-nitrotoluene was not achieved in CH_3CN (Table 2, entry 7). It is noted that compounds **7** and **8** were produced under various reaction conditions, indicating that these species might be the reaction intermediates. For the catalyst loading, 0.5 mol % appeared to be the best choice for full conversion within 6 h (Table 2, entries 12−14).

We also evaluated the ability of various palladium complexes for this reduction of *p*-nitrotoluene under the optimal conditions (Table 3). As expected, complexes **1** and **2** have similar activities. To our delight, in addition to complex **1**, quite a few monopalladium complexes show good catalytic activity in the reduction of nitroarenes. For example, the catalytic activity of $[Pd(bpy)(CF_3COO)_2]$ and [Pd(dien)Cl]Cl (dien = diethylenetriamine) are similar to that of **1** under the same conditions. Unlike the case for [Pd(dien)Cl]Cl, the metal center chelated by a terpyridine ligand in $[Pd(tpy)Cl]PF_6$ does not have any activity at all.

Having observed the differences in product distribution under various reaction conditions, we tried to find out more about the mechanism of this catalytic process. Thus, experiments to determine the nature of the catalyst and possible intermediates were investigated. First, a study of the kinetics of the resultant reaction profile for the reduction of *p*-nitrotoulene catalyzed by **1** was performed (Figure 2). This catalytic system showed an induction period of ca. 25 min followed by a slow conversion and then a rapid transformation. It is noted that both *p*-nitrosotoluene and *p,p′*-azoxytoluene remained at low concentrations during the catalysis and converted into the product at the end of the reaction, indicating that both

Table 3. Activities of Various Palladium Complexes[a]

entry	Pd complex (loading (mol %))	conversn (%)[b]	yield (%)[b] 7	8	9
1	**1** (0.5)	100	0	0	100
2	**2** (0.5)	100	0	0	100
3[c]	**6** (1)	100	0	0	100
4	$[Pd(tpy)Cl]PF_6$ (1)[d]	0	0	0	0
5	$[Pd(bpy)(CF_3COO)_2]$ (1)[e]	100	0	0	100
6	$[Pd(bpy)Cl_2]$ (1)	92	0	0	92
7	[Pd(dien)Cl]Cl (1)[f]	100	5	0	95
8	$[Pd(PPh_3)_2Cl_2]$ (1)	0	0	0	0
9	$[Pd(CH_3CN)_2Cl_2]$ (1)	57	0	<5	50
10	$Pd(OAc)_2$ (1)	89	<5	<5	65

[a]Reaction conditions unless specified otherwise: a mixture of *p*-nitrotoluene (0.5 mmol) and Pd complex in MeOH (0.5 mL) was stirred under an H_2 atmosphere (1 atm) for 6 h. [b]Based on NMR integration. [c]24 h. [d]tpy = terpyridine. [e]bpy = bipyridine. [f]dien = diethylenetriamine.

compounds are intermediates in this reduction. The induction period for this catalytic system is presumably due to the reduction of Pd(II) to a lower oxidation state under a hydrogen atmosphere.

As depicted in Scheme 2, the well-documented mechanism for reduction of nitroarenes comprises multistep pathways.[11] Reduction of the nitro group to nitrosoarene is the first step followed by the subsequent reduction to yield hydroxyaminoarene. Once formed, the hydroxyamino compound can undergo two competing routes for further reductions. One involves the direct reduction of hydroxyaminoarenes leading to the final product (Scheme 2, pathway A). Alternatively, the condensation of nitroso- and hydroxyaminoarenes occurs to generate azoxybenzene, which is further reduced to azobenzene, diarylhydrazine, and finally aniline (Scheme 2, pathway B). The observation of *p,p′*-azoxytoluene during the catalysis operated by **1** indicates that the reaction might proceed

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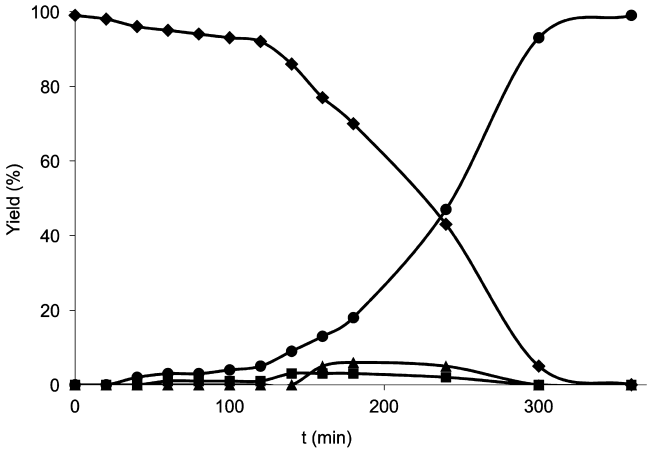
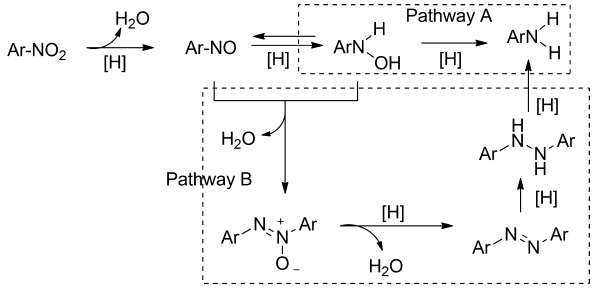


Figure 2. Reaction profile of reduction of *p*-nitrotoluene catalyzed by **1** (0.5 mol %) in MeOH at 50 °C under H_2 (1 atm): (◆) *p*-nitrotoluene; (●) *p*-toluidine; (■) *p*-nitrosotoluene; (▲) *p,p′*-azoxytoluene.

Scheme 2. Proposed Reaction Pathway of Catalytic Reduction of Nitro Compounds



through pathway B. In order to test this assumption, we set up a few experiments, as illustrated in the following.

First, a time-dependence study of the product distribution under the optimal catalytic conditions was carried out with *p,p′*-azoxytoluene as the substrate (Figure 3). As expected, we did observe an induction period (ca. 60 min) for the reaction to proceed and a full conversion of the substrate into toluidine. Additionally, the intermediates azotoluene and di-*p*-tolylhydrazine were both formed after the induction period and the concentration of these two species slowly increased. As shown in Figure 3, di-*p*-tolylhydrazine remains in a fair amount during the catalysis, whereas the azotoluene is present in a small amount, indicating that the rate of N−N bond cleavage is slower than that of the reduction of N═N into NH−NH (hydrazine). The final product, toluidine, started to form after a period of 130 min and then the amount increased immediately, correlating well with the decrease in the amount of the substrate and intermediates. Furthermore, when hydroxyaminobenzene was used as a substrate, the palladium complex **1** granted a full conversion of the substrate, leading to a mixture of various products (eq 1). This observation clearly suggests that the reduction of nitrobenzenes catalyzed by **1** prefers to undergo pathway B instead of direct reduction (pathway A).

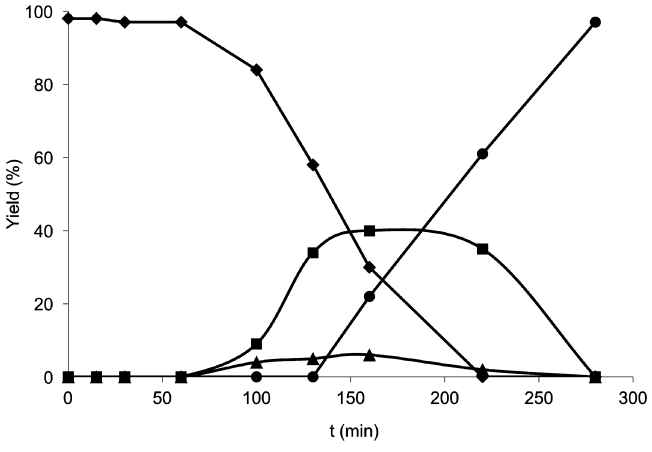


Figure 3. Reaction profile starting from *p,p′*-azoxytoluene with 0.5 mol % of **1** at 50 °C under H_2 (1 atm): (◆) *p,p′*-azoxytoluene; (●) *p*-toluidine; (■) azotoluene; (▲) di-*p*-tolylhydrazine.

For comparison, the catalytic activities of the mononuclear complex $[Pd(bpy)(CF_3COO)_2]$ under the optimized reduction conditions was examined. Thus, the reaction profile of reduction of *p*-nitrotoluene catalyzed by $[Pd(bpy)(CF_3COO)_2]$ (1 mol %) in MeOH at 50 °C under H_2 (1 atm) was revealed (Figure 4). Again, we observed an induction period (~90 min) and a full conversion for this monopalladium complex. However, in this catalytic reaction, we did not observe any intermediate as the reaction proceeded, which is not similar to catalysis by the dipalladium complex **1**. In addition, when azobenzene was used as a substrate, the catalyst $[Pd(bpy)(CF_3COO)_2]$ showed no activity at all with full recovery of the starting substrate, but the complex delivered a full conversion to aniline when hydroxyaminobenzene was used as a substrate. Furthermore, $[Pd(bpy)(CF_3COO)_2]$ exhibited a poor reactivity in the reduction of azobenzene. These observations clearly suggest the preference of pathway A operating by this mononuclear palladium complex.

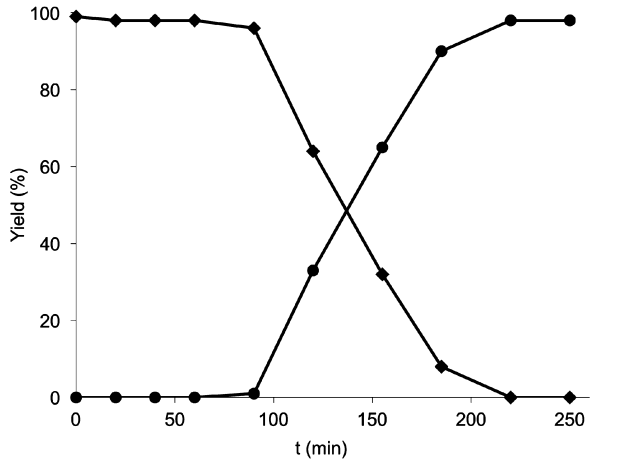


Figure 4. Reaction profile of reduction of *p*-nitrotoluene catalyzed by $[Pd(bpy)(CF_3COO)_2]$ (1 mol %) in MeOH at 50 °C under H_2 (1 atm): (◆) *p*-nitrotoluene; (●) *p*-toluidine.

From the above studies, it appears that the preference for pathway A or B in the catalytic reduction of aromatic nitro compounds depends on the number of metal centers of the catalyst. The mononuclear species seems to react preferentially through pathway A via a direct conversion of phenylhydroxyamine to aniline, whereas the dipalladium complex **1** predominantly reacts via pathway B. Since the two palladium ions in **1** are separated by 3.17 Å, the coordinating intermediates of nitrosoarene and hydroxyaminoarene on each metal ion readily undergo the coupling reaction leading

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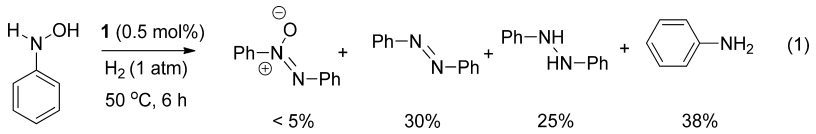


to azoxybenzene (Figure 5). Presumably, this is one of the factors favored by dipalladium **1** to undergo pathway B, illustrating the synergistic effect of dimetallic systems.

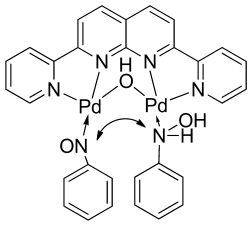
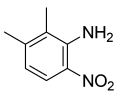
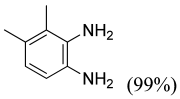


Figure 5. Synergistic assistance on the formation of azoxybenzene in complex **1**.

With the optimized conditions, the scope of the reduction of various nitroarenes catalyzed by **1** was explored (Table 4).

Table 4. Reduction of Substituted Nitroarenes Catalyzed by 1[a]

entry	substrate	Product (yield)[b]
1	$C_6H_5NO_2$	$C_6H_5NH_2$ (95%)
2	*p*-$MeC_6H_4NO_2$	*p*-$MeC_6H_4NH_2$ (96%)
3	*p*-$HOC_6H_4NO_2$	*p*-$HOC_6H_4NH_2$ (99%)
4[c]	*p*-$H_2NC_6H_4NO_2$	*p*-$H_2NC_6H_4NH_2$ (95%)
5	*p*-$FC_6H_4NO_2$	*p*-$FC_6H_4NH_2$ (89%)
6	*p*-$ClC_6H_4NO_2$	*p*-$ClC_6H_4NH_2$ (28%) + $C_6H_5NH_2$ (30%)
7	*p*-$NCCH_2C_6H_4NO_2$	*p*-$NCCH_2C_6H_4NH_2$ (100%)
8[c]	*p*-$CH_3COC_6H_4NO_2$	*p*-$CH_3COC_6H_4NH_2$ (88%)
9	*p*-$MeOOCC_6H_4NO_2$	*p*-$MeOOCC_6H_4NH_2$ (86%)
10	2,6-$Me_2C_6H_4NO_2$	2,6-$Me_2C_6H_4NH_2$ (100%)
11	1-nitronaphthylene	1-aminonaphthylene (100%)
12[c]		 (99%)
13[c]	1,3-$C_6H_4(NO_2)_2$	1,3-$C_6H_4(NH_2)_2$

[a]Reaction conditions unless specified otherwise: substrate (0.5 mmol) and complex **1** (2.5×10^{-3} mmol) in methanol (0.5 mL) at 50 °C under atmospheric pressure of H_2 for 12 h. [b]Isolated yield. [c]Catalyst **1** (5×10^{-3} mmol, 1 mol %) .

Various substituted nitrobenzenes were found to undergo the reduction to afford the corresponding aniline in excellent yields, except for those with a chloro substituent (Table 4, entry 6). Functional groups such as hydroxyl, cyano, keto, and carboxylate were tolerated under the catalytic conditions. Dinitrobenzenes could also be reduced to the corresponding phenylenediamines in excellent yields. However, reduction of *p*-chloronitrobenzene gave two products: *p*-chloroaniline and aniline, indicating that the chloro substituent was replaced.

Palladium-catalyzed dehalogenation of aryl halides using molecular hydrogen as a hydride source is also well-documented.[12] The reaction is generally carried out under a high pressure of H_2, with a few reactions taking place at atmospheric pressure.[12a] The catalytic system developed in this work is active for the dehalogenation at atmospheric pressure of H_2, but in a poor yield. Apparently, the catalytic system was poisoned by the dehalogenation process. Presumably, the side product HX produced from the dehalogenation process caused this effect. Indeed, when bases were added to the reaction mixture, the product yield increased dramatically. Typically, the addition of 2 equiv of DABCO (1,4-diazabicyclo[2.2.2]octane) to the reduction of *p*-chloronitrobenzene under the optimal conditions provided aniline in 96% yield. Similarly, the quantitative conversion of 1,3,5-tribromobenzene to benzene could be achieved by using these catalytic conditions with 3 equiv of DABCO.

CONCLUSIONS

In summary, a series of hydroxyl-bridged dipalladium complexes hosted by a **bpnp** ligand have been prepared and structurally characterized. In addition, a convenient and highly efficient protocol for the reduction of aromatic nitro compounds catalyzed by dipalladium complexes leading to the corresponding anilines under mild conditions, typically atmospheric pressure of H_2 at 50 °C in methanol, has been developed. Various substrates with other reducible functionalities such as keto, nitrile, and ester, but not halides, were unaffected during the reduction. A series of controlled experiments and a kinetic study revealed that the dipalladium catalytic system preferentially proceeds through the azoxybenzene intermediate generated by the condensation of nitrosoarene and hydroxyaminoarene. Such a reaction pathway operated by precatalyst **1** is believed to be due to the synergistic effect of the dimetallic system.

EXPERIMENTAL SECTION

General Information. Chemicals and solvents were of analytical grade and were used without further purification. Nuclear magnetic resonance spectra were recorded on a 400 MHz spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR. Complexes $[Pd(tpy)Cl]PF_6$,[13a] $[Pd(bpy)(CF_3COO)_2]$,[13b] $[Pd(bpy)Cl_2]$,[13c] and $[Pd(dien)Cl]Cl$[13d] were prepared according to the reported methods.

Complex 1. A mixture of **bpnp** (12.5 mg, 4.4×10^{-2} mmol), $Pd(CH_3COO)_2$ (20.2 mg, 0.09 mmol), and CF_3COOH (0.25 mL) in methanol (1 mL) was heated to 50 °C with stirring for 30 min. After removal of solvents, the residue was washed with Et_2O (1 mL × 3) to yield the desired complex as a yellow solid (32 mg, 98%). ^1H NMR (400 MHz, DMSO-d_6): δ 9.38 (d, J = 8.4 Hz, 2H), 9.13 (d, J = 8.4 Hz, 2H), 8.90 (d, J = 8 Hz, 2H), 8.56 (t, J = 8 Hz, 2H), 8.29 (s, br, 2H), 8.20−7.85 (m, 2H), 4.68 (s, br, 1H); ^{19}F NMR (375 MHz, DMSO-d_6) δ - 73.43 (s, br). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.73, 156.45, 151.40, 150.26 (q, J = 23 Hz), 149.24, 146.46, 142.81, 129.61, 128.69, 126.45, 124.06, 40.48 (q, J = 200 Hz). HRMS (ESI): m/z $[M - CF_3COO]^+$ calcd for $C_{22}H_{13}F_6N_4O_5Pd_2$, 738.8869; found, 738.8890. Anal. Calcd for [**1** + $2H_2O$]: C, 32.42; H, 1.93; N, 6.30. Found: C, 32.30; H, 1.57; N, 6.01.

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Complex 2. To a solution of **bpnp** (19.9 mg, 0.07 mmol) in DMF (1 mL) was added $Pd(ACN)_4(BF_4)_2$ (62.2 mg, 0.14 mmol) under stirring at room temperature. The reaction mixture was stirred at room temperature for 5 min. After completion of the reaction, the solvent was completely removed under reduced pressure and the residue was washed with acetone and methanol. Upon drying under vacuum, the pure complex **2** was obtained as a brown-yellow powder (60.8 mg, 0.066 mmol, 94%). ^{1}H NMR (400 MHz, DMF-d_7): δ 9.62 (d, J = 8.7 Hz, 2H), 9.34 (d, J = 8.7 Hz, 2H), 9.11 (d, J = 8.1 Hz, 2H), 8.75−8.71 (m, 4H), 8.17−8.14 (m, 2H). ^{13}C NMR (100 MHz): δ 164.44, 162.57, 156.36, 156.03, 149.94, 146.68, 143.10, 129.71, 128.67, 126.49, 123.97, 35.71, 30.58. Recrystallization of **2** from DMF/methanol at room temperature gave crystals suitable for X-ray determination. Thus, the structure of **2** was further confirmed by crystallography. Anal. Calcd for [**2** + 2 DMF]: C, 33.77; H, 3.87; N, 10.50. Found: C, 33.40; H, 3.55; N, 10.61.

Complex 5. A mixture of **1** (25.4 mg, 0.03 mmol) and KCl (5.0 mg, 0.06 mmol) in predried CH_3CN (2 mL) was stirred at room temperature under N_2 for 3 h. The solution was centrifuged and decanted. The residue was washed with Et_2O and dried under vacuum to provide a yellow solid (18.8 mg, 90%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.34 (d, J = 8 Hz, 2H), 9.09 (d, J = 8 Hz, 2H), 8.93−8.74 (m, 4H), 8.45 (t, J = 8 Hz, 2H), 7.83 (t, J = 7 Hz, 2H). ^{19}F NMR (375 MHz, DMSO-d_6): δ −73.84 (s). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.7, 156.5, 151.9, 149.9, 145.6, 141.8, 128.8, 128.2, 126.2, 123.6. HRMS (ESI): m/z [M − TFA]$^+$ calcd for $C_{18}H_{13}Cl_2N_4OPd_2$, 582.8536; found, 582.8590.

Complex 6. A mixture of **2** (32.5 mg, 3.5×10^{-2} mmol) and KCl (13.2 mg, 0.18 mmol) in dimethylformamide (1 mL) was stirred at room temperature under N_2 for 3 h. After removal of dimethylformamide, the residue was washed with water and Et_2O to give the desired product as an orange-yellow solid (21.7 mg, 98%). This complex is insoluble in most organic solvents, even dmso. HRMS (ESI): m/z [M − Cl]$^+$ calcd for $C_{18}H_{13}Cl_2N_4OPd_2$, 582.8536; found, 582.8504.

Catalysis Reduction of Nitroarenes. A mixture of nitro compound (0.5 mmol) and complex **1** (2.5×10^{-3} mmol) in methanol (0.5 mL) was loaded in a reaction vessel with a stirring bar. The reaction vessel was flushed with hydrogen gas through an adapter with a 100 mL balloon filled with H_2. The mixture was stirred at 50 °C for 12 h. After the reaction, methanol was removed under reduced pressure. The residue was extracted with ether (3 mL × 3), and the combined organic extracts were dried and concentrated. The residue was analyzed by NMR spectroscopy. For the purification, chromatography on silica gels provided the desired compound in pure form. The spectral data of the organic products are essentially identical with those reported. ^{1}H and ^{13}C NMR spectral data for all compounds are deposited in the Supporting Information.

General Kinetic Procedures. A mixture of substrate (1 mmol) and complex **1** (5×10^{-3} mmol) in methanol (2 mL) was loaded in a reaction vessel with a stirring bar. The reaction vessel was flushed with hydrogen gas through an adaptor with a 100 mL balloon filled with H_2. The mixture was stirred at 50 °C. At appropriate time intervals, 0.1 mL aliquots were removed using a syringe and quickly passed through Celite to remove the metal complexes with elution of ether. The filtrate was then concentrated under reduced pressure and analyzed by ^{1}H NMR spectroscopy.

Crystallography. A crystal suitable for X-ray determination was obtained for **2**·2DMF. Cell parameters were determined with a Siemens SMART CCD diffractometer. The structure was solved using the SHELXS-97 program[14] and refined using the SHELXL-97 program[15] by full-matrix least-squares on F^2 values. Crystal data of **2**·2DMF: $C_{30}H_{40}B_3F_{12}N_8O_5Pd_2$, mol wt 1065.93, triclinic, space group $P\bar{1}$; a = 12.7021(4) Å, b = 13.2940(3) Å, c = 13.8549(5) Å, α = 96.541(2)°, β = 103.247(3)°, γ = 93.220(2)°; V = 2254.28(12) Å^3; Z = 2; ρ_{calcd} = 1.570 Mg m^{-3}; $F(000)$ = 1062; crystal size 0.25 × 0.20 × 0.20 mm^3; 22435 reflections collected; 9983 independent reflections (R(int) = 0.0384); θ range 3.05−27.50°; goodness of fit on F^2 1.067; final R indices ($I > 2\sigma(I)$) R1 = 0.0605, wR2 = 0.1610; R indices (all data) R1 = 0.0922, wR2 = 0.1821. CCDC 1558483. Other crystallographic data are deposited as Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00460.

^{1}H and ^{13}C NMR spectral data for organic products of catalysis and bond distances and angles for complex **2** (PDF)

Accession Codes

CCDC 1558483 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge 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.

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Notes

The authors declare no competing financial interest.

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