ORGANOMETALLICS
Article
Cite This: Organometallics XXXX, XXX, XXX−XXX
pubs.acs.org/Organometallics

Fluorene Complexes of Group 9 Metals: Fluorene Effect and Application for Reductive Amination

Vladimir B. Kharitonov,[†,‡] Evgeniya Podyacheva,[†] Yulia V. Nelyubina,[†] Dmitry V. Muratov,[†] Alexander S. Peregudov,[†] Gleb Denisov,[∥] Denis Chusov,[†,§,∥] and Dmitry A. Loginov*[,†]

[†]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilova str., Moscow 119991, Russian Federation

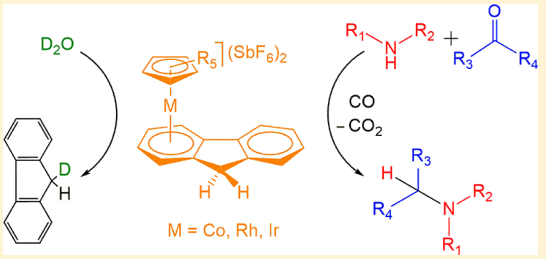
[‡]Dmitry Mendeleev University of Chemical Technology of Russia, 9 Miusskaya sq., Moscow 125047, Russian Federation

[§]G.V. Plekhanov Russian University of Economics, 36 Stremyanny per., Moscow 117997, Russian Federation

[∥]National Research University - Higher School of Economics, 20 Miasnitskaya str, Moscow 101000, Russian Federation

Supporting Information

ABSTRACT: The η^6-fluorene cyclopentadienyl complexes $[(\eta^5\text{-}C_5R_5)M(\eta^6\text{-fluorene})](SbF_6)_2$ (**1**: M = Co, R = Me; **2a**: M = Rh, R = H; **2b**: M = Ir, R = H) were synthesized by the iodide abstraction from $[(\eta^5\text{-}C_5R_5)MI_2]_n$ with $AgSbF_6$ in the presence of fluorene. The procedure is also suitable for the synthesis of the indenyl derivatives $[(\eta^5\text{-indenyl})M(\eta^6\text{-fluorene})](SbF_6)_2$ (**3a**: M = Rh; **3b**: M = Ir) starting from $[(\eta^5\text{-indenyl})MI_2]_n$. The structures of $[\mathbf{1}](SbF_6)_2$ and $[\mathbf{2b}](SbF_6)_2$ were determined by X-ray diffraction. The rhodium complex $[\mathbf{2a}](SbF_6)_2$ readily undergoes the replacement of the fluorene ligand by mesitylene, being more reactive than the benzene derivative $[CpRh(\eta^6\text{-}C_6H_6)](SbF_6)_2$. According to experimental data and DFT calculations, the fluorene elimination proceeds via a cascade of $\eta^6 \rightarrow \eta^5 \rightarrow \eta^1$ haptotropic rearrangements. The complex $[\mathbf{2b}](SbF_6)_2$ (at 1 mol % loading) effectively catalyzes the reductive amination reaction between aldehydes (or ketones) and primary aromatic (or secondary aliphatic) amines in the presence of carbon monoxide, giving the corresponding secondary and tertiary amines in the range of yields 59−91%. This protocol uses water as a solvent.



INTRODUCTION

The indenyl effect, which is expressed in higher chemical and catalytic activity of indenyl complexes compared to cyclopentadienyl analogues, is well-known.[1] The enhanced reactivity of indenyl complexes is attributed to easy slippage of indenyl ligand from η^5 to η^3 coordination mode, which provides an additional free coordination site at the metal atom. The main driving force of this transformation is the recovery of the benzene ring aromaticity. Recently, we have found that indenyl rhodium complexes exhibit a high catalytic activity in the reductive amination of aldehydes or ketones in the presence of carbon monoxide as a reducing agent.[2] Unlike conventional catalysts, these complexes showed the highest catalytic activity when water was used as a solvent.

Fluorenide anion is another perspective polyaromatic system for catalyst design, in which four types (η^1, η^3, η^5, and η^6) of coordination with a metal atom may be realized. Moreover, fluorene is ecologically friendly because it does not display mutagenic activity in contrast to many other polycyclic aromatic hydrocarbons.[3] However, fluorenyl complexes are less studied in catalysis than indenyl analogues, which can be explained by their low stability. For example, manganese and zirconium complexes easily undergo fluorenyl slippage from η^5 to η^1 coordination mode with subsequent total elimination of the metal to give bifluorenyl derivatives.[4] Moreover, the interaction of lithium fluorenides with $CoCl_2$ is the basis of the general approach to bifluorenes.[5] The 9-substituted fluorenes with bulky substituents, e.g., Pr^i and $SiMe_3$, also proved to be suitable for this reaction. Therefore, fluorene can be considered as a good leaving moiety in catalytic reactions to generate free coordination sites at the metal atom.

At the same time, complexes of group 9 metals with labile arene ligands are known to be efficient catalysts for many organic transformations. Elimination of arene ligand results in three vacant coordination sites. For example, Matsunaga and Kanai showed that the cobalt complex $[Cp^*Co(\eta^6\text{-}C_6H_6)]^{2+}$ effectively catalyzes selective C−H activation of aromatic compounds under chelation assistance of a directing group (e.g., pyridyl and carbamoyl).[6,7] We found that the rhodium benzene complex $[(\eta^5\text{-indenyl})Rh(\eta^6\text{-}C_6H_6)]^{2+}$ shows a higher catalytic activity in the reductive amination of carbonyl compounds as compared with the iodide derivative $[(\eta^5\text{-indenyl})RhI_2]_n$.[2a] Herein, we report the synthesis and reactivity of η^6-fluorene complexes $[(\eta^5\text{-}C_5R_5)M(\eta^6\text{-fluorene})]^{2+}$ (M = Co, Rh, Ir; R = H, Me) and $[(\eta^5\text{-indenyl})M(\eta^6\text{-fluorene})]^{2+}$

Received: June 5, 2019

DOI: 10.1021/acs.organomet.9b00378
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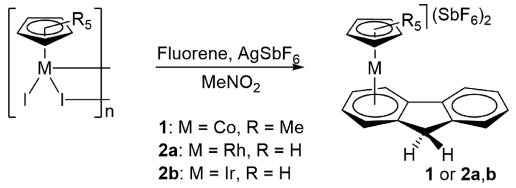
(M = Rh, Ir), as well as their application in the catalytic reductive amination of aldehydes and ketones. The formation of catalytic species is due to the high thermal lability of fluorene ligand.

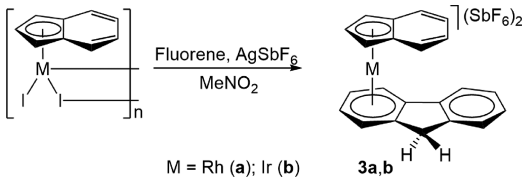
RESULTS AND DISCUSSION

Synthesis and Reactivity. Recently, we have developed a general approach to the bis(indenyl)rhodium and iridium complexes $[M(\eta^5\text{-indenyl})_2]^+$ based on the spontaneous deprotonation of the η^6-derivative $[(\eta^5\text{-indenyl})M(\eta^6\text{-indene})]^{2+}$ and the subsequent $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement.[8] Maitlis with co-workers showed that the η^6-fluorene complexes $[Cp^*M(\eta^6\text{-fluorene})]^{2+}$ (M = Rh, Ir) are stable and do not eliminate protons.[9] Moreover, it has been found that acetone induces a rapid displacement of fluorene from the rhodium complex, giving the solvate $[Cp^*Rh(acetone)_3]^{2+}$ even at 0 °C. For a comprehensive study of this phenomenon, we synthesized the related η^6-fluorene complexes $[Cp^*Co(\eta^6\text{-fluorene})](SbF_6)_2$ ($[\mathbf{1}](SbF_6)_2$), $[CpM(\eta^6\text{-fluorene})](SbF_6)_2$ ($[\mathbf{2a}](SbF_6)_2$, M = Rh; $[\mathbf{2b}](SbF_6)_2$, M = Ir), and $[(\eta^5\text{-indenyl})M(\eta^6\text{-fluorene})](SbF_6)_2$ ($[\mathbf{3a}](SbF_6)_2$, M = Rh; $[\mathbf{3b}](SbF_6)_2$, M = Ir) using iodide abstraction from $[Cp^*CoI_2]_2$, $[CpMI_2]_n$, and $[(\eta^5\text{-indenyl})MI_2]_n$ by $AgSbF_6$ in the presence of fluorene (Schemes 1 and 2). It should be noted that the use

Scheme 1. Synthesis of the Cyclopentadienyl η^6-Fluorene Complexes $[\mathbf{1}](SbF_6)_2$ and $[\mathbf{2a,b}](SbF_6)_2$



Scheme 2. Synthesis of the Indenyl η^6-Fluorene Complexes $[\mathbf{3a,b}](SbF_6)_2$

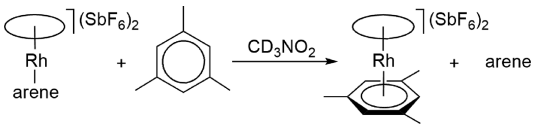


of a more nucleophilic hexafluorophosphate anion also allowed fluorene complexes to be prepared but in lower yields and in impure form. We were not able to synthesize the non-methylated cobalt complex $[CpCo(\eta^6\text{-fluorene})](SbF_6)_2$ due to its low stability.

The fluorene complexes $[\mathbf{1}](SbF_6)_2$, $[\mathbf{2a,b}](SbF_6)_2$, and $[\mathbf{3a,b}](SbF_6)_2$ were isolated as solvates with one molecule of nitromethane. They are indefinitely stable in the solid state but readily undergo solvolysis by coordinating solvents (such as acetone, acetonitrile, and dimethylsulfoxide) with the removal of free fluorene, indicating the substitutional lability of this ligand. The ^1H and ^{13}C NMR spectra display 9 and 13 different resonances, respectively, for the fluorene ligand, which is in accordance with its η^6-coordination with one metal atom. The signals for fluorene protons are downfield shifted as compared with free fluorene (that is in accordance with a high positive charge of the complexes), being less shifted for the indenyl derivatives. In contrast, the signals of the coordinated carbon atoms of the fluorene moiety are upfield shifted compared to the corresponding signals of the uncoordinated atoms. In the case of the cobalt complex $[\mathbf{1}](SbF_6)_2$, the signals for hydrogen and carbon atoms, which are close to the metal atom, are strongly broadened, probably due to the quadrupole broadening by the ^{59}Co nucleus.

Usually, the arene ligand is more labile in rhodium complexes than in cobalt and iridium congeners.[10] To estimate the lability of the fluorene ligand in the complexes prepared, we carried out the ^1H NMR study of arene exchange in the rhodium complexes $[\mathbf{2a}](SbF_6)_2$ and $[\mathbf{3a}](SbF_6)_2$ (Table 1).

Table 1. Arene Exchange in $[\mathbf{2a}](SbF_6)_2$, $[\mathbf{3a}](SbF_6)_2$, and Related Rhodium Complexes[a]



entry	complex	time (days)	conversion[b] (%)
1	$[\mathbf{2a}](SbF_6)_2$	7	59
2	$[CpRh(\eta^6\text{-}C_6H_6)](SbF_6)_2$	7	9
3	$[\mathbf{3a}](SbF_6)_2$	7	28
4	$[(\eta^5\text{-indenyl})Rh(\eta^6\text{-}C_6H_6)](SbF_6)_2$	1	74[c]

[a]Reagents and conditions: rhodium complex (0.016 mmol), mesitylene (0.14 mmol), nitromethane-d_3 (0.5 mL), room temperature. [b]Determined by ^1H NMR spectroscopy. [c]Reference 2a.

As a model reaction, we chose the reaction of these complexes with an excess of mesitylene in nitromethane-d_3. It was found that the fluorene ligand in the cyclopentadienyl complex $[\mathbf{2a}](SbF_6)_2$ is considerably more labile than the benzene ligand in $[CpRh(\eta^6\text{-}C_6H_6)](SbF_6)_2$ (entry 1 vs entry 2), suggesting the crucial role of fluorene as a leaving ligand in the arene exchange. Unexpectedly, the indenyl complex $[\mathbf{3a}](SbF_6)_2$ proved to be less reactive than the cyclopentadienyl analogue $[\mathbf{2a}](SbF_6)_2$ (entry 3 vs entry 1), which can be explained by the strong steric hindrance of two bulky ligands (indenyl and fluorene). Accordingly, the fluorene ligand in this complex is considerably less labile than the benzene ligand in $[(\eta^5\text{-indenyl})Rh(\eta^6\text{-}C_6H_6)](SbF_6)_2$ (entry 3 vs entry 4).

The iridium complex $[\mathbf{2b}](SbF_6)_2$ proved to be less reactive in the arene exchange than the rhodium analogue; the degree of conversion is ca. 2% after 8 h in refluxing nitromethane. However, an addition of a catalytic amount of acetonitrile leads to an increase of conversion up to 83% after 2 days.

To elucidate the lability of the fluorene ligand and the mechanism of its replacement, we performed the DFT calculations at the BP86/TZP level. First of all, we estimated the energies of the M−arene bonds by energy decomposition analysis[11] for the η^6-fluorene complexes and their benzene analogues (Table 2). It was found that for all complexes the bonding with fluorene is stronger than that with benzene by ca. 15−25 kcal mol^{-1} (for example, see entry 3 vs entry 4). At the same time, the complex $[\mathbf{2a}](SbF_6)_2$ has a higher reactivity in the arene exchange than $[CpRh(\eta^6\text{-}C_6H_6)](SbF_6)_2$ (vide supra), suggesting that kinetic factors, rather than thermodynamic ones, affect the displacement of fluorene.

A question arises: What is a mechanism of easy elimination of the fluorene ligand? We propose that the displacement of fluorene starts with the spontaneous elimination of a proton from the methylene group with the formation of intermediate

DOI: 10.1021/acs.organomet.9b00378
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Table 2. Calculated Dissociation Energies (D_e, in kcal mol^{-1}) for the M–Arene Interaction in Cations $[(L)M(\eta^6\text{-Fluorene})]^{2+}$ and $[(L)M(\eta^6\text{-}C_6H_6)]^{2+}$ at the BP86/TZP Level

entry	M	L	arene	D_e
1 ($[\mathbf{1}]^{2+}$)	Co	Cp*	fluorene	103.80
2	Co	Cp*	C_6H_6	88.63
3 ($[\mathbf{2a}]^{2+}$)	Rh	Cp	fluorene	122.57
4	Rh	Cp	C_6H_6	99.29[a]
5 ($[\mathbf{3a}]^{2+}$)	Rh	indenyl	fluorene	98.28
6	Rh	indenyl	C_6H_6	78.30[a]
7 ($[\mathbf{2b}]^{2+}$)	Ir	Cp	fluorene	129.35
8	Ir	Cp	C_6H_6	107.62
9 ($[\mathbf{3b}]^{2+}$)	Ir	indenyl	fluorene	105.16
10	Ir	indenyl	C_6H_6	86.38

[a]Reference 2a.

A, which can be represented as two resonance structures (Scheme 3). The subsequent $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement leads to η^5-fluorenyl intermediate **B**, which is unstable and undergoes subsequent transformation into η^1-fluorenyl derivative **C** with further removal of free fluorene after back protonation. To confirm our hypothesis, we estimated the energies (ΔE) of the formation of intermediates **A** and **B** for cyclopentadienyl complexes (Table 3). The formation of intermediate **A** is slightly endothermic for all complexes (entries 1, 3, and 5), being less endothermic for the rhodium derivative (entry 3). The subsequent $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement is even exothermic (entries 2, 4, and 6), which implies easy deprotonation and rearrangement of the fluorene complexes. The mechanism of the $\eta^6 \rightarrow \eta^5$ transformation has previously been thoroughly studied theoretically and experimentally for the fluorenyl complexes of iron and ruthenium.[12] Unfortunately, our attempts to isolate intermediates **A** or **B** have failed. For example, the deprotonation of $[\mathbf{2b}](SbF_6)_2$ with sodium hydride gave a mixture of unidentified products. Nevertheless, we found that the decomposition of $[\mathbf{2a}](SbF_6)_2$ by D_2O resulted in the elimination of 9-D-fluorene. At the same time, the treatment of free fluorene as well as the stable iridium complex $[\mathbf{2b}](SbF_6)_2$ with D_2O for at least 1 week did not lead to deutero exchange in the methylene group of fluorene, thus confirming the proposed mechanism.

Scheme 3. Supposed Pathway for Displacement of Fluorene from $[\mathbf{2a}](SbF_6)_2$

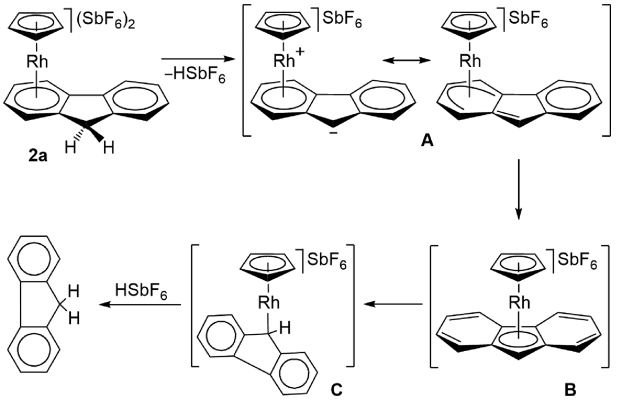

Table 3. Calculated Reaction Energies (ΔE, in kcal mol^{-1}) for the Formation of Intermediates A and B for the Cyclopentadienyl Complexes $[\mathbf{1}]^{2+}$ and $[\mathbf{2a,b}]^{2+}$ at the BP86/TZP Level

entry	complex	reaction	ΔE
1	$[\mathbf{1}]^{2+}$	$[\mathbf{1}]^{2+} + H_2O \rightarrow \mathbf{A} + [H_3O]^+$	24.11
2	$[\mathbf{1}]^{2+}$	$\mathbf{A} \rightarrow \mathbf{B}$	−5.23
3	$[\mathbf{2a}]^{2+}$	$[\mathbf{2a}]^{2+} + H_2O \rightarrow \mathbf{A} + [H_3O]^+$	18.96
4	$[\mathbf{2a}]^{2+}$	$\mathbf{A} \rightarrow \mathbf{B}$	−6.58
5	$[\mathbf{2b}]^{2+}$	$[\mathbf{2b}]^{2+} + H_2O \rightarrow \mathbf{A} + [H_3O]^+$	21.44
6	$[\mathbf{2b}]^{2+}$	$\mathbf{A} \rightarrow \mathbf{B}$	−5.48

X-ray Diffraction. The structures of $[\mathbf{1}](SbF_6)_2$ and $[\mathbf{2b}](SbF_6)_2$ were determined by X-ray diffraction (Figures 1 and 2). The structure of cation $[\mathbf{1}]^{2+}$ is the first example of a (cyclopentadienyl)(arene)cobalt complex. The cobalt atom is not quite symmetrically coordinated with the six-membered ring of the fluorene ligand, with the bonds of the Co atom with C2, C3, and C4 atoms (av. 2.104 Å) being noticeably shorter than those with C1, C4a, and C9a atoms (av. 2.137 Å). This coordination is in accordance with the structure of intermediate **A** (see Scheme 3). The Co···Cp* distance in $[\mathbf{1}](SbF_6)_2$ (1.664 Å) is close to the same distance in the oxocyclohexadienyl complex $[Cp^*Co\{\eta^5\text{-}C_6Me_4(O)(OH)\}]PF_6$ (1.670 Å).[13]

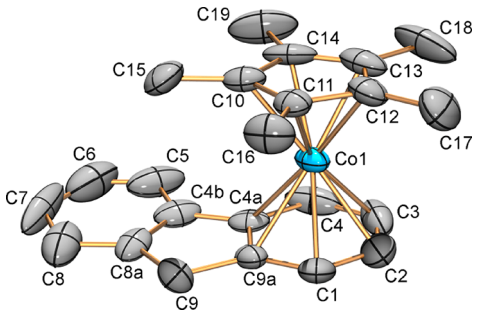

Figure 1. Crystal structure of complex $[\mathbf{1}](SbF_6)_2$ in 50% thermal ellipsoids. Counterions, solvent molecules of nitromethane, and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Co1–C1 2.117(8), Co1–C2 2.102(9), Co1–C3 2.095(8), Co1–C4 2.114(8), Co1–C4a 2.144(7), Co1–C9a 2.150(7), Co1–C10 2.070(7), Co1–C11 2.072(7), Co1–C12 2.058(8), Co1–C13 2.056(8), Co1–C14 2.055(7), C1–C2 1.365(13), C1–C9a 1.403(12), C2–C3 1.348(17), C3–C4 1.430(16), C4–C4a 1.452(12), C4a–C4b 1.464(12), C9a–C4a 1.412(10), C4b–C8a 1.397(13), C4b–C5 1.351(13), C5–C6 1.332(19), C6–C7 1.35(2), C7–C8 1.48(2), C8–C8a 1.388(13), C9–C8a 1.500(11), C9–C9a 1.501(10).

The structure of the cation $[\mathbf{2b}]^{2+}$ is close to the structure of various other (cyclopentadienyl)(arene)iridium complexes $[Cp^*Ir(arene)]^{2+}$ (arene = benzene derivatives, tyrosine, phenanthrene, pyrene, etc.).[14] Similar to the cobalt complex $[\mathbf{1}](SbF_6)_2$, the fluorene ligand in $[\mathbf{2b}](SbF_6)_2$ is η^6-coordinated to the iridium atom with considerable slippage toward C2, C3, and C4 atoms.

As expected, in both complexes, the C–C bonds within the coordinated six-membered ring of the fluorene ligand (av. 1.402 Å for $[\mathbf{1}](SbF_6)_2$ and av. 1.418 Å for $[\mathbf{2b}](SbF_6)_2$) are longer than those within the uncoordinated one (av. 1.383 Å for $[\mathbf{1}](SbF_6)_2$ and av. 1.377 Å for $[\mathbf{2b}](SbF_6)_2$) due to the loosening of π bonds upon coordination.

DOI: 10.1021/acs.organomet.9b00378
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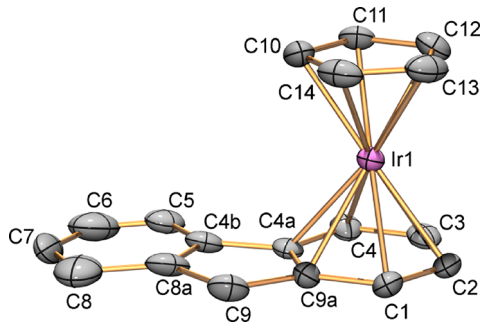


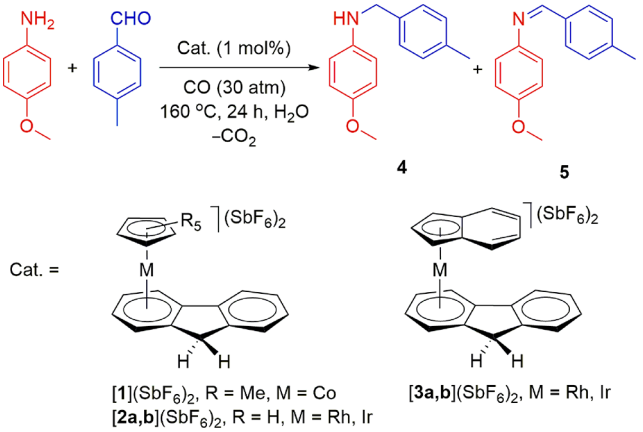
Figure 2. Crystal structure of complex $[\mathbf{2b}](SbF_6)_2$ in 50% thermal ellipsoids. Counterions, solvent molecules of nitromethane, and all hydrogen atoms are omitted for clarity. Selected interatomic distances for a major part of the disordered fluorene fragment (Å): Ir1−C1 2.245(10), Ir1−C2 2.233(12), Ir1−C3 2.202(12), Ir1−C4 2.215(12), Ir1−C4a 2.280(10), Ir1−C9a 2.267(10), Ir1−C10 2.172(5), Ir1−C11 2.177(5), Ir1−C12 2.179(5), Ir1−C13 2.184(5), Ir1−C14 2.164(5), C1−C2 1.417(17), C1−C9a 1.397(15), C2−C3 1.425(19), C3−C4 1.419(18), C4−C4a 1.406(16), C4a−C4b 1.471(17), C9a−C4a 1.441(16), C4b−C8a 1.385(18), C4b−C5 1.360(16), C5−C6 1.268(17), C6−C7 1.400(11), C7−C8 1.343(10), C8−C8a 1.504(19), C9−C8a 1.516(17), C9−C9a 1.504(15).

Application to Direct Reductive Amination. Reductive amination[15] with carbon monoxide as a reducing agent is a highly effective catalytic process without an external hydrogen source. Carbon monoxide as a scavenger of oxygen atoms provides a high atom precision, tolerance to potentially reducible functional groups, and economy of atoms and steps, which is important for industry.[16]

It is known that several arene complexes are effective in CO-assisted reductive amination. Some examples[2a,17] were presented which suggest that the stage of removal of the arene ligand can influence the catalytic activity of the complex. Therefore, we decided to test new complexes $[\mathbf{1}](SbF_6)_2$, $[\mathbf{2a,b}](SbF_6)_2$, and $[\mathbf{3a,b}](SbF_6)_2$ with fluorene ligand in direct reductive amination. As a model reaction, we chose the reaction between *p*-tolualdehyde and *p*-anisidine. At an early stage of the research, the reaction was conducted in THF as a solvent, and only traces of amine **4** were obtained. Schiff base **5** was the main product, whereas conversion was 100%. Taking into account that fluorene complexes can undergo solvolysis by coordinating solvents (acetone, acetonitrile, and dimethyl sulfoxide) and previous data[2] that reductive amination with CO under indenyl rhodium catalysis can be carried out in water,[2] we decided to test water as a solvent and/or reagent. Before the autoclave is heated, the reaction mixture is biphasic. It is hard to tell if the reaction is going in water or on water. The reduced product **4** was obtained in 30% yield using iridium and rhodium catalysts and only 7% yield using Co-complex at 120 °C (see the Supporting Information). The reaction temperature was increased for all catalysts from 120 to 160 °C. We identified that iridium catalysts demonstrated higher activity (88 and 77%) than rhodium ones (55 and 35%) which in turn were more effective than cobalt catalyst (12%) (Table 4). The lower activity of the indenyl complexes $[\mathbf{3a,b}](SbF_6)_2$ can be explained by strong steric hindrance of two bulky ligands (indenyl and fluorene), as was mentioned above. Herein, we confirmed that the new fluorene-containing complexes represent active species in such an eco-friendly, nontoxic, nonflammable, and easily accessible solvent like water in CO-assisted reductive amination. Other implementations of reductive amination in water are described.[18]

The complex $[\mathbf{2b}](SbF_6)_2$ was chosen for the substrate scope screening. We found that the process can be applied to aromatic aldehydes with aromatic amines and aliphatic ketones with aromatic and aliphatic amines (74−91%) (Figure 3).

Table 4. Screening of Fluorene Complexes in the Reductive Amination Reaction



catalyst[a]	yield,[b] 4	yield,[b] 5
$[\mathbf{1}](SbF_6)_2$[c]	12%	79%
$[\mathbf{2a}](SbF_6)_2$[d]	55%	33%
$[\mathbf{3a}](SbF_6)_2$[d]	35%	38%
$[\mathbf{2b}](SbF_6)_2$[c]	88%	3%
$[\mathbf{3b}](SbF_6)_2$[c]	77%	15%

[a]22.7−27.0 mg (0.18−0.22 mmol) of *p*-anisidine, 14.5−17.3 μL (0.12−0.15 mmol) of *p*-tolylaldehyde, 1 mol % of catalyst, 133−158 μL of water. [b]Yields were determined by ^{1}H NMR with mesitylene as the internal standard. [c]Catalysts were stored at −20 °C in plastic vessels. [d]The catalysts were freshly prepared.

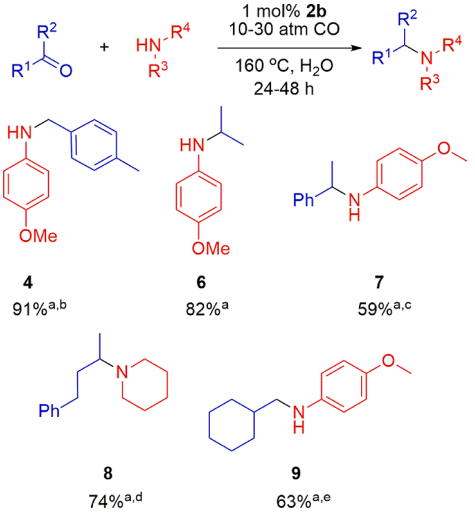


Figure 3. Products synthesized by reductive amination using carbon monoxide as a reducing agent and $[\mathbf{2b}](SbF_6)_2$ as a catalyst. Conditions: 1 mol % of $[\mathbf{2b}](SbF_6)_2$, 160 °C, 30 atm of CO, 24 h, water as a solvent; exception: compound **8** - 160 °C, 10 atm of CO, 48 h. [a]Yields were determined by ^{1}H NMR with mesitylene as an internal standard. [b]The average yield of five experiments. [c]The average yield of six experiments. [d]The average yield of four experiments. [e]The average yield of two experiments.

DOI: 10.1021/acs.organomet.9b00378
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However, it should be noted that lower yields (59−63%) were obtained in the case of aliphatic aldehydes and aromatic ketones. Recently, we have found that simple reductive amination between benzylacetone and piperidine can be problematic for classical reducing systems.[19] Therefore, we tried to make some additional optimization. We managed to increase the yield of **8** (from 60 to 74%) by reducing the pressure and increasing the reaction time (see the Supporting Information). Despite the additional optimization of conditions for the synthesis of **7** and **9**, we did not get a significant improvement. Also, it is important to use a freshly prepared catalyst; otherwise, there are significant discrepancies in the results. The complex [**2b**]$(SbF_6)_2$ is the most active for the reductive amination with CO as a reducing agent among all iridium catalysts.[20] The highest turnover number (TON) is 82 per iridium, whereas the previously achieved value was 48 for $[CpIrI_2]_n$.[20b]

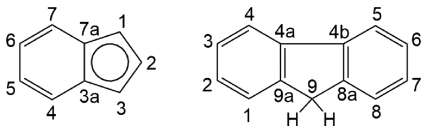
CONCLUSIONS

We developed a general approach to the η^6-fluorene complexes $[(L)M(\eta^6\text{-fluorene})](SbF_6)_2$ (L = Cp, Cp*, indenyl; M = Co, Rh, Ir) based on the reaction of iodides $[(L)MI_2]_n$ with fluorene in the presence of $AgSbF_6$. The fluorene ligand in the rhodium complex $[CpRh(\eta^6\text{-fluorene})](SbF_6)_2$ proved to be considerably more labile than benzene in $[CpRh(\eta^6\text{-}C_6H_6)](SbF_6)_2$. The facilitation of the fluorene replacement is reached as a result of its spontaneous deprotonation and subsequent $\eta^6 \rightarrow \eta^5 \rightarrow \eta^1$ haptotropic rearrangements. The observed "fluorene effect" makes fluorene a good leaving group, the removal of which opens the way to a highly active system for homogeneous catalysis. At the same time, this effect is of a different nature than the classical indenyl and fluorenyl effects, where generation of vacant coordination sites on the catalyst results from a reversible change of the ligand hapticity. The fluorene complexes proved to be active catalysts in the reaction of reductive amination with carbon monoxide in water. The activity of the synthesized (fluorene)rhodium catalysts is less than that of the previously described (indenyl)rhodium ones, whereas the (fluorene)iridium catalysts have shown the highest activity among all iridium catalysts known.

EXPERIMENTAL SECTION

General. 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 Varian Inova 400 spectrometer operating at 400.13 and 100.61 MHz, respectively. Chemical shifts are reported in ppm using the residual signals of the solvents as internal standards. The signals of indenyl and fluorene systems in the NMR spectra and X-ray diffraction data were assigned according to the IUPAC recommendation (Scheme 4).[21] Starting materials $[Cp^*CoI_2]_2$,[22] $[CpRhI_2]_n$,[23] $[CpIrI_2]_n$,[24] $[(\eta^5\text{-indenyl})RhI_2]_n$,[2b] and $[(\eta^5\text{-indenyl})IrI_2]_n$[25] were prepared as described in the literature. 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).

Scheme 4. Numbering Scheme of the Carbon Atoms in the Indenyl and Fluorene Ligands



$[(\eta^5\text{-}C_5R_5)M(\eta^6\text{-Fluorene})](SbF_6)_2$ ([1]$(SbF_6)_2$ and [2a,b]$(SbF_6)_2$). $MeNO_2$ (4 mL) was added to a mixture of the iodide complex $[(\eta^5\text{-}C_5R_5)MI_2]_n$ (0.149 mmol), fluorene (27 mg, 0.163 mmol), and $AgSbF_6$ (107 mg, 0.311 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 reprecipitated twice from nitromethane by ether and dried in vacuo. Compounds [**1**]$(SbF_6)_2$ and [**2a,b**]$(SbF_6)_2$ were obtained as colored solids.

[1]$(SbF_6)_2$. M = Co, R = Me, yellow solid, yield 67 mg (50%). ^1H NMR (CD_3NO_2): δ 8.29 (d, ^3J = 8.0 Hz, 1H, C5 or C8, fluorene), 8.00 (d, ^3J = 8.0 Hz, 1H, C5 or C8, fluorene), 7.90 (m, 1H, C6 or C7, fluorene), 7.83 (m, 1H, C6 or C7, fluorene), 7.63 (br. s, 1H, C1 or C4, fluorene), 7.50 (br. s, 1H, C1 or C4, fluorene), 7.27 (br. s, 2H, C2 and C3, fluorene), 4.43 (d, ^2J = 24.0 Hz, 2H, C9, fluorene), 4.34 (s, 3H, $MeNO_2$), 1.97 (s, 15H, Cp*). ^{13}C NMR (CD_3NO_2): δ 146.7 (s, C4b or C8a, fluorene), 134.6 (s, C5−C8, fluorene), 130.1 (s, C4b or C8a, fluorene), 129.6 (s, C5−C8, fluorene), 126.7 (s, C5−C8, fluorene), 125.3 (s, C5−C8, fluorene), 123.0 (br. s, C4a and C9a, fluorene), 110.8 (br. s, $\underline{C}_5Me_5$), 104.0 (br. s, C1−C4, fluorene), 35.2 (s, C9, fluorene), 8.1 (s, $C_5\underline{Me}_5$). Anal. Calcd for $C_{23}H_{25}CoF_{12}Sb_2\cdot MeNO_2$: C, 32.28; H, 3.16. Found: C, 32.33; H, 3.31.

[2a]$(SbF_6)_2$. M = Rh, R = H, green solid, yield 60 mg (46%). ^1H NMR (CD_3NO_2): δ 8.30 (d, ^3J = 8.0 Hz, 1H, fluorene), 8.24 (d, ^3J = 8.0 Hz, 1H, fluorene), 8.11 (d, ^3J = 6.0 Hz, 1H, fluorene), 7.83 (m, 2H, fluorene), 7.69 (m, 1H, fluorene), 7.63 (m, 1H, fluorene), 7.54 (m, 1H, fluorene), 6.61 (s, 5H, Cp), 4.50 (s, 2H, C9, fluorene), 4.34 (s, 3H, $MeNO_2$). ^{13}C NMR (CD_3NO_2): δ 146.8 (s, C4b or C8a, fluorene), 135.0 (s, C5−C8, fluorene), 131.2 (s, C4b or C8a, fluorene), 128.9 (s, C5−C8, fluorene), 126.7 (d, $^1J_{Rh-C}$ = 4.0 Hz, C4a or C9a, fluorene), 126.5 (d, $^1J_{Rh-C}$ = 4.0 Hz, C4a or C9a, fluorene), 126.4 (s, C5−C8, fluorene), 125.0 (s, C5−C8, fluorene), 102.9 (d, $^1J_{Rh-C}$ = 4.0 Hz, C1−C4, fluorene), 102.8 (d, $^1J_{Rh-C}$ = 4.0 Hz, C1−C4, fluorene), 100.7 (d, $^1J_{Rh-C}$ = 4.0 Hz, C1−C4, fluorene), 96.2 (d, $^1J_{Rh-C}$ = 7.0 Hz, Cp), 96.1 (d, $^1J_{Rh-C}$ = 4.0 Hz, C1−C4, fluorene), 37.7 (s, C9, fluorene). Anal. Calcd for $C_{18}H_{15}F_{12}RhSb_2\cdot MeNO_2$: C, 26.33; H, 2.09. Found: C, 26.27; H, 2.37.

[2b]$(SbF_6)_2$. M = Ir, R = H, cream solid, yield 101 mg (71%). ^1H NMR (CD_3NO_2): δ 8.41 (d, ^3J = 8.0 Hz, 1H, fluorene), 8.20 (m, 2H, fluorene), 7.83 (m, 2H, fluorene), 7.72 (m, 2H, fluorene), 7.59 (m, 1H, fluorene), 6.64 (s, 5H, Cp), 4.39 (s, 3H, $MeNO_2$), 4.25 (d, ^2J = 24.0 Hz, 2H, C9, fluorene). ^{13}C NMR (CD_3NO_2): δ 146.2 (s, C4b or C8a, fluorene), 135.0 (s, C5−C8, fluorene), 130.6 (s, C4b or C8a, fluorene), 128.7 (s, C5−C8, fluorene), 126.1 (s, C5−C8, fluorene), 125.1 (s, C5−C8, fluorene), 120.6 (s, C4a or C9a, fluorene), 118.3 (s, C4a or C9a, fluorene), 94.6 (s, C1−C4, fluorene), 94.5 (s, C1−C4, fluorene), 93.1 (s, C1−C4, fluorene), 89.2 (s, Cp), 87.9 (s, C1−C4, fluorene), 37.5 (s, C9, fluorene). Anal. Calcd for $C_{18}H_{15}F_{12}IrSb_2\cdot MeNO_2$: C, 23.87; H, 1.89. Found: C, 24.26; H, 1.90.

$[(\eta^5\text{-Indenyl})M(\eta^6\text{-Fluorene})](SbF_6)_2$ ([3a,b]$(SbF_6)_2$). $MeNO_2$ (4 mL) was added to a mixture of the iodide complex $[(\eta^5\text{-indenyl})MI_2]_n$ (0.148 mmol), fluorene (27 mg, 0.163 mmol), and $AgSbF_6$ (107 mg, 0.311 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 reprecipitated twice from nitromethane by ether and dried in vacuo. Compounds [**3a,b**]$(SbF_6)_2$ were obtained as yellow solids.

[3a]$(SbF_6)_2$. M = Rh, yield 75 mg (57%). ^1H NMR (CD_3NO_2): δ 7.91 (m, 5H, fluorene and indenyl), 7.78 (m, 2H, C4−C7, indenyl), 7.65 (m, 1H, fluorene), 7.49 (m, 3H, fluorene), 7.31 (m, 1H, fluorene), 7.25 (br. s, 1H, C1 or C3, indenyl), 7.19 (m, 1H, fluorene), 7.14 (br. s, 1H, C1 or C3, indenyl), 6.60 (br. s, 1H, C2, indenyl), 4.39 (s, 3H, $MeNO_2$), 4.13 (d, ^2J = 24.0 Hz, 2H, C9, fluorene). ^{13}C NMR (CD_3NO_2): δ 146.5 (s, C4b or C8a, fluorene), 140.4 (s, C4−C7, indenyl), 139.7 (s, C4−C7, indenyl), 134.7 (s, C5−C8, fluorene), 128.9 (s, C5−C8, fluorene), 127.9 (s, C4b or C8a, fluorene), 126.0 (s, C4−C7, indenyl), 125.9 (s, C4−C7, indenyl), 125.1 (d, $^1J_{Rh-C}$ = 4.0 Hz, C4a or C9a, fluorene), 123.6 (d, $^1J_{Rh-C}$ = 4.0 Hz, C4a or C9a,

DOI: 10.1021/acs.organomet.9b00378
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fluorene), 122.6 (s, C5−C8, fluorene), 121.0 (s, C5−C8, fluorene), 106.5 (d, $^1J_{Rh-C}$ = 6.0 Hz, C3a or C7a, indenyl), 105.7 (d, $^1J_{Rh-C}$ = 6.0 Hz, C3a or C7a, indenyl), 102.4 (d, $^1J_{Rh-C}$ = 4.0 Hz, C1−C4, fluorene), 101.5 (d, $^1J_{Rh-C}$ = 6.0 Hz, C1−C4, fluorene), 98.7 (d, $^1J_{Rh-C}$ = 6.0 Hz, C1−C4, fluorene), 97.6 (d, $^1J_{Rh-C}$ = 4.0 Hz, C1−C4, fluorene), 92.1 (d, $^1J_{Rh-C}$ = 8.0 Hz, C2, indenyl), 88.9 (d, $^1J_{Rh-C}$ = 8.0 Hz, C1 or C3, indenyl), 88.6 (d, $^1J_{Rh-C}$ = 8.0 Hz, C1 or C3, indenyl), 34.5 (s, C9, fluorene). Anal. Calcd for $C_{22}H_{17}F_{12}RhSb_2 \cdot MeNO_2$: C, 30.13; H, 2.20. Found: C, 30.22; H, 2.32.

[3b](SbF$_6$)$_2$. M = Ir, yield 52 mg (35%). ^{1}H NMR (CD_3NO_2): δ 8.02 (d, ^3J = 8.0 Hz, 1H, fluorene), 7.92 (d, ^3J = 8.0 Hz, 1H, fluorene), 7.82 (m, 2H, C4−C7, indenyl), 7.68 (m, 1H, fluorene), 7.63 (m, 2H, C4−C7, indenyl), 7.45 (m, 1H, fluorene), 7.36 (m, 2H, fluorene), 7.18 (br. s, 1H, C1 or C3, indenyl), 7.14 (m, 1H, fluorene), 7.09 (br. s, 1H, C1 or C3, indenyl), 7.02 (m, 1H, fluorene), 6.63 (br. s, 1H, C2, indenyl), 4.35 (s, 3H, $MeNO_2$), 3.79 (d, ^2J = 24.0 Hz, 1H, C9, fluorene), 3.00 (d, ^2J = 24.0 Hz, 1H, C9, fluorene). ^{13}C NMR (CD_3NO_2): δ 148.7 (s, C4b or C8a, fluorene), 141.5 (s, C4−C7, indenyl), 140.8 (s, C4−C7, indenyl), 137.6 (s, C5−C8, fluorene), 131.3 (s, C5−C8, fluorene), 130.3 (s, C4b or C8a, fluorene), 128.6 (s, C4−C7, indenyl), 128.3 (s, C4−C7, indenyl), 123.9 (s, C5−C8, fluorene), 122.4 (s, C5−C8, fluorene), 121.9 (s, C4a or C9a, fluorene), 118.2 (s, C4a or C9a, fluorene), 105.6 (s, C3a or C7a, indenyl), 104.7 (s, C3a or C7a, indenyl), 96.9 (s, C1−C4, fluorene), 95.5 (s, C1−C4, fluorene), 93.8 (s, C1−C4, fluorene), 92.1 (s, C1−C4, fluorene), 88.4 (s, C2, indenyl), 83.8 (s, C1 or C3, indenyl), 83.6 (s, C1 or C3, indenyl), 37.0 (s, C9, fluorene). Anal. Calcd for $C_{22}H_{17}F_{12}IrSb_2 \cdot MeNO_2$: C, 27.96; H, 1.81. Found: C, 27.87; H, 1.77.

Arene Exchange Experiments. Mesitylene (0.02 mL, 0.14 mmol) was added to a solution of the complex (0.016 mmol) in nitromethane-d_3 (0.5 mL). The reactions were monitored by ^{1}H NMR spectroscopy. The results are summarized in Table 1.

Decomposition of [2a](SbF$_6$)$_2$ by D$_2$O. A solution of [**2a**](SbF$_6$)$_2$ (76 mg, 0.09 mmol) and D_2O (0.04 mL, 2.0 mmol) in nitromethane-d_3 (0.5 mL) was stirred for 1 week. The solvent was removed in vacuo, and the solid residue was extracted with petroleum ether (40 mL). The solution obtained was passed through a silica gel (10 cm). After removal of solvent in vacuo, 9-D-fluorene was obtained as a white solid. Yield 13.4 mg (ca. 89%).

General Procedure for Catalytic Reductive Amination. [**2b**](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 0.4 mL portion of water was added, and the autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm of CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 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 (4 × 1 mL); the product was extracted with dichloromethane (2 × 1 mL), the combined organic layers were dried with anhydrous sodium sulfate and filtered through a silica gel pad, and 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[26] and the correlation functional of Perdew[27] (BP86). The 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.[28] The calculations were carried out using the ADF 2010.01 program package.[29]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00378.

Crystallographic data, experimental procedures for catalytic reactions, and copies of NMR spectra (PDF)

Accession Codes

CCDC 1916687−1916688 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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dloginov@ineos.ac.ru.

ORCID

Yulia V. Nelyubina: 0000-0002-9121-0040
Dmitry V. Muratov: 0000-0002-8872-1608
Denis Chusov: 0000-0001-6770-5484

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (Grant No. 19-73-20212). The NMR studies were performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for Molecular Composition Studies of INEOS RAS.

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DOI: 10.1021/acs.organomet.9b00378
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