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Synthesis and Characterization of *N*-Trifluoromethyl N-Heterocyclic Carbene Ligands and Their Complexes

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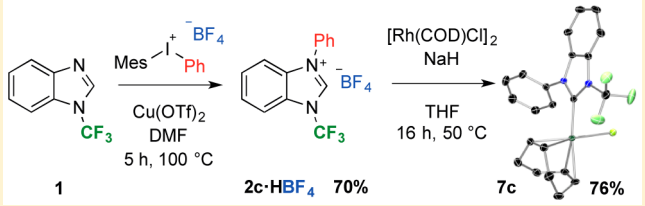
Supporting Information

ABSTRACT: Starting from *N*-trifluoromethyl benzimidazole (**1**), a series of *N*-trifluoromethyl benzimidazolium salts **2a−f·HA** have been prepared and fully characterized. These were engaged in the formation of [Ir(CO)$_2$(NHC)Cl], [Rh(COD)(NHC)Cl], [Se(NHC)], and [Au(NHC)Cl] derivatives. IR analysis of [Ir(CO)$_2$(NHC)Cl] complexes revealed that the trifluoromethyl substituent on nitrogen significantly decreases the σ-donating ability of the carbene carbon. On the other hand, the π-acceptor property of these novel ligands is enhanced. Examination of the ^{77}Se NMR resonance of [Se(NHC)] adducts and the redox potentials of [Rh(NHC)(COD)Cl] complexes further supports this assumption. In addition, the efficiency of these new *N*-trifluoromethyl NHC ligands was investigated in π-acidic Au(I)-catalyzed hydroalkoxylation of cyclohexene. The gold complexes bearing NHCs **2a** and **2c−e** compete with [Au(PPh$_3$)Cl] in terms of catalytic activity.



INTRODUCTION

The discovery by Arduengo et al.[1] that carbenes are not invariably reactive, unstable reaction intermediates has led to the preparation of a myriad of N-heterocyclic carbenes (NHCs) and ignited the curiosity of researchers toward possible applications of NHCs as ligands in homogeneous catalysis,[2] as well as components for medicinal,[3] luminescent, and functional materials.[4] This is reflected by the abundance of publications on NHCs and the vast structural diversity of commercially available NHC precursors nowadays.[5] The striking success of NHCs in transition metal catalysis was initially ascribed to their excellent σ-electron-donating properties, which leads to very strong metal carbene bonds,[6] hence preventing decomposition of the catalyst and giving rise to high catalytic activity. However, recent reports on the electronic nature of NHCs have also highlighted the significance of π-bonding in transition metal catalysis.[7] With the introduction of electron-withdrawing groups in the backbone structure or on the substituents at the nitrogen atoms of the NHCs, one can significantly improve metal-to-carbene π-back-donation.[8] As a consequence of this increased π-acidity of the ligand, the metal center becomes more electron-deficient, which has been shown to lead to an accelerated or increased reactivity for, for example, π-acid-catalyzed cyclizations.[9] As an interesting example, by tuning the π-acceptor properties of ancillary NHC ligands, Alcarazo et al.[10] could selectively modulate the outcome of three mechanistically distinct gold(I)-catalyzed processes. In order to evaluate the electronic effects of NHCs, Gusev[11] used computational methods to calculate the Tolman electronic parameter (TEP) of a diverse group of representative NHC ligands in [Ni(CO)$_3$(NHC)] complexes. Interestingly, this study also included NHCs that have not yet been synthesized, such as the *N*-bis(trifluoromethyl) NHC ImN(CF$_3$)$_2$ shown in Figure 1. These calculations predict that ImN(CF$_3$)$_2$ is a significantly weaker donor ligand compared to its methyl analogue ImN(Me)$_2$. The ability of the nitrogen lone pair to hyperconjugate into the σ^*_{C-F} antibonding orbital is considered to decrease the π-overlap of this nitrogen with the vacant p-orbital of the carbene. This in turn leads to an increased π-acidity, as reflected by the substantially higher TEP values for ImN(CF$_3$)$_2$ as compared to ImN(CH$_3$)$_2$.[12]

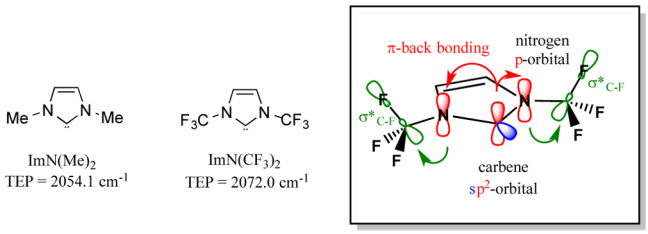


Figure 1. Calculated Tolman electronic parameters (TEP) of Ni(CO)$_3$(NHC) complexes bearing the NHC ligands ImN(Me)$_2$ and ImN(CF$_3$)$_2$ and schematic representation of crucial orbital interactions.

The larger TEP value of ImN(CF$_3$)$_2$ compared to ImN(Me)$_2$ is assumed to be a consequence of the negative hyperconjugation from the nitrogen lone pair of ImN(CF$_3$)$_2$ into the σ^*_{CF} antibonding orbital of the CF$_3$ group, which leads to a depletion of the electron density at the vacant p-orbital of the carbene carbon. These considerations clearly call for a synthetic

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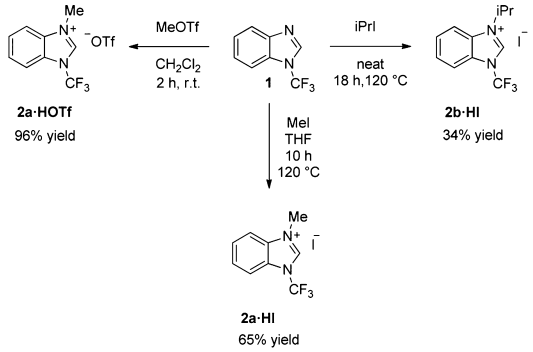
method to access *N*-trifluoromethyl NHCs, since a major impact on the behavior of the NHC as a ligand in transition metal catalysis is anticipated.

We report herein the synthesis of a series of *N*-trifluoromethyl NHC ligand precursors and their complexes starting from *N*-trifluoromethyl benzimidazole (**1**), which can be synthesized on a multigram scale following the procedure for direct *N*-trifluoromethylation of azoles recently reported by our group.[13] This study includes an evaluation of the electronic properties of these new *N*-trifluoromethyl NHC ligands and a comparison with well-established NHCs and phosphines.

RESULTS AND DISCUSSION

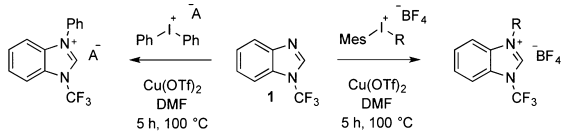
Treatment of *N*-trifluoromethyl benzimidazole (**1**) with an excess of methyl triflate in CH_2Cl_2 afforded benzimidazolium salt **2a·HOTf** as a bench-stable white solid in 96% yield. In addition, alkyl iodides could successfully be applied for the direct alkylation of **1**, however, under harsher reaction conditions and giving lower yields (Scheme 1).

Scheme 1. Synthesis of *N*-Trifluoromethyl Benzimidazolium Salts 2a·HOTf, 2a·HI, and 2b·HI



Disappointingly, it was not possible to arylate benzimidazole **1** with aryl halides. However, using diaryliodonium salts under copper(II) catalysis, as recently presented by Gao,[14] benzimidazolium salt **2c·HOTf** was initially prepared in 83% yield (Scheme 2). The synthesis of benzimidazolium salts **2d·HBF$_4$**, **2e·HBF$_4$**, and **2f·HBF$_4$** required the use of $[Cu(OTf)_2]$ instead of $[Cu(OAc)_2{\cdot}H_2O]$. Presumably, deprotonation of the newly formed benzimidazolium salt by acetate and consecutive complexation of the NHC to the copper catalyst inhibited the reaction.

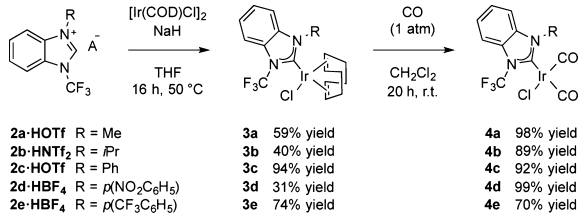
Scheme 2. Synthesis of *N*-Trifluoromethyl Benzimidazolium Salts 2c·HOTf, 2c·HBF$_4$, 2d·HBF$_4$, 2e·HBF$_4$, and 2f·HBF$_4$[a]



[a]Use of $[Cu(OAc)_2{\cdot}H_2O]$ instead of $[Cu(OTf)_2]$.

Determination of the π-Acceptor Properties of *N*-Trifluoromethyl NHC Ligands via IR and NMR Analysis. Iridium carbonyl complexes $[IrCl(CO)_2(NHC)]$ have become the standard model system for estimating the electronic properties of NHC ligands by measuring their average carbonyl stretching frequency, ν_{av}, using IR spectroscopy.[15] Iridium complexes **3a–e** were obtained by reaction of the *in situ* generated free carbenes with $[Ir(COD)Cl]_2$ using an excess of NaH in THF (Scheme 3). Unfortunately, this protocol could not be applied for **2b·HI**, which instead gave the undesired $[IrI(COD)(\mathbf{2b})]$ complex, containing an iodide ligand. To obtain iridium complex **3b**, an anion exchange of I^- with NTf_2^- prior to the reaction of **2b·HI** with $[Ir(COD)Cl]_2$ was necessary.

Scheme 3. Synthesis of [IrCl(COD)(NHC)] 3a–e and [IrCl(CO)$_2$(NHC)] 4a–e



Interestingly, the synthesis of iridium complex **3d** also afforded minor quantities of the dihydrobenzimidazole **2d·red** (Figure 2). The formation of this byproduct is not unusual, considering the ability of NaH to act both as a base and as a reductant.[16] However, treatment of benzimidazolium salt **2d·BF$_4$** with NaH in the absence of $[Ir(COD)Cl]$ did not lead to the formation of dihydrobenzimidazole **2d·red**.

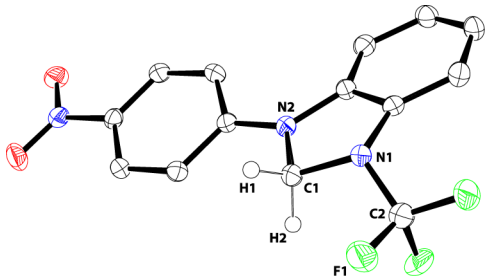


Figure 2. ORTEP drawing of **2d·red**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set to 50% probability. Selected bond lengths [Å], bond angles [deg], and torsion angles [deg]: C1–N1 1.474(2), C1–N2 1.471(2), N1–C2 1.394(3), C2–F1 1.337(3), N2–C1–N1 103.65(15), N2–C1–N1–C2–144.45(18).

Subsequent exposure of a solution of iridium complexes **3a–e** in CH_2Cl_2 to carbon monoxide afforded the respective $[Ir(CO)_2(NHC)Cl]$ complexes **4a–e**. The corresponding TEP parameters of complexes **4a–e** were determined by applying a relation established by Nolan and Plenio,[17] correlating the average CO stretching frequencies of $[IrCl(CO)_2(NHC)]$ complexes to the traditionally used $[Ni(CO)_3(L)]$ system (Table 2). Known TEP values of typical tertiary phosphines span over a relatively large range between 2056.1 cm^{-1} (PCy_3) and 2110.8 cm^{-1} (PF_3),[18] while the lower TEP values of standard NHCs are distributed over a relatively small range of ca. 10 cm^{-1} (Figure 3). *N*-Trifluoromethyl NHCs **2a–e**, on the other hand, are found at higher TEP values, thereby accounting for their less electron-donating nature. Furthermore, a significant difference between the TEP parameters of NHCs **2a–e** and that of NHC **5** (1,3-bis(2-propyl)-1*H*-benzimidazo-

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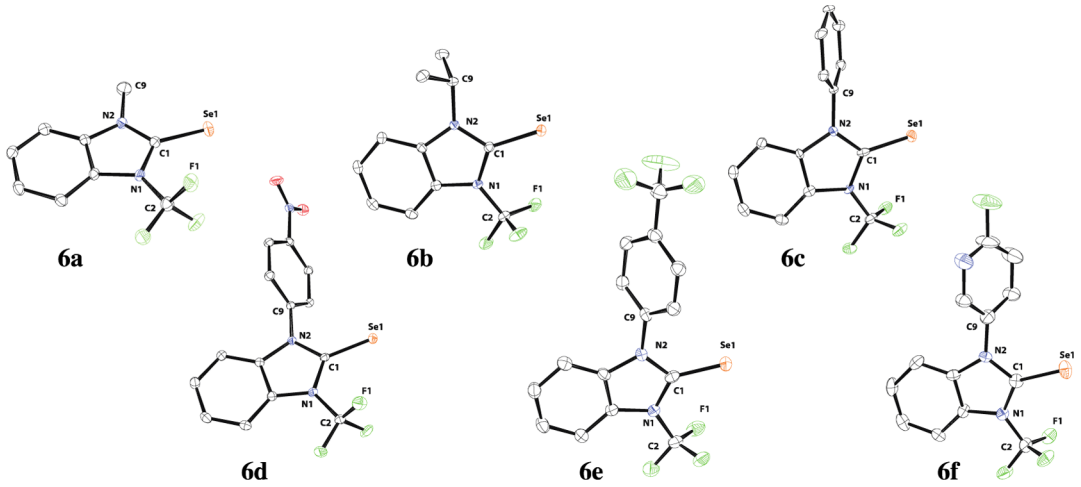
Table 1. Important Bond Lengths, Bond Angles, and Torsion Angles of Selenium Adducts 6a−f



	6a	6b	6c	6d	6e	6f
			Bond Lengths [Å]			
Se1−C1	1.820(3)	1.820(2)	1.804(4)	1.809(2)	1.814(5)	1.816(7)
N1−C2	1.418(4)	1.424(2)	1.418(5)	1.431(2)	1.439(6)	1.436(9)
N2−C9	1.467(4)	1.482(2)	1.437(5)	1.429(2)	1.435(6)	1.435(9)
			Bond Angles [deg]			
N1−C1−N2	105.7(2)	105.6(1)	105.1(3)	105.0(1)	105.7(4)	105.6(5)
			Torsion Angles [deg]			
Se1−C1−N1−C2	2.5(2)	2.5(2)	1.3(5)	1.7(2)	0.7(7)	−3.1(9)

lylidene) can be noted (Table 2). This finding suggests that the presence of a trifluoromethyl substituent at the nitrogen atom can lead to a higher d → π*(NHC) back-donation and hence a reduced d → π*(CO) back-donation compared to standard NHCs.

In order to quantify the contribution of the d → π* interactions for NHC−metal bonds, Ganter[8] has established an alternative model system to compare the π-acceptor strength of different types of NHCs. It has been demonstrated that the ^{77}Se NMR chemical shift of the corresponding NHC selenium adducts correlates with the π-acceptor character of the respective carbene. Furthermore, the ^{77}Se NMR chemical shift can be measured with far greater accuracy as compared to IR data. The NHC selenium adducts **6a−f** were obtained in one synthetic step by deprotonation of the NHC precursors **2a−f·HA** with NaHMDS in the presence of selenium black (Scheme 4). Interestingly, benzimidazolium salts having a triflate counterion could not be converted to the corresponding selenium adducts. Instead, decomposition of the benzimidazolium salts was observed under the applied reaction conditions.

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the corresponding selenium adducts **6a−f** in $CDCl_3$. ORTEP representations, as well as selected bond lengths and angles of selenium derivatives **6a−f**, are shown in Table 1. The Se−C bond lengths of compounds **6a−f** are all very similar and do not show any significant deviation from the value found for [Se(IPr)] (1.853(7) Å) and [Se(SIPr)] (1.820(8) Å).[19] The ^{77}Se NMR chemical shifts of derivatives **2a−f** range from 196 to 276 ppm, as presented in Table 2. Thus, compared to the selenium adduct of NHC **5**, the ^{77}Se resonance of, for example, **6b** is shifted by 148 ppm to lower field.

This is a consequence of the increased π-acidity induced by the trifluoromethyl group in **6b**. On the other hand, the electron-donating isopropyl groups of NHC **5** lead to an electronically more shielded selenium atom. Accordingly, the ^{77}Se NMR resonance of the selenium adduct of NHC **5** is shifted to higher field. Moreover, the introduction of an additional electron-withdrawing *p*-nitrophenyl (**2d**), *p*-trifluoromethyl (**2e**), or pyridinyl (**2f**) substituent at the second nitrogen atom leads to a further increase of the π-acidity of the respective NHCs. While the respective ^{77}Se NMR resonance of adducts **6a−f** are gradually shifted to lower field with increasing π-acidity, the TEP values of **2a−e** are barely affected. Interestingly, the TEP parameters of NHCs **2a−e** do not correlate with the ^{77}Se NMR and ^{13}C NMR chemical shifts of the carbene atoms in **6a−e**. Hence, comparison of the TEP values of imidazolylidenes with those of benzimidazolylidenes might be biased by the different nature of the metal to ligand bonding of these two NHC classes. This can best be illustrated by correlating the TEP values of SIPr and NHC **2b** to the respective ^{77}Se NMR chemical shifts. While the TEP values of SIPr and **2b** deviate substantially, the corresponding ^{77}Se NMR chemical shifts of the selenium adduct of SIPr and **2b** are only 6 ppm apart, implying a similar degree of π-accepting character. This observation can however be accounted for by the fact that saturated NHCs such as SIPr are slightly better σ-donors than their unsaturated analogues, which results in stronger metal to NHC bonding.[22]

Electrochemical Analysis of Complexes 7a−e. The redox potential $E_{1/2}$ of metal complexes is highly sensitive to the electron density at the metal center, which is in turn affected by the acceptor and donor properties of its ligands. More electronegative ligands remove electron density from the metal center, thereby increasing the energy barrier toward oxidation of the complex.[23] In order to gain further insight into the electronic properties of the *N*-trifluoromethyl NHC ligands, rhodium complexes **7a−e** were synthesized and their redox

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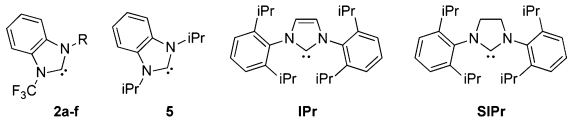
Table 2. Tolman Electronic Parameters (TEP) and NMR Data of Selected Carbenes



		[IrCl(CO)$_2$(NHC)]	[Se(NHC)]	
	ligand	TEP [cm^{-1}][a]	δ(^{13}C) [ppm][b]	δ(^{77}Se) [ppm][b]
2a	R = Me	2059.0	166.3	215
2b	R = *i*Pr	2058.6	165.2	196
2c	R = Ph	2058.0	167.4	249
2d	R = 4-NO$_2$Ph	2060.8	167.5	276
2e	R = 4-CF$_3$Ph	2059.9	167.4	264
2f	R = 4-F-py	n.d.	168.2	275
5[c]		2053.3	164.9	67
IPr[d]		2051.5	162.3	90
SIPr[d]		2052.2	184.3	190
IDNP[e]		2060.2		
IDA[f]		2069.0	182.3	856
PPh$_3$[g]		2068.9		

[a]TEP parameters were calculated from the symmetric and antisymmetric carbonyl stretching frequencies of the corresponding [IrCl(CO)$_2$(NHC)] complexes, using the relation TEP = 0.847 × ν_{av}(CO) + 336 cm^{-1}.[20] The IR spectra of complexes **4a–e** were measured in CH_2Cl_2. [b]The ^{77}Se NMR and ^{13}C carbene NMR chemical shifts of selenium adducts **6a–f** were measured in $CDCl_3$. [c]The symmetric and antisymmetric carbonyl stretching frequencies, as well as the ^{13}C and ^{77}Se chemical shifts, have been reported in ref 21. [d]The TEP parameters, as well as the ^{13}C and ^{77}Se chemical shifts, have been reported in ref 19. [e]IDNP = 1,3-bis(2,4-dinitrophenyl)-1*H*-imidazolylidene. The TEP parameter has been reported in ref 9c. [f]IDA = 1,3-dimesityl-4,5-dioxo-4,5-dihydro-1*H*-imidazolylidene. The TEP parameters, as well as the ^{13}C and ^{77}Se chemical shifts, have been reported in ref 8. [g]The TEP parameter has been reported in ref 18.

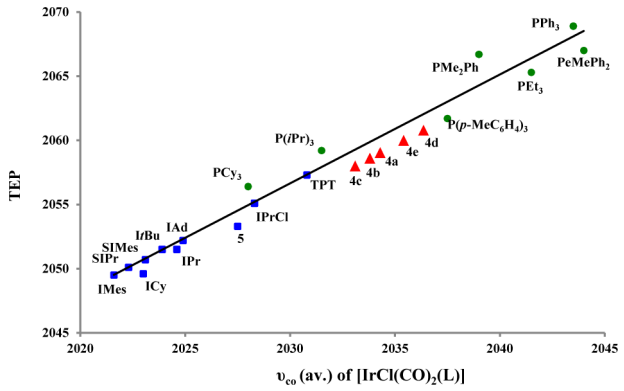
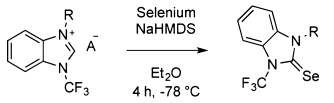


Figure 3. Correlation of the average carbonyl stretching frequency ν_{co} values of [IrCl(CO)$_2$(L)] complexes with the Tolman electronic parameter (TEP): (▲) *N*-trifluoromethyl NHCs **2a–e**; (◆) standard NHCs; (●) tertiary phosphines.

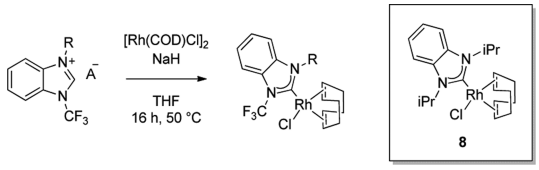
potentials were determined by cyclic voltammetry (Table 3). Except for rhodium complex **7a**, the Rh(I/II) redox process of **7b–e** turned out to be reversible. Notably, the redox potential changes by 0.239 mV when replacing the electron-donating isopropyl group on the nitrogen of **5** with a trifluoromethyl group in complex **7b**. Due to the fact that the Cl and COD ligands remain constant in the [RhCl(COD)(NHC)] complexes examined, the shift to higher redox potentials can be

Scheme 4. Synthesis of Selenium Adducts 6a–f



2a·HNTf$_2$	R = Me	**6a**	87% yield
2b·HI	R = *i*Pr	**6b**	86% yield
2c·HBF$_4$	R = Ph	**6c**	32% yield
2d·HBF$_4$	R = *p*(NO$_2$C$_6$H$_5$)	**6d**	62% yield
2e·HBF$_4$	R = *p*(CF$_3$C$_6$H$_5$)	**6e**	55% yield
2f·HBF$_4$	R = *p*(FC$_5$NH$_4$)	**6f**	49% yield

Table 3. Redox Potentials $E_{1/2}$ [V] of [RhCl(COD)(NHC)] Complexes 7a–e and 8



				[RhCl(COD)(NHC)]	
	ligand	A	R	yield (%)	$E_{1/2}$[a] (V)
7a	**2a**	OTf	Me	72	n.d.
7b	**2b**	I	*i*Pr	65	1.012
7c	**2c**	BF$_4$	Ph	76	0.858
7d	**2d**	BF$_4$	*p*(NO$_2$C$_6$H$_5$)	57	1.053
7e	**2e**	BF$_4$	*p*(CF$_3$C$_6$H$_5$)	58	1.025
8					0.773

[a]Calibrated against Fc/Fc$^+$ $E_{1/2}$ = 0.46,[26] 0.1 M Bu$_4$NPF$_6$ in CH_2Cl_2.

attributed to the increased electron-withdrawing property of the trifluoromethyl substituent of NHC **2b**. Interestingly, the redox potential of rhodium complex **7c** (Figure 4) is lowered by 0.167–0.195 mV compared to complexes **7d** and **7e**.

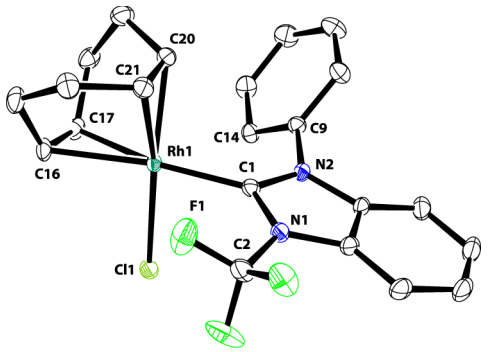


Figure 4. ORTEP drawing of **7c**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set to 50% probability. Selected bond lengths [Å], bond angles [deg], and torsion angles [deg]: Rh1–C1 2.015(2), Rh1–C16 2.208(2), Rh1–C17 2.175(2), Rh1–C20 2.125(2), Rh1–C21 2.107(2), C1–N1 1.380(3), C1–N2 1.350(3), N1–C2 1.425(3), N2–C9 1.437(3), N1–C1–N2 104.25(2), C1–Rh1–C21 95.62(8), N1–C1–Rh1–Cl1–76.2(2), C1–N2–C9–C14–56.9(3).

When trying to rationalize the observed reduction potentials, π-conjugation could easily be ruled out: First of all, the metal center and the electron-withdrawing group at the C_{para} are separated by 7 bonds. Second, the near orthogonality of the two aromatic systems renders their conjugation quite unlikely. Finally, when comparing the N2–C3 bond distances of the selenium adducts **6a–f**, no change in bond length can be

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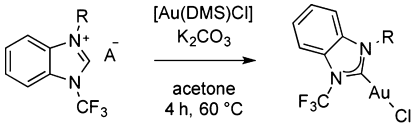
observed, likewise hinting at a negligible π-conjugation. Similar observations were made by Plenio,[24] who proposed that the interaction between the NHC ligand and the metal center could occur through π-face donation from an electron-rich *N*-aryl moiety, hence increasing the electron density at the metal center and possibly stabilizing higher oxidation states during catalysis. Recently, Cavallo[25] further examined this mode of interaction with the help of DFT calculations. His findings suggest a π-face donation from the C_{ipso} of the *N*-aryl moiety to an empty d-orbital of the metal center, this phenomenon increasing for more electron donating para substituents. This assumption is supported by the observation that the redox potential of complex **7b** is higher by 0.154 mV compared to that of complex **7c**, although an isopropyl group is generally considered to be a better σ-electron donor than a phenyl group. Indeed, in contrast to the phenyl group (**7c**), C_{ipso} of the isopropyl group (**7b**) does not possess any π-orbital to donate electron density to the metal center.

Au-Catalyzed Hydroxyalkoxylation of Alkenes. We were interested in comparing the influence on reactivity of the novel *N*-trifluoromethyl NHC ligands with that of known NHCs in π-acid gold catalysis. Similarly to a recent report by Sato et al.,[27] we expected that the significant extent of Au-NHC d → π* back-bonding would enhance the π-acidity of the metal center, giving superior catalysts. The Au(I)-NHC complexes **9a–e** were synthesized by *in situ* deprotonation of the corresponding benzimidazolium salts with K_2CO_3 in the presence of [Au(DMS)Cl] (Scheme 5).

Scheme 5. Synthesis of Au-NHC Gold Complexes 9a–e



2a·HOTf	R = Me	**9a**	36%
2c·HOTf	R = Ph	**9b**	45%
2d·HBF$_4$	R = *p*($NO_2C_6H_5$)	**9c**	34%
2e·HBF$_4$	R = *p*($CF_3C_6H_5$)	**9d**	41%
2f·HBF$_4$	R = *p*(FC_5NH_4)	**9e**	44%

Single crystals of **9a** suitable for X-ray diffraction analysis were obtained by sublimation. The ORTEP representation of **9a** is shown in Figure 5. Both the C1–Au bond length (1.982(6) Å) and the Au–Cl bond length (2.2778(14) Å) in **9a** are comparable to those in [Au(IPr)Cl] ($C_{carbene}$–Au = 1.998(4) Å and Au–Cl = 2.2718(11) Å).[28] The catalytic activity of the Au(I)-NHC complexes **9a–e** was then evaluated in the intermolecular hydroalkoxylation of cyclohexene as a model reaction, using the same reaction conditions as reported by Sato et al.[29] For comparison, the catalytic activities of the Au(I) complexes bearing PPh_3, IDNP, IPr, and NHC **5** are also provided in Table 4.

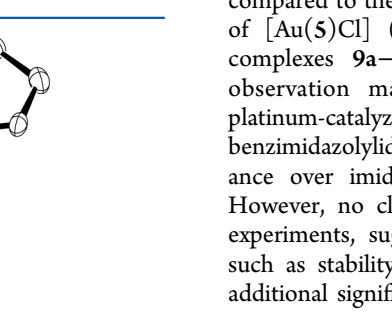
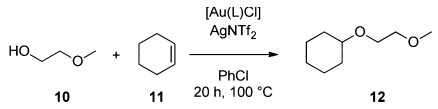


Figure 5. ORTEP drawing of **9a**. Hydrogen atoms are omitted for clarity, and thermal ellipsoids are set to 50% probability. Selected bond lengths [Å] and bond angles [deg]: Au1–C1 1.982(6), Au1–Cl1 2.2778(14), C1–N1 1.360(8), C1–N2 1.346(7), N1–C2 1.417(7), N2–C9 1.456(8), N1–C1–N2 106.4(5).

Table 4. Au(I)-Catalyzed Intermolecular Hydroalkoxylation of Cyclohexene[a]



entry	[Au(L)Cl]	yield[b] (%)
1	**9a**, L = **2a**	70
2	**9b**, L = **2c**	74
3	**9c**, L = **2d**	75
4	**9d**, L = **2e**	77
5	**9e**, L = **2f**	11
6	L = **5**	77
7	L = IPr	35 (lit: 7)[c]
8	L = PPh_3	76 (lit: 63)[c]
9	L = IDNP[d]	64 (lit: 66)[c]
10	none	0

[a]Reaction conditions: **10** (0.25 mmol), **11** (2.5 mmol), gold complex (0.0125 mmol), and $AgNTf_2$ (0.0125 mol) in PhCl (0.25 mL) for 20 h. [b]Yields were determined by GC analysis, using *n*-tetradecane as an internal standard. [c]See ref 29. [d]IDNP = 1,3-bis(2,4-dinitrophenyl)-1*H*-imidazolylidene.

From the corresponding results, we conclude that the *N*-trifluoromethyl NHCs **2a** and **2c–e** induce an intermediate π-acidity between that of standard NHCs and phosphines. If the catalytic activity were solely dependent on the π-acidity of the gold complexes, one would therefore expect a correlation between the analytical data and the reaction outcome. The gold complex bearing the weakest π-accepting NHC, IPr, indeed shows the lowest catalytic efficiency (35% yield). Interestingly, the catalytic activities of the gold complexes **9a–d** (70–77% yield) were found to surpass that of [Au(IDNP)Cl] (64% yield) and compete with that of [Au(PPh_3)Cl] (76% yield). Au(I) complex **9e**, bearing the pyridinyl N-substituent, on the other hand, leads to a yield of only 11%. Furthermore, although the analytical data suggest that NHC **5** is a weaker π-acceptor compared to the *N*-trifluoromethyl NHCs, the catalytic activity of [Au(**5**)Cl] (77% yield) is comparable to that of gold complexes **9a–d**. This result can be rationalized by an observation made by Hahn et al.[30] in palladium- and platinum-catalyzed cross-coupling reactions, suggesting that benzimidazolylidene ligands generally show improved performance over imidazolylidene ligands in such transformations. However, no clear trend can be inferred from these simple experiments, suggesting that, besides π-acidity, other factors such as stability and solubility of the active catalyst play an additional significant role.

CONCLUSIONS

A series of *N*-trifluoromethyl NHC ligand precursors **2a–f·HA** have been synthesized and fully characterized starting from *N*-trifluoromethyl benzimidazole **1**. In order to explore the π-accepting properties of the corresponding NHC ligands, they

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have been engaged in the formation of several organometallic complexes. The spectroscopic analysis of [IrCl(CO)$_2$(NHC)] complexes revealed that NHCs bearing a trifluoromethyl substituent are significantly weaker donor ligands compared to standard NHCs, as reflected by their higher TEP values. The decreased σ-donating ability of the carbene carbon is considered to be a consequence of the diminished π-overlap with the nitrogen lone pair, due to hyperconjugation of the nitrogen lone pair into the σ^*_{C-F} antibonding orbital of the trifluoromethyl group. Concurrently, the π-accepting property of these novel ligands is enhanced, which was verified by examining the ^{77}Se NMR resonance of [Se(NHC)] adducts and the redox potentials of [RhCl(COD)(NHC)] complexes. To further evaluate and compare the electronic properties of our *N*-trifluoromethyl NHCs to those of well-established NHCs and PPh_3, the intermolecular hydroalkoxylation of cyclohexene with 2-methoxyethanol using Au(I) complexes was carried out. The gold complexes **9a−d** were found to be catalytically active and compete with [Au(PPh_3)Cl] and [Au(**5**)Cl] complexes on the basis of product formation.

EXPERIMENTAL SECTION

General Information. All experiments were performed under an argon atmosphere using standard Schlenk techniques. Solvents were distilled and dried prior to utilization (CH_2Cl_2 from CaH_2; Et_2O, THF, and toluene from Na/benzophenone; chlorobenzene from P_2O_5). Unless otherwise stated all commercially available chemicals were used without further purification. Cyclohexene and 2-methoxyethanol were purified by atmospheric distillation prior to use. The following reagents and metal complexes were synthesized according to reported procedures: 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole,[31] diaryliodonium triflates,[32] NaHMDS,[33] [Ir(COD)Cl]$_2$,[34] [Rh(COD)Cl]$_2$,[35] [Rh(**5**)(COD)Cl],[36] [Au(IDNP)Cl],[37] [Au(IPr)Cl].[38] Diaryliodonium trilfates were converted to the corresponding diaryliodonium tetrafluoroborates following a procedure reported by Olofsson.[39] Neutral aluminum oxide activity I was purchased from ICN Biomedicals GmbH. Silica gel 60 (230−400 mesh) was purchased from Fluka. TLC plates were obtained from Merck (silica gel 60 F254). NMR spectra were recorded on Bruker DPX-200, DPX-300, DPX-400, and DPX-500 instruments operating at the denoted spectrometer frequency given in MHz for the specified nucleus. The ^{1}H and ^{13}C chemical shifts are referred to TMS and calibrated with the residual solvent peak. For ^{19}F NMR, $CFCl_3$ was used as an external standard. The chemical shifts are reported in parts per million (ppm), and coupling constants *J* are given in hertz (Hz). High-resolution mass spectra were measured by the MS-service of the "Laboratorium für Organische Chemie der ETH Zürich". Values are given as *m*/*z* and the intensity *I*% of the base peak. Elemental analysis was performed by the microelemental anaylsis service of the "Laboratorium für Organische Chemie der ETH Zürich and the Mikroelementalanalytisches Laboratorium der ETH Zürich". Melting points were determined on a Büchi melting point B-540 apparatus in open capillaries and are uncorrected. IR spectra were recorded on a Thermo Fischer Scientific Nicolet 6700 FT-IR equipped with a PIKE Technologies GladiATR or on a PerkinElmer BX II using ATR FT-IR technology and are reported as absorption maxima in cm^{-1}. X-ray diffraction structural analysis was carried out on a Siemens CCD diffractometer (Siemens SMART PLATFORM, with CCD detector, graphite monochromator, Mo Kα radiation). Details of the data collection and refinement can be found in the Supporting Information. The GC yields of ether **12** were determined by addition of *n*-tetradecane as an internal standard on a Thermo Fischer Trace GC 2000 equipped with a flame ionization detector, using a ZB-5 column with guardian (L: 30 m × i.d.: 0.25 mm, DF = 0.25 μm) and helium as the carrier gas with a constant flow of 1.1 mL/min.

1-(Trifluoromethyl)-1*H*-benzo[*d*]imidazole (1). A 250 mL two-necked round-bottom flask equipped with a reflux condenser was charged with benzimidazole (6000 mg, 50.8 mmol, 1.1 equiv), silica sulfuric acid (150 mg), and HMDS (50 mL, 157.2 mmol, 3.4 equiv). The reaction mixture was heated to reflux for 6 h. Subsequently, the reaction was cooled to room temperature and filtered through a cannula with a filter into a 200 mL Schlenk flask. The 250 mL two-necked round-bottom flask was washed with toluene (2 × 10 mL). The solvent and the HMDS were removed under reduced pressure (15 mbar) to give the trimethylsilylated benzimidazole, which was then dried for an additional 30 min under high vacuum (4.2×10^{-2} mbar). In a glovebox, the trimethylsilylated benzimidazole was dissolved in CH_2Cl_2 (15 mL), and $LiNTf_2$ (155 mg, 0.924 mmol, 0.02 equiv) was added. After shaking, 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (15 200 mg, 46.2 mmol, 1 equiv) and $HNTf_2$ (1560 mg, 15.54 mmol, 0.12 equiv) were added, and the neck of the Schlenk flask was rinsed with CH_2Cl_2 (5 mL). The resulting clear solution was then stirred at 35 °C for 20 h. The reaction mixture was then cooled to rt and concentrated on a rotatory evaporator (650 mbar). The residue was purified by column chromatography (Pentane/Et_2O, 10:1 to 2:1) and subsequent bulb-to-bulb distillation (60 °C, 5×10^{-2} mbar) to afford **1** (6128 mg, 46.2 mmol, 71.3% isolated yield) as a colorless liquid. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.15 (s, 1H, NCHN), 7.86 (d, *J* = 9.2 Hz, 1H, ArH), 7.60 (d, *J* = 7.3 Hz, 1H, ArH), 7.42 (m, 2H, ArH). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −57.04. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ = 143.78 (C), 138.21 (NCHN), 130.32 (C), 125.58 (CH), 124.73 (CH), 124.13(CH), 118.90 (q, J = 263.5 Hz, NCF_3), 111.40 (q, *J* = 2.1 Hz, CH). IR (neat): 3090.3, 1376.9, 1320.9, 1292.2, 1231.8, 1150.9, 1000.6, 739.5 cm^{-1}. HRMS (ESI): [M + H$^+$] calcd for $C_8H_6F_3N_2$ 187.05; found 187.0490. Anal. Calcd (%) for $C_8H_5F_3N_2$: C, 51.62; H, 2.71; N, 15.05. Found: C, 51.79; H, 2.82; N, 15.18.

3-Methyl-1-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-3-ium Triflate (2a·HOTf). A 50 mL Young Schlenk flask was charged with **1** (1021 mg, 5.48 mmol, 1 equiv) and CH_2Cl_2 (10 mL). Subsequently, the reaction mixture was cooled to 0 °C, and methyl trifluoromethanesulfonate (0.95 mL, 8.23 mmol, 1.5 equiv) was added dropwise over 10 min. The reaction mixture was stirred at room temperature for 3 h. Subsequently, all volatiles were removed under reduced pressure (9×10^{-3} mbar) to give **2a·HOTf** (1836 mg, 5.24 mmol, 95.6%) as a white solid. ^{1}H NMR (300.13 MHz, MeOD-d_4): δ = 10.40 (s, 1H, NCHN), 8.15−8.12 (m, 1H, ArH), 8.07−8.05 (m, 1H, ArH), 7.95−7.86 (m, 2H, ArH), 4.27 (s, 3H, NCH_3). ^{19}F NMR (282.38 MHz, MeOD-d_4): δ = −59.54 (NCF_3), −80.18 (SCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, MeOD-d_4): δ = 143.64−142.97 (apt m, NCHN), 133.69 (C), 130.62 (CH), 129.83 (CH), 128.80 (C), 121.12 (q, *J* = 318.56 Hz, CF_3), 118.87 (q, *J* = 268.5 Hz, CF_3), 115.65 (CH), 114.49 (CH), 34.99 (NCH_3). IR (neat): 3177.9, 3116.9, 1260.0, 1210.1, 1150.4, 1025.9, 754.5, 635.4 cm^{-1}. HRMS (ESI): [M$^+$ − CF_3O_3S] calcd for $C_9H_8F_3N_2$ 201.06; found 201.0642. Anal. Calcd (%) for $C_{10}H_8N_2O_3F_6S$: C, 34.29; H, 2.30; N, 8.00. Found: C, 34.29; H, 2.29; N, 8.05. Mp: 135.8 °C.

3-Methyl-1-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-3-ium Iodide (2a·HI). A septum cap vial (5 mL) tube was charged with **1** (160.0 mg, 0.86 mmol, 1 equiv) and THF (2 mL). Subsequently, methyl iodide (0.2 mL, 3.19 mmol, 3.7 equiv) and the reaction mixture were stirred at 120 °C for 12 h. Subsequently, the precipitate was collected, washed with acetone (3 × 10 mL), and dried *in vacuo* to afford **2a·HI** (184.1 mg, 0.56 mmol, 65.3%) as a white, crystalline solid. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 10.71 (s, 1H, NCHN), 8.25−8.21 (m, 1H, ArH), 8.13−8.09 (m, 1H, ArH), 7.89−7.86 (m, 2H, ArH), 4.18 (s, 3H, NCH_3). ^{19}F NMR (282.38 MHz, DMSO-d_6): δ = −59.45 (NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ 143.46 (apt d, *J* = 3.1 Hz, NCHN), 131.87 (C), 128.98 (CH), 128.08 (CH), 126.65 (C), 116.99 (apt d, *J* = 268.0 Hz, NCF_3), 114.93 (CH), 113.16 (CH), 34.34 (NCH_3). IR (neat): 3013.7, 2980.1, 2924.1, 1363.5, 1235.2, 1184.1, 1135.8, 1083.2, 762.2 cm^{-1}. HRMS (ESI): [M$^+$ − I] calcd for $C_9H_8F_3N_2$ 201.06; found 201.0634. Anal. Calcd (%) for $C_9H_8N_2F_3I$: C, 32.95; H, 2.46; N, 8.54. Found: C, 32.74; H, 2.34; N, 8.40. Mp: 239.6 °C.

3-Isopropyl-1-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-3-ium Iodide (2b·HI). A septum cap vial (5 mL) tube was charged with **1**

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(700 mg, 3.76 mmol) and 2-iodopropane (2 mL, 19.84 mmol). The reaction mixture was then stirred at 120 °C for 18 h. Subsequently, diethyl ether (3 mL) was added. The resulting precipitate was filtered off and recrystallized from MeOH/Et_2O to afford **2b·HI** (455.1 mg, 33.9%) as a white, crystalline solid. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 10.59 (s, 1H, NCHN), 8.36−8.32 (m, 1H, ArH), 8.12−8.0 (m, 1H, ArH), 7.88−7.5 (m, 2H, ArH), 5.19 (hept, J = 6.7 Hz, NCH), 1.69 (d, J = 6.7 Hz, 6H, $C(CH_3)_2$). ^{19}F NMR (282.38 MHz, DMSO-d_6): δ = −57.19 (NCF_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, DMSO-d_6): δ = 141.72 (NCHN), 130.58 (C), 128.97 (CH), 128.01 (CH), 127.15 (C), 117.04 (q, J = 268.2 Hz, NCF_3), 115.30 (CH), 113.40−113.36 (m, CH), 52.51 (NCH), 21.06 (CH_3). IR (neat): 3119.6, 3017.8, 2981.2, 1556.9, 1423.9, 1356.7, 1219.5, 1171.4, 1057.5, 754.1 cm^{-1}. HRMS (MALDI/ESI): [M^+ − I] calcd for $C_{11}H_{12}F_3N_2$ 229.09; found 229.0942. Anal. Calcd (%) for $C_{11}H_{12}N_2F_3I$: C, 37.10; H, 3.40; N, 7.87. Found: C, 36.97; H, 3.36; N, 7.74. Mp: 228.9 °C.

*General Procedure A. Synthesis of Benzimidazolium Salts **2c−f**.* Benzimidazolium salts **2c−f** were synthesized starting from **1** following a modified procedure previously reported by Gao.[40] To a solution of the corresponding diaryl iodonium salt (1.5 equiv) in DMF (0.2 M) were added **1** (1 equiv) and $Cu(OTf)_2$ (5 mol %). The resulting reaction mixture was stirred at 100 °C for 6 h. Subsequently, Et_2O was added to precipitate the product, which was filtered off and washed thoroughly with CH_2Cl_2. Subsequent recrystallization from acetone/Et_2O afforded the product as a white solid.

*1-(Trifluoromethyl)-3-(phenyl)-1H-benzo[d]imidazol-3-ium Triflate (**2c·HOTf**).* Synthesized according to general procedure A from **1** (500 mg, 2.69 mmol) and diphenyliodonium triflate (1733.4 mg, 4.03 mmol). The product was obtained as a white solid (919.9 mg, 2.23 mmol, 83%). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 11.14 (s, 1H, NCHN), 8.24 (dt, J = 9.1, 1.6 Hz, 1H, ArH), 7.97−7.80 (m, 8H, ArH). ^{19}F NMR (282.38 MHz, DMSO-d_6): δ = −57.54 (NCF_3), −77.77 (SCF_3). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ = 162.54 (C), 143.62 (apt d, J = 3.2 Hz, NCHN), 132.01 (CH), 131.53 (C), 131.45 (CH), 130.40 (CH), 129.28 (CH), 128.87 (CH), 126.80 (CH), 125.59 (CH), 120.63 (apt d, J = 322.5 Hz, CF_3), 117.07 (apt d, J = 268.9 Hz, CF_3), 115.29 (CH), 113.54 (CH). IR (neat): 3132.6, 3064.6, 3010.6, 1566.9, 1475.8, 1286.7, 1240.4, 1202.5, 1156.6, 1031.3, 744.7, 637.9 cm^{-1}. HRMS (ESI): [M^+ − CF_3O_3S] calcd for $C_{14}H_{10}F_3N_2$ 263.08; found 263.0791. Anal. Calcd (%) for $C_{15}H_{10}N_2F_6O_3S$: C, 43.70; H, 2.44; N, 6.79. Found: C, 43.52; H, 2.29; N, 6.82. Mp: 181.8 °C

*1-(Trifluoromethyl)-3-(phenyl)-1H-benzo[d]imidazol-3-ium Tetrafluoroborate (**2c·HBF$_4$**).* Synthesized according to general procedure A from **1** (120.1 mg, 0.64 mmol) and diphenyliodonium tetrafluoroborate (355.85 mg, 0.97 mmol). The product was obtained as a white solid (157.5 mg, 0.45 mmol, 70.3%). ^{1}H NMR (300.13 MHz, acetone-d_6): δ = 10.76 (s, 1H, NCHN) 8.27 (d, J = 8.64 Hz, 1H, ArH), 8.06−7.94 (m, 5H, ArH), 7.84 (apt d, J = 3.1 Hz, 3H, ArH). ^{19}F NMR (282.38 MHz, acetone-d_6): δ = −58.87 (NCF_3), −151.85 (BF_4). $^{13}C\{^1H\}$ NMR (75.48 MHz, acetone-d_6): δ = 142.91 (d, J = 3.3 Hz, C), 133.29 (d, J = 5.7 Hz, NCHN), 132.69 (C), 131.50 (CH), 130.68(C), 130.16, (CH), 128.54, (C), 126.65 (CH), 118.52 (q, J = 269.1 Hz, CF_3), 115.80 (CH), 114.58 (q, J = 1.6 Hz, CH). IR (neat): 3148.5, 3089.0, 3044.7, 1565.2, 1409.7, 1364.3, 1239.0, 1211.5, 1059.1, 1019.1, 753.9, 689.9 cm^{-1}. HRMS (ESI): [M^+ − BF_4] calcd for $C_{14}H_{10}F_3N_2$263.08; found 263.0788. Mp: 175.2 °C.

*3-(4-Nitrophenyl)-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ium Tetrafluoroborate (**2d·HBF$_4$**).* Synthesized according to general procedure A from **1** (545.4 mg, 2.93 mmol) and mesityl(4-nitrophenyl)iodonium tetrafluoroborate (2000.0 mg, 4.39 mmol). The product was obtained as a white solid (818.2 mg, 2.07 mmol, 70.7%). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 11.30 (s, 1H, NCHN), 8.67 (d, J = 8.6 Hz, 2H, ArH), 8.28 (d, J = 7.8 Hz, 1H, ArH), 8.18 (d, J = 8.6, 2H, ArH), 8.03−7.91 (m, 3H, ArH). ^{19}F NMR (282.38 MHz, DMSO-d_6): δ = −57.69 (NCF_3), −148.40 (BF_4). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ = 148.94 (C), 144.31 (apt d, J = 3.2 Hz, NCHN), 136.76 (C), 131.21 (C), 129.56 (CH), 129.14 (CH), 127.41 (2C, CH), 126.75 (C), 125.75 (2C, CH), 117.05 (apt d, J = 269.3 Hz, CF_3), 114.67 (CH), 113.68 (CH). IR (neat): 3140.6, 3080.3, 3038.6, 1530.6, 1357.2, 1239.6, 1205.6, 1022.8, 460.4, 692.9 cm^{-1}. HRMS (ESI): [M^+ − BF_4] calcd for $C_{14}H_9F_3N_3O_2F_3$ 308.07; found 308.0641. Mp: 243.8 °C.

*1-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1H-benzo[d]-imidazol-3-ium Tetrafluoroborate (**2e·HBF$_4$**).* Synthesized according to general procedure A from **1** (545.2 mg, 2.93 mmol) and mesityl(4-(trifluoromethyl)phenyl)iodonium tetrafluoroborate (2100 mg, 4.39 mmol). The product was obtained as a white solid (749.7 mg, 1.79 mmol, 61.2%). ^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 11.23 (s, 1H, NCHN), 8.26 (apt t, J = 8.7 Hz, 3H, ArH), 8.13 (apt d, J = 8.3 Hz, 2H, ArH), 7.91 (m, 3H, ArH). ^{19}F NMR (282.38 MHz, DMSO-d_6): δ = −57.67 (NCF_3), −61.34 ($ArCF_3$), −148.40 (BF_4). $^{13}C\{^1H\}$ NMR (100.62 MHz, DMSO-d_6): δ = 144.15 (apt d, J = 2.9 Hz, NCHN), 135.34 (C), 131.70 (C), 131.34 (C), 129.50 (CH), 129.07 (CH), 127.71 (2C, q, J = 3.8 Hz, CH), 126.98 (2C, CH), 126.77 (C), 123.55 (apt d, J = 272.8 Hz, CF_3), 117.08 (apt d, J = 269.1 Hz, CF_3), 114.75 (CH), 113.63 (CH). IR (neat): 3144.0, 3072.3, 3017.8, 1567.3, 1326.7, 1212.2, 1127.6, 1068.8, 1023.7, 853.8, 753.1 cm^{-1}. HRMS (ESI): [M^+ − BF_4] calcd for $C_{15}H_9F_6N_2$ 331.07; found 331.0670. Mp: 224.5 °C.

*3-(6-Fluoropyridin-3-yl)-1-(trifluoromethyl)-1H-benzo[d]-imidazol-3-ium Tetrafluoroborate (**2f·HBF$_4$**).* Synthesized according to general procedure A from **1** (723.1 mg, 3.88 mmol) and (6-fluoropyridin-3-yl)(mesityl)iodonium tetrafluoroborate (2500.0 mg, 5.83 mmol). The product was obtained as a white solid (250.9 mg, 0.68 mmol, 17.5%). ^{1}H NMR(400.13 MHz, acetone-d_6): δ = 10.77 (s, 1H, NCN), 8.73 (s, 1H, ArH), 8.63 (ddd, J = 9.1, 6.6, 2.8 Hz, 1H, ArH), 8.27 (d, J = 8.0 Hz, 1H, ArH), 8.04 (m, 2H, ArH), 7.59 (dd, J = 8.8, 3.1 Hz, 1H, ArH), 7.46 (dd, J = 8.8, 3.1 Hz, 1H, ArH). ^{19}F NMR (376.46 MHz, acetone-d_6): δ = −59.02 (NCF_3), −64.99 (ArF), −151.74 (BF_4). $^{13}C\{^1H\}$ NMR (100.62 MHz, acetone-d_6): δ = 165.37 (apt d, J = 242.8 Hz, CF), 146.63 (d, J = 17.9 Hz, CCHN), 143.80 (apt d, J = 3.3 Hz, NCHN), 141.20 (d, J = 9.9 Hz, CH), 133.67 (C), 130.86 (CH), 130.37 (CH), 128.68 (apt d, J = 4.7 Hz, C), 128.36 (C), 117.56 (apt d, J = 272.5 Hz, CF_3), 114.83 (CH), 113.71 (q, J = 1.5 Hz, CH), 111.61 (d, J = 40.3 Hz, CH). IR (neat): 3150.7, 3086.9, 3048.0, 1569.2, 1495.0, 1474.9, 1422.8, 1365.4, 1287.6, 1242.9, 1210.5, 1165.6, 1064.9, 1012.3, 919.3, 832.8, 760.0 cm^{-1}. HRMS (ESI): [M^+ − BF_4] calcd for $C_{13}H_8F_4N_3$ 282.07; found 282.0651. Mp: 251.6 °C with decomposition.

*General Procedure B. Synthesis of N-Trifluoromethyl Benzimidazolium Triflimides (**2a·HNTf$_2$** and **2b·HNTf$_2$**).* *N*-Trifluoromethylated benzimidazolium triflimides **2a·HNTf$_2$** and **2b·HNTf$_2$** were synthesized via anion exchange from their corresponding triflate and iodide analogues following a modified procedure previously reported by Yagupolskii.[41] To an aqueous solution (0.16 M) of the corresponding benzimidazolium salt (1 equiv) was added $LiNTf_2$ (2 equiv). The mixture was then stirred at room temperature for 6 h. The white precipitate formed during the reaction was filtered off and recrystallized from acetone/Et_2O to afford the *N*-trifluoromethylated benzimidazolium triflimides as a white solid.

*3-Methyl-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ium Triflimide (**2a·HNTf$_2$**).* Synthesized according to general procedure B from **2a·HOTf** (1200 mg, 3.43 mmol) and $LiNTf_2$ (1969.4 mg, 6.86 mmol). The product was obtained as a white solid (1393.9 mg, 2.89 mmol, 84.5%). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 10.66 (s, 1H, NCHN), 8.23−8.20 (m, 1H, ArH), 8.12−8.10 (m, 1H, ArH), 7.91−7.84 (m, 2H, ArH), 4.17 (s, 3H, NCH_3). ^{19}F NMR (282.38 MHz, DMSO-d_6): δ = −57.53 (NCF_3), −78.75 (SCF_3). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): δ = 143.49 (app d, J = 2.9 Hz, NCHN), 131.88 (C), 129.01(C), 128.11 (CH), 126.72 (C), 119.46 (q, J = 321.9 Hz, CF_3), 117 (apt d, J = 267.7 Hz, CF_3) 114.88 (CH), 113.17 (CH), 34.16 (CH_3). IR (neat): 3122.2, 1582.6, 1464.4, 1341.1, 1186.7, 1133.1, 1081.8, 1057.9, 882.1, 757.2, 604.9 cm^{-1}. HRMS (ESI): [M^+ − $N(SO_2CF_3)_2$] calcd for $C_9H_8F_3N_2$ 201.06; found 201.0634. Anal. Calcd (%) for $C_{11}H_8N_3O_4F_9S_2$: C, 27.45; H, 1.68; N, 8.73. Found: C, 27.55; H, 1.67; N, 8.68. Mp: 73.4 °C.

*3-Isopropyl-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ium Triflimide (**2b·HNTf$_2$**).* Synthesized according to general procedure B from **2b·HI** (320.0 mg, 0.89 mmol) and $LiNTf_2$ (511.1 mg, 1.78 mmol).

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The product was obtained as a white, crystalline solid (278.5 mg, 0.55 mmol, 60.9%). ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 10.58 (s, 1H, NCHN), 8.34−8.31 (m, 1H, ArH), 8.13−8.09 (m, 1H, ArH), 7.90−7.83 (m, 2H, ArH), 5.18 (p, J = 6.7 Hz, 1H, NCH), 1.69 (d, J = 6.7 H, 6H, C(CH_3)$_2$). ^{19}F NMR (282.38 MHz, DMSO-d_6): δ = −57.25 NCF_3, −78.73 (SCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, DMSO-d_6): δ = 141.75 (d, J = 3.1 Hz, NCHN), 130.61 (C), 128.97 (CH), 128.01 (CH), 127.18 (C), 119.46 (q, J = 321.9 Hz, CF_3), 117.07 (app d, J = 268.3 Hz, CF_3), 115.22 (CH), 113.06 (CH), 52.47 (NCH), 21.04 (CH_3). IR (neat): 3143.1, 3086.2, 2990.3, 1565.9, 1347.7, 1188.9, 1135.8, 1049.3, 757.2 cm^{-1}. HRMS (ESI): [M$^+$ − N(SO_2CF_3)$_2$] calcd for $C_{11}H_{12}F_3N_2$ 229.09; found 229.0947. Anal. Calcd (%) for $C_{13}H_{12}N_3O_4F_9S_2$: C, 30.65; H, 2.37; N, 8.25. Found: C, 30.67; H, 2.47; N, 8.21. Mp: 83.8 °C.

General Procedure C. Synthesis of [Ir(COD)(NHC)Cl] Complexes. The corresponding *N*-trifluoromethylated benzimidazolium salt (1 equiv), [Ir(COD)Cl]$_2$ (0.5 equiv), NaH (1.5 equiv), and THF (0.2 M) were added to a Young Schlenk flask, and the resulting reaction mixture was stirred at 50 °C for 16 h. Subsequently, all volatiles were removed under vacuum, and the residue was purified by flash column chromatography (EtOAc/hexane = 1:0−2:1 v/v), followed by subsequent recrystallization from CH_2Cl_2/pentane to afford the desired [Ir(COD)(NHC)Cl] complexes.

*Chloro(η^4-cycloocta-1,5-diene)[3-methyl-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ylidene]iridium (**3a**).* Synthesized according to general procedure C from **2a·OTf** (208 mg, 0.59 mmol) and [Ir(COD)Cl]$_2$ (200 mg, 0.29 mmol). The product was obtained as a yellow solid (187.6 mg, 0.35 mmol, 59.3%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.57−7.57 (m, 1H, ArH), 7.39−7.26 (m, 3H, ArH), 4.87−4.79 (m, 2H, CH_{COD}), 4.39 (s, 3H, NCH_3), 3.19−3.14 (m, 1H, CH_{COD}), 3.00−2.94 (m, 1H, CH_{COD}), 2.35−2.22 (m, 4H, CH_{COD}), 1.92−1.66 (m, 4H, $CH_{2\ COD}$). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −52.58 (NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 194.26 (dd, J = 4.1 Hz, Ir−C), 135.15 (C), 132.01 (C), 125.04 (CH), 124.50 (CH), 119.68 (apt d, J = 265.7 Hz, CF_3), 112.38 (q, J = 3.1 Hz, CH), 110.29 (CH), 87.71 (CH_{COD}), 87.53 (CH_{COD}), 53.61 (CH_{COD}), 53.30 (apt d, J = 2.2 Hz, CH_{COD}), 33.72 ($CH_{2\ COD}$), 33.36 ($CH_{2\ COD}$), 29.63 ($CH_{2\ COD}$), 29.17 ($CH_{2\ COD}$). IR (neat): 2960.7, 2912.7, 2884.8, 2837.5, 1462.9, 1425.4, 1322.5, 1216.7, 1163.8, 1090.6, 965.3, 762.0 cm^{-3}. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{17}H_{19}N_2F_3ClIr$ 536.08; found 536.0805. Anal. Calcd (%) for $C_{17}H_{19}N_2F_3ClIr$: C, 38.09; H, 3.57; N, 5.23. Found: C, 37.81; H, 3.65; N, 5.22. Mp: 176.5 °C with decomposition.

*Chloro(η^4-cycloocta-1,5-diene)[3-isopropyl-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ylidene]iridium (**3b**).* Synthesized according to general procedure C from **2b·HNTf$_2$** (250 mg, 0.70 mmol) and [Ir(COD)Cl]$_2$ (235.9 mg, 0.35 mmol). The product was obtained as a yellow solid (195.6 mg, 0.35 mmol, 49.6%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.57 (dd, J = 6.7, 2.3 Hz, 2H, ArH), 7.36−7.29 (m, 2H, ArH), 6.72 (hept, J = 7.1 Hz, 1H, NCH), 4.86−4.72 (m, 2H, CH_{COD}), 3.22−3.16 (m, 1H, CH_{COD}), 3.12−3.07 (m, 1H, CH_{COD}), 2.37−2.18 (m, 4H, $CH_{2\ COD}$), 1.94−1.58 (m, 4H, $CH_{2\ COD}$), 1.83 (d, J = 7.1 Hz, CH_3), 1.72 (d, J = 7.0 Hz, CH_3). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −52.57 (d, J = 1.9 Hz, NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 192.85 (app d, J = 4.1 Hz, Ir−C), 133.33 (C), 132.61(C), 124.51 (CH), 124.10 (CH), 119.66 (app d, J = 266.2 Hz, CF_3), 112.86 (CH), 87.13 (NCH), 86.31 (CH_{COD}), 57.09 (CH_{COD}), 53.22 (CH_{COD}), 53.07 (q, J = 2.4 Hz, CH_{COD}), 34.26 ($CH_{2\ COD}$), 32.90 ($CH_{2\ COD}$), 29.65 ($CH_{2\ COD}$), 29.06 ($CH_{2\ COD}$), 21.37 (CH_3), 20.42 (CH_3). IR (neat): 2985.3, 2939.2, 2906.2, 2839.2, 1404.5, 1359.6, 1316.3, 1287.8, 1162.8, 1098.8, 1053.8, 753.1 cm^{-3}. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{19}H_{23}N_2F_3ClIr$ 564.11; found 564.1126. Anal. Calcd (%) for $C_{19}H_{23}N_2F_3ClIr$: C, 40.46; H, 4.11; N, 4.97. Found: C, 40.29; H, 4.16; N, 4.87. Mp: 224.8 °C with decomposition.

*Chloro(η^4-cycloocta-1,5-diene)[1-(trifluoromethyl)-3-(phenyl)-1H-benzo[d]imidazol-3-ylidene]iridium (**3c**).* Synthesized according to general procedure C from **2c·OTf** (200 mg, 0.48 mmol) and [Ir(COD)Cl]$_2$ (148 mg, 0.22 mmol). The product was obtained as a yellow solid (123 mg, 0.45 mmol, 94%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.44−7.5 (br m, 5H, ArH), 7.44−7.31 (m, 2H, ArH), 7.33−7.21 (br m, ArH), 4.83 (td, J = 7.5, 4.4, 1 Hz, 1H, CH_{COD}), 4.60 (td, J = 7.9, 3.9 Hz, 1H, CH_{COD}), 3.27−3.15 (m, 1H, CH_{COD}), 2.43 (td, J = 7.3, 4.0 Hz, 1H, CH_{COD}), 2.34−2.09 (m, 2H, $CH_{2\ COD}$), 1.75−1.54 (m, 4H, $CH_{2\ COD}$), 1.38−1.14 (m, 2H, $CH_{2\ COD}$). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −53.0 (NCF_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ = 194.51 (d, J = 4.1 Hz, Ir−C), 137.64 (C), 135.66 (C), 131.86 (C), 129.36 (CH), 129.05 (br s, 4C, CH), 125.17 (CH), 124.83 (CH), 119.7 (q, J = 267 Hz, CF_3), 112.45 (q, J = 3.4 Hz, CH), 111.43 (CH), 88.16 (2C, CH_{COD}), 86.09 (2C, CH_{COD}), 34.21 ($CH_{2\ COD}$), 32.10 ($CH_{2\ COD}$), 29.57 ($CH_{2\ COD}$), 28.36 ($CH_{2\ COD}$). IR (neat): 2933.2, 2880.3, 2832.6, 1358.8, 1320.8, 1165.9, 750.2 cm^{-1}. HRMS (ESI): [M$^+$] calcd m/z for $C_{22}H_{21}F_3IrN_2$: 598.0961; found 598.0968. Anal. Calcd (%) for $C_{22}H_{21}F_3IrN_2$: C, 44.18; H, 3.54; N, 4.68. Found: C, 44.46; H, 3.20; N, 5.01 (solvent impurities accounted for deviation). Mp: 189.2 °C.

*Chloro(η^4-cycloocta-1,5-diene)[3-(4-nitrophenyl)-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ylidene]iridium (**3d**).* Synthesized according to general procedure C from **2d·BF$_4$** (150 mg, 0.36 mmol) and [Ir(COD)Cl]$_2$ (120.9 mg, 0.18 mmol). The product was obtained as an orange solid (70.7 mg, 0.11 mmol, 30.5%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.48 (d, J = 8.8 Hz, 2H, ArH), 8.36 (br s, 2H, ArH), 7.68 (d, J = 8.2, 1H, ArH), 7.41 (dt, J = 23.1, 7.5 Hz, 2H, ArH), 7.22 (d, J = 8.0 Hz, 2H, ArH), 4.89 (q, J = 5.9 Hz, 1H, CH_{COD}), 4.72−4.66 (m, 1H, CH_{COD}), 3.19 (t, J = 6.7 Hz, 1H, CH_{COD}), 2.29−2.19 (m, 4H, $CH_{2\ COD}$ and CH_{COD}), 1.71−1.62 (m, 4H, $CH_{2\ COD}$), 1.41−1.35 (m, 1H, $CH_{2\ COD}$), 1.28−1.18 (m, 1H, $CH_{2\ COD}$). ^{19}F NMR (376.46 MHz, $CDCl_3$): δ = −53.14 (NCF_3). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 195.11 (Ir−C), 147.81 (C), 143.07 (C), 134.85 (C), 131.98 (C), 125.65 (2C, CH), 125.49 (CH), 124.24 (4C, CH), 119.66 (d, J = 267.6 Hz, CF_3), 112.82 (q, J = 3.4 Hz, CH), 110.91 (CH), 89.67 (CH_{COD}), 88.4 (CH_{COD}), 54.36 (d, J = 1.8 Hz, CH_{COD}), 54.15 (CH_{COD}), 33.85 ($CH_{2\ COD}$), 32.52 ($CH_{2\ COD}$), 29.47 ($CH_{2\ COD}$), 28.47 ($CH_{2\ COD}$). IR (neat): 2974.0, 2920.8, 2885.8, 2835.5, 1528.7, 1378.5, 1212.6, 1160.8, 1022.1, 750.4 cm^{-1}. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{23}H_{20}N_3F_3O_2ClIr$ 643.08; found 643.0825. Anal. Calcd (%) for $C_{23}H_{20}N_3F_3O_2ClIr$: C, 41.09; H, 3.13; N, 6.53. Found: C, 41.03; H, 3.23; N, 6.54. Mp: 217.8 °C decomposition.

*Chloro(η^4-cycloocta-1,5-diene)[1-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-3-ylidene]iridium (**3e**).* Synthesized according to general procedure C from **2e·BF$_4$** (150 mg, 0.36 mmol) and [Ir(COD)Cl]$_2$ (120.6 mg, 0.18 mmol). The product was obtained as a yellow solid (167.3 mg, 0.26 mmol, 73.6%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.24 (br s, 3H, ArH), 7.89 (d, J = 8.1 Hz, 1H, ArH), 7.66 (d, J = 8.1 Hz, 1H, ArH), 7.39 (dt, J = 22.2, 7.5 Hz, 2H, ArH), 7.23 (d, J = 8.0 Hz, 1H, ArH), 4.85 (q, J = 6.5, 6.1 Hz, 1H, CH_{COD}), 4.65−4.60 (m, 1H, CH_{COD}), 3.18 (t, J = 7.3 Hz, 1H, CH_{COD}), 2.30−2.11 (m, 3H, CH_{COD} and $CH_{2\ COD}$), 1.71−1.60 (m, 4H, $CH_{2\ COD}$) 1.35−1.27 (m, 1H, $CH_{2\ COD}$), 1.24−1.14 (m, 1H, $CH_{2\ COD}$). ^{19}F NMR (376.46 MHz, $CDCl_3$): δ = −53.15 (NCF_3), −62.71 ($ArCF_3$). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 195.05 (Ir−C), 140.77 (C), 143.07 (C), 135.17 (C), 131.93 (CH), 131.78 (CH), 131.46 (C), 126.14 (C, CH), 125.48 (CH), 125.23 (2C, CH), 123.82 (q, J = 272.5 Hz, CF_3), 119.73 (q, J = 267.2 Hz, CF_3), 112.71 (CH), 111.08 (CH), 89.22 (CH_{COD}), 87.32 (CH_{COD}), 54.18 (CH_{COD}), 53.85 (CH_{COD}), 34.15 ($CH_{2\ COD}$), 32.18 ($CH_{2\ COD}$), 29.53 ($CH_{2\ COD}$), 28.28 ($CH_{2\ COD}$). IR (neat): 2950.3, 2927.5, 1882.5, 2834.2, 1321.5, 1156.8, 1123.9, 1066.3, 1023.9, 747.7 cm^{-1}. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{23}H_{20}N_2F_6ClIr$ 666.08; found 666.0844. Anal. Calcd (%) for $C_{23}H_{20}N_2F_6ClIr$: C, 41.47; H, 3.03; N, 4.21. Found: C, 41.75; H, 3.18; N, 4.26 (solvent impurities accounted for deviation). Mp: 203.1 °C with decomposition.

General Procedure D. Synthesis of [Ir(CO)$_2$(NHC)Cl] Complexes. The appropriate [Ir(COD)(NHC)Cl] complex (1 equiv) was dissolved in CH_2Cl_2 (0.03 M) in a Young Schlenk flask. The solution was cooled to −78 °C, and the atmosphere inside the Young Schlenk was replaced with CO. The solution was then allowed to warm to room temperature and stirred for 20 h. Subsequently, all volatiles were removed under vacuum and the residue was washed with pentane.

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Subsequent recrystallization from CH_2Cl_2/pentane afforded the desired [Ir(CO)$_2$(NHC)Cl] complex.

*Chlorodicarbonyl[3-methyl-1-(trifluoromethyl)-1H-benzo[d]-imidazol-3-ylidene]iridium (**4a**).* Synthesized according to general procedure D from **3a** (80 mg, 0.15 mmol). The product was obtained as a yellow solid (71.1 mg, 0.15 mmol, 98.3%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.76−7.72 (m, 1H, ArH), 7.57−7.52 (m, 3H, ArH), 4.31 (s, 3H, NCH_3). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −51.51 (NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 184.63 (Ir−C), 179.68 (CO), 167.56 (CO), 134.39 (C), 131.32 (C), 126.46 (CH), 126.31 (CH), 119.12 (q, J = 309.3 Hz, CF_3), 117.07 (CH), 111.67 (CH), 37.48 (NCH_3). IR (neat): 2073.2 (C═O), 1988.0 (C═O), 1352.5, 1186.8, 1093.4 cm^{-1}. IR (CH_2Cl_2): 2075.4 (C═O), 1993.2 (C═O) cm^{-1}. HRMS (MALDI/ESI): [M + Na$^+$] calcd for $C_{11}H_9N_2NaF_3O_2ClIr$ 506.97; found 506.9661. Anal. Calcd (%) for $C_{11}H_9N_2F_3O_2ClIr$: C, 27.31; H, 1.46; N, 5.79. Found: C, 27.12; H, 1.56; N, 5.63.

*Chlorodicarbonyl[3-isopropyl-1-(trifluoromethyl)-1H-benzo[d]-imidazol-3-ylidene]iridium (**4b**).* Synthesized according to general procedure D from **3b** (70 mg, 0.12 mmol). The product was obtained as a yellow solid (56.2 mg, 0.11 mmol, 88.5%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.75−7.73 (m, 2H, ArH), 7.50−7.48 (m, 2H, ArH), 6.28 (hept, J = 7.0 Hz, 1H, NCH), 1.76 (dd, J = 7.1, 5.0 Hz, 6H, $C(CH_3)_2$). ^{19}F NMR (376.46 MHz, $CDCl_3$): δ = −51.36 (d, J = 1.9 Hz, NCF_3). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 182.82 (d, J = 3.9 Hz, Ir−C), 179.57 (CO), 167.56 (CO), 132.66 (C), 131.85 (C), 126.06 (CH), 125.72 (CH), 119.37 (d, J = 268.1 Hz, CF_3), 114.10 (CH), 113.92 (q, J = 4.3 Hz, CH), 58.20 (NCH), 20.67 (CH_3), 20.32 (CH_3). IR (neat): 2988.6, 2069.5, 1985.7, 1346.3, 1210.9, 1184.8, 1100.5, 1058.3, 758.7 cm^{-1}. IR (CH_2Cl_2): 2075.0 (C═O), 1992.6 (C═O) cm^{-1}. HRMS (MALDI/ESI): [M + Na$^+$] calcd for $C_{13}H_{11}N_2NaF_3O_2ClIr$ 535.00; found 534.9974. Anal. Calcd (%) for $C_{13}H_{11}N_2F_3O_2ClIr$: C, 30.50; H, 2.17; N, 5.47. Found: C, 30.46; H, 2.08; N, 5.35.

*Chlorodicarbonyl[1-(trifluoromethyl)-3-(phenyl)-1H-benzo[d]-imidazol-3-ylidene]iridium (**4c**).* Synthesized according to general procedure D from **3c** (50 mg, 0.08 mmol). The product was obtained as a yellow solid (39 mg, 0.07 mmol, 92%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.83 (ddq, J = 8.4, 1.9, 0.9 Hz, 1H, ArH), 7.9−7.5 (br m, 4H, ArH), 7.59 (ddd, J = 8.4, 7.4, 1.1 Hz, 1H, ArH), 7.50 (ddd, J =8.3, 7.4, 1.0 Hz, 1H, ArH), 7.31−7.25 (m, 2H, ArH). ^{19}F NMR (376.46 MHz, $CDCl_3$): δ = −51.8 (NCF_3). ^{13}C{^{1}H} NMR (100.62, $CDCl_3$): δ = 184.80 (d, J = 3.9 Hz, Ir−C), 179.47 (CO), 167.59 (CO), 136.47 (C), 135.39 (C), 131.04 (C), 130.73 (CH), 130.15−129.65 (4C, CH), 126.64 (CH), 126.54 (CH), 119.4 (q, J = 268 Hz, CF_3), 113.39 (q, J = 3.9 Hz, CH), 112.81 (CH). IR (neat): 2066.7 (CO) 1984.2 (CO), 1363.0, 1166.5, 753.3 cm^{-1}. IR (CH_2Cl_2): 2074.35 (CO), 1991.84 (CO) cm^{-1}. HRMS (ESI): [M$^+$] calcd m/z for $C_{16}H_9F_3IrN_2O_2$: 545.9934; found 545.9930. Anal. Calcd (%) for $C_{16}H_9F_3IrN_2O_2$: C, 35.20; H, 1.66; N; 5.13. Found: C, 35.63; H, 1.71; N, 5.10.

*Chlorodicarbonyl[3-(4-nitrophenyl)-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ylidene]iridium (**4d**).* Synthesized according to general procedure D from **3d** (60 mg, 0.09 mmol). The product was obtained as a green solid (55.2 mg, 0.09 mmol, 99.9%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.52 (d, J = 9.1 Hz, 1H, ArH), 7.93 (br s, 2H, ArH) 7.86 (d, J = 8.3 Hz, 1H, ArH), 7.63 (t, J = 7.9 Hz, 1H, ArH), 7.54 (t, J = 7.8 Hz, 1H, ArH), 7.25 (d, J = 6.4 Hz, 1H, ArH). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −51.82 (NCF_3). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 185.17 (Ir−C), 178.86 (CO), 167.32 (CO), 148.96 (C), 141.53 (C), 134.73 (C), 131.11 (C), 127.24 (2C, CH), 127.08 (2C, CH), 125.30 (2C, CH), 119.30 (apt d, J = 267.6 Hz, CF_3), 113.82 (apt d, J = 3.4 Hz, CH), 112.26 (CH). IR (neat): 2071.5 (C═O), 1972.1 (C═O), 1530.1, 1348.2, 1197.2, 1161.4, 1025.9, 758.3, 734.2, 694.6 cm^{-1}. IR (CH_2Cl_2): 2077.9 (C═O), 1994.8 (C═O) cm^{-1}. HRMS (MALDI/ESI): [M + K$^+$] calcd for $C_{16}H_8N_3KF_3O_4ClIr$ 629.94; found 629.9407. Anal. Calcd (%) for $C_{16}H_8N_3F_3O_4ClIr$: C, 32.52; H, 1.36; N, 7.11. Found: C, 33.81; H, 1.92; N, 6.32 (solvent impurities accounted for deviation).

*Chlorodicarbonyl[1-(trifluoromethyl)-3-(4-(trifluoromethyl)-phenyl)-1H-benzo[d]imidazol-3-ylidene]iridium (**4e**).* Synthesized according to general procedure D from **3e** (85 mg, 0.13 mmol). The product was obtained as a green solid (55.2 mg, 0.09 mmol, 69.6%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.3 Hz, 2H, ArH), 7.84 (d, J = 8.4 Hz, 2H, ArH), 7.60 (t, J = 8.2 Hz, 1H, ArH), 7.51 (t, J = 7.8 Hz, 1H, ArH), 7.24 (d, J = 8.3 Hz, 1H, ArH). ^{19}F NMR (376.46 MHz, $CDCl_3$): δ = −51.84 (NCF_3), −62.77 ($ArCF_3$). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 185.14 (Ir−C), 179.14 (CO), 167.45 (CO), 139.45 (C), 135.02 (C), 132.92 (q, J = 33.2 Hz, C), 131.07 (C), 127.23 (2C, CH), 127.02 (2C, CH), 126.87 (2C, CH), 123.54 (q, J = 272.8 Hz, CF_3), 119.34 (q, J = 269.3 Hz, CF_3), 113.64 (q, J = 3.8 Hz, CH), 112.46 (CH). IR (neat): 2071.5 (C═O), 1974.1 (C═O), 1616.5, 1347.7, 1327.7, 1218.1, 1166.8, 1130.8, 1109.8, 1068.7, 1025.2, 859.7, 756.6, 617.0 cm^{-1}. IR (CH_2Cl_2): 2076.9 (C═O), 1993.9 (C═O) cm^{-1}. HRMS (MALDI/ESI): [M + Na$^+$] calcd for $C_{17}H_8N_2NaF_6O_2ClIr$ 636.97; found 636.9692. Anal. Calcd (%) for $C_{17}H_8N_2F_6O_2ClIr$: C, 33.26; H, 1.31; N, 4.56. Found: C, 44.43; H, 1.34; N, 4.53.

General Procedure E. Synthesis of Selenones. The selenium complexes **5a−f** were synthesized from the corresponding benzimidazolium salts **2a−f** according to a modified procedure previously reported by Ganter.[42] A mixture of benzimidazolium salt **2a−f** (1 equiv), selenium powder (5 equiv), and Et_2O (0.06 M) was cooled to −78 °C. Subsequently, a solution of NaHMDS (1.1 equiv, 0.2 M in Et_2O) was added dropwise to the reaction mixture. The resulting solution was stirred for 20 min at −78 °C; then the cooling bath was removed, and the suspension was stirred for 4 h and allowed to warm to room temperature. All volatiles were then removed *in vacuo* and the residue was purified by flash column chromatography (CH_2Cl_2/pentane, 0:1−2:1 v/v), followed by subsequent recrystallization from CH_2Cl_2/pentane to afford the desired product.

*1-Methyl-3-(trifluoromethyl)-1H-benzo[d]imidazole-2(3H)-selenone (**6a**).* Synthesized according to the general procedure E, starting from **2a·HNTf$_2$** (230 mg, 0.48 mmol). The product was obtained as a white solid (116.3 mg, 0.2 mmol, 86.9%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.93 Hz, 1H, ArH), 7.41−7.29 (m, 2H, ArH), 7.27 (d, J = 8.12 Hz, 1H, ArH), 3.87 (s, CH_3, 3H, NCH_3). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −54.23 (NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 166.26 (Se−C), 133.60 (C), 130.14 (C), 125.47 (CH), 124.91 (CH), 119.91 (q, J = 267.2 Hz, CF_3), 112.53 (q, J = 5.6 Hz, CH), 110.08 (CH), 33.33 (CH_3). ^{77}Se NMR (76.36 MHz, $CDCl_3$): 214.62 (q, J = 15.5 Hz). HRMS (MALDI/ESI): [M$^+$] calcd for $C_9H_7N_2F_3Se$ 279.97; found 279.9721. Anal. Calcd (%) for $C_9H_7N_2F_3Se$: C, 38.73; H, 2.53; N, 10.04. Found: C, 38.76; H, 2.42; N, 9.91. Mp: 181.9 °C.

*1-Isopropyl-3-(trifluoromethyl)-1H-benzo[d]imidazole-2(3H)-selenone (**6b**).* Synthesized according to the general procedure E, starting from **2b·HI** (50 mg, 0.14 mmol). The product was obtained as a white, crystalline solid (36.9 mg, 0.12 mmol, 85.6%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.55 (apt dd, J = 6.7, 2.1 Hz, 2H, ArH), 7.35−7.27 (m, 2H, ArH), 6.02 (dt, J = 14.6, 7.4 Hz, 1H, NCH), 1.62 (d, J = 7.2 Hz, 6H, $C(CH_3)_2$). ^{19}F NMR (376.46 MHz, $CDCl_3$): δ = −53.74 (NCF_3). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 165.21 (Se−C), 131.31 (C), 130.69 (C), 124.82 (CH), 124.44 (CH), 119.91 (q, J = 266.9 Hz, CF_3), 112.75 (q, J = 6.1 Hz, CH), 111.54 (CH), 51.53 (NCH), 19.45 (2C, CH_3). ^{77}Se NMR (76.36 MHz, $CDCl_3$): δ = 195.63. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{11}H_{11}N_2F_3Se$ 308.00; found 308.0034. Anal. Calcd (%) for $C_9H_7N_2F_3Se$: C, 43.01; H, 3.61; N, 9.12. Found: C, 42.98; H, 3.62; N, 9.12. Mp: 120.6 °C.

*1-Phenyl-3-(trifluoromethyl)-1H-benzo[d]imidazole-2(3H)-selenone (**6c**).* Synthesized according to the general procedure E, starting from **2a·HBF$_4$** (84 mg, 0.24 mmol). The product was obtained as an off-white solid (26.5 mg, 0.08 mmol, 32.4%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.66−7.56 (m, 4H, ArH), 7.48−7.45 (m, 2H, ArH), 7.36−7.24 (m, 2H, ArH), 6.92 (d, J = 7.7 Hz, 1H, ArH). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −54.03 (d, J = 2.1 Hz, NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 167.36 (Se−C), 135.70 (C), 134.88 (C), 130.48 (C), 130.21 (2C, CH), 130.17 (CH), 128.47 (2C, CH), 125.55 (CH), 125.06 (CH), 120.04 (app d, J = 267.4 Hz, CF_3), 112.44 (q, J = 5.7 Hz, CH), 111.01 (CH). ^{77}Se NMR (76.36 MHz, $CDCl_3$): δ = 249.41 (q, J = 14.8 Hz). IR (neat): HRMS (MALDI/ESI): [M$^+$]

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calcd for $C_{14}H_9N_2F_3Se$ 341.99; found 341.9878. Anal. Calcd (%) for $C_{14}H_9N_2F_3Se$: C, 49.28; H, 2.66; N, 8.21. Found: C, 49.02; H, 2.54; N, 8.02 (solvent impurities accounted for deviation). Mp: 132.9 °C.

*1-(4-Nitrophenyl)-3-(trifluoromethyl)-1H-benzo[d]imidazole-2(3H)-selenone (**6d**).* Synthesized according to the general procedure E, starting from **2d·HBF$_4$** (100 mg, 0.25 mmol). The product was obtained as a orange solid (60.8 mg, 0.16 mmol, 62.1%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.50 (d, J = 8.9 Hz, 2H, ArH), 7.74 (d, J = 8.9 Hz, 2H, ArH), 7.61 (d, J = 8.1 Hz, 1H, ArH), 7.35 (dtd, J = 21.2, 7.6, 1.2 Hz, 2H, ArH), 6.92 (d, J = 7.3 Hz, 1H, ArH). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −54.26 (NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 167.43 (Se−C), 148.41 (C), 141.04 (C), 133.99 (C), 130.63 (C), 130.05 (2C, CH), 125.93 (CH), 125.67 (CH), 125.56 (2C, CH), 119.93 (app d, J = 267.8 Hz, CF_3), 112.80 (q, J = 5.7 Hz, CH), 110.46 (CH). ^{77}Se NMR (76.36 MHz, $CDCl_3$): δ = 276.03 (q, J = 15.1 Hz). IR (neat): 3117.4, 1613.9, 1590.2, 1519.9, 1493.7, 1478.1, 1351.2, 1323.6, 1277.3, 1188.3, 1164.6, 1108.2, 1015.1, 944.2, 851.7, 752.9, 731.7, 695.9, 614.4 cm^{-1}. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{14}H_8N_3F_3O_2Se$ 386.97; found 386.9729. Anal. Calcd (%) for $C_{14}H_8N_3F_3O_2Se$: C, 43.54; H, 2.09; N, 10.88. Found: C, 43.69; H, 1.98; N, 10.91. Mp: 226.5 °C.

*1-(Trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1H-benzo[d]-imidazole-2(3H)-selenone (**6e**).* Synthesized according to the general procedure E, starting from **2e·HBF$_4$** (100 mg, 0.24 mmol). The product was obtained as a white solid (54.1 mg, 0.13 mmol, 55.2%). ^{1}H NMR (400.20 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.3 Hz, 2H, ArH), 7.65 (d, J = 8.4 Hz, 2H, ArH), 7.60 (d, J = 7.2 Hz, ArH), 7.33 (dt, J = 28.0, 7.6 Hz, ArH), 6.92 (d, J = 8.0 Hz, ArH). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −54.23 (NCF_3), −62.81 ($ArCF_3$). ^{13}C{^{1}H} NMR (100.64 MHz, $CDCl_3$): δ = 167.35 (Se−C), 138.75 (d, J = 1.7 Hz, C), 134.33 (C), 132.20 (q, J = 33.1 Hz, C), 130.52 (C), 129.29 (2C, CH), 127.42 (q, J = 3.7 Hz, 2C, CH), 125.78 (CH), 125.44 (CH), 123.62 (q, J = 272.7 Hz, CF_3), 119.96 (q, J = 267.4 Hz, CF_3) 112.64 (q, J = 5.7 Hz, CH), 110.66 (CH). ^{77}Se NMR (76.36 MHz, $CDCl_3$): δ = 263.71 (q, J = 14.8 Hz). IR (neat): 3044.8, 1738.5, 1613.9, 1477.9, 1372.8, 1316.6, 1281.1, 1217.0, 1153.8, 1125.0, 1103.5, 1064.4, 1019.3, 944.4, 827.3, 743.8, 715.7, 622.2 cm^{-1}. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{15}H_{18}N_2F_6Se$ 409.98; found 409.9752. Anal. Calcd (%) for $C_{15}H_{18}N_2F_6Se$: C, 44.03; H, 1.97; N, 6.85. Found: C, 43.97; H, 1.90; N, 6.85. Mp: 218.7 °C.

*1-(6-Fluoropyridin-3-yl)-3-(trifluoromethyl)-1H-benzo[d]-imidazole-2(3H)-selenone (**6f**).* Synthesized according to the general procedure E, starting from **2f·HBF$_4$** (25 mg, 0.07 mmol). The product was obtained as a white solid (12.6 mg, 0.03 mmol, 49.9%). ^{1}H NMR (400.20 MHz, $CDCl_3$): δ = 8.37 (s, 1H, ArH), 8.01 (td, J = 8.0, 6.8, 2.7 Hz, 1H, ArH), 7.60 (d, J = 8.2 Hz, 1H, ArH), 7.35 (dt, J = 22.3, 7.5 Hz, 2H, ArH), 7.22 (dd, J = 8.6, 3.2 Hz, 1H, ArH), 6.94 (d, J = 8.2 Hz, 1H, ArH). ^{19}F NMR (376.56 MHz, $CDCl_3$): δ = −54.41 (NCF_3), −64.32 (ArF). ^{13}C{^{1}H} NMR (100.63 MHz, $CDCl_3$): δ = 168.21 (Se−C), 163.46 (d, J = 244.4 Hz, CF), 147.80 (d, J = 16.3 Hz, CH), 141.99 (d, J = 9.2 Hz, CH), 134.32 (C), 130.49 (CH), 125.98 (CH), 125.60 (CH), 119.90 (d, J = 267.9 Hz CF_3), 112.77 (q, J = 5.7 Hz CH), 111.21 (d, J = 39.4 Hz CH), 110.41 (CH). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = 275.18 (q, J = 14.5 Hz). HRMS (MALDI/ESI): [M$^+$] calcd for $C_{13}H_7N_3F_4Se$ 360.97; found 360.9736. Anal. Calcd (%) for $C_{13}H_7N_3F_4Se$: C, 43.35; H, 1.96; N, 11.67. Found: C, 43.18; H, 1.96; N, 11.51.

General Procedure F. Synthesis of [Rh(COD)(NHC)Cl] Complexes. The corresponding *N*-trifluoromethylated benzimidazolium salt (1 equiv), $[Rh(COD)Cl]_2$ (0.5 equiv), NaH (1.5 equiv), and THF (0.2 M) were added to a Young Schlenk flask, and the resulting reaction mixture was stirred at room temperature for 4 h. Subsequently, all volatiles were removed *in vacuo* and the residue was purified by flash column chromatography (EtOAc/hexane, 1:0−2:1 v/v), followed by subsequent recrystallization from CH_2Cl_2/pentane to afford the desired [Rh(COD)(NHC)Cl] complex.

*Chloro(η^4-cycloocta-1,5-diene)[3-methyl-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ylidene]rhodium (**7a**).* Synthesized according to general procedure F from **2a·HOTf** (100 mg, 0.29 mmol) and $[Rh(COD)Cl]_2$ (70.4 mg, 0.14 mmol). The product was obtained as a yellow solid (91.2 mg, 0.21 mmol, 71.5%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.08 Hz), 7.41−7.30 (m, 3H, ArH), 5.18 (s, 2H, CH_{COD}), 4.55 (s, 3H, NCH_3), 3.55−3.51 (m, 1H, CH_{COD}), 3.46−3.41 (m, 1H, CH_{COD}), 2.54−2.39 (m, 4H, $CH_{2\ COD}$), 2.06−1.97 (m, 4H, $CH_{2\ COD}$). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −53.60 (NCF_3). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 194.26 (d, J = 4.1 Hz, Rh−C), 135.15 (C), 132.01 (C), 125.04 (CH), 124.50 (CH), 119.68 (apt d, J = 266.1 Hz, CF_3) 112.38 (q, J = 3.4 Hz, CH), 110.29 (CH), 70.18 (CH_{COD}), 69.99 (CH_{COD}), 69.25 (CH_{COD}), 69.11 (q, J = 2.1 Hz, CH_{COD}), 36.79 ($CH_{2\ COD}$), 33.41 ($CH_{2\ COD}$), 33.32 ($CH_{2\ COD}$), 28.94 ($CH_{2\ COD}$), 28.89 (CH_3). IR (neat): 3052.8, 2913.3, 2882.4, 2836.9, 1462.9, 1427.8, 1349.4, 1326.1, 1255.7, 1215.4, 1164.3, 1134.1, 1090.3, 965.6, 764.4 cm^{-1}. HRMS (MALDI/ESI): [M$^+$] calcd for $C_{17}H_{19}N_2F_3ClRh$ 446.02; found 446.0238. Anal. Calcd (%) for $C_{17}H_{19}N_2F_3ClRh$: C, 45.71; H, 4.29; N, 6.27. Found: C, 45.21; H, 4.41; N, 6.32 (solvent impurities accounted for deviation). Mp: 162.8 °C.

*Chloro(η^4-cycloocta-1,5-diene)[3-isopropyl-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ylidene]rhodium (**7b**).* Synthesized according to general procedure F from **2b·HNTf$_2$** (100 mg, 0.28 mmol) and $[Rh(COD)Cl]_2$ (69.3 mg, 0.14 mmol). The product was obtained as a yellow solid (86.4 mg, 0.18 mmol, 64.9%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.56 (apt d, J = 6.8 Hz, 2H, ArH), 7.31 (td, J = 6.9, 5.9, 3.8 Hz, 2H, ArH), 6.96 (dt, J = 13.9, 6.9 Hz, 1H, NCH), 5.13 (m, 2H, CH_{COD}), 3.54 (br s, 2H, CH_{COD}), 2.45 (m, 4H, $CH_{2\ COD}$), 1.94−1.58 (m, 4H, $CH_{2\ COD}$), 1.85 (d, J = 7.1 Hz, 3H, CH_3), 1.78 (d, J = 6.9 Hz, 3H, CH_3). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −53.57 (NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 198.11 (dd, J = 48.7, 5.0 Hz, Rh−C), 133.40 (C), 132.31 (C), 124.42 (CH), 124.07 (CH), 119.60 (apt d, J = 265.7 Hz, CF_3), 112.58 (q, J = 3.2 Hz, CH), 99.55 (d, J = 7.0 Hz, $CH_{2\ COD}$)), 98.98 (d, J = 7.4 Hz, $CH_{2\ COD}$), 69.39 (app dd, J = 24.2, 14.4 Hz, NCH), 57.27 (CH_{COD}), 33.71 ($CH_{2\ COD}$), 31.98 ($CH_{2\ COD}$), 29.24 ($CH_{2\ COD}$), 28.49 ($CH_{2\ COD}$), 21.29 (CH_3), 20.66 (CH_3). IR (neat): 3049.76, 2980.03, 2939.44, 2833.51, 1476.45, 1402.49, 1350.17, 1320.14, 1286.67, 1258.28, 1165.31, 1140.72, 1098.10, 1051.92, 992.68, 960.28, 858.19, 751.70, 701.15 cm^{-1}. HRMS (MALDI/ESI): [M$^+$ − Cl] calcd for $C_{19}H_{23}N_2F_3Rh$ 439.09; found 439.0863. Anal. Calcd (%) for $C_{19}H_{23}N_2F_3ClRh$: C, 48.07; H, 4.88; N, 5.90. Found: C, 47.81; H, 4.91; N, 5.70 (solvent impurities accounted for deviation). Mp: 217.5 °C with decomposition.

*Chloro(η^4-cycloocta-1,5-diene)[1-(trifluoromethyl)-3-(phenyl)-1H-benzo[d]imidazol-3-ylidene]rhodium (**7c**).* Synthesized according to general procedure F from **2c·BF$_4$** (170 mg, 0.49 mmol) and $[Rh(COD)Cl]_2$ (119.7 mg, 0.24 mmol). The product was obtained as a yellow solid (187.3 mg, 0.37 mmol, 76%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.14 (br s, 2H, ArH), 7.63 (dt, J = 14.1, 6.0 Hz, 4H, ArH), 7.36−7.23 (m, 3H, ArH), 5.08 (apt q, J = 7.8 Hz, 1H, CH_{COD}), 4.96 (apt q, J = 7.7 Hz, 1H, CH_{COD}), 3.53 (apt t, J = 7.2 Hz, 1H, CH_{COD}), 2.76 (apt dt, J = 7.5, 4.1 Hz, 1H, CH_{COD}), 2.46−2.21 (m, 2H, $CH_{2\ COD}$), 1.90−1.68 (m, 4H, $CH_{2\ COD}$), 1.56−1.48 (m, 1H, $CH_{2\ COD}$), 1.32 (apt td, J = 14.4, 7.7 Hz, 1H, $CH_{2\ COD}$). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −53.86 (NCF_3). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ = 200.54 (dd, J = 51.0, 5.1 Hz, Rh−C), 137.93 (C), 135.41 (C), 131.92 (C), 129.59 (2C, CH), 129.33 (CH), 125.13 (2C, CH), 124.79 (2C, CH), 119.71 (q, 266.3 Hz, CF_3), 112.17 (q, J = 3.0 Hz, CH), 111.37 (CH), 99.79 (d, J = 7.3 Hz, CH_{COD}), 98.83 (d, J = 7.0 Hz, CH_{COD}), 70.00 (d, J = 14.4 Hz, CH_{COD}), 69.40 (apt dd, J = 14.3, 1.9 Hz, CH_{COD}), 33.16 ($CH_{2\ COD}$), 31.55 ($CH_{2\ COD}$), 28.95 ($CH_{2\ COD}$), 28.06 ($CH_{2\ COD}$). IR (neat): 2938.3, 2836.4, 1357.0, 1322.9, 1163.5, 1032.1, 754.1, 696.4 cm^{-1}. HRMS (MALDI/ESI): [M$^+$ − Cl] calcd for $C_{22}H_{21}N_2F_3ClRh$ 473.07; found 473.0704. Anal. Calcd (%) for $C_{22}H_{21}N_2F_3ClRh$: C, 51.94; H, 4.16; N, 5.51. Found: C, 51.77; H, 4.10; N, 5.41. Mp: 196.7 °C.

*Chloro(η^4-cycloocta-1,5-diene)[3-(4-nitrophenyl)-1-(trifluoro-methyl)-1H-benzo[d]imidazol-3-ylidene]rhodium (**7d**).* Synthesized according to general procedure F from **2d·HBF$_4$** (120 mg, 0.29 mmol) and $[Rh(COD)Cl]_2$ (70.4 mg, 0.14 mmol). The product was obtained as an orange solid (91.8 mg, 0.17 mmol, 58%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.56 (apt d, J = 6.6 Hz, 4H, ArH), 7.67 (d, J = 7.6 Hz, 1H, ArH), 7.46−4.35 (m, 2H, ArH), 7.27−7.24 (m, 1H, ArH),

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5.18−5.04 (m, 2H, CH_{COD}) 3.55 (apt t, J = 7.0 Hz, 1H, CH_{COD}), 2.69 (dt, J = 7.4, 4.4 Hz 1H, CH_{COD}), 2.39 (apt tt, J = 16.9, 7.7 Hz, 2H, $CH_{2\ COD}$), 1.95−1.78 (m, 4 H, $CH_{2\ COD}$), 1.67−1.57 (m, 1H, $CH_{2\ COD}$), 1.42−1.23 (m, 1H, $CH_{2\ COD}$). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −53.94 (NCF_3). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ = 201.77 (d, J = 51.2 Hz, Rh−C), 148.13 (C), 143.25 (C), 134.73 (C), 132.03 (C), 129.13 (br s, 2C, CH), 125.66 (CH), 125.48 (CH), 124.55 (2C, CH), 119.58 (d, J = 267.4 Hz, CF_3), 112.56 (q, J = 3.1 Hz, CH), 110.89 (CH), 100.82 (d, J = 7.2 Hz, CH_{COD}), 100.59 (d, J = 6.8 Hz, CH_{COD}), 70.43 (d, J = 14.3 Hz, CH_{COD}), 69.99 (d, J = 14.2 Hz, CH_{COD}), 32.78 ($CH_{2\ COD}$), 32.06 ($CH_{2\ COD}$), 28.89 ($CH_{2\ COD}$), 28.21 ($CH_{2\ COD}$). IR (neat): 3062.79, 2987.08, 1694.84, 1591.60, 1530.09, 1342.75, 1325.85, 1164.93, 1110.01, 1020.84, 853.20, 748.61, 731.70, 695.32 cm^{-1}. HRMS (MALDI/ESI): [M^+ − Cl] calcd for $C_{23}H_{20}N_3F_3O_2ClRh$ 518.06; found 518.0557. Anal. Calcd (%) for $C_{23}H_{20}N_3O_2F_3ClRh$: C, 47.72; H, 3.64; N, 6.40. Found: C, 48.46; H, 3.68; N, 8.01 (solvent impurities accounted for deviation) Mp: 227.2 °C with decomposition.

*Chloro(η^4-cycloocta-1,5-diene)[1-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-3-ylidene]rhodium (**7e**).* Synthesized according to general procedure F from **2e·HBF$_4$** (120 mg, 0.29 mmol) and [Rh(COD)Cl]$_2$ (70.4 mg, 0.14 mmol). The product was obtained as a yellow solid (96.2 mg, 0.17 mmol, 57%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.38 (br s, 2H, ArH), 7.93 (d, J = 8.3 Hz, 2H, ArH), 7.61 (d, J = 7.5 Hz, 1H, ArH), 7.39−7.30 (m, 2H, ArH), 7.26−7.21 (m, 1H, ArH) 5.10 (q, J = 7.1, 6.5 Hz, 1H, $CH_{2\ COD}$), 4.99 (q, J = 7.6 Hz, 1H, $CH_{2\ COD}$), 3.51 (app t, J = 7.2 Hz, 1H, $CH_{2\ COD}$), 2.65 (dt, J = 7.5, 4.2 Hz, 1H, $CH_{2\ COD}$), 2.50−2.25 (m, 2H, CH_{COD}), 1.94−1.79 (m, 4H, CH_{COD}), 1.63−1.53 (m, 1H, CH_{COD}), 1.39−1.26 (m, 1H, CH_{COD}). ^{19}F NMR (282.38 MHz, $CDCl_3$): δ = −53.95 (NCF_3), 62.63 ($ArCF_3$). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ = 201.38 (d, J = 56.6 Hz, Rh−C), 141.02 (C), 134.98 (C), 134.98 (C), 131.99 (C), 131.88 (q, J = 33.1 Hz, CH), 128.64 (br, 2C, CH), 126.42 (apt d, J = 3.9 Hz, CH), 125.47 (CH), 125.21 (CH), 123.79 (d, J = 272.7 Hz, CF_3), 119.63 (apt d, J = 266.8 Hz, CF_3), 112.43 (q, J = 3.2 Hz, CH), 111.03 (CH), 100.51 (d, J = 7.3 Hz, $CH_{2\ COD}$), 99.77 (d, J = 6.9 Hz, $CH_{2\ COD}$), 70.18 (d, J = 14.5 Hz, $CH_{2\ COD}$), 69.82 (d, J = 14.0 Hz, CH_{COD}), 33.05 ($CH_{2\ COD}$), 31.69 ($CH_{2\ COD}$), 28.92 ($CH_{2\ COD}$), 28.04 ($CH_{2\ COD}$). IR (neat): 2933.5, 2881.7, 2836.2, 1617.3, 1476.6, 1358.3, 1318.9, 1185.7, 1170.7, 1107.0, 1024.1, 851.0, 752.1, 713.0 cm^{-1}. HRMS (MALDI/ESI): [M^+] calcd for $C_{23}H_{20}N_2F_6ClRh$ 576.03; found 576.0268. Anal. Calcd (%) for $C_{23}H_{20}N_2F_6ClRh$: C, 47.90; H, 3.50; N, 4.86. Found: C, 47.82; H, 3.44; N, 4.72. Mp: 213.0 °C with decomposition.

General Procedure G. Synthesis of [Au(NHC)Cl] Complexes. The gold complexes were synthesized from the corresponding benzimidazolium salts **2a** and **2c−f** according to a modified procedure previously reported by Nolan.[43] The corresponding benzimidazolium salt (1 equiv), [Au(DMS)Cl] (1 equiv), K_2CO_3 (3 equiv), and acetone (0.05 M) were added to a Schlenk flask, and the resulting reaction mixture was stirred at 60 °C for 4 h in the dark. Subsequently, all volatiles were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and filtered through a small pad of neutral aluminum oxide. The clear solution was then concentrated to dryness under reduced pressure. Subsequent recrystallization of the residue from acetone/pentane afforded the desired [Au(CNHC)Cl] complex.

*Chloro[3-methyl-1-(trifluoromethyl)-1H-benzo[d]imidazol-3-ylidene]gold (**9a**).* Synthesized according to the general procedure G, starting from **2a·HOTf** (160 mg, 0.68 mmol) and [Au(DMS)Cl] (200 mg, 0.68 mmol). The product was obtained as a white solid (112.8 mg, 0.26 mmol, 38.4%). ^{1}H NMR (400.13 MHz, DMSO-d_6, 60 °C): δ = 7.98−7.94 (m, 1H, ArH), 7.87−7.84 (m, 1H, ArH), 7.69−7.64 (m, 2H, ArH), 4.17 (s, 3H, NCH_3). ^{19}F NMR (282.4 MHz, DMSO-d_6, 60 °C): δ = −52.53 (d, J = 1.8 Hz, NCF_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, DMSO-d_6, 60 °C): δ = 177.04 (d, J = 5.8 Hz, Au−C), 132.86 (C), 129.19 (C), 126.56 (CH), 126.22 (CH), 118.75 (app d, J = 265.5 Hz, CF_3), 113.25 (CH), 112.71 (q, J = 4.0 Hz, CH), 36.77 (CH_3). HRMS (MALDI/ESI): [M + Na^+] calcd for $C_9H_7AuF_3ClNNa$ 454.99; found 454.9809. Anal. Calcd (%) for $C_9H_7AuF_3ClN$: C, 24.99; H, 1.63; N, 6.48. Found: C, 24.82; H, 1.63; N, 6.56. Mp: 324.2 °C with decomposition.

*Chloro[1-(trifluoromethyl)-3-(phenyl)-1H-benzo[d]imidazol-3-ylidene]gold (**9b**).* Synthesized according to the general procedure G, starting from **2c·HOTf** (278.9 mg, 0.68 mmol) and [Au(DMS)Cl] (200 mg, 0.68 mmol). The product was obtained as a white solid (150.2 mg, 0.30 mmol, 44.7%). ^{1}H NMR (500.26 MHz, DMSO-d_6, 60 °C): δ = 7.96 (d, J = 9.2 Hz, 1H, ArH), 7.84−7.82 (m, 2H, ArH) 7.73−7.69 (m, 4H, ArH), 7.62 (t, J = 7.8, 1H, ArH), 7.39 (d, J = 8.3, 1H, ArH). ^{19}F NMR(470.67 MHz, acetone-d_6): δ = −52.82 (NCF_3). $^{13}C\{^1H\}$ NMR (125.80 MHz, DMSO-d_6, 60 °C): δ = 177.44 (q, J = 6.0 Hz, Au−C), 136.19 (C), 135.51 (C), 130.26 (2C, CH), 129.77 (2C, CH), 129.11 (C), 126.81 (2C, CH), 126.77 (CH), 126.73 (CH), 118.83 (q, J = 266.3, CF_3), 113.01 (CH). HRMS (MALDI/ESI): [M − Cl + $C_{14}H_9F_3N_2$] calcd for $C_{28}H_{18}AuF_6N_4$ 721.11; found 721.1095. Anal. Calcd (%) for $C_{14}H_9AuF_3ClN_2$: C, 33.99; H, 1.63; N, 5.66. Found: C, 33.76; H, 1.95; N, 5.60 (solvent impurities accounted for deviation). Mp: 274.8 °C with decomposition.

*Chloro[3-(4-nitrophenyl)-1-(trifluoromethyl)-1H-benzo[d]-imidazol-3-ylidene]gold (**9c**).* Synthesized according to the general procedure G, starting from **2d·HBF$_4$** (282.9 mg, 0.45 mmol) and [Au(DMS)Cl] (176.9 mg, 0.45 mmol). The product was obtained as an off-white solid (82.1 mg, 0.15 mmol, 33.9%). ^{1}H NMR (400.13 MHz, DMSO-d_6, 60 °C): δ = 8.58−8.54 (m, 2H, ArH), 8.20−8.16 (m, 2H, ArH), 8.00−7.97 (m, 1H, ArH), 7.73 (ddd, J = 8.4, 7.4, 1H, ArH), 7.64 (ddd, J = 8.3, 7.4, 1H, ArH), 7.48 (dt, J = 8.3, 0.9 Hz, 1H, ArH). ^{19}F NMR (376.46 MHz, DMSO-d_6, 60 °C): δ = −53.01 (NCF_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, DMSO-d_6, 60 °C): δ = 177.79 (d, J = 6.0 Hz, Au−C), 148.33 (C), 141.25 (C), 133.27 (C), 129.19 (C), 128.74 (2C, CH), 126.98 (CH), 126.87 (CH), 125.06 (2C, CH), 118.76 (q = 266.6 Hz, CF_3), 113.07 (q, J = 3.9 Hz, CH), 112.96 (CH). HRMS (MALDI/ESI): [M − Cl + $C_{14}H_8F_3N_3O_2$] calcd for $C_{28}H_{16}AuF_6N_6O_4$ 811.12; found 811.1188. Anal. Calcd (%) for $C_{14}H_8AuF_3ClN_3O_2$: C, 36.16; H, 1.49; N, 7.79. Found: C, 36.30; H, 1.66; N, 7.80. Mp: 316.5 °C with decomposition.

*Chloro[1-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-3-ylidene]gold (**9d**).* Synthesized according to the general procedure G, starting from **2e·HBF$_4$** (282.9 mg, 0.68 mmol) and [Au(DMS)Cl] (200 mg, 0.68 mmol). The product was obtained as a white solid (156.2 mg, 0.28 mmol, 41.1%). ^{1}H NMR (500.26 MHz, acetone-d_6): δ = 8.18−8.12 (m, 4H, ArH), 8.01 (ddt, J = 8.4, 1.8, 0.8 Hz, ArH) 7.77 (ddd, J = 8.4, 7.4, 1.1 Hz, 1H, ArH), 7.69 (ddd, J = 8.3, 7.4, 1.0 Hz, 1H, ArH), 7.58 (dt, J = 8.3, 0.9 Hz, 1H, ArH). ^{19}F NMR (470.67 MHz, acetone-d_6): δ = −54.19 (NCF_3), −63.22 ($ArCF_3$). $^{13}C\{^1H\}$ NMR (125.80 MHz, acetone-d_6): δ = 180.01 (q, J = 6.1 Hz, Au−C), 141.19 (C), 134.98 (C), 132.70 (q, J = 32.8 Hz, C), 130.90 (C), 129.36 (2C, CH), 128.29 (q, J = 3.8 Hz, 2C, CH), 128.07 (CH), 127.90 (CH), 124.80 (apt d, J = 271.9 Hz, CF_3), 120.45 (apt d, J = 265.9 Hz, CF_3), 114.30 (q, J = 4.1 Hz, CH), 114.15 (CH). HRMS (MALDI/ESI): [M − Cl + $C_{15}H_8F_6N_2$] calcd for $C_{30}H_{16}AuF_{12}N_4$ 857.08; found 857.0819. Anal. Calcd (%) for $C_{15}H_8AuF_6ClN_2$: C, 32.02; H, 1.43; N, 4.98. Found: C, 31.99; H, 1.45; N, 4.87. Mp: 335.6 °C with decomposition.

*Chloro[3-(6-fluoropyridin-3-yl)-1-(trifluoromethyl)-1H-benzo[d]-imidazol-3-ylidene]gold (**9e**).* Synthesized according to the general procedure G, starting from **2f·HBF$_4$** (84.9 mg, 0.23 mmol) and [Au(DMS)Cl] (67.9 mg, 0.23 mmol). The product was obtained as an off-white solid (51.5 mg, 0.10 mmol, 43.6%). ^{1}H NMR (500.26 MHz, DMSO-d_6, 60 °C): δ = 8.79 (s, 1H, ArH), 8.52 (m, 1H), 7.98 (d, J = 8.0, 1H, ArH), 7.73 (t, J = 8.0 Hz, 1H, ArH), 7.65 (t, J = 7.8 Hz, 1H, ArH), 7.60−7.53 (m, 2H, ArH). ^{19}F NMR (470.67 MHz, DMSO-d_6, 60 °C): δ = −53.09 (NCF_3), −65.54 (dd, J = 7.4 Hz, 3.5 Hz, ArF). $^{13}C\{^1H\}$ NMR (125.80 MHz, DMSO-d_6, 60 °C): δ = 178.45 (d, J = 6.5 Hz, Au−C), 162.90 (d, J = 240.9 Hz, CF), 146.30 (d, J = 16.9 Hz, C), 141.10 (d, J = 9.7 Hz, C), 133.69 (C), 131.73 (d, J = 4.6 Hz, CH), 129.07 (CH), 126.93 (d, J = 6.7 Hz, CH), 118.73 (q, J = 266.5 Hz, CF_3), 113.10 (CH), 112.97 (q, J = 4.0 Hz, CH), 111.02 (CH), 110.71 (CH). HRMS (MALDI/ESI): [M + Na^+] calcd for $C_{13}H_7AuF_4ClN_3Na$ 535.98; found 535.9822. Anal. Calcd (%) for $C_{13}H_7AuF_4ClN_3$: C, 30.40; H, 1.37; N, 8.18. Found: C, 28.32; H, 1.22;

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N, 7.37 (solvent impurities accounted for deviation). Mp: 335.3 °C with decomposition.

*General Procedure H. Au(I)-Catalyzed Intermolecular Hydroalkoxylation of Cyclohexene (**10**) with 2-Methoxyethanol (**11**).* A septum cap vial tube (2 mL) wrapped in aluminum foil was charged the corresponding Au(I) complex **9a**−**e** (0.0125 mmol), $AgNTf_2$ (4.9 mg, 0.0125 mmol), and chlorobenzene (0.25 mL), and the mixture was stirred for 5 min. Then cyclohexene (**10**, 205 mg, 2.50 mmol) and 2-methoxyethanol (**11**, 19.0 mg, 0.250 mmol) were added to the mixture. The vial tube was sealed and stirred at 100 °C for 20 h. Subsequently, the mixture was cooled to room temperature. Then, *n*-tetradecane was added to the mixture as an internal standard. The yield of the resulting (2-methoxyethoxy)cyclohexane (**12**) was determined by GC analysis.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for new compounds; crystallographic data (CIF files) for **2d·red**, **6a**−**f**, **7a**, and **9a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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