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Cationic Iridium and Rhodium Complexes with C−N Chelating Primary Benzylic Amine Ligands as Potent Catalysts for Hydrogenation of Unsaturated Carbon−Nitrogen Bonds

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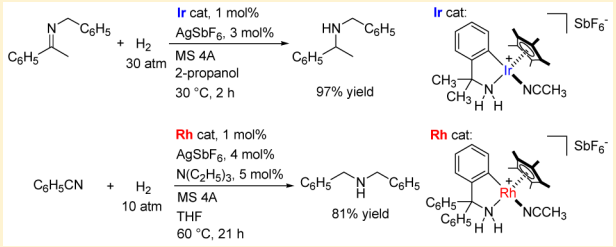
Supporting Information

ABSTRACT: Cationic half-sandwich C−N chelating Ir and Rh complexes $[Cp^*M(NCCH_3)\{\kappa^2(N,C)\text{-}NH_2CR_2\text{-}2\text{-}C_6H_4\}]^+SbF_6^-$ (**1a**, M = Ir, R = CH_3; **1b**, M = Ir, R = C_6H_5; **2a**, M = Rh, R = CH_3; **2b**, M = Rh, R = C_6H_5) are synthesized by $AgSbF_6$-mediated halide abstraction from neutral azametallacycles derived from tritylamine or cumylamine and are fully characterized by NMR spectroscopy and X-ray crystallography. The treatment of the cationic complex **1b** with H_2 gas under ambient conditions in the presence of triethylamine in THF-d_8 quantitatively yielded hydrido(amine) complex $[Cp^*Ir(H)\{\kappa^2(N,C)\text{-}NH_2C(C_6H_5)_2\text{-}2\text{-}C_6H_4\}]$ (**4**). The C−N chelating Ir complex shows a higher catalytic activity than an N−N chelating complex, $[Cp^*Ir(NCCH_3)(Tscydn)]^+SbF_6^-$ (**3**; Tscydn = *N*-(*p*-toluenesulfonyl)-1,2-cyclohexanediamine), that has been previously used for the asymmetric hydrogenation of acyclic imines. For example, the cationic Ir complex **1a** promoted the hydrogenation of *N*-(1-phenylethylidene)benzylamine under 30 atm at 30 °C in the presence of excess $AgSbF_6$ to produce the corresponding amine in 97% yield within 2 h. The cationic Rh complexes **2** serve as efficient catalysts for hydrogenative condensation of nitriles in the presence of $AgSbF_6$, producing dibenzylamines selectively even at 60 °C.



INTRODUCTION

Metal/NH bifunctional catalysis has received much attention as a pivotal concept for redox transformations based on hydrogen transfer between secondary alcohols and ketones.[1] A fundamental hydrogen delivery process alternating between 16*e* amido and 18*e* hydrido(amine) complexes has been thoroughly explored in in-depth studies on the prototype catalyst bearing chiral *N*-sulfonyldiamines (N−N chelating ligands) developed by Noyori and Ikariya.[2] We have systematically investigated interconversion operation for a range of group 8 and 9 metal complexes with protic amine chelates and examined ligand modification by significantly changing the chelating atom influences on the catalyst performance.[3] In particular, bifunctional Cp*Ir and Rh complexes containing a five-membered C−N chelate ring that were synthesized by cyclometalation of protic benzylamine derivatives have been successfully designed for use as highly efficient hydrogen transfer catalysts.[4] Remarkable enhancement of catalytic activity of the amido complexes derived from the neutral chloro(amine) complexes was observed in transfer hydrogenation of ketones using 2-propanol[4a] and in aerobic oxidation of alcohols,[4b,c] compared to the results obtained with the original N−N chelating Ir complex. Pfeffer and co-workers have independently reported that the related cationic C−N chelating complexes can also be utilized for transfer hydrogenation of ketones and imines.[5] The rapid hydrogen transfer from alcohols to the amidoiridium and from the hydrido(amine)iridium to ketones is induced by the high basicity of the amido moiety[4a,6] as well as the strong nucleophilicity of the hydrido ligand caused by a pronounced σ-donor nature of the chelating carbon atom. It should be noted that these outstanding features accommodate dynamic kinetic resolution of racemic secondary alcohols through a combination of the reactions described above with enzymatic transformations.[7]

Due to the similarities between the hydrogen transfer and H_2-hydrogenation mechanisms,[8] we anticipated that C−N chelating complexes can serve as good hydrogenation catalysts in the case where the hydrido(amine) complexes can be generated directly from H_2. In the case of the N−N chelate system, we and other groups independently reported that direct hydrogenation is promoted by the protonation of 16*e* amido complexes with the help of Brønsted acids or alcoholic media[9,10] and by the formation of cationic complexes using silver salts.[11] This is true even if the original transfer hydrogenation catalysts only slightly activate H_2 gas. For the N−N chelating Ir complex $[Cp^*IrCl\{(S,S)\text{-Tscydn}\}]$, a combined use of silver salts in catalytic asymmetric hydrogenation of acyclic imines proved to promote the activity and selectivity.[11b] As shown in Scheme 1, mechanistic studies revealed that formation of cationic species allows heterolytic bond cleavage of H_2 to generate a hydrido

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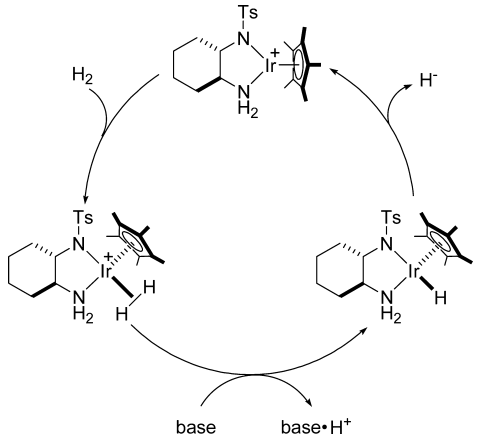
Scheme 1. Hydrogen Activation Mechanism of Cationic N−N Chelating Ir Complexes



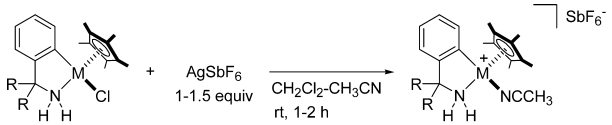
intermediate and that the activation of the imine substrates by the silver cation facilitates the subsequent H^- transfer.

In this paper, we describe the synthesis of new cationic iridacycles and rhodacycles derived from tritylamine or cumylamine to develop the H_2-hydrogenation system based on the C−N chelating complexes. The cationic Ir complex exhibited a higher catalytic activity in the hydrogenation of *N*-(1-phenylethylidene)benzylamine in the presence of $AgSbF_6$ than the previously reported N−N chelating complex. The combination of the cationic Rh complex with excess $AgSbF_6$ was also found to catalyze the selective hydrogenative condensation of nitriles to secondary amines.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cationic C−N Chelating Ir and Rh Complexes. Prior to the evaluation of the applicability of the C−N chelating complexes for catalytic hydrogenation, we first synthesized a series of cationic Ir and Rh complexes from neutral chloro(amine) complexes that have been employed as catalytic precursors for redox transformations of ketones or alcohols in our previous work.[4a,c] Treatment of the chloroiridium complexes $[Cp^*Ir(Cl)\{\kappa^2(N,C)\text{-}NH_2CR_2\text{-}2\text{-}C_6H_4\}]$ (R = CH_3 and C_6H_5) with 1−1.5 equiv of $AgSbF_6$ in a mixed solution of CH_2Cl_2 and CH_3CN at room temperature gave the corresponding yellow cationic complexes, $[Cp^*Ir(NCCH_3)\{\kappa^2(N,C)\text{-}NH_2CR_2\text{-}2\text{-}C_6H_4\}]^+SbF_6^-$ (**1a**, R = CH_3,; **1b**, R = C_6H_5), in 67% and 47% yields, respectively (Scheme 2).

Scheme 2. Synthesis of Cationic C−N Chelating Complexes



1a: M = Ir, R = CH_3, 67% yield
1b: M = Ir, R = C_6H_5, 47% yield
2a: M = Rh, R = CH_3, 77% yield
2b: M = Rh, R = C_6H_5, 72% yield

The cationic C−N chelating Rh analogues, $[Cp^*Rh(NCCH_3)\{\kappa^2(N,C)\text{-}NH_2CR_2\text{-}2\text{-}C_6H_4\}]^+SbF_6^-$ (**2a**, R = CH_3; **2b**, R = C_6H_5), were also prepared through chloride abstraction from the well-defined neutral complexes by using $AgSbF_6$ and successfully isolated as yellow crystals in 77% and 72% yields after recrystallization from ether and dichloromethane.

The isolated products were fully characterized by ^1H and $^{13}C\{^1H\}$ NMR, IR spectroscopy, X-ray crystallography, and elemental analysis. The ORTEP diagrams of the cationic complexes **1** and **2** presented in Figure 1 show a distorted octahedral geometry with coordination of Cp*, chelating carbon and nitrogen, and CH_3CN as observed in the analogous N−N chelating Ir complex $[Cp^*Ir(NCCH_3)\{(S,S)\text{-Tscydn}\}]^+SbF_6^-$ (**3**).[11b] The principal bond lengths and angles are summarized in Table 1. The bond distances between the metal center and C−N chelating ligands are similar to those of the parent neutral complexes.[4a,c] The cationic Ir complexes **1a** and **1b** show Ir−$NCCH_3$ distances of 2.046(5) and 2.059 Å (mean value), which are slightly shorter than that of complex **3** (2.079(2) Å), reflecting the stronger steric effect of the Tscydn ligand compared to those of the C−N chelating ligands.

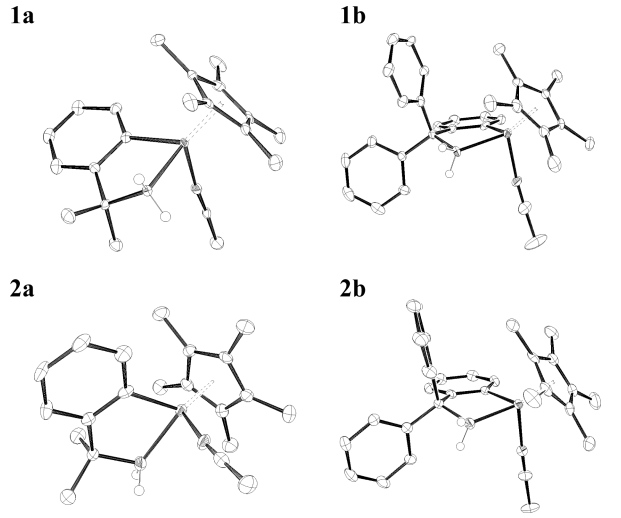


Figure 1. ORTEP drawings of cationic C−N chelating complexes **1a**, **1b**, **2a**, and **2b**. Counter anion and hydrogen atoms other than the amine protons are omitted for clarity, and the ellipsoids represent 50% probability.

Table 1. Selected Bond Lengths and Angles of Cationic Ir and Rh Complexes 1a, 1b, 2a, and 2b

complex	M−C [Å]	M−N [Å]	M−$NCCH_3$ [Å]	N−M−C [deg]
1a	2.056(5)	2.132(4)	2.046(4)	78.27(19)
1b[a]	2.068	2.135	2.059	77.97
2a	2.045(5)	2.126(4)	2.067(5)	78.51(15)
2b	2.048(5)	2.118(4)	2.081(4)	78.15(15)

[a]Mean value.

The cationic C−N chelating complexes **1** and **2** are coordinatively saturated 18*e* species and are thermally stable in a solid state, yet appear fluxional in solution. The ^1H NMR spectrum of **1a** in CD_2Cl_2 at room temperature exhibits a singlet signal due to the CH_3CN at 2.42 ppm, and the IR spectrum recorded with a KBr pellet shows a CN stretching band at 2331 cm^{-1}. In contrast to the reported $[Cp^*Ir(NCCH_3)\{(S,S)\text{-Tscydn}\}]^+SbF_6^-$ (**3**) N−N chelating complex, the NH_2 protons were detected as a broad singlet signal at 4.20 ppm in the ^1H NMR spectroscopy. Furthermore, a broad signal corresponding to two methyl substituents on the cumylamine framework

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was observed at 1.46 ppm, possibly due to the rapid stereochemical inversion of the configuration at the Ir center caused by the liberation of the coordinating CH_3CN ligand.

The proposed dynamic behavior was confirmed by variable-temperature ^1H NMR spectroscopy. As shown in Figure 2, the

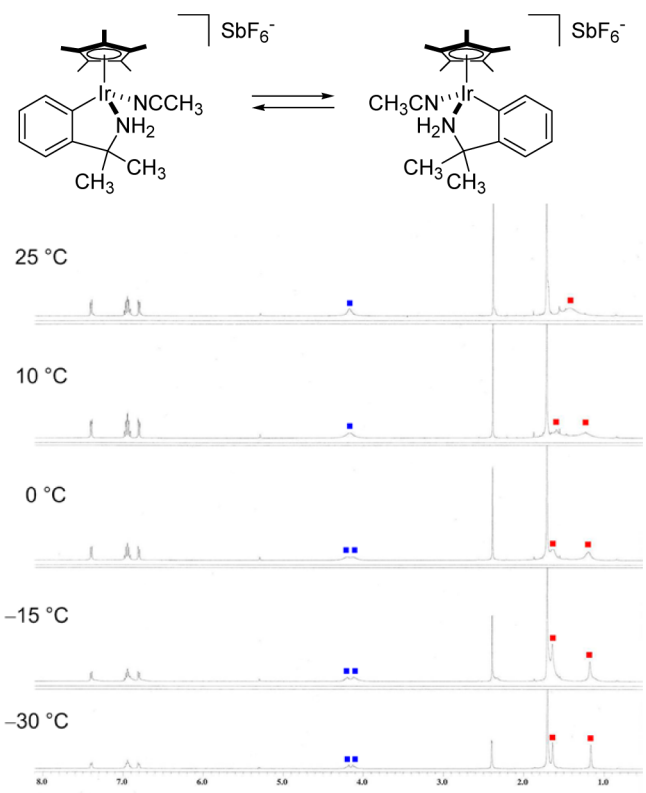
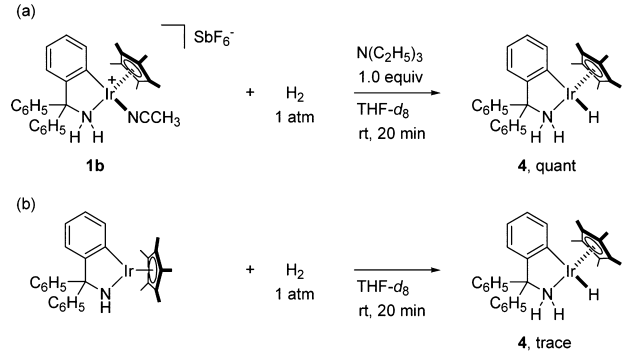


Figure 2. Dynamic behavior of **1a** in CD_2Cl_2 observed by variable-temperature ^1H NMR spectra at 25, 10, 0, −10, and −30 °C.

^1H NMR spectrum of **1a** recorded at −30 °C displayed the two signals assigned to the diastereotopic methyl protons (red dots) at 1.16 and 1.64 ppm, indicating that the Ir center is configurationally stable on the NMR time scale. A set of two doublets due to the NH_2 protons (blue dots) at 4.08 and 4.20 ppm with a geminal coupling constant of 11.9 Hz also supports the chelating structure of the amine ligand. The coalescence temperature of these signals is 15 °C. Similar trends in temperature-dependent spectra were observed for the related cationic Ir and Rh analogues **1b**, **2a**, and **2b** (see Supporting Information). Therefore, this confirms that the acetonitrile ligand easily dissociates from the metal center in solution and opens a coordination site for the incoming molecular hydrogen.

Stoichiometric Reaction of H_2 Gas with the C−N Chelating Complexes. To confirm the formation of a hydrido complex from molecular hydrogen, reactivity of the cationic Ir complex **1b** was investigated under a H_2 atmosphere. Although ^1H NMR monitoring of a mixture of **1b** with atmospheric H_2 in THF-d_8 at room temperature did not support the formation of either the η^2-hydrogen complex or the corresponding hydrido complex, addition of an equimolar amount of $N(C_2H_5)_3$ gave rise to the rapid appearance of a singlet signal at −13.14 ppm ascribed to the hydrido(amine)-Ir complex **4** (Scheme 3a). The same complex has been identified in the reaction of the 16*e* amido complex [Cp*Ir{κ^2(*N*,*C*)-NHC(C_6H_5)$_2$-2-C_6H_4}] in 2-propanol.[4a] In contrast to the smooth and quantitative formation of **4** from

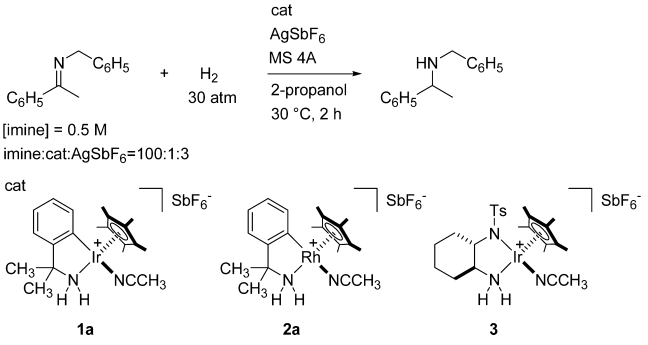
Scheme 3. Reactions of Cationic C−N Chelating Complex 1b or a 16*e* Amidoiridium Complex under a Hydrogen Atmosphere



1b, only a trace amount of the hydrido complex was generated from the basic amido complex with H_2 under identical conditions, indicating that the amido/metal bifunctional effect will not operate sufficiently in the H_2 activation step (Scheme 3b). The instantaneous transformation of the hydrido(amine) complex from the cationic complex **1b** and H_2 in the presence of $N(C_2H_5)_3$ will be attributed to a mechanism involving the heterolytic cleavage of the H−H bond on the cationic metal center with the aid of the base, as realized for the N−N chelating complex shown in Scheme 1.

Comparison of Catalytic Activities of C−N and N−N Chelating Ir and Rh Complexes for Imine Hydrogenation. To demonstrate the advantageous catalytic performance of the newly synthesized C−N chelating complexes, hydrogenation of *N*-(1-phenylethylidene)benzylamine was tested following the procedure described in our previous report (Table 2).[11b] For the

Table 2. Catalytic Hydrogenation of *N*-(1-Phenylethylidene)-benzylamine



entry	catalyst	% yield[a]
1	**1a**	97
2[b]	**1a**	37
3	**2a**	29
4	**3**	14

[a]Yields were determined by ^1H NMR using triphenylmethane as an internal standard. [b]The reaction without H_2 gas.

imine hydrogenation using the N−N chelating Ir catalyst, it has been demonstrated that an extra amount of $AgSbF_6$ can participate not only in formation of the cationic species effective for the facile heterolytic cleavage of H_2 but also in the activation of the substrate imine as a Lewis acid. The imine hydrogenation under 3.0 MPa of H_2 in 2-propanol containing **1a** in the presence

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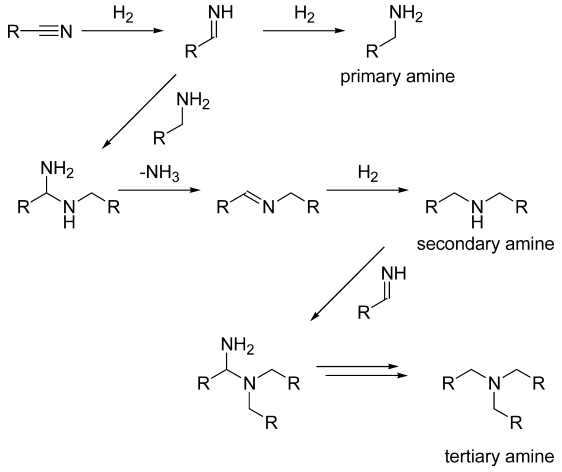
of $AgSbF_6$ (substrate/$AgSbF_6$/catalyst = 100:3:1) and 4A molecular sieves at 30 °C proceeded efficiently to give the corresponding amine in 97% yield after 2 h (entry 1). The reaction conducted under an argon atmosphere resulted in lowering of the yield (37%), suggesting that the imine should be reduced via the hydrogenation in preference to the transfer hydrogenation from 2-propanol by using the cationic complex (entry 2). The cationic Rh complex **2a** also was used to obtain the hydrogenated product in yields of 29% (entry 3). The catalytic activity of **1a** was found to be much higher than that of N−N chelating complex **3** (14% yield) under the same conditions (entry 4). The strong σ-donating ability of the C−N chelating ligands will affect the smooth hydride transfer from the nucleophilic hydrido complexes to the imine substrate that should play a vital role in the catalysis.

Catalytic Hydrogenation of Nitriles with a Combination of Cationic Rh Complexes and $AgSbF_6$. Stimulated by the satisfactory hydrogenation activity of the cationic C−N chelating complexes combined with $AgSbF_6$, we set out to explore the catalytic hydrogenation of nitriles, which represents an economical and environmentally benign process for amines.[12] The nitriles can be generally reduced with stoichiometric amounts of metal hydrides such as $LiAlH_4$ or with heterogeneous catalysts based on Pd, Ni, and Co.[13] With respect to the homogeneous catalytic nitrile reductions, relatively limited examples using Mo,[14] W,[14] Re,[15] Fe,[16] Ru,[17] Co,[18] Rh,[19] Ir,[20] Ni,[21] and Pd[22] complexes have been reported. In most cases, somewhat harsh reaction conditions such as high pressure and elevated temperature are required to activate the unreactive nitrile substrates and to overcome catalyst poisoning by the amine products. Moreover, hydrogenation often suffers from the formation of mixtures of primary, secondary, and tertiary amines and imine intermediates through a repetitive hydrogenation/condensation sequence as depicted in Scheme 4.[23] In 2007,

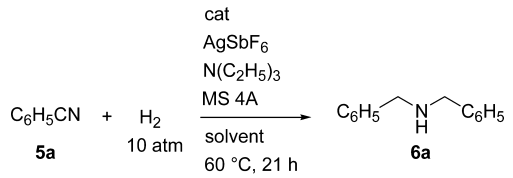
Scheme 4. Possible Reaction Pathways for Formation of Primary, Secondary, and Tertiary Amines in the Catalytic Hydrogenation of Nitriles



Morris' group reported that a Ru catalyst with a P−NH−NH−P tetradentate ligand can catalyze hydrogenation of benzonitrile to afford benzylamine with complete conversion.[17d] Beller and co-workers developed a Ru catalyst system composed of $[Ru(cod)(methylallyl)_2]$ with phosphines or N-heterocyclic carbenes for selective hydrogenation of nitriles to primary amines in the presence of *t*-BuOK.[17e−g] In a study of a base-free system, it was also reported that the transformation from benzonitrile into benzylamine could be accomplished by using a dihydrido(dihydrogen)ruthenium complex, $[RuH_2(H_2)(PCyp_3)_2]$ ($PCyp_3$ = tricyclopentylphosphine).[17h] Alternatively, direct and selective synthesis of secondary amines from nitriles is also attractive due to its operational simplicity[24,25] compared to other traditional C−N bond formation methods via the alkylation of primary amines.

As a pilot experiment, hydrogenation was carried out with 1.0 mmol of benzonitrile (**5a**) as a substrate, using Rh or Ir catalysts for the evaluation of the catalytic potential of the cationic C−N chelating complexes. THF solutions containing triethylamine catalyst and **5a** in a ratio of 1:5:100 were pressurized with 10 atm of H_2 in the presence of 4A molecular sieves (400 mg) and heated at 60 °C for 21 h. The results are outlined in Table 3. The addition of $AgSbF_6$ (Ag/cat = 1)

Table 3. Catalytic Hydrogenation of Benzonitrile 5a



$[C_6H_5CN]$ = 0.1 M
C_6H_5CN:cat:$N(C_2H_5)_3$=100:1:5

entry	catalyst	$AgSbF_6$, mol %	solvent	% yield[a]
1	**2a**	0	THF	0
2	**2a**	1	THF	31
3	**2b**	1	THF	65
4	**2b**	1	CH_3OH	44
5	**2b**	1	$(CH_3)_2CHOH$	30
6	**2b**	1	toluene	0
7	**2b**[b]	0	THF	0
8	**1a**	1	THF	0
9	$[Cp^*RhCl_2]_2$	3	THF	9
10		4	THF	0
11	**2b**	4	THF	81

[a]Yields were determined by ^1H NMR using triphenylmethane as an internal standard. [b]One equivalent of *t*-BuOK was added to **2b** as base instead of $N(C_2H_5)_3$.

allowed the hydrogenation to produce dibenzylamine (**6a**) in 31% yield together with a trace of *N*-benzylidenebenzylamine, which agrees with the hydrogenation pathway shown in Scheme 4 (entries 1 and 2). Even better catalytic performance (65% yield) was obtained with an easily accessible in situ catalyst composed of **2b** and $AgSbF_6$ (entry 3). Unlike the case of imine hydrogenation, alcoholic solvents slightly reduced the catalytic activity (entries 4 and 5). The hydrogenation in toluene was unsuccessful, possibly due to the limited solubility of the silver salt (entry 6). Because the use of *t*-BuOK instead of $N(C_2H_5)_3$ involves the preferential formation of an amidoiridium species, **5a** remained intact after the reaction (entry 7). The combination of the Ir complex **1a** with $AgSbF_6$ did not catalyze the hydrogenation under identical conditions (entry 8). The effectiveness of metal/NH cooperation for the C−N chelating complexes was confirmed by a reduced catalytic activity in the hydrogenation using $[Cp^*RhCl_2]_2$ with 3 mol amounts of $AgSbF_6$ (entry 9). The amine product **6a** was not obtained in a separate experiment using $AgSbF_6$ without the Rh catalyst (entry 10). An addition of extra $AgSbF_6$ (Ag/cat = 4) was beneficial for the enhancement of

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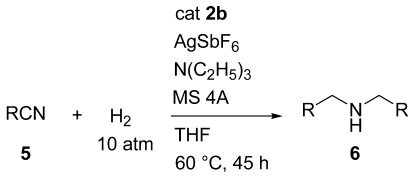
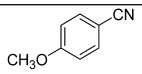
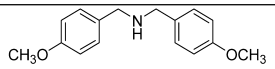
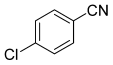
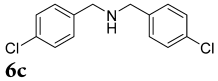
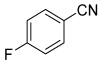
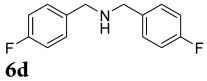
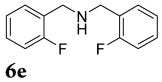
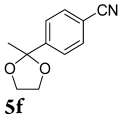
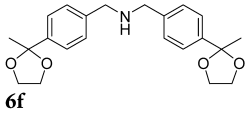
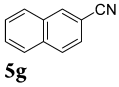
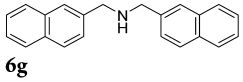
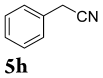
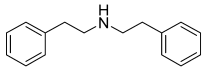
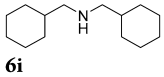
catalytic activity, producing **6a** in 81% yield without formation of primary and tertiary amines (entry 11).

The substrate scope was examined using optimized hydrogenation conditions with the combined catalyst system of **2b** and $AgSbF_6$ under 1.0 MPa of H_2 at 60 °C. As shown in Table 4,

Table 4. Selective Formation of Secondary Amines in the Catalytic Hydrogenation of Nitriles



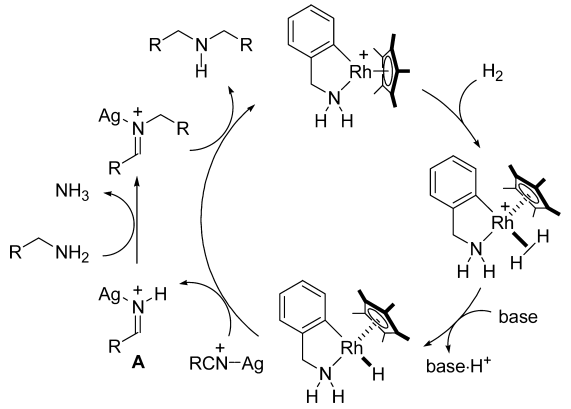
entry	substrate	product	% yield[a]
1[b]	 **5b**	 **6b**	87
2	 **5c**	 **6c**	32
3[b]	 **5d**	 **6d**	50
4[b]	 **5e**	 **6e**	72
5[b]	 **5f**	 **6f**	67
6	 **5g**	 **6g**	74
7[b,c]	 **5h**	 **6h**	49
8[b,c]	 **5i**	 **6i**	59

[a]Isolated yield. [b]S/C = 50. [c]69 h.

benzonitrile derivatives with methoxy, fluoro, and acetal groups (**5b**, **5d**–**f**) and 2-cyanonaphthalene (**5g**) were substantially converted to obtain the desired secondary amines (**6b**, **6d**–**g**) in satisfactory yields after purification, whereas the hydrogenation of 4-chlorobenzonitrile (**5c**) was not completed after the same conditions (entries 1–6). Although the reactivity of aliphatic nitriles such as benzyl cyanide and cyclohexanecarbonitrile was slightly lowered, the use of 2 mol % of the catalyst **2a** with elongation of the reaction time to 69 h was effective for increasing the yield of secondary amine products (**6h** and **6i**; entries 7 and 8).

Analogously to the imine hydrogenation by the combined catalyst system of **1** and $AgSbF_6$, the mechanism of the nitrile hydrogenation is considered to involve the heterolytic bond cleavage of H_2 on a cationic complex to generate a hydrido intermediate with the subsequent H^- transfer to the nitrile substrates activated by the silver center. As shown in Scheme 5, the

Scheme 5. Reaction Pathway for Hydrogenation of Nitriles Using C–N Chelating Rh Catalysts



dominant formation of the secondary amines will be intimately associated with the silver-mediated activation of the primary hydrogenation products (**A**), which become susceptible to nucleophilic attack by primary amines, leading to further hydrogenation. Although the details of the process proceeding through multiple hydrogenation stages remains unclear, the further conversion into tertiary amines via condensation of imine with sterically demanding secondary amines is not favorable under mild reaction conditions.

CONCLUSIONS

We demonstrated that the cationic C–N chelating Ir and Rh complexes derived from tritylamine and cumylamine are effective hydrogenation catalysts. The cationic complexes can promote the heterolytic cleavage of molecular hydrogen in the presence of base under atmospheric pressure at ambient temperature to generate the hydrido(amine) complexes; such heterolytic cleavage is effective for the reduction of polar bonds. Actually, the Ir complexes serve as highly efficient catalysts for the imine hydrogenation instead of the complex bearing *N*-sulfonyldiamine ligands. Furthermore, the cationic Rh complex **2b** was successfully used for the hydrogenation of nitriles. The combined use of cationic Rh complex and silver salt efficiently and selectively converted nitriles into secondary amines under mild conditions. Silver salts will facilitate the condensation of imines, with primary amines accompanied by the elimination of ammonia as well as the subsequent nucleophilic attack to imine by hydrido-Rh complexes. The powerful reducing nature of the C–N chelating complexes is highly promising for the development of catalytic transformations of hardly reducible substrates, and further research on this is currently in progress in our laboratory.

EXPERIMENTAL SECTION

General Procedures. Reactions requiring air-sensitive manipulations were conducted under an argon atmosphere following standard Schlenk techniques. Dichloromethane and acetonitrile were distilled under argon after drying over P_2O_5. Diethyl ether and THF were dried and deoxygenated by refluxing and distilling from sodium benzophenone ketyl under argon. Other reagents were purchased and used as delivered unless otherwise noted. The starting Ir and Rh complexes $Cp^*IrCl[\kappa^2(N,C)\text{-}\{NH_2C(CH_3)_2\text{-}2\text{-}C_6H_4\}]$,[4a] $Cp^*IrCl[\kappa^2(N,C)\text{-}\{NH_2C(C_6H_5)_2\text{-}2\text{-}C_6H_4\}]$,[4a] $Cp^*RhCl[\kappa^2(N,C)\text{-}\{NH_2C(CH_3)_2\text{-}2\text{-}C_6H_4\}]$,[4c] $Cp^*RhCl[\kappa^2(N,C)\text{-}\{NH_2C(C_6H_5)_2\text{-}2\text{-}C_6H_4\}]$,[4c] and $Cp^*Ir[\kappa^2(N,C)\text{-}\{NHC(C_6H_5)_2\text{-}2\text{-}C_6H_4\}]$[4a] were prepared according to the procedures described in the literature with modifications. The N–N

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chelating complex **3** was prepared according to the procedure described in a previous work.[10b] ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-ECX400 spectrometer. The NMR chemical shifts were referenced to $SiMe_4$ by using residual protio impurities in the deuterated solvent. Elemental analyses were carried out using a PE2400 Series II CHNS/O analyzer (PerkinElmer). IR spectra were recorded on a JASCO FT/IR-610 spectrometer. Mass spectra (MS) were obtained with a JEOL JMS-SX102A instrument. Recyclable preparative high-performance liquid chromatography was performed on a Japan Analytical Industry LC-9225 NEXT system equipped with JAIGEL-1H and -2H columns using $CHCl_3$ as an eluent at a flow rate of 14 mL min^{-1}.

Synthesis of [Cp*Ir(NCCH$_3$){κ^2(*N*,*C*)-(NH$_2$C(CH$_3$)$_2$-2-C$_6$H$_4$)}](SbF$_6$) (1a). The chloride complex Cp*IrCl[κ^2(*N*,*C*)-{NH$_2$C(CH$_3$)$_2$-2-C$_6$H$_4$}] (359.1 mg, 0.722 mmol), $AgSbF_6$ (252.5 mg, 0.735 mmol), and acetonitrile (0.5 mL) were added to a CH_2Cl_2 solution (5.0 mL) at room temperature. After the reaction mixture was stirred for 1 h at room temperature, a yellow suspension was dried under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 and filtrated through a Celite pad. Removal of solvents gave the crude product. Recrystallization from CH_2Cl_2 and ether gave pale yellow crystals (360.1 mg, 67% yield). ^{1}H NMR (399.8 MHz, CD_2Cl_2, RT): δ 1.46 (br, 6H; NH$_2$C(C*H*$_3$)$_2$C$_6$H$_4$), 1.75 (s, 15H; C$_5$(C*H*$_3$)$_5$), 2.42 (s, 3H; C*H*$_3$CN), 4.20 (br, 2H; N*H*$_2$C(CH$_3$)$_2$C$_6$H$_4$), 6.83−7.44 (m, 4H; NH$_2$C(CH$_3$)$_2$C$_6$*H*$_4$) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, RT): δ 4.1 (*C*H$_3$CN), 9.1 (C$_5$(*C*H$_3$)$_5$), 31.0 (NH$_2$C(*C*H$_3$)$_2$C$_6$H$_4$), 67.8 (NH$_2$*C*(CH$_3$)$_2$C$_6$H$_4$), 90.0 (*C*$_5$(CH$_3$)$_5$), 118.7, 122.5, 124.2, 127.6, 136.1, 147.1, 156.7 ppm. IR (KBr) ν: 3327, 3282, 3051, 3038, 2969, 2928, 2331, 1592, 1578, 1455, 1429, 1386, 1367, 1284, 1255, 1168, 1118, 1077, 1026, 946, 864, 763, 741, 655 cm^{-1}. Anal. Calcd for $C_{21}H_{30}F_6N_2IrSb$: C, 34.16; H, 4.09; N, 3.79. Found: C, 34.01; H, 4.06; N, 3.74.

Synthesis of [Cp*Ir(NCCH$_3$){κ^2(*N*,*C*)-(NH$_2$C(C$_6$H$_5$)$_2$-2-C$_6$H$_4$)}](SbF$_6$) (1b). The chloride complex Cp*IrCl[κ^2(*N*,*C*)-{NH$_2$C(C$_6$H$_5$)$_2$-2-C$_6$H$_4$}] (399.4 mg, 0.643 mmol), $AgSbF_6$ (262.0 mg, 0.763 mmol), and acetonitrile (0.6 mL) were added to a CH_2Cl_2 solution (6.0 mL) at room temperature. After the reaction mixture was stirred for 1 h at room temperature, a yellow suspension was dried under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 and filtrated through a Celite pad. Removal of solvents gave the crude product. Recrystallization from CH_2Cl_2 and ether gave pale yellow crystals (360.1 mg, 67% yield). ^{1}H NMR (399.8 MHz, CD_2Cl_2, RT): δ 1.46 (s, 15H; C$_5$(C*H*$_3$)$_5$), 2.51 (s, 3H; C*H*$_3$CN), 5.32 (br, 2H; N*H*$_2$C(C$_6$H$_5$)$_2$C$_6$H$_4$), 6.32−7.58 (m, 14H; NH$_2$C(C$_6$*H*$_5$)$_2$C$_6$*H*$_4$) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, −30 °C): δ 4.4 (*C*H$_3$CN), 8.4 (C$_5$(*C*H$_3$)$_5$), 80.6 (NH$_2$*C*(C$_6$H$_5$)$_2$C$_6$H$_4$), 90.0 (*C*$_5$(CH$_3$)$_5$), 119.0, 123.4, 127.5, 127.8, 128.0, 128.2, 128.6, 128.9, 128.97, 129.00, 136.3, 143.7, 146.4, 150.4, 154.2 ppm. IR (KBr) ν: 3340, 3287, 3059, 2991, 2920, 2330, 1970, 1909, 1820, 1568, 1494, 1446, 1383, 1293, 1272, 1235, 1157, 1082, 1049, 1032, 1001, 980, 917, 862, 848, 768, 754, 738, 706, 658 cm^{-1}. Anal. Calcd for $C_{31}H_{34}F_6N_2IrSb$: C, 43.16; H, 3.97; N, 3.25. Found: C, 43.04; H, 3.88; N, 3.20.

Synthesis of [Cp*Rh(NCCH$_3$){κ^2(*N*,*C*)-(NH$_2$C(CH$_3$)$_2$-2-C$_6$H$_4$)}](SbF$_6$) (2a). The chloride complex Cp*RhCl[κ^2(*N*,*C*)-{NH$_2$C(CH$_3$)$_2$-2-C$_6$H$_4$}] (177.6 mg, 0.436 mmol), $AgSbF_6$ (158.9 mg, 0.462 mmol), and acetonitrile (0.2 mL) were added to a CH_2Cl_2 solution (5.0 mL) at room temperature. After the reaction mixture was stirred for 1 h at room temperature, a yellow suspension was dried under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 and filtrated through a Celite pad. Removal of solvents gave the crude product. Recrystallization from CH_2Cl_2 and ether gave orange crystals (217.5 mg, 77% yield). ^{1}H NMR (399.8 MHz, CD_2Cl_2, RT): δ 1.45 (br, 6H; NH$_2$C(C*H*$_3$)$_2$C$_6$H$_4$), 1.70 (s, 15H; C$_5$(C*H*$_3$)$_5$), 2.27 (s, 3H; C*H*$_3$CN), 3.62 (br, 2H; N*H*$_2$C(CH$_3$)$_2$C$_6$H$_4$), 6.80−7.44 (m, 4H; NH$_2$C(CH$_3$)$_2$C$_6$*H*$_4$) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, RT): δ 3.9 (*C*H$_3$CN), 9.5 (C$_5$(*C*H$_3$)$_5$), 31.5 (NH$_2$C(*C*H$_3$)$_2$C$_6$H$_4$), 65.6 (NH$_2$*C*(CH$_3$)$_2$C$_6$H$_4$), 97.3 (*C*$_5$(CH$_3$)$_5$, $^1J_{CRh}$ = 5.7 Hz), 122.8, 122.9, 124.5, 127.7, 136.0, 157.0, 162.8 (NH$_2$C(CH$_3$)$_2$*C*$_6$H$_4$, $^1J_{CRh}$ = 27.8 Hz) ppm. IR (KBr) ν: 3336, 3289, 3036, 2969, 2930, 2315, 2286,1590, 1574, 1523, 1451,1427, 1385, 1367, 1307, 1281, 1254, 1180,1146, 1110, 1077, 1021, 947, 865, 762, 736, 657 cm^{-1}. Anal. Calcd for $C_{21}H_{30}F_6N_2RhSb$: C, 38.86; H, 4.66; N, 4.32. Found: C, 38.59; H, 4.67; N, 4.10.

Synthesis of [Cp*Rh(NCCH$_3$){κ^2(*N*,*C*)-(NH$_2$C(C$_6$H$_5$)$_2$-2-C$_6$H$_4$)}](SbF$_6$) (2b). Cp*RhCl[κ^2(*N*,*C*)-{NH$_2$C(C$_6$H$_5$)$_2$-2-C$_6$H$_4$}] (279.5 mg, 0.526 mmol), $AgSbF_6$ (193.0 mg, 0.5617 mmol), and acetonitrile (0.5 mL) were added to a CH_2Cl_2 solution (5.0 mL) at room temperature. After the reaction mixture was stirred for 1 h at room temperature, a yellow suspension was dried under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 and filtrated through a Celite pad. Removal of solvents gave the crude product. Recrystallization from CH_2Cl_2 and ether gave orange crystals (293.4 mg, 72% yield). ^{1}H NMR (399.8 MHz, CD_2Cl_2, RT): δ 1.41 (s, 15H; C$_5$(C*H*$_3$)$_5$), 2.33 (s, 3H; C*H*$_3$CN), 4.58−4.74 (br, 2H; N*H*$_2$C(C$_6$H$_5$)$_2$C$_6$H$_4$), 6.27−7.59 (m, 14H; NH$_2$C(C$_6$*H*$_5$)$_2$C$_6$*H*$_4$) ppm. ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, −30 °C): δ 4.1 (*C*H$_3$CN), 8.7 (C$_5$(*C*H$_3$)$_5$), 78.1 (NH$_2$*C*(CH$_3$)$_2$C$_6$H$_4$), 97.2 (*C*$_5$(CH$_3$)$_5$, J_{CRh} = 5.8 Hz), 123.1 (*C*H$_3$CN, $^2J_{CRh}$ = 6.7 Hz), 123.7, 127.9 (overlapped), 128.6, 128.7, 128.9, 129.1, 136.3, 144.2, 146.9, 154.3, 166.2 (NH$_2$C(CH$_3$)$_2$*C*$_6$H$_4$, $^1J_{CRh}$ = 28.7 Hz) ppm. IR (KBr) ν: 3351, 3296, 3058, 3035, 2987, 2919, 2318, 2288, 1573, 1514, 1492, 1444, 1379, 1228, 1132, 1042, 1024, 768, 754, 734, 705, 657 cm^{-1}. Anal. Calcd for $C_{31}H_{34}F_6N_2RhSb$: C, 48.15; H, 4.43; N, 3.62. Found: C, 48.14; H, 4.45; N, 3.73.

Formation of Hydrido(amine)iridium Complex 4 by Treatment of Cationic Iridium Complex 1b and H$_2$. An NMR tube equipped with a J-Young valve was loaded with **1b** (7.0 mg, 8.1 × 10^{-3} mmol) and triethylamine (0.8 mg, 7.9 × 10^{-3} mmol) in 0.50 mL of THF-d_8. After the solution was degassed via freeze−pump−thaw cycles, the system was then filled with H_2 at room temperature for 20 min. The ^{1}H NMR spectrum acquired immediately afterward at room temperature showed the formation of **4**.

NMR Monitoring of a Mixture of Amidoiridium Complex and H$_2$. An NMR tube equipped with a J-Young valve was loaded with Cp*Ir[κ^2(*N*,*C*)-{NHC(C$_6$H$_5$)$_2$-2-C$_6$H$_4$}] (4.3 mg, 7.3 × 10^{-3} mmol) in 0.50 mL of THF-d_8, and the solution was degassed via freeze−pump−thaw cycles with liquid nitrogen. After the NMR tube was then filled with H_2 at room temperature for 20 min, ^{1}H NMR spectra were recorded.

General Procedure for Hydrogenation of *N*-(1-Phenylethylidene)benzylamine. In a typical experiment, a 50 mL stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer was loaded with the cationic complex **1a** (1.0 × 10^{-2} mmol), *N*-(1-phenylethylidene)benzylamine (209 mg, 1.00 mmol), and 4A molecular sieves (0.4 g) under an argon atmosphere. After the loading of $AgSbF_6$ (10.3 mg, 3.0 × 10^{-2} mmol) in 2-propanol (2 mL), the autoclave was flushed with H_2 and then pressurized to 3.0 MPa. The reaction mixture was stirred in a water bath at 30 °C for 2 h. After carefully venting hydrogen, a sample of the reaction mixture was passed through a small amount of Celite and dried under reduced pressure. The yield was determined by ^{1}H NMR using triphenylmethane (244.3 mg, 1.00 mmol) as an internal standard.

General Procedure for Hydrogenation of Nitriles. In a typical experiment, a 50 mL stainless steel autoclave equipped with a pressure gauge and a magnetic stirrer was loaded with the cationic complex (1.0 × 10^{-2} mmol), the nitrile substrate **5** (1.00 mmol), and 4A molecular sieves (0.4 g) under an argon atmosphere. After the loading of $AgSbF_6$ (13.7 mg, 4.0 × 10^{-2} mmol) in THF (2 mL) and triethylamine (5.1 mg, 5.0 × 10^{-2} mmol), the autoclave was flushed with H_2 and then pressurized to 1.0 MPa. The reaction mixture was stirred in a water bath at 60 °C. After carefully venting hydrogen, a sample of the reaction mixture was passed through a small amount of Celite and dried under reduced pressure. The yield of **6a** was determined by ^{1}H NMR using triphenylmethane (24.4 mg, 0.100 mmol) as an internal standard. Other product amines **6b−i** were obtained after purification by a recycling preparative HPLC.

Spectroscopic Data of *N*,*N*-Bis[{4-(1,1-ethylenedioxy)ethyl}-phenyl]amine (6f). Isolated yield: 67% yield. ^{1}H NMR (399.8 MHz, $CDCl_3$, RT): δ 1.64 (s, 6H; CH_3), 3.75−3.76 (m, 4H; O CH_2 CH_2O), 3.80 (s, 4H; CH_2), 4.01−4.02 (m, 4H; O CH_2 CH_2O), 7.31, 7.43 (each d, 4H; C_6H_4, $^3J_{HH}$ = 8.3 Hz). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, RT): δ 27.7,

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52.8, 64.5, 108.9, 125.5, 128.2, 139.5, 142.2. HR-ESI-MS (ESI+): m/z 370.2032 $[M + H]^+$ (m_{theor} = 370.2018).

X-ray Structure Determination of 1a, 1b, 2a, and 2b. All measurements were performed using a Rigaku Saturn CCD area detector equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 70 Å) under a nitrogen stream at 193 K. Indexing was performed from seven images. The crystal-to-detector distance was 45.05 mm. Data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of the data was carried out by using ω scans from −110.0° to 70.0° in 0.5° steps at χ = 45.0° and ϕ = 0.0°. A second sweep was performed by using ω scans from −110.0° to 70.0° in 0.5° steps at χ = 45.0° and ϕ = 90.0°. Intensity data were collected for the Lorentz−polarization effects as well as for the absorption. Structure solution and refinement were performed using the CrystalStructure program package. The heavy-atom positions were determined by a direct-program method (SIR2002), and the remaining non-hydrogen atoms were determined by the subsequent use of Fourier techniques (DIRDIF99). An empirical absorption correction based on equivalent reflections was applied to all data. All non-hydrogen atoms were refined anisotropically by full-matrix least-squared techniques based on F^2. All hydrogen atoms were constrained to be attached to their parent atom. The relevant crystallographic data are compiled in Tables S1 and S2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00133.

Text and figures giving characterization data and NMR spectra for new compounds (PDF)

Crystallographic data for **1a**, **1b**, **2a**, and **2b** (CIF)

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Notes

The authors declare no competing financial interest.

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