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Indenyl Rhodium Complexes with Arene Ligands: Synthesis and Application for Reductive Amination

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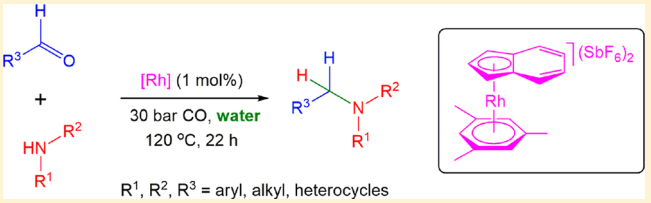
Supporting Information

ABSTRACT: An efficient protocol for synthesis of indenyl rhodium complexes with arene ligands has been developed. The hexafluoroantimonate salts $[(\eta^5\text{-indenyl})\text{Rh(arene)}](SbF_6)_2$ (arene = benzene (**2a**), *o*-xylene (**2b**), mesitylene (**2c**), durene (**2d**), hexamethylbenzene (**2e**), and [2.2]-paracyclophane (**2g**)) were obtained by iodide abstraction from $[(\eta^5\text{-indenyl})RhI_2]_n$ (**1**) with $AgSbF_6$ in the presence of benzene and its derivatives. The procedure is also suitable for the synthesis of the dirhodium arene complex $[(\mu\text{-}\eta\text{:}\eta'\text{-1,3-dimesitylpropane})\{Rh(\eta^5\text{-indenyl})\}_2](SbF_6)_4$ (**3**) starting from 1,3-dimesitylpropane. The structures of $[\mathbf{2e}](SbF_6)_2$, $[\mathbf{2g}](SbF_6)_2$, and $[\mathbf{3}](SbF_6)_4$ were determined by X-ray diffraction. The last species has a sterically unfavorable conformation, in which the bridgehead carbon atoms of the indenyl ligand are arranged close to the propane linker between two mesitylene moieties. Experimental and DFT calculation data revealed that the benzene ligand in **2a** is more labile than that in the related cyclopentadienyl complexes $[(C_5R_5)Rh(C_6H_6)]^{2+}$. Complex **2c** effectively catalyzes the reductive amination reaction between aldehydes and primary (or secondary) amines in the presence of carbon monoxide, giving the corresponding secondary and tertiary amines in very high yields (80–99%). This protocol is the most active in water.



INTRODUCTION

The catalytic applications of indenyl metal complexes are well-known.[1] For example, Gimeno and co-workers[2] have shown that the ruthenium derivative $(\eta^5\text{-indenyl})\text{Ru(cod)Cl}$ effectively catalyzes the cycloaddition reactions and hydration of alkynes, with yields and selectivity being considerably higher than those in the reactions catalyzed by cyclopentadienyl congeners.

The enhanced catalytic activity of indenyl complexes in comparison to cyclopentadienyl analogs is attributed to easy slippage of the indenyl ligand from an η^5 to an η^3 coordination mode (the so-called indenyl effect).[3] The structural flexibility of the indenyl ligand facilitates the ligand substitution and catalytic reactions. In addition, the indenyl moiety can play the role of a sterical bulky ligand in the chiral reactions. For example, the heptamethylindenyl rhodium complex $[(\eta^5\text{-}C_9Me_7)RhCl_2]_2$ proved to be an effective catalyst for the diastereoselective coupling of O-substituted arylhydroxamates and cyclopropenes.[4] Though it has been a very long time since the indenyl effect was discovered by Hart-Davis and Mawby in 1969,[5] the indenyl complexes of transition metals are still poorly studied in catalysis, which can be explained by their limited commercial availability. Therefore, the development of effective synthetic methods to prepare indenyl complexes is a very important challenge of organometallic chemistry.

At the same time, the strongly bonded halide anions can decrease the activity of the catalyst by blocking of vacant coordination sites at the metal atom. In general, the use of silver salts as halogen scavengers is necessary for the generation of catalytically active species.[6] In contrast, more weakly bonded neutral ligands, e.g. carbonyl, acetonitrile, olefins, and arenes, do not have this disadvantage due to their easy thermal lability.[7] To the best of our knowledge, indenyl rhodium complexes with arenes are known only for the 1,2,3,4,7-pentamethylindenyl ligand.[8] In particular, we have found earlier that the benzene complex $[(\eta^5\text{-}C_9H_2Me_5)Rh(C_6H_6)]^{2+}$ shows moderate catalytic activity in the oxidative coupling of benzoic acid with diphenylacetylene, giving 1,2,3,4-tetraphenylnaphthalene.[9] Herein we report the synthesis of parent arene rhodium complexes with an unsubstituted indenyl ligand and their application in catalytic reductive amination of aldehydes.

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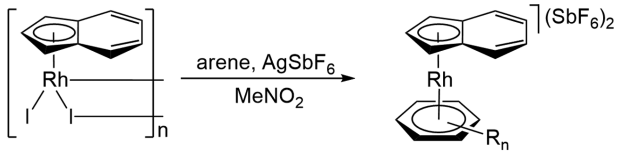
Very recently, we have found that the iodide $[(\eta^5\text{-indenyl})RhI_2]_n$ (**1**) has high catalytic activity in the reductive amination of aldehydes or ketones in the presence of carbon monoxide as a reducing agent.[10] The classical two-step synthesis of amines includes Schiff base formation and its subsequent hydrogenation. The method where CO is used as a reducing agent instead of H_2 gas or hydride reagents has a number of advantages in comparison with the classical method. In the first place, it provides high selectivity due to the absence of an external hydrogen source, which makes hydrogenation of functional groups present in the substrates impossible.[11−13] Second, carbon monoxide, the reducing agent in the aforementioned method, is widely available and inexpensive in comparison to hydride reducing agents such as $NaBH_3CN$. Moreover, the method is highly atom economical and the only stochiometric byproduct is carbon dioxide. CO-mediated reductive addition has been applied to the synthesis of a number of practically important compounds, including chiral ligands[14] and drugs.[15,16]

However, in terms of green chemistry atom economy has been the only advantage of this reductive amination reaction until now. Moreover, from an ecological point of view it had a serious disadvantage—low yields of the desired amines if the experiment is conducted in ecologically friendly solvents. Surprisingly, with the use of the new indenyl rhodium complexes as catalysts for the reductive amination, various solvents were tested and water was found to be the best solvent for the reaction among them. Using this approach, we were able to prepare both aliphatic and aromatic amines.

RESULTS AND DISCUSSION

Synthesis and Reactivity. Recently, we have shown that iodide complex **1** is a useful synthon of the $(\eta^5$-indenyl)Rh fragment, as illustrated by the preparation of the cyclopentadienyl derivatives and rhodacarboranes.[10,17] In the present study, we used **1** for the synthesis of arene complexes. Thus, iodide abstraction from **1** by $AgSbF_6$ in the presence of benzene or its derivatives in nitromethane gives the dicationic mononuclear arene complexes $[(\eta^5$-indenyl)Rh(arene)$](SbF_6)_2$ ($[\mathbf{2a–e}](SbF_6)_2$, Scheme 1). Apparently, the reaction

Scheme 1. Synthesis of the Mononuclear Arene Complexes $[\mathbf{2a–e}](SbF_6)_2$

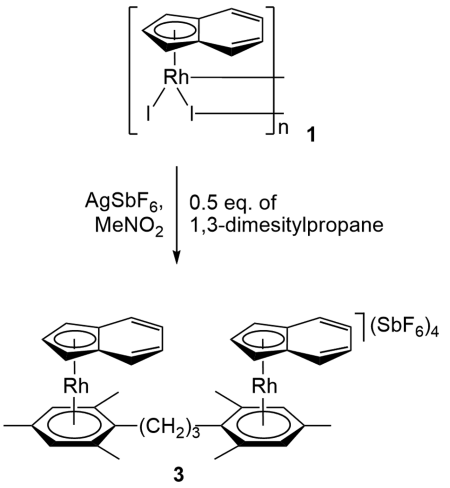


R_n = H (**a**); 1,2-Me_2 (**b**); 1,3,5-Me_3 (**c**); 1,2,4,5-Me_4 (**d**); Me_6 (**e**)

proceeds via intermediate formation of the nitromethane solvate $[(\eta^5$-indenyl)Rh$(MeNO_2)_3](SbF_6)_2$[18] which is an analogue of the well-known cyclopentadienyl derivatives $[(\eta^5\text{-}C_5R_5)Rh(MeNO_2)_3]^{2+}$.[19] However, the step-by-step procedure with preliminary generation of the solvate (due to its low stability) did not give the desired arene complexes. It is worth noting that the nature of the counterion significantly affects the outcome of the reaction. For example, arene complexes were not obtained with the use of silver salts with nucleophilic anions, e.g. AgOAc and AgOTf, instead of $AgSbF_6$. The use of $AgBF_4$ or $AgPF_6$ leads to the desired products, but in lower yields and in impure form. We propose that these products are contaminated by solvate complexes which may be formed as a result of arene replacement with the assistance of the counterion.

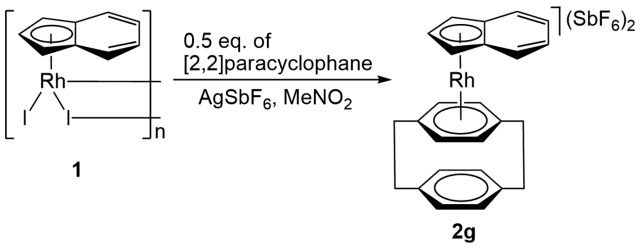
Further investigation showed that this procedure is also suitable for the synthesis of the dinuclear complex $[(\mu\text{-}\eta\text{:}\eta'\text{-}1,3\text{-dimesitylpropane})\{Rh(\eta^5\text{-indenyl})\}_2](SbF_6)_4$ ($[\mathbf{3}](SbF_6)_4$), in which two $(\eta^5$-indenyl)Rh fragments are coordinated to different aromatic rings (Scheme 2). An attempt to prepare

Scheme 2. Synthesis of the Dinuclear Arene Complex $[\mathbf{3}](SbF_6)_4$



the mononuclear complex $[(\eta^5$-indenyl)Rh(1,3-dimesitylpropane)$](SbF_6)_2$ ($[\mathbf{2f}](SbF_6)_2$) by using a 4-fold excess of 1,3-dimesitylpropane led to formation of an inseparable mixture of $[\mathbf{2f}](SbF_6)_2$ and $[\mathbf{3}](SbF_6)_4$ in a 2:1 ratio. At the same time, the reaction of an excess of **1** with [2.2]paracyclophane exclusively leads to the mononuclear complex $[(\eta^5$-indenyl)Rh([2.2]paracyclophane)$](SbF_6)_2$ ($[\mathbf{2g}](SbF_6)_2$), in which one of the aromatic rings remains uncoordinated (Scheme 3).

Scheme 3. Reaction of 1 with [2.2]Paracyclophane



The arene complexes $[\mathbf{2a–g}](SbF_6)_2$ and $[\mathbf{3}](SbF_6)_4$ are indefinitely stable in the solid state, but they readily undergo solvolysis by coordinating solvents (such as acetone, acetonitrile, and dimethyl sulfoxide) with elimination of free arene, indicating substitutional lability of the arene ligand. Higher lability of the arene can have a good effect on the catalytic activity. The arene exchange reaction, in which one arene ligand is replaced by another arene, is well-known for rhodium complexes.[20] In particular, examples of such reactions have been described for cyclopentadienyl, carborane, and

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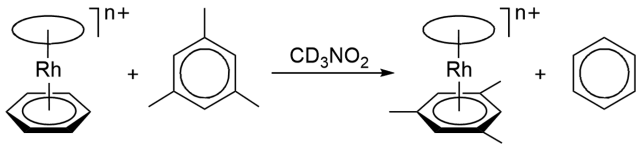
triple-decker derivatives. To estimate the lability of arene ligand in the indenyl complexes, we carried out the comparative ^{1}H NMR study of arene exchange in the benzene derivatives [**2a**](SbF$_6$)$_2$, [**2a**](BF$_4$)$_2$, and related rhodium complexes (Table 1). The reaction of the complex with an excess of mesitylene in nitromethane-d_3 was chosen as a model.

Table 1. Comparative Study of Arene Exchange in [2a](SbF$_6$)$_2$, [2a](BF$_4$)$_2$, and Related Rhodium Complexes[a]



entry	complex	time, h	conversion,[b] %
1	[**2a**](SbF$_6$)$_2$	5	17
2	[**2a**](SbF$_6$)$_2$	24	74
3	[**2a**](BF$_4$)$_2$	5	32
4	[**2a**](BF$_4$)$_2$	24	92
5	[Cp*Rh(C$_6$H$_6$)](SbF$_6$)$_2$	5	8
6	[Cp*Rh(C$_6$H$_6$)](SbF$_6$)$_2$	48	61
7	[Cp*Rh(C$_6$H$_6$)](BF$_4$)$_2$	5	53
8	[CpRh(C$_6$H$_6$)](BF$_4$)$_2$	5	9
9	[(C$_9$H$_2$Me$_5$)Rh(C$_6$H$_6$)](BF$_4$)$_2$[c]	5	62
10	[CpCo(μ-1,3-C$_3$B$_2$Me$_5$)Rh(C$_6$H$_6$)](BF$_4$)$_2$	5	<1
11	[(7,8-C$_2$B$_9$H$_{11}$)Rh(C$_6$H$_6$)]BF$_4$	5	44
12	[(9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)Rh(C$_6$H$_6$)](BF$_4$)$_2$	5	49[d]

[a]Reagents and conditions: rhodium complex (0.016 mmol), mesitylene (0.14 mmol), nitromethane-d_3 (0.5 mL), room temperature. [b]Determined by ^{1}H NMR spectroscopy. [c]C$_9$H$_2$Me$_5$ denotes 1,2,3,4,7-pentamethylindenyl. [d]Significant decomposition of the carborane derivative was observed.

It was found that the benzene ligand in the indenyl complexes is more labile than in the cyclopentadienyl analogs (Table 1, entry 3 vs entry 8 as well as entry 9 vs entry 7). In general, the methylated derivatives have a higher rate of the arene exchange in comparison with the parent analogs (entry 7 vs entry 8 as well as entry 9 vs entry 3) that can be explained by the highest dissociation energies of the Rh−C$_6$H$_6$ bond for the parent compounds (vide infra). The carborane and triple-decker derivatives showed lower reactivity in the arene exchange reaction in comparison to the cyclopentadienyl and indenyl complexes (entries 10−12 vs entries 7 and 9). In general, the salts with a tetrafluoroborate anion are considerably more reactive than those with a hexafluoroantimonate anion (entry 3 vs entry 1 as well as entry 7 vs entry 5), suggesting the crucial participation of counterions in replacement of the arene ligand.[21] The latter is in accordance with the difficulty in isolating cations **2a−e** as salts with the BF$_4^-$ anion in pure form (vide supra).

Recently, we have shown that the thermal arene exchange in the (indenyl)iron complexes [(η^5-indenyl)Fe(arene)]$^+$ proceeds by an associative mechanism via arene slippage from η^6 to η^3 coordination mode rather than indenyl slippage.[21e] We consider that the rhodium complexes undergo arene exchange in the same manner. Otherwise, methyl groups in the indenyl ligand should suppress the indenyl slippage and thereby decrease the reaction rate. However, the methylated complex [(C$_9$H$_2$Me$_5$)Rh(C$_6$H$_6$)](BF$_4$)$_2$ proved to be more reactive than the parent analog [**2a**](BF$_4$)$_2$ (Table 1, entry 9 vs entry 3).

To elucidate the influence of the ligand at the rhodium atom on the Rh−C$_6$H$_6$ bonding, we performed energy decomposition analysis (EDA)[22] for **2a** and the related rhodium complexes (Table 2). According to the EDA method, the interaction energy between the bonding fragments ΔE_{int} can be divided into three main components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

ΔE_{elstat} is the electrostatic interaction energy between the fragments with a frozen electron density distribution, ΔE_{Pauli} presents the repulsive four-electron interactions between occupied orbitals (Pauli repulsion), and ΔE_{orb} refers to the stabilizing orbital interactions. The ratio $\Delta E_{elstat}/\Delta E_{orb}$ indicates the electrostatic/covalent character of the bond. The bond dissociation energy D_e is defined as

$$D_e = -(\Delta E_{int} + \Delta E_{prep})$$

where ΔE_{prep} (the fragment preparation energy) is the energy that is necessary to promote the fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state that they have in the optimized structure.

We found that in agreement with the highest reactivity of the indenyl complexes in the arene exchange reaction they have weaker Rh−C$_6$H$_6$ bond than cyclopentadienyl analogs (Table 2, entries 1 and 2 vs entries 3 and 4). The loosening of the bond is mainly caused by the decrease in orbital interactions and the increase in Pauli repulsion. The introduction of methyl groups in the indenyl ring leads to the following decrease of ΔE_{orb} and thereby ΔE_{int} (entry 2 vs entry 1). The decrease in ΔE_{orb} upon methylation can be explained by the decrease in benzene-to-rhodium donation. The ΔE_{int} values correlate well with the dissociation energies, since the preparation energy is almost the same in all cases. Surprisingly, EDA data for complexes with boron-heterocyclic

Table 2. Results of EDA (Energy Values in kcal mol^{-1}) of Cations [(L)Rh(C$_6$H$_6$)]$^{n+}$ Using [(L)Rh]$^{n+}$ and C$_6$H$_6$ as Interacting Fragments at the BP86/TZP Level

entry	L	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}[a]	ΔE_{orb}[a]	ΔE_{prep}	D_e
1	indenyl (**2a**)	−81.27	118.46	−83.03 (41.6)	−116.70 (58.4)	2.97	78.30
2	C$_9$H$_2$Me$_5$	−62.59	115.12	−80.28 (45.2)	−97.42 (54.8)	2.80	59.79
3	Cp	−102.53	113.72	−81.48 (37.7)	−134.76 (62.3)	3.24	99.29
4	Cp*	−68.81	108.71	−76.95 (43.3)	−100.57 (56.7)	2.59	66.22
5	CpCo(μ-1,3-C$_3$B$_2$Me$_5$)	−62.19	115.45	−78.85 (44.4)	−98.79 (55.6)	3.83	58.36
6	7,8-C$_2$B$_9$H$_{11}$	−54.46	117.95	−81.50 (47.3)	−90.90 (52.7)	4.69	49.77
7	9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$	−69.77	111.24	−77.77 (43)	−103.24 (57.0)	6.30	63.47

[a]The values in parentheses give the percentage contribution to the total attractive interactions.

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and carborane ligands (entries 5−7) did not agree with the experimental data. For example, the rhodacarborane $[(7,8\text{-}C_2B_9H_{11})Rh(C_6H_6)]^+$ with the weakest Rh−C_6H_6 bond had lower reactivity in the arene exchange in comparison with the indenyl and cyclopentadienyl complexes, which can be explained by kinetic factors due to better positive charge delocalization in polyhedral compounds.[20d]

X-ray Diffraction. The structures of $[\mathbf{2e}](SbF_6)_2$, $[\mathbf{2g}](SbF_6)_2$, and $[\mathbf{3}](SbF_6)_4$ were determined by X-ray diffraction (Figures 1−3). In $[\mathbf{2e}](SbF_6)_2$, the cations pack into infinite columns bound by the anions into the 3D framework by a number of weak C−H···F contacts. The latter are supported by F···π contacts with indenyl rings, the smallest C···F distance being 2.930 Å. In $[\mathbf{3}](SbF_6)_4$, only cation−anion interactions contribute to the crystal formation: most of them are C−H···F contacts with a F···π interaction involving the indenyl rings (C···F 3.121 Å).

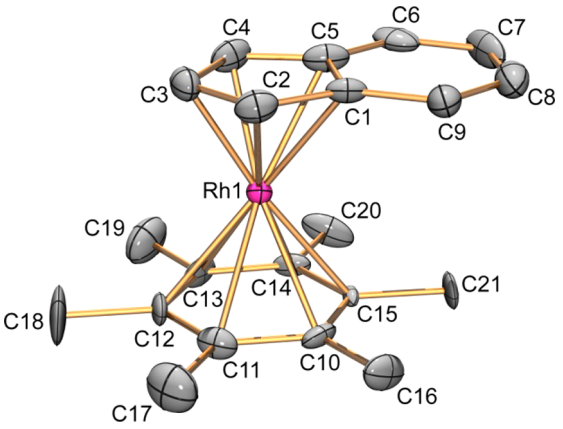

Figure 1. Crystal structure of complex $[\mathbf{2e}](SbF_6)_2$ with 50% thermal ellipsoids. Counterions and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Rh1−C1 2.230(7), Rh1−C2 2.131(8), Rh1−C3 2.047(9), Rh1−C4 2.082(8), Rh1−C5 2.207(8), Rh1−C10 2.285(7), Rh1−C11 2.317(7), Rh1−C12 2.333(8), Rh1−C13 2.314(7), Rh1−C14 2.284(7), Rh1−C15 2.238(7), C1−C2 1.408(12), C1−C5 1.506(11), C2−C3 1.407(11), C3−C4 1.418(11), C4−C5 1.406(13).

The indenyl ligand in these complexes is almost planar; the hinge angles[23,24] are 0.1, 3.2, and 3.5°, respectively. At the same time, the slip parameter,[21e,24,25] which is used to describe the slip-fold distortion in the indenyl complexes, has a considerably higher value for the hexamethylbenzene derivative $[\mathbf{2e}](SbF_6)_2$ (0.13 Å) in comparison with other complexes (0.07 for $[\mathbf{2g}](SbF_6)_2$ and $[\mathbf{3}](SbF_6)_4$), which can be expected from the higher steric hindrance of hexamethylbenzene.

The Rh···C_6Me_6 distance in $[\mathbf{2e}](SbF_6)_2$ (1.78 Å) is also longer than the same distance in the cyclopentadienyl analog $[CpRh(C_6Me_6)](BF_4)_2$ (1.689 Å),[19b] suggesting weaker bonding of hexamethylbenzene with the $[Rh(\eta^5\text{-indenyl})]^{2+}$ fragment than with $[RhCp]^{2+}$. In contrast, the Rh···indenyl and Rh···Cp distances in these complexes are very close (1.76 Å).

Both benzene rings of the paracyclophane ligand in cation **2g** deviate from planarity toward a boat conformation, similar to the case for the free ligand[26] and its known complexes.[27] The C−C bonds of the coordinated six-membered ring (average 1.42 Å) are slightly longer than those of the uncoordinated ring (average 1.40 Å) due to the loosening of π bonds upon coordination. In contrast to hexamethylbenzene

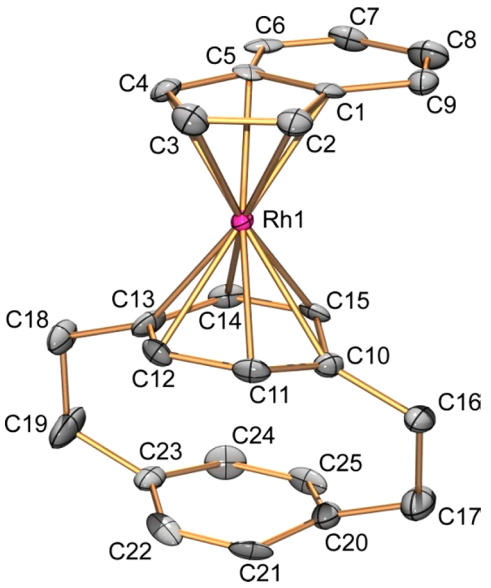

Figure 2. Crystal structure of complex $[\mathbf{2g}](SbF_6)_2$ with 50% thermal ellipsoids. Counterions and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Rh1−C1 2.233(9), Rh1−C2 2.169(9), Rh1−C3 2.167(9), Rh1−C4 2.145(9), Rh1−C5 2.221(9), Rh1−C10 2.411(10), Rh1−C11 2.209(9), Rh1−C12 2.227(9), Rh1−C13 2.359(11), Rh1−C14 2.220(9), Rh1−C15 2.213(9), C1−C2 1.434(14), C1−C5 1.460(14), C2−C3 1.412(14), C3−C4 1.503(13), C4−C5 1.410(14), C10−C11 1.405(13), C10−C15 1.426(13), C11−C12 1.443(14), C12−C13 1.437(12), C13−C14 1.394(15), C14−C15 1.407(15), C20−C21 1.409(15), C20−C25 1.407(14), C21−C22 1.365(15), C22−C23 1.394(15), C23−C24 1.448(15), C24−C25 1.359(16).

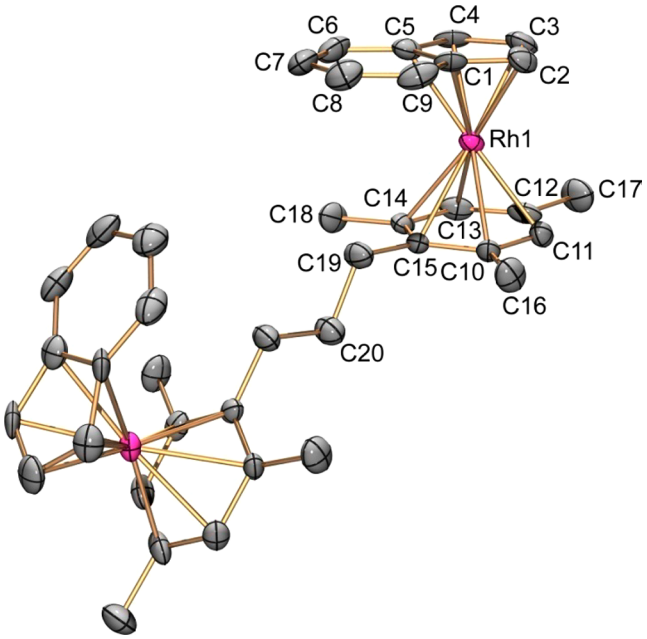

Figure 3. Crystal structure of complex $[\mathbf{3}](SbF_6)_4$ with 50% thermal ellipsoids. Counterions and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Rh1−C1 2.232(9), Rh1−C2 2.158(9), Rh1−C3 2.158(9), Rh1−C4 2.176(8), Rh1−C5 2.232(9), Rh1−C10 2.278(8), Rh1−C11 2.250(9), Rh1−C12 2.246(10), Rh1−C13 2.226(9), Rh1−C14 2.286(8), Rh1−C15 2.254(8), C1−C2 1.427(13), C1−C5 1.446(13), C2−C3 1.418(14), C3−C4 1.431(14), C4−C5 1.450(13).

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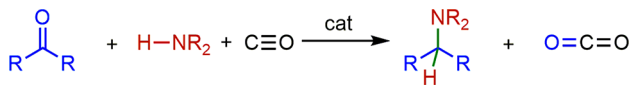
derivatives, the Rh···paracyclophane distance in $[\mathbf{2g}](SbF_6)_2$ (1.78 Å) is somewhat shorter than the corresponding distances in the related complexes [Cp*Rh([2.2]paracyclophane)]-$(BF_4)_2$ (1.805 Å)[27c] and $[(\eta\text{-}7,8\text{-}C_2B_9H_{11})Rh([2.2]\text{-}paracyclophane)]BF_4$ (1.817 Å).[20c]

Recently, we have found that (indenyl)rhodacarboranes adopt the sterically unfavorable eclipsed cisoid conformation, in which the bridgehead carbon atoms of the indenyl ligand are located close to the carborane cage carbon atoms.[17] This phenomenon was explained by the trans effect and the symmetry of molecular orbitals of indenyl and carborane ligands. Surprisingly, the arene dinuclear complex $[\mathbf{3}](SbF_6)_4$ also has a sterically unfavorable conformation, in which the bridgehead carbon atoms of the indenyl ligand are arranged close to the propane linker between two mesitylene moieties. As a result of the trans effect, the Rh1−C10, Rh1−C14, and Rh1−C15 bonds (average 2.27 Å) are considerably longer than the Rh1−C11, Rh1−C12, and Rh1−C13 bonds (average 2.24 Å). Nevertheless, we consider that the sterically unfavorable conformation in this case is due to crystal-packing effects rather than thermodynamic factors. In particular, this correlates well with the 2D ROESY NMR study of $[\mathbf{3}](SbF_6)_4$ (see Figure S8 in the Supporting Information), which showed the absence of spin interactions between the protons of the indenyl ligand and the propane linker.

Application to Direct Reductive Amination. Since reductive amination is one of the most convenient and versatile methods of C−N bond formation, we have investigated the catalytic activity of several rhodium complexes in the reductive amination reaction using carbon monoxide as a reducing agent (Scheme 4).[28] Such reductive amination does not need an external hydrogen source and has become one of the most selective approaches for the amine synthesis (even more selective than sodium cyanoborohydride).[11]

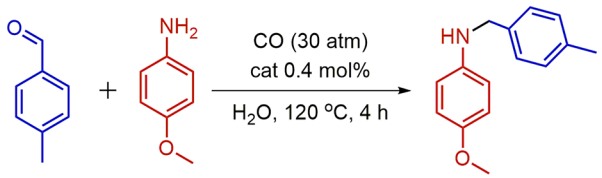
Scheme 4. Reductive Amination Using Carbon Monoxide as a Reducing Agent



However, usually this protocol does not work in water.[12,15] Even the water-gas shift reaction could not provide such a transformation in pure water.[29] Recently, we have reported the first example of such a transformation in water, which is important since it is a highly accessible, nontoxic, and nonflammable solvent.[10] Herein, we report that the new rhodium arene complexes are the most active species in such reactions.

As a model reaction we chose the reaction between *p*-tolylaldehyde and *p*-anisidine (Table 3). Since 1 mol % of the iodide complex **1** was shown to give full conversion in such a transformation,[10] we decided to decrease the catalyst loading to 0.4 mol %. Complex **1** gave only a 34% yield of the desired product. Screening of various indenyl rhodium complexes with arene ligands showed higher activity, in general (entries 2−8 vs entry 1). The mesitylene complex $[\mathbf{2c}](SbF_6)_2$ led to an 84% yield, and the use of the durene and [2.2]paracyclophane complexes $[\mathbf{2d}](SbF_6)_2$ and $[\mathbf{2g}](SbF_6)_2$ respectively led to 80% and 81% yields. The dimeric complex $[\mathbf{3}](SbF_6)_4$ also exhibited relatively high catalytic activity and furnished the product in 83% yield. However, the use of the hexamethylbenzene complex $[\mathbf{2e}](SbF_6)_2$ led to only a 57% yield of the desired amine (entry 4). This can be explained by the strong binding of the hexamethylbenzene ligand to the rhodium atom, which inhibits the removal of the arene ligand. Therefore, we can suggest that catalytic efficiency is limited by the stage of removal of the arene ligand. At the same time, a change of the counterion to BF_4^- did not have a significant effect on the yield (entries 7 and 8 vs entries 2−6). The benzene complex $[\mathbf{2a}](BF_4)_2$ furnished the desired amine in 68% yield. The methylated derivative $[(C_9H_2Me_5)Rh(C_6H_6)](BF_4)_2$ showed somewhat higher activity in comparison to the parent complex (entry 8 vs entry 7), which is in accordance with the lower dissociation energy of the Rh−C_6H_6 bond in the former (vide supra).

Table 3. Screening of Rhodium Complexes in Reductive Amination Reactions



entry	complex	yield, %
1	**1**	34
2	$[\mathbf{2c}](SbF_6)_2$	84
3	$[\mathbf{2d}](SbF_6)_2$	81
4	$[\mathbf{2e}](SbF_6)_2$	57
5	$[\mathbf{2g}](SbF_6)_2$	80
6	$[\mathbf{3}](SbF_6)_4$	83
7	$[\mathbf{2a}](BF_4)_2$	68
8	$[(C_9H_2Me_5)Rh(C_6H_6)](BF_4)_2$	79

The complex $[\mathbf{2c}](SbF_6)_2$ was used for the substrate scope screening. We found that aromatic and aliphatic aldehydes as well as aromatic and aliphatic amines (both primary and secondary) are suitable for the reaction. The methodology takes advantage of the unique deoxygenative potential of carbon monoxide, which enables full compatibility with a range of functional groups prone to reduction (e.g., *N*-benzyl and halocyclopropanes) (Figure 4).

On the basis of previous studies by our group[12,30] and that of Denmark,[31] we hypothesize that the cycle starts with the formation of hydroxide anion and ammonium cation (Figure 5). An intermolecular attack of hydroxide on the precatalytic species leads to intermediate **A**, and intramolecular attack on the carbonyl group leads to species **B**. Subsequent elimination of carbon dioxide yields hydride **C**, which reacts with an iminium cation/Schiff base, leading to the formation of the product. We believe that the key step of both processes involves changing the configuration of the complex from η^5 to η^3.

Attempts of C−H Activation. Finally, we tested the catalytic activity of indenyl arene complexes for the C−H activation of various aromatic substrates with directing group (such as −NHAc, −C(O)NHOBoc, and −C(O)OH). Unfortunately, it was found that even the most labile benzene derivative, $[\mathbf{2a}](SbF_6)_2$, exhibited very low reactivity (Scheme 5). For example, the reaction of acetanilide with 1-phenyl-1-propyne in dichloromethane at a 5.0 mol % loading of $[\mathbf{2a}](SbF_6)_2$ gave the corresponding indole derivative in 34% yield, which is comparable with that for the classical catalyst $[Cp^*RhCl_2]_2$[32] but is lower than that for the functionalized

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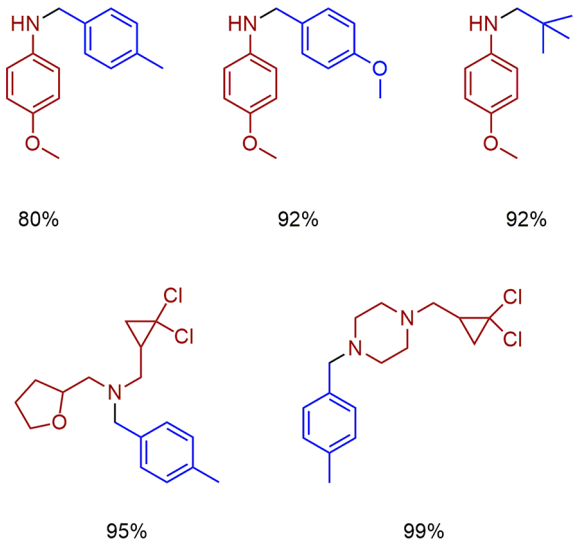


Figure 4. Products synthesized by reductive amination using carbon monoxide as the reducing agent and $[\mathbf{2c}](SbF_6)_2$ as the catalyst. Conditions: 120 °C, 30 bar of CO. Yields of amines are given for 1.0 mol % catalyst loading with the exception of 4-methoxy-*N*-(4-methylbenzyl)aniline, for which 0.4 mol % of the catalyst was employed.

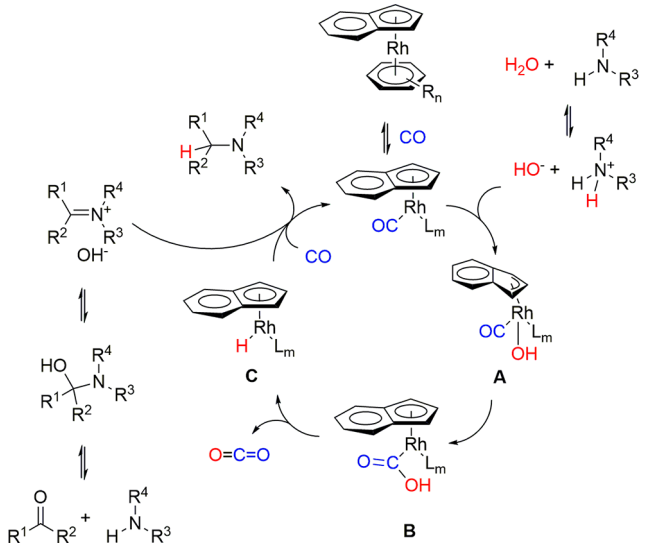
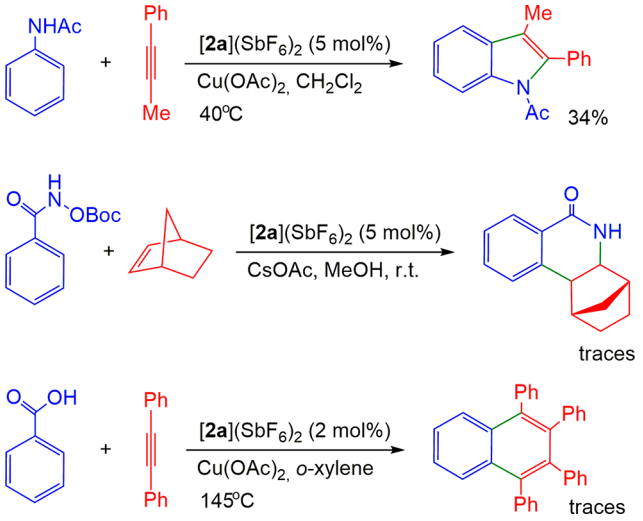


Figure 5. Plausible reaction mechanism. Counterions for the rhodium species are omitted for clarity.

indenyl derivative $[(\eta^5\text{-indenyl}^E)RhI_2]_2$ (indenyl^E is 1-(COOEt)-2-Me-3-benzylindenyl).[1c] The use of acetone or 1,2-dichloroethane as a solvent as well as the addition of KOAc, CsOAc, or KI did not improve the yield of the product. Similarly, the low catalytic activity of $[\mathbf{2a}](SbF_6)_2$ was observed for the couplings of O-Boc-phenylhydroxamic acid with norbornene[33] or benzoic acid with diphenylacetylene,[34] which gave only a trace amount of the corresponding dihydroisoquinolin-1-one or naphthalene, respectively. At the same time, the use of an equimolar quantity of $[\mathbf{2a}](SbF_6)_2$ in the last reaction increased the yield of naphthalene up to almost quantitative. Therefore, we can conclude that the low catalytic activity in C−H activation reactions is probably connected with the low stability of the catalytic species. A similar pattern was observed earlier for (indenyl)iridium and (cyclohexadienyl)rhodium complexes.[24c,35]

Scheme 5. Attempted C−H Activation Reactions



CONCLUSIONS

The reaction of the iodide complex $[(\eta^5\text{-indenyl})RhI_2]_n$ (**1**) with arenes in the presence of $AgSbF_6$ has been shown to be an effective method for the synthesis of mono- and binuclear indenyl rhodium complexes with arene ligands. The outcome of the reaction strongly depends on the nature of the counterion. For example, strongly nucleophilic anions, e.g. acetate and triflate anions, did not afford arene complexes, while the use of a non-nucleophilic hexafluoroantimonate anion allowed us to prepare the desired complexes in pure form. In accordance with the weaker Rh−C_6H_6 bonding in $[(\eta^5\text{-indenyl})Rh(C_6H_6)]^{2+}$ (**2a**) in comparison to that in cyclopentadienyl analogs, the cation **2a** readily undergoes an arene exchange reaction. Indenyl arene complexes proved to be the most active catalysts in the reaction of reductive amination with carbon monoxide in water. The methodology enables full compatibility with a range of functional groups prone to reduction (e.g., *N*-benzyl, PMB, halocyclopropanes).

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an argon atmosphere in anhydrous solvents, which were purified and dried using standard procedures. Isolation of all products was carried out in air. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 500.13 and 125.8 MHz, respectively. Chemical shifts are reported in ppm using the residual signals of the solvents as internal standards. The signals of the carbon atoms of the indenyl ligand in the ^{13}C NMR spectra were assigned by analogy with the (indenyl)iron complexes according to the conventional numbering scheme.[21e] 2D ROESY NMR experiments were performed on a Bruker Avance 600 spectrometer at 298 K. Complex **1**[10] was prepared by the literature procedure. All other reagents were purchased from Acros or Aldrich and used as received. Column chromatography was carried out using Macherey−Nagel silica gel 60 (0.04−0.063 mm particle size).

$[(\eta^5\text{-indenyl})Rh(arene)](SbF_6)_2$ ([2a−e,g](SbF$_6$)$_2$). $MeNO_2$ (1 mL) was added to a mixture of **1** (57 mg, 0.121 mmol), $AgSbF_6$ (83 mg, 0.241 mmol), and arene (0.5 mL of benzene, *o*-xylene, or mesitylene; 30 mg of durene, hexamethylbenzene, or [2.2]-paracyclophane). The reaction mixture was vigorously stirred for 1 h, and the precipitate of AgI was centrifuged off. Then an excess of ether was added. The precipitate that formed was washed with

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CH_2Cl_2 (2 × 2 mL), reprecipitated from nitromethane by ether, and dried in vacuo. Compounds [**2a**−**g**]$(SbF_6)_2$ were obtained as an pale yellow solids.

[2a](SbF$_6$)$_2$: arene = benzene, yield 49 mg (53%). ^{1}H NMR (CD_3NO_2): δ 8.13 (m, 2H, C_9H_7), 8.02 (m, 2H, C_9H_7), 7.41 (s, 6H, C_6H_6), 7.40 (m, 2H, C_9H_7), 6.64 (m, 1H, C_9H_7). ^{13}C NMR (CD_3NO_2): δ 142.8 (s, C4/7), 127.6 (s, C5/6), 111.2 (d, $^1J_{Rh-C}$ = 6.3 Hz, C8/9), 108.9 (d, $^1J_{Rh-C}$ = 5.0 Hz, C_6H_6), 95.0 (d, $^1J_{Rh-C}$ = 7.5 Hz, C2), 92.3 (d, $^1J_{Rh-C}$ = 7.5 Hz, C1/3). Anal. Calcd for $C_{15}H_{13}F_{12}RhSb_2$: C, 23.47; H, 1.71. Found: C, 23.86; H, 1.81.

[2b](SbF$_6$)$_2$: arene = *o*-xylene, yield 68 mg (71%). ^{1}H NMR (CD_3NO_2): δ 8.28 (m, 2H, C_9H_7), 7.80 (m, 2H, C_9H_7), 7.43 (m, 2H, $C_6H_4Me_2$), 7.31 (m, 2H, $C_6H_4Me_2$), 7.23 (m, 2H, C_9H_7), 6.61 (m, 1H, C_9H_7), 1.96 (s, 6H, $C_6H_4Me_2$). ^{13}C NMR (CD_3NO_2): δ 141.9 (s, C4/7), 126.1 (s, C5/6), 124.5 (d, $^1J_{Rh-C}$ = 3.8 Hz, $C_6H_4Me_2$), 110.1 (d, $^1J_{Rh-C}$ = 6.3 Hz, C8/9), 109.2 (d, $^1J_{Rh-C}$ = 5.0 Hz, $C_6H_4Me_2$), 104.9 (d, $^1J_{Rh-C}$ = 5.0 Hz, $C_6H_4Me_2$), 95.2 (d, $^1J_{Rh-C}$ = 7.5 Hz, C2), 91.7 (d, $^1J_{Rh-C}$ = 7.5 Hz, C1/3), 17.7 (s, $C_6H_4Me_2$). Anal. Calcd for $C_{17}H_{17}F_{12}RhSb_2$: C, 25.66; H, 2.15. Found: C, 25.71; H, 2.20.

[2c](SbF$_6$)$_2$: arene = mesitylene, yield 64 mg (66%). ^{1}H NMR (CD_3NO_2): δ 8.19 (m, 2H, C_9H_7), 7.89 (m, 2H, C_9H_7), 7.15 (m, 2H, C_9H_7), 7.02 (s, 3H, $C_6H_3Me_3$), 6.59 (m, 1H, C_9H_7), 2.46 (s, 9H, $C_6H_3Me_3$). ^{13}C NMR (CD_3NO_2): δ 140.5 (s, C4/7), 125.2 (s, C5/6), 124.7 (d, $^1J_{Rh-C}$ = 5.0 Hz, $C_6H_3Me_3$), 108.8 (d, $^1J_{Rh-C}$ = 6.3 Hz, C8/9), 104.8 (d, $^1J_{Rh-C}$ = 5.0 Hz, $C_6H_3Me_3$), 94.5 (d, $^1J_{Rh-C}$ = 7.5 Hz, C2), 91.0 (d, $^1J_{Rh-C}$ = 7.5 Hz, C1/3), 19.5 (s, $C_6H_3Me_3$). Anal. Calcd for $C_{18}H_{19}F_{12}RhSb_2$: C, 26.69; H, 2.37. Found: C, 26.84; H, 2.48.

[2d](SbF$_6$)$_2$: arene = durene, yield 56 mg (56%). ^{1}H NMR (CD_3NO_2): δ 8.26 (m, 2H, C_9H_7), 7.76 (m, 2H, C_9H_7), 7.27 (s, 2H, $C_6H_2Me_4$), 7.18 (m, 2H, C_9H_7), 6.43 (m, 1H, C_9H_7), 2.30 (s, 12H, $C_6H_2Me_4$). ^{13}C NMR (CD_3NO_2): δ 138.6 (s, C4/7), 123.2 (s, C5/6), 119.4 (d, $^1J_{Rh-C}$ = 4.0 Hz, $C_6H_2Me_4$), 106.7 (d, $^1J_{Rh-C}$ = 6.0 Hz, C8/9), 106.3 (d, $^1J_{Rh-C}$ = 6.0 Hz, $C_6H_2Me_4$), 94.4 (d, $^1J_{Rh-C}$ = 8.0 Hz, C2), 89.1 (d, $^1J_{Rh-C}$ = 8.0 Hz, C1/3), 16.1 (s, $C_6H_2Me_4$). Anal. Calcd for $C_{19}H_{21}F_{12}RhSb_2$: C, 27.70; H, 2.57. Found: C, 28.08; H, 2.40.

[2e](SbF$_6$)$_2$: arene = hexamethylbenzene, yield 89 mg (87%). ^{1}H NMR (CD_3NO_2): δ 8.23 (m, 2H, C_9H_7), 7.72 (m, 2H, C_9H_7), 6.86 (m, 2H, C_9H_7), 6.36 (m, 1H, C_9H_7), 2.24 (s, 18H, C_6Me_6). ^{13}C NMR (CD_3NO_2): δ 140.9 (s, C4/7), 124.9 (s, C5/6), 120.4 (d, $^1J_{Rh-C}$ = 5.0 Hz, C_6Me_6), 108.6 (d, $^1J_{Rh-C}$ = 6.3 Hz, C8/9), 97.3 (d, $^1J_{Rh-C}$ = 7.5 Hz, C2), 92.3 (d, $^1J_{Rh-C}$ = 7.5 Hz, C1/3), 18.4 (s, C_6Me_6). Anal. Calcd for $C_{21}H_{25}F_{12}RhSb_2$: C, 29.61; H, 2.96. Found: C, 29.48; H, 2.97.

[2g](SbF$_6$)$_2$: arene = [2.2]paracyclophane, yield 74 mg (69%). ^{1}H NMR (CD_3NO_2): δ 8.00 (m, 2H, C_9H_7), 7.86 (m, 2H, C_9H_7), 7.13 (m, 2H, C_9H_7), 6.91 (s, 4H, C_6H_4), 6.31 (s, 4H, C_6H_4), 6.26 (m, 1H, C_9H_7), 3.37 (m, 8H, CH_2). ^{13}C NMR (CD_3NO_2): δ 143.7 (d, $^1J_{Rh-C}$ = 2.5 Hz, C_6H_4), 140.9 (s, C_6H_4), 140.2 (s, C4/7), 135.6 (s, C_6H_4), 126.4 (s, C5/6), 108.1 (d, $^1J_{Rh-C}$ = 6.3 Hz, C8/9), 99.7 (d, $^1J_{Rh-C}$ = 6.3 Hz, C_6H_4), 91.6 (d, $^1J_{Rh-C}$ = 7.5 Hz, C2), 90.5 (d, $^1J_{Rh-C}$ = 7.5 Hz, C1/3), 35.4 (s, CH_2), 33.9 (s, CH_2). Anal. Calcd for $C_{25}H_{23}F_{12}RhSb_2$: C, 33.41; H, 2.69. Found: C, 33.73; H, 2.77.

[(*μ*-*η*:*η*′-1,3-dimesitylpropane){Rh(*η*^{5}-indenyl)}$_2$](SbF$_6$)$_4$ ([3](SbF$_6$)$_4$). $MeNO_2$ (1 mL) was added to a mixture of **1** (85 mg, 0.180 mmol), $AgSbF_6$ (124 mg, 0.360 mmol), and 1,3-dimesitylpropane (25 mg, 0.090 mmol). The reaction mixture was vigorously stirred for 1 h, and the precipitate of AgI was centrifuged off. Then an excess of ether was added. The precipitate that formed was washed with CH_2Cl_2 (2 × 2 mL), reprecipitated from nitromethane by ether, and dried in vacuo. Compound [**3**]$(SbF_6)_4$ was obtained as an orange solid. Yield: 119 mg (80%). ^{1}H NMR (CD_3NO_2): δ 8.27 (m, 4H, C_9H_7), 7.84 (m, 4H, C_9H_7), 7.17 (s, 4H, $C_6H_2Me_3$), 7.10 (m, 4H, C_9H_7), 6.54 (m, 2H, C_9H_7), 2.53 (s, 6H, $C_6H_2Me_3$), 2.51 (m, 4H, CH_2), 2.39 (s, 12H, $C_6H_2Me_3$), 1.7 (m, 2H, CH_2). ^{13}C NMR (CD_3NO_2): δ 140.5 (s, C4/7), 124.7 (s, C5/6), 123.3 (d, $^1J_{Rh-C}$ = 3.8 Hz, $C_6H_2Me_3$), 122.4 (d, $^1J_{Rh-C}$ = 5.0 Hz, $C_6H_2Me_3$), 118.3 (d, $^1J_{Rh-C}$ = 3.8 Hz, $C_6H_2Me_3$), 108.5 (d, $^1J_{Rh-C}$ = 6.3 Hz, C8/9), 106.2 (d, $^1J_{Rh-C}$ = 5.0 Hz, $C_6H_2Me_3$), 95.0 (d, $^1J_{Rh-C}$ = 7.5 Hz, C2), 91.1 (d, $^1J_{Rh-C}$ = 7.5 Hz, C1/3), 27.8 (s, CH_2), 24.4 (s, CH_2), 19.7 (s, $C_6H_2Me_3$), 18.0 (s, $C_6H_2Me_3$). Anal. Calcd for $C_{39}H_{42}F_{24}Rh_2Sb_4$: C, 28.22; H, 2.56. Found: C, 28.39; H, 2.54.

General Procedure for Catalytic Reductive Amination. [**2c**]$(SbF_6)_2$ (1.0 mol %), *p*-anisidine (150 mol %), and *p*-tolualdehyde (100 mol %) were charged into a glass vial in a 10 mL stainless steel autoclave. A 0.2 mL portion of water was added, and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar of CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask, and the autoclave was washed with dichloromethane (2 × 1 mL); the product was extracted with dichloromethane (3 × 1 mL), the combined organic layers were filtered through a silica gel pad, and the solvent was removed on a rotary evaporator. The residue was purified by column chromatography.

Computational Details. The geometries have been optimized without constraints at the gradient corrected DFT level of theory using the exchange functional of Becke[36] and the correlation functional of Perdew[37] (BP86). An all-electron triple-ζ basis set augmented by one polarization function TZP was used. The bonding interactions were studied by means of Morokuma−Ziegler energy decomposition analysis.[38] The calculations were carried out using the ADF 2010.01 program package.[39]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00311.

Crystallographic data and NMR spectra (PDF)
Cartesian coordinates for optimized structures (XYZ)

Accession Codes

CCDC 1838580−1838582 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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