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Article

NHC-Palladium(II) Mononuclear and Binuclear Complexes Containing Phenylene-Bridged Bis(thione) Ligands: Synthesis, Characterization, and Catalytic Activities

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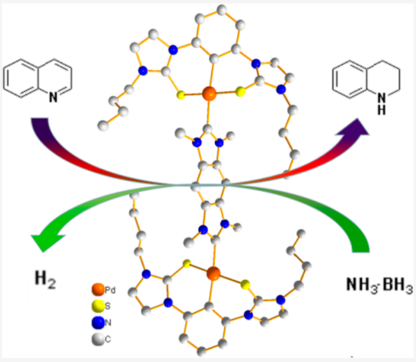
ABSTRACT: A series of mono- and binuclear Pd(II) complexes with N-heterocyclic carbene (NHC) and phenylene-bridged bis(thione) (SCS) ligands were prepared and characterized by ^{1}H and ^{13}C NMR spectroscopy, IR, and mass spectrometry. The molecular structures of **1b**, **2a**, and **3b** have been determined by the single-crystal X-ray diffraction method. The catalytic activities of the synthesized palladium complexes in the regioselective reduction of quinolines to the corresponding 1,2,3,4-tetrahydroquinolines were thoroughly investigated with ammonia−borane under mild reaction conditions. It is observed that the activities of the binuclear Pd(NHC) complexes were higher than those of the corresponding mononuclear complexes under the same conditions.



■ INTRODUCTION

N-heterocyclic carbene (NHC) transition-metal complexes have found ubiquitous applications in the fields of drugs, materials science, and catalysis.[1−10] NHCs are effective and versatile ligands to transition metals due to their strong σ-donating and weak π-accepting ability. The NHC ligand's donor strength and electronic and steric bulk can be easily modified via the substituents at the nitrogen atom or the carbon skeleton, which in turn influences the properties and reactivities of the resulting transition-metal complexes.[11−13]

In recent years, palladium complexes with NHC ligands have been demonstrated to be efficient catalysts that have been used in organic transformations, such as hydrogen transfer reactions,[14−17] olefin metathesis,[18,19] cross-coupling reactions,[20−23] and other transformations.[24−26] A number of organic transformations have been successfully catalyzed by palladium complexes bearing monodentate NHCs. While monodentate NHC palladium complexes show good catalytic activity, those bearing polydentate, chelating coordinated ligands such as tricarbene ligands exhibit superior stability toward heat and moisture.[27−34] To enhance the practical utility of palladium complexes with NHC ligands in catalytic reactions, the development of multinuclear palladium complexes with poly-NHC-ligand catalysts has received greater attention.

Recently, we reported a new family of palladium complexes with phenylene-bridged bis(thione) ligands as highly efficient catalysts for nitro compound reduction.[35] Encouraged by the above results and continuing our interest in the reactivity of the Pd(SCS)Cl complex, we herein investigate the reactivity of the Pd(SCS)Cl complex with mono- and dicarbene ligands. Four mononuclear and two binuclear Pd(II)-NHC complexes were synthesized and characterized successfully. The solid-state structures of the Pd(II)-NHC were also confirmed by single-crystal X-ray diffraction studies. Moreover, the catalytic activities of obtained palladium complexes were investigated, and the results showed that the palladium complexes with mono-NHC or bi-NHC ligands are good candidates in the regioselective reduction of quinolines to the corresponding 1,2,3,4-tetrahydroquinolines. Binuclear palladium complexes with dicarbene units were significantly more active than the corresponding mononuclear complexes under the same conditions.

■ RESULTS AND DISCUSSION

As we previously reported, the precursor Pd(SCS)Cl complexes were conveniently prepared through reactions of phenylene-bridged bis(thione) (SCS) ligands and palladium chloride in one step.[35] Mononuclear and binuclear palladium complexes with the NHC ligands were readily prepared with Pd(SCS)Cl by addition of an NHC precursor in the presence of Cs_2CO_3 in CH_3CN solvent (Scheme 1). The palladium

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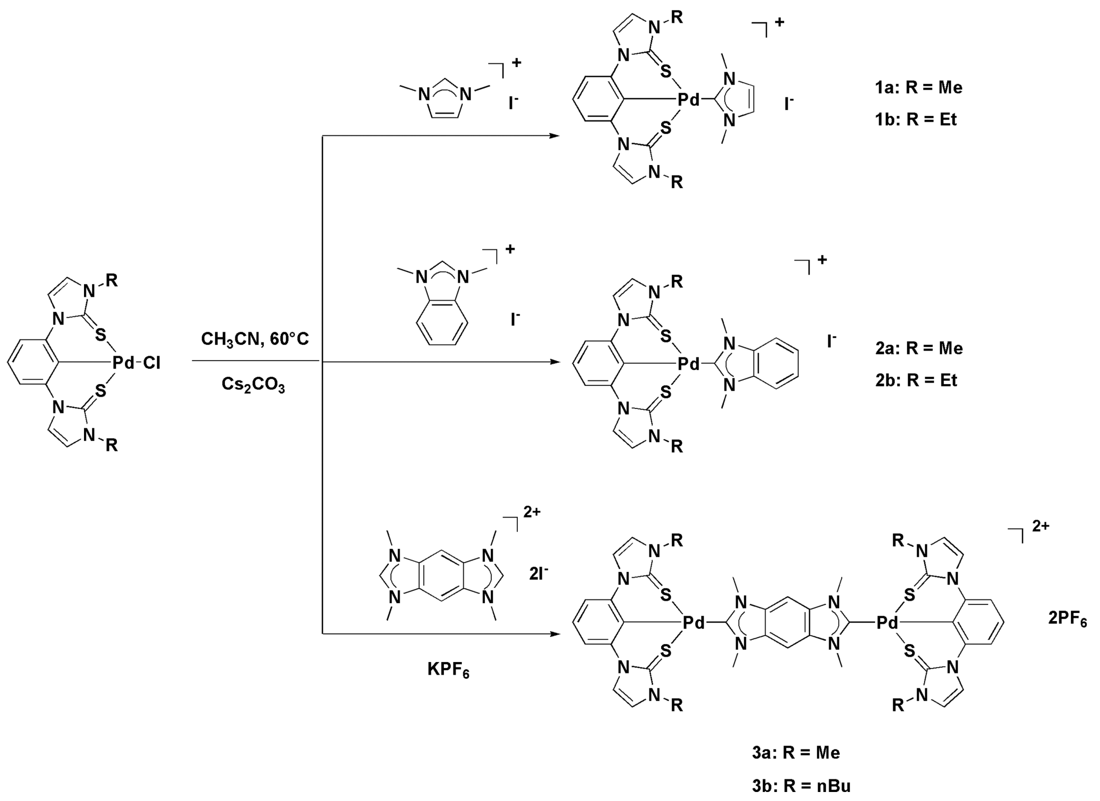
Scheme 1. Synthesis of Pd-NHC Mononuclear and Binuclear Complexes with Phenylene-Bridged Bis(thione) Ligands



complexes **1** and **2** were isolated as pale yellow iodide salts. In the cases of the binuclear palladium **3**, the anion metathesis reaction with KPF$_6$ afforded the desired palladium complexes in moderate yields. The products were characterized by a combination of ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry, IR, and X-ray crystallography. The palladium complexes are stable to moisture and air and soluble in polar organic solvents (e.g., MeOH and DMSO).

The NMR data of all palladium complexes were successfully obtained in the corresponding deuterated solvents. The proton signal of the imidazole was observed as a doublet at δ 7.68 and 8.04 ppm in **2a**, which was shifted downfield by $\Delta\delta_H = 0.08$ and 0.12 ppm for the imidazole protons in comparison to those in the parent complexes. The downfield shift of these C−H protons in the ^{1}H NMR spectrum in comparison to their precursor complexes indicated that the NHC coordinates to the metal center. The ^{13}C═S resonances of the palladium complexes are observed at 149.9 (**1a**), 149.7 (**2a**), and 150.6 (**3a**) ppm, respectively (Figure 1). They are consistent with the previous ^{13}C═S resonances compounds reported.[36−42] The ^{13}C═S resonance of the parent palladium complex is at 152.5 ppm. The ^{13}C═S resonances of the Pd-NHC complexes indicate an increase in the NHC donor strength from tetramethylbenzobis(imidazolium) to 1,3-dimethylimidazolium and 1,3-dimethylbenzimidazolium, which is in agreement with the HEP (Huynh electronic parameter) value reported by Huynh.[43,44] These complexes were also confirmed by positive-mode electrospray ionization mass spectrometry (ESI-MS), which showed base peaks due to the [M − PF$_6$]$^+$ and [M − 2PF$_6$]$^{2+}$ fragments (Supporting Information). ESI-MS spectra of the complexes showed peaks at *m*/*z* 599.1251 and 1343.2188 for **3b**, and these were assigned to [M − 2PF$_6$]$^{2+}$ and [M − PF$_6$]$^+$ ions, respectively.

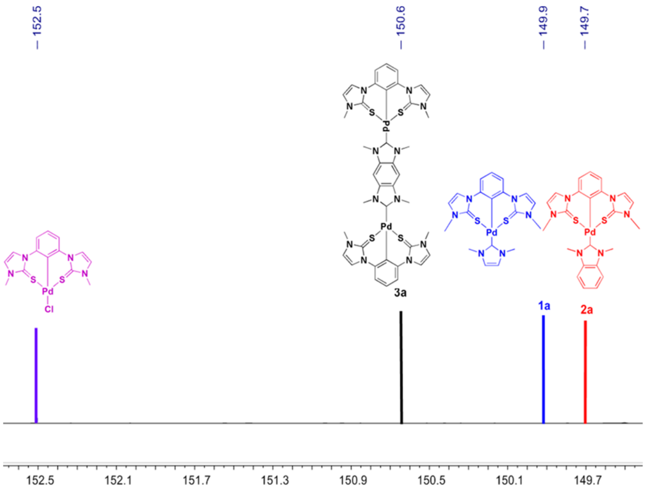
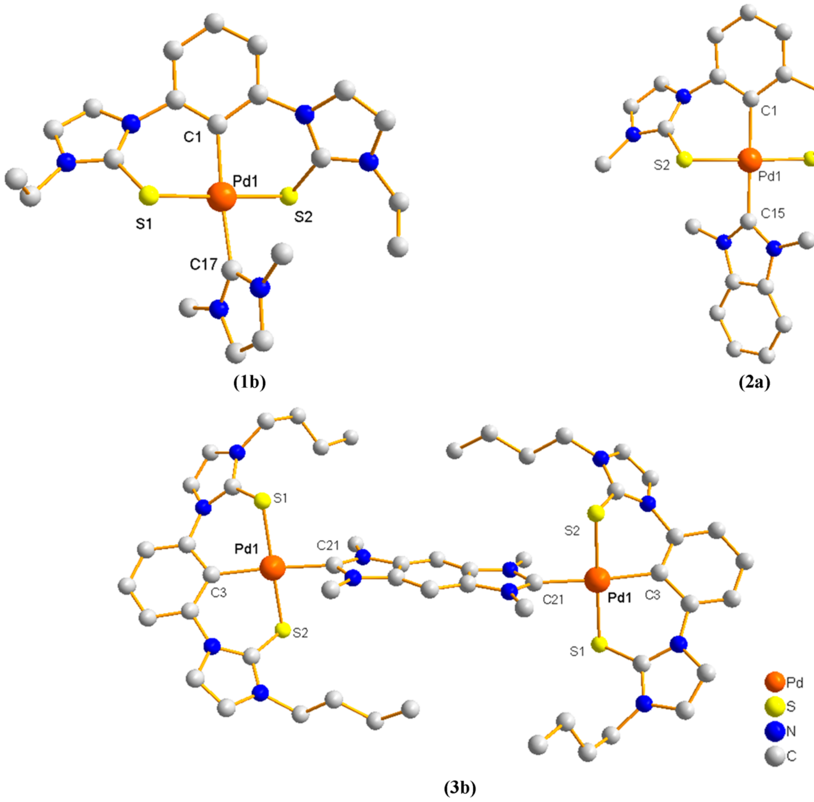


Figure 1. C signal of C═S at the ^{13}C NMR scale in palladium complexes.

Crystals of **1b**, **2a**, and **3b** suitable for X-ray crystallographic diffraction were obtained by slow diffusion of Et$_2$O into a concentrated solution of the complexes in DMSO solution. The crystallographic data for complexes **1b**, **2a**, and **3b** are summarized in Table S1, and selected bond lengths and angles are given in Table S2. The molecular structures of **1b**, **2a**, and **3b** are shown in Figure 2.

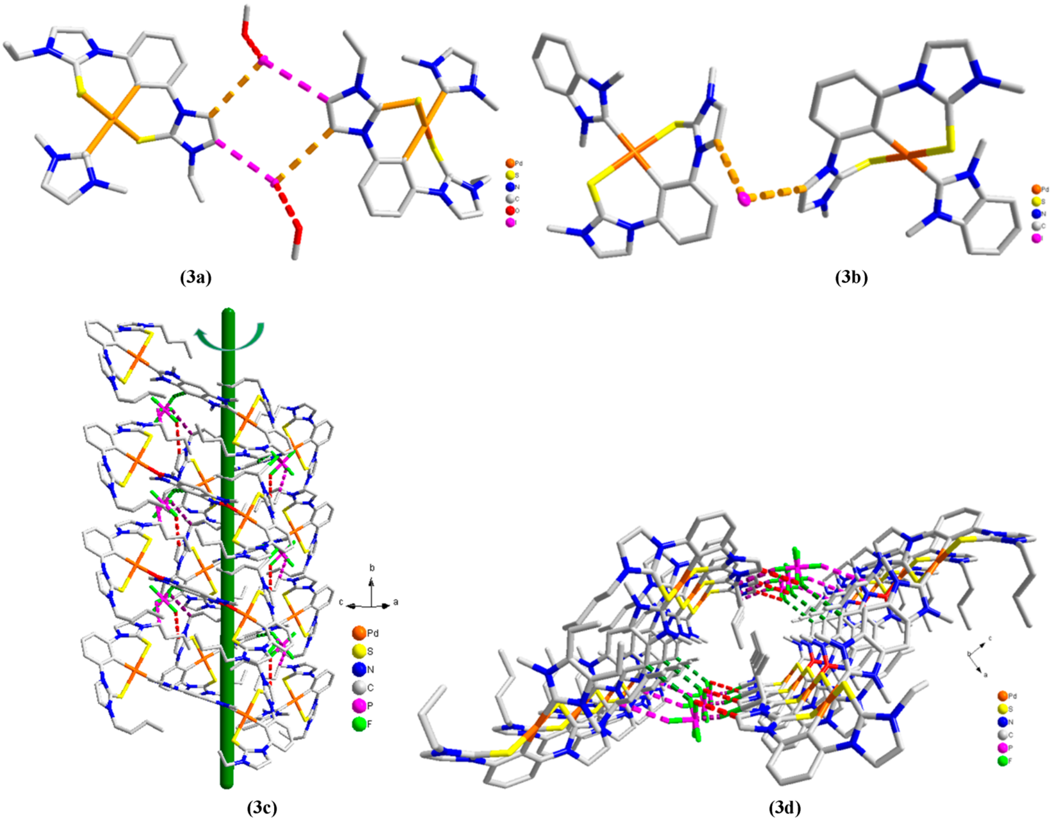
The coordination environment of the complex of Pd(II) ions with NHCs is shown inFigure 2, and it can be seen that each Pd(II) is four-coordinated to two sulfurs and one carbon atom of the SCS ligand and one carbon of the NHC. The Pd(II) adopts a square conformation with two six-membered metallacycles formed by coordination of the ligands to the



(1b) (2a)

(3b)

Figure 2. Molecular structures of complexes **1b**, **2a**, and **3b**. Hydrogen atoms in all structures and the noncoordinating anion are not shown.



(3a) (3b)

(3c) (3d)

Figure 3. (a) Dimer structure of **1b** mediated through C−H···I hydrogen bonding interactions. (b) Dimer structure of **2a** mediated through C−H···I hydrogen bonding interactions (c) Lateral view of the helical arrangement in **3b**. Dashed lines indicate the hydrogen bonds. (d) 2D structure of **3b** mediated through C−H···F hydrogen bonding interactions along the *b* direction.

palladium center. The $C_{carbene}$−Pd(1)−C(1) and S(1)−Pd(1)−S(2) angles are almost close to 180°, while the $C_{carbene}$−Pd(1)−S(1), $C_{carbene}$−Pd(1)−S(2), C(1)−Pd(1)−S(1), and C(1)−Pd(1)−S(2) angles are almost close to 90°. The NHC planes in both complexes are perpendicular to the $PdCS_2C$ coordination plane with dihedral angles of 89.8 and 87.4° in complexes **1b** and **3b**, respectively. In complex **2a**, the NHC planes tilt toward the center Pd coordination plane with dihedral angles of 62.3°. The Pd−C(benzene) bond lengths of the Pd-NHC complexes are in the range of 2.0063−2.0461 Å and are consistent with Pd−C bond length values reported for palladium complexes with benzene-based pincer ECE ligands.[45−48] The $C_{carbene}$−Pd(1) bond lengths for **1b** and **2a** are 2.063(8) and 2.065(4) Å, respectively, both of which are slightly longer than that observed in complex **3b** (2.022(8) Å) due to the weak coordination ability of the $C_{carbene}$ atom,[49] which is validated by the ^{13}C═S resonance results. The Pd−S bond lengths (2.279(3)−2.3374(10) Å) of the complexes are quite comparable to those of related Pd(II) complexes reported.[35,50−53]

As seen in Figure 3a,b, there are intermolecular hydrogen bonds between palladium complexes in **1b** and **2a**. The iodide as a bridging atom links two adjacent molecular structures. Intermolecular nonclassical C−H···I intermolecular hydrogen bonds play crucial roles in the construction of a 1D structure in the solid state (details in Table 1). Complex **3b** crystallized in the monoclinic space group $P2_1/n$, with four molecules in the unit cell. As shown in Figure 3c,d, each PF_6^- anion interacts with four hydrogens from four adjacent palladium complexes in the unit cell of **3b**. The molecular complex units are linked into a helical chain along the *b* axis via nonclassical C−H···F hydrogen bonds with adjacent molecules. Each helix is linked by C−H···F intermolecular hydrogen bonds along the *a* axis to form a 2D architecture (Figure 3c).

Table 1. Hydrogen Bond Parameters for Palladium Complexes

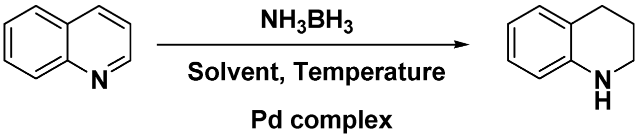
complex	D−H···A[a]	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	D−H···A (deg)
1b	O(1)−H(1)···I(2)^{‡1}	0.82	2.66	3.454(8)	165
	C(29)−H(29)···I(2)	0.93	3.01	3.935(9)	178
	C(30)−H(30)···I(2)	0.93	3.03	3.806(8)	143
2a	C(12)−H(12)···I(1)^{‡2}	0.93	3.05	3.968(4)	171
3b	C(8)−H(8B)···F(2) (pink)^{‡3}	0.97	2.44	3.298(19)	147
	C(16)−H(16)···F(1) (red)	0.93	2.54	3.403(19)	154
	C(17)−H(17B)···F(3) (violet)	0.97	2.41	3.282(19)	150
	C(25)−H(25)···F(4) (green)	0.93	2.28	3.211(15)	176

[a] Complex **1b**: (‡*1*) 1 + *x*, 1 + *y*, *z*. Complex **2a**: (‡*2*) 1 − *x*, 2 − *y*, 1 − *z*. Complex **3b**: (‡*3*) 0.5 + *x*, 1.5 − *y*, 0.5 + *z*.

1,2,3,4-Tetrahydroquinoline and its derivatives are known for their importance as synthetically valuable intermediates for pharmaceuticals and agrochemicals.[54,55] Catalytic hydrogenation of quinoline is highly atom economical, and heterogeneous palladium catalyst systems are commonly used for the hydrogenation of quinoline.[56−59] In this work, ammonia−borane ($NH_3·BH_3$, AB) as an environmentally benign transfer hydrogenation source substituting the flammable hydrogen for hydrogenation of quinoline was used,[60,61] in conjunction with our synthesized palladium catalyst complex. To our knowledge, this homogeneous catalytic system is relatively unexplored.[62−64] Thus, we examined the catalytic activity of the palladium complexes for transfer hydrogenation of quinolines beginning with quinoline and AB to screen for optimal reaction conditions.

Initially, a model reaction of quinoline with 10 equiv of AB under a nitrogen atmosphere was explored. To our delight, the desired product was obtained in 78% yield and the selectivity for 1,2,3,4-tetrahydroquinoline reduction is about 100% with catalyst **1a** at 100 °C for 3 h in toluene (Table 2, entry 1). As shown in Table 2, complex **3b** performed as an ideal catalyst toward quinoline reduction under the same reaction conditions. Our screening also showed that nonpolar toluene was the suitable solvent (Table 2, entry 6). The same reaction gave lower yields in polar solvents such as MeCN, MeOH, THF, *i*-PrOH, H_2O, and mixed solvents (Table 2, entries 7−12). Slightly lower yields were obtained with a decrease in reaction temperature, and decreased yields were observed when the amount of AB was decreased (Table 2, entries 13−15). Under an H_2 balloon at standard pressure, only less than 5% of the product was obtained (Table 2, entry 16). When the reaction was carried out in air, the yield of product was decreased slightly to only an 81% yield (Table 2, entry 17).

Table 2. Optimization of Reaction Conditions for Transfer Hydrogenation of Quinoline with Palladium Complexes[a]

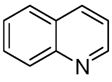
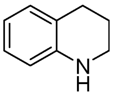
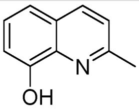
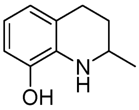
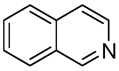
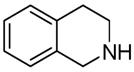
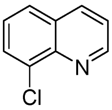
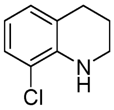
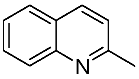
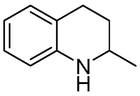
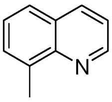
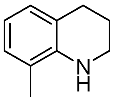
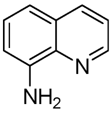
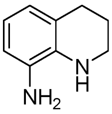
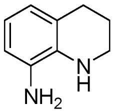
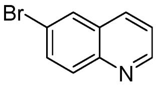
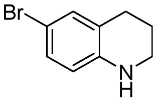
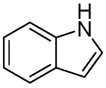
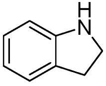
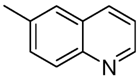
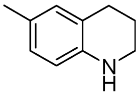
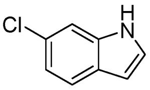
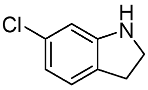
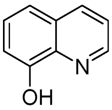
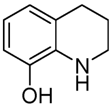
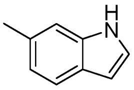
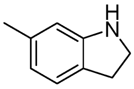


entry	catalyst	atmosphere	solution	$NH_3·BH_3$ (equiv)	temp (°C)	time (h)	yield (%)[b]
1	**1a**	N_2	toluene	10	100	3	78
2	**1b**	N_2	toluene	10	100	3	86
3	**2a**	N_2	toluene	10	100	3	71
4	**2b**	N_2	toluene	10	100	3	76
5	**3a**	N_2	toluene	10	100	3	93
6	**3b**	N_2	toluene	10	100	3	95
7	**3b**	N_2	MeCN	10	100	3	21
8	**3b**	N_2	MeOH	10	100	3	<10
9	**3b**	N_2	THF	10	100	3	84
10	**3b**	N_2	1/1 MeCN/H_2O	10	100	3	<10
11	**3b**	N_2	*i*-PrOH	10	100	3	<5
12	**3b**	N_2	H_2O	10	100	3	7
13	**3b**	N_2	toluene	10	80	3	73
14	**3b**	N_2	toluene	3	100	12	40
15	**3b**	N_2	toluene	10	120	3	82
16	**3b**	H_2	toluene		100	3	<5
17	**3b**	air	toluene	10	100	3	81

[a] Reaction conditions: quinoline (0.1 mmol), catalyst (based on Pd: 1 mol %), $NH_3·BH_3$, solvent (2 mL). [b] Determined by GC-MS.

Having identified the optimal reaction conditions, the generality and scope of the reaction were then explored. The results are shown in Table 3. It was found that the transformation with isoquinoline was efficient, which proceeded smoothly to give the desired product in 90% yield (Table 3, entry 2). The reaction was also compatible with

Table 3. Screening of Substrates for Transfer Hydrogenation of Nitrogen Heterocyclic Compounds Catalyzed by Complex 3b[a,b]

Entry	Substrate	Product	Time/Yield (%)	Entry	Substrate	Product	Time/Yield (%)
1			3 h/95	8			24 h/60
2			3 h/90	9			3 h/32
3			15 h/87	10			15 h/60
4			15 h/99	11			24 h/58
5			3 h/83	12			15 h/90
6			15 h/68	13			15 h/93
7			3 h/30	14			15 h/94

[a] Reaction conditions: 0.1 mmol of quinoline or its derivatives or nitrogen heterocyclic compounds, 10 mmol of AB, **3b** (based on Pd: 2 mol %), toluene (2 mL), 100 °C. [b] The yields were determined by GC/MS.

quinolines bearing 2- or 6-methyl, 6-bromo, and 8-amino substituents, providing the corresponding products in 68−99% yields (Table 3, entries 3−6). However, the results were not satisfactory when 8-substituted quinolines such as hydroxy, methyl, and chlorine were employed as the substrates (Table 3, entries 7−10). When the reaction time was prolonged from 3 to 24 h, the yield was not improved much (Table 3, entry 7 vs entry 8). For quinoline with an 8-nitro group, the $-NO_2$ group was also reduced, leading to the corresponding product in moderate yield (58%, Table 3, entry 11). The reactions of other nitrogen heterocyclic compounds, including indole, 6-chloroindole, and 6-methylindole, were also performed. All reactions worked well to produce the corresponding indoline derivatives in excellent yields after 15 h (90−94% yields, Table 3, entries 12−14).

■ CONCLUSION

Palladium(II) complexes with NHC and phenylene-bridged bis(thione) (SCS) ligands were synthesized and fully characterized. Spectroscopic and X-ray crystallographic studies confirmed the molecular structures of all palladium complexes. The Pd(II) complexes are highly active toward the transfer hydrogenation of quinolines to the corresponding 1,2,3,4-tetrahydroquinolines using AB as an alternative hydrogen source under mild reaction conditions. The binuclear Pd-(NHC) complexes were more active than the mononuclear Pd(NHC) complexes under the same reaction conditions.

■ EXPERIMENTAL SECTION

Materials and Measurements. All the operations were carried out under a pure nitrogen atmosphere using standard Schlenk techniques. All solvents were purified and degassed by standard procedures. The palladium precursor Pd(SCS)Cl,[35] 1,3-dialkylimidazolium,[65] 1,3-dialkylbenzimidazolium iodide,[65] and tetramethylbenzobis(imidazolium) bromide[66] were synthesized according to the literature. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AV 400 spectrometer at room temperature. Chemical shifts (δ) are given as parts per million (ppm) and refer to the shift of the hydrogen or carbon atoms in the solvents used (CD_3OD and DMSO-d_6). The following abbreviations were used for the assignment of the signals and their multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The given coupling constants *J* are listed as the average of the experimental findings. The IR (KBr pellet) spectrum was recorded (400−4000 cm^{-1} region) on a Bruker TENSOR 27 FT-IR spectrometer. Elemental analyses were performed on a PerkinElmer 2400 CHN analyzer. Electrospray ionization mass spectra (ESI-MS) were recorded on Bruker micrOTOF-Q II 10280 and Bruker micrOTOF II 10257 mass spectrometers.

General Procedure for the Synthesis of Pd-NHC Complexes (1a,b and 2a,b). A solution of Pd(SCS)Cl (0.1 mmol), 1,3-dialkylimidazolium or 1,3-dialkylbenzimidazolium iodide (0.12 mmol), and Cs_2CO_3 (98.0 mg, 0.3 mmol) in MeCN (15 mL) was purged with N_2 and then stirred at 333 K for 18 h. Then the solvent was removed with a rotary evaporator. The reminding green solid was washed with 3 × 10 mL of H_2O and was then dried under vacuum pumping to give the corresponding product.

1a. Yield: 49.0 mg, 90%. ^1H NMR (400 MHz, MeOD-d_4): δ 7.74 (d, J = 2.4 Hz, 2H), 7.39 (d, J = 2.4 Hz, 2H), 7.36 (s, 3H), 7.22 (s, 2H), 3.82 (s, 6H), 3.75 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ

172.9, 149.9, 140.7, 139.2, 126.8, 123.2, 122.0, 121.3, 119.4, 37.2, 35.5. IR (KBr, cm^{-1}): 3150 (w), 3076 (s), 2955 (s), 2924 (s), 1601 (w), 1577 (m), 1466 (vs), 1442 (s), 1315 (m), 1294 (s), 791 (m), 735 (s), 708 (s), 675 (s). Anal. Calcd for $C_{19}H_{22}N_6PdS_2I$: C, 36.12; H, 3.51; N, 13.30. Found: C, 36.20; H, 3.47; N, 13.25. ESI-MS *m*/*z*: calcd for $[C_{19}H_{22}N_6PdS_2]^+$ $[M - I]^+$, 503.0305; found, 503.0378.

1b. Yield: 61.0 mg, 92%. ^1H NMR (400 MHz, MeOD-d_4): δ 7.75 (d, J = 2.4 Hz, 2H), 7.46 (d, J = 2.4 Hz, 2H), 7.37 (s, 3H), 7.22 (s, 2H), 4.19 (q, J = 7.2 Hz, 4H), 3.18(s, 6H), 1.43 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.2, 149.0, 140.6, 139.1, 126.8, 123.2, 121.4, 120.5, 119.8, 43.5, 37.1, 14.4. IR (KBr, cm^{-1}): 3156 (w), 3116 (m), 3069 (s), 2973 (m), 1614 (w), 1575 (m), 1446 (s), 1352 (m), 1307 (m), 1279 (s), 790 (w), 731 (s), 711 (s). Anal. Calcd for $C_{21}H_{26}N_6PdS_2I$: C, 38.22; H, 3.97; N, 12.73. Found: C, 38.28; H, 3.92; N, 12.65. ESI-MS *m*/*z*: calcd for $[C_{21}H_{26}N_6PdS_2]^+$ $[M - I]^+$, 531.0618; found, 531.0701.

2a. Yield: 60.0 mg, 88%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.05 (s, 2H), 7.71 (dd, J = 6.0, 2.4 Hz, 2H), 7.69(d, J = 2.4 Hz, 2H), 7.46−7.41 (m, 5H), 4.01 (s, 6H), 3.70 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 185.5, 149.7, 140.5, 139.2, 134.5, 127.0, 123.3, 122.1, 121.4, 119.5, 111.0, 35.6, 34.5. IR (KBr cm^{-1}): 3173 (w), 3069 (m), 3013 (m), 2922 (s), 1614 (w), 1582 (m), 1471 (vs), 1441 (s), 1380 (s), 1265 (m), 789 (s), 740 (s), 706 (s). Anal. Calcd for $C_{23}H_{24}N_6PdS_2I$: C, 40.51; H, 3.55; N, 12.32. Found: C, 40.56; H, 3.54; N, 12.36. ESI-MS *m*/*z*: calcd for $[C_{23}H_{24}N_6PdS_2]^-$ $[M - I]^+$, 553.0463; found, 553.0443.

2b. Yield: 64.0 mg, 90%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.08 (d, J = 2.0 Hz, 2H), 7.77 (d, J = 2.4 Hz, 2H), 7.72 (dd, J = 6.0, 3.2 Hz, 2H), 7.47−7.40 (m, 5H), 4.13 (q, J = 7.2 Hz, 4H), 4.00 (s, 6H), 1.33 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 185.8, 148.8, 140.5, 139.0, 134.5, 127.0, 123.3, 121.6, 120.6, 120.0, 111.0, 43.6, 34.4, 14.4. IR (KBr, cm^{-1}): 3153 (w), 3113 (w), 3065 (m), 2976 (m), 2931 (m), 1612 (w), 1580 (w), 1462 (s), 1442 (s), 1346 (m), 1275 (m), 787 (w), 744 (s), 716 (m), 680 (m). Anal. Calcd for $C_{25}H_{28}N_6PdS_2I$: C, 42.29; H, 3.98; N, 11.84. Found: C, 42.33; H, 3.96; N, 11.89. ESI-MS *m*/*z*: calcd for $[C_{25}H_{28}N_6PdS_2]^+$ $[M - I]^+$, 581.0776; found, 581.0755.

General Procedure for the Synthesis of Pd-NHC Complexes (3a,b). A solution of Pd(SCS)Cl (0.1 mmol), tetramethylbenzobis(imidazolium) bromide (0.05 mmol), and Cs_2CO_3 (98.0 mg, 0.3 mmol) in MeCN (15 mL) was purged with N_2 and then stirred at room temperature for 0.5 h and at 333 K for 18 h. Then the solvent was removed with a rotary evaporator. The reminding green solid was washed with H_2O (3 × 10 mL) and Et_2O (3 × 5 mL), which was then dried under vacuum pumping to give the intermediate product. The resulting product was poured into 1/1 $MeOH/CH_2Cl_2$ (v/v) solution, the undissolved precipitate was removed by filtration, excess aqueous KPF_6 (5 mL) was added, and a thick orange precipitate was obtained by filtration and washed with H_2O (3 × 5 mL) and Et_2O (3 × 5 mL). The solid was dried under vacuum pumping to give the corresponding product.

3a. Yield: 36.6 mg, 55%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.14−8.06 (m, 6H), 7.70 (s, 4H), 7.45 (s, 6H), 4.11−4.02 (m, 12H), 3.72 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 189.2, 150.6, 140.9, 139.8, 132.5, 127.6, 122.7, 122.0, 120.0, 93.6, 36.0, 35.4. IR (KBr cm^{-1}): 3426 (m), 3163 (vw), 2940 (vw), 1625 (w), 1474 (m), 1389 (m), 1304 (vw), 1231 (w), 1107 (w), 839 (s), 721 (w), 669 (w), 577 (m), 472 (vw). Anal. Calcd for $C_{40}H_{42}N_{12}P_2F_{12}Pd_2S_4$: C, 36.34; H, 3.20; N, 12.72. Found: C, 36.32; H, 3.26; N, 12.75. ESI-MS *m*/*z*: calcd for $[C_{40}H_{42}N_{12}Pd_2S_4]^{2+}$ $[M - 2PF_6]^{2+}$, 515.0227; found, 515.0316.

3b. Yield: 39.4 mg, 53%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.16−8.10 (m, 6H), 7.77 (d, J = 2.4, 4H), 7.49−7.42 (m, 6H), 4.14−3.97 (m, 20H), 1.76−1.68 (m, 8H), 1.31−1.21 (m, 8H), 0.85−0.78 (m, 12H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 189.2, 149.5, 140.7, 139.5, 132.4, 122.2, 121.7, 120.4, 93.6, 82.6, 48.4, 35.4, 31.2, 19.4, 13.9. IR (KBr cm^{-1}): 3417 (m), 3148 (w), 2951 (m), 2859 (w), 2176 (w), 1710 (vw), 1618 (vw), 1578 (w), 1461 (s), 1415 (m), 1381 (m), 1250 (w), 1106 (m), 844 (s), 718 (w), 672 (w), 561 (s). Anal. Calcd for $C_{52}H_{66}N_{12}P_2F_{12}Pd_2S_4$: C, 41.91; H, 4.46; N, 11.28. Found: C, 41.90; H, 4.48; N, 11.33. ESI-MS *m*/*z*: calcd for $[C_{52}H_{66}F_6N_{12}PPd_2S_4]^+$ $[M - PF_6]^+$, 1343.2132; found, 1343.2188; calcd for $[C_{52}H_{66}N_{12}Pd_2S_4]^{2+}$ $[M - 2PF_6]^{2+}$, 599.1168; found, 599.1251.

General Procedure for the Reduction of Quinoline Compounds with Palladium Complex. The palladium complex (0.001 mmol, 1 mol %), quinoline or a derivative (0.1 mmol), *n*-dodecane (0.1 mmol), and ammonia−borane (1 mmol) were added to toluene (2 mL) in a Schlenk tube and kept at 100 °C to stir for 3 h under a nitrogen atmosphere. The resulting mixture was filtered through a small pad of silica using EtOAc and analyzed by GC-MS.

X-ray Structure Determination. Diffraction data of **1b**, **2a**, and **3b** were collected on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area detector using Cu Kα radiation (λ = 1.54184) for **1b** and Mo Kα radiation (λ = 0.71073 Å) for **2a** and **3b**. All of the data were collected at 298 K, and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL).[67] SADABS[68] absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. All calculations were performed using the Bruker Smart program.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00091.

Crystal data and summary of data collection and refinement, absorption spectra, NMR data, and MS of palladium complexes (PDF)

Accession Codes

CCDC 1976090−1976092 contain 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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