Diverse Coordination Modes of Bidentate COC and Tridentate CNC Ligands Comprising 1,2,3-Triazol-5-ylidenes

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S Supporting Information

ABSTRACT: Two readily available bis(1,2,3-triazol-5-ylidene) ligand precursors $[H_2(COC)](PF_6)_2$ and $[H_2(C^HNC)](PF_6)_2$, bridged by an ether or amine functionality, respectively, were prepared. Their coordination versatility was evaluated predominantly by reacting Rh(I) and Ir(I) metal precursors with the in situ deprotonated salt precursors or in exceptional cases, via transmetallation from silver, to obtain those complexes not accessible via the preferred one-step route. A divergence in reactivity and coordination was observed for both ligand precursors depending on the base and metal employed. The carbon–ether–carbon (**COC**) ligand afforded mono- and bimetallic complexes of Rh(I) and Ir(I), chelates or bridges two metal centers. Conversely, the carbon–amine–carbon (**C^HNC**) ligand displayed a greater predisposition for rhodium binding and poor coordination ability to iridium. As a result, two unusual bimetallic Rh(I) complexes bearing two metal centers bridged by the central (deprotonated) amido functionality, along with a monometallic Rh(I) containing the neutral amino-CNC pincer ligand were isolated. In contrast, only monometallic Ir(I) complexes bearing a pendant triazolium arm could be prepared.
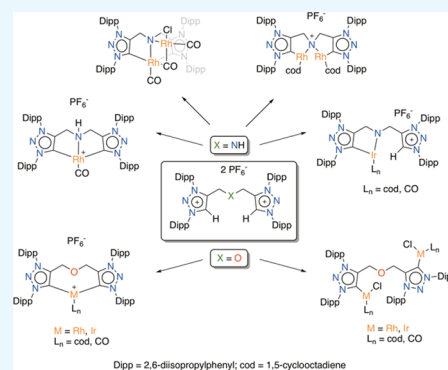
INTRODUCTION

N-heterocyclic carbene ligands (NHCs) have been widely used as ligands for the preparation of organometallic compounds,[1] specifically in the arena of efficient homogeneous catalyst development. The continuous efforts to modify the electronic properties and modulate the substitution pattern (sequence and number of the heteroatoms) of the classical Arduengo-type imidazolylidenes have led to the development of different NHC frameworks such as the cyclic(alkyl)(amino) carbenes[2] and mesoionic carbenes (MICs).[3] Among them, mesoionic 1,2,3-triazolylidene ligands have recently received considerable attention due to their intrinsic mesoionic character provisioning them as strong σ-donors. The particular advantage of this class of ligands is the potential for ligand–metal cooperativity combined with their synthetic versatility, giving access to readily available mono-, bi-, and tridentate ligands.[4] In this context, the isolation of the first stable "click" chemistry-derived mesoionic bis(triazolylidene) (i-bitz) bearing two carbene units directly bound to the C4 carbon of the triazolylidene and its related monometallic [Rh(i-bitz)(cod)]-[OTf] and [Rh(i-bitz)(CO)₂][OTf] complexes reported by Bertrand and co-workers[5] spurred the development of several metal complexes based on poly(triazolylidene) ligands. Several examples, by varying the number of carbene moieties (two[6] or three[7]), the substituents at the N1 and N3 (alkyl or aryl) of the

triazolylidene, as well the spacer or scaffold employed (flexible or rigid), have been reported since. We have recently isolated the potassium adduct of an anionic CNC bis(triazolylidene) pincer ligand based on a rigid carbazole scaffold,[6j] readily available upon deprotonation of the corresponding bistriazolium amine salt. Its coordination versatility and extraordinary electronic properties were demonstrated by the preparation of a range of complexes,[6g–j] notably including reactive species such as the Ni(II)[6j] and Au(III) hydrides[6g] as well as Rh(I) oxygen adducts.[6i] Notwithstanding the significant catalytic implications demonstrated by related ancillary aliphatic pincer ligands,[8] the number of metal complexes featuring poly(triazolylidene) ligands linked by a flexible aliphatic spacer bearing none or any additional functionality is still limited.[9] Herein, we report the synthesis of readily available ether- and amine-bridged bis(triazolium) ligand precursors that were employed for the preparation of several mono- and binuclear rhodium and iridium complexes, including a [(**CNC**)Rh(I)-(CO)] metal complex containing an aliphatic CNC pincer ligand.
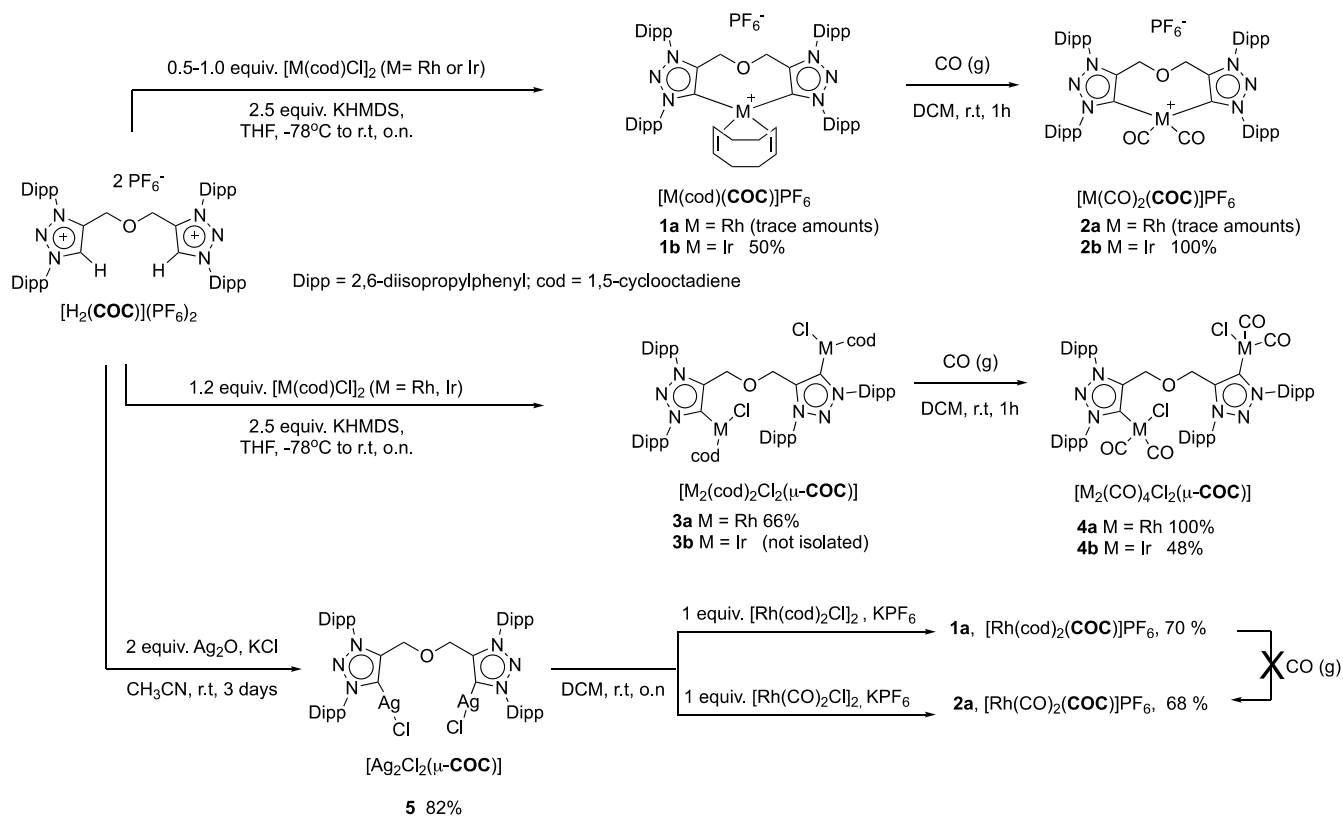
Scheme 1. Synthesis of Ligand Salt Precursors $[H_2(COC)](PF_6)_2$ and $[H_2(C^HNC)](PF_6)_2$
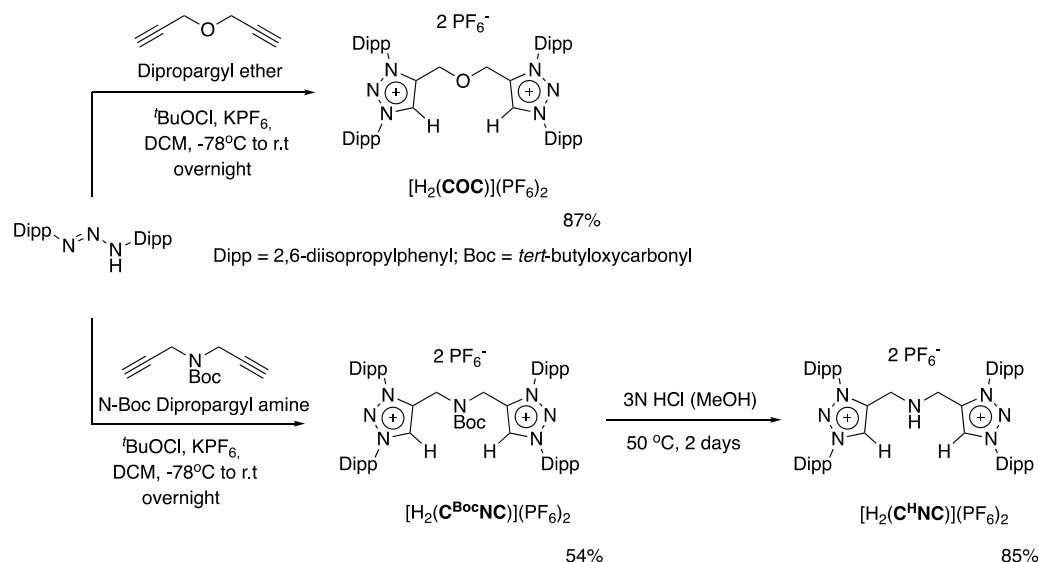
Scheme 2. Synthesis of Metal Complexes 1−5

RESULTS AND DISCUSSION

The ether-bridged bistriazolium salt $[H_2(COC)](PF_6)_2$ was obtained in 87% yield by using an adapted version of a 1,3-dipolar cycloaddition between 1,3-bis-(2,6-diisopropylphenyl)-triaz-1-ene and dipropargyl ether (Scheme 1).[3d] The amino-bridged bistriazolium salt was prepared in two steps starting with a 1,3-dipolar cycloaddition between 1,3-bis-(2,6-diisopropylphenyl)triaz-1-ene and N-(tert-butyloxy)carbonyl dipropargylamine that gives $[H_2(C^{Boc}NC)](PF_6)_2$, followed by a deprotection step involving the removal of the tert-butyloxycarbonyl (Boc) protecting group using a 3 N

methanolic solution of hydrochloric acid to produce $[H_2(C^HNC)](PF_6)_2$ in 85% yield.[9e] The detailed synthetic procedure and characterization data, including the X-ray diffraction (XRD) crystal structures of $[H_2(L)](PF_6)_2$ (with L = COC, $C^{Boc}NC$, and C^HNC), are included in the Supporting Information (SI). The bistriazolium salts $[H_2(COC)](PF_6)_2$ and $[H_2(C^HNC)](PF_6)_2$ were selected as ligand precursors for the preparation of the corresponding Rh(I) and Ir(I) complexes.

We initially evaluated the coordination ability of salt $[H_2(COC)](PF_6)_2$ against two metal precursors $[M(cod)Cl]_2$

(with M = Rh, Ir, cod = 1,5-cyclooctadiene), using a synthetic method involving the in situ deprotonation of the salt in the presence of potassium hexamethyldisilazide (KHMDS) as base (Scheme 2). Aiming to obtain the corresponding cationic monometallic complexes [M(cod)(**COC**)](PF$_6$) (with M = Rh, Ir), we used less than 0.5 equiv of precursor [M(cod)Cl]$_2$ (with M = Rh, Ir) with respect to ligand salt. However, we found that only trace amounts of monometallic Rh(I) complex **1a** [Rh(cod)(**COC**)](PF$_6$) were obtained (Scheme 2). Efforts to isolate its dicarbonyl derivative **2a** [Rh(CO)$_2$(**COC**)](PF$_6$) after treating the crude mixture with CO(g) produced a residual amount of **2a** [Rh (CO)$_2$(**COC**)](PF$_6$). Recrystallization of this fraction yielded single crystals of **2a** suitable for XRD analysis. In view of these results, we decided to explore their synthesis by varying the amount of metal precursor, from 0.5 to 1.2 equiv. We found that only cationic monometallic Ir(I) complex **1b** [Ir(I)(cod) (**COC**)](PF$_6$) could be obtained in 50% yield after 1.0 equiv of [Ir(cod)Cl]$_2$ was employed, which could be easily converted into its dicarbonyl derivative **2b** [Ir(CO)$_2$(**COC**)](PF$_6$) in 100% after treating a solution of **1b** in dichloromethane with CO(g). Unfortunately, the related Rh(I) **1a** was not accessible following this strategy and it was obtained via transmetallation from silver (vide infra). Interestingly, we observed that when 1.2 equiv of metal precursor was employed, neutral binuclear Rh(I) complex **3a** [Rh$_2$(cod)$_2$Cl$_2$(μ-**COC**)] was obtained in 66% yield. Conversely, the related bimetallic iridium complex **3b** [Ir$_2$(cod)$_2$Cl$_2$(μ-**COC**)] could only be extracted from the crude mixture using n-hexane as solvent and subsequently used in the next step, without further purification. The corresponding tetracarbonyl derivatives **4a** and **4b** with formula [M$_2$(CO)$_4$Cl$_2$(μ-**COC**)] (with M = Rh, Ir) were obtained in 100 and 48% yield, respectively, after bubbling CO(g) through a dichloromethane solution containing either **3a** or **3b**. It is noteworthy to mention that complexes **3a** and **4a** were also accessible in similar yields (69 and 100%, respectively) by using a methodology that entails the generation of the free biscarbene by deprotonation of the ligand salt precursor [H$_2$(**COC**)](PF$_6$)$_2$ with KHMDS, followed by the addition of the metal precursors [Rh(cod)Cl]$_2$ or [Rh(CO)$_2$Cl]$_2$ in tetrahydrofuran (THF) (see Experimental Section).

Our endeavor to obtain complex **1a** involved the exploration of alternative synthetic routes such as transmetallation from silver. Thus, we first reacted [H$_2$(**COC**)](PF$_6$)$_2$ with Ag$_2$O in the presence of KCl as halide source in acetonitrile, which afforded the bimetallic complex **5** [Ag$_2$Cl$_2$(μ-**COC**)] in 82% yield after 3 days at room temperature (RT). Then, **5** was reacted with [Rh(cod)Cl]$_2$ and [Rh(CO)$_2$Cl] in dichloromethane at RT to afford both complexes **1a** [Rh(cod)(**COC**)](PF$_6$) (70%) and **2a** [Rh(CO)$_2$(**COC**)](PF$_6$) (68%), respectively. Attempts to convert compound **1a** to **2a** by bubbling CO(g) through a dichloromethane solution of **1a** proved to be unsuccessful.

Complexes **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, and **4b** were characterized spectroscopically by NMR, high-resolution mass spectrometry (HRMS), and Fourier transform infrared (FTIR) spectroscopy. The carbene carbon atom resonance for complex **1a**[Rh(cod)(**COC**)](PF$_6$) appears as a doublet at 169.4 ppm (J = 41.2 Hz), while that for **1b** [Ir(cod)(**COC**)](PF$_6$) appears as a singlet at 166.7 ppm (see Figures S8 and S10, SI). The carbene carbon for the dicarbonyl complex **2a** [Rh-(CO)$_2$(**COC**)](PF$_6$) resonates at 167.6 ppm (J = 45.5 Hz), similar to that of **2b** [Ir (CO)$_2$(**COC**)](PF$_6$), appearing as a

singlet at 166.2 ppm. The carbonyl ligands for **2a** display a doublet at 183.8 ppm (J = 56.4 Hz), while that of **2b** resonates as a singlet at 176.5 ppm in the ^{13}C NMR spectra (see Figures S12 and S14, SI).

The IR spectra for both **2a** and **2b** display two strong bands at 2016 and 1998 cm^{-1} ($\nu_{(CO)av}$ 2007 cm^{-1}) in the former case and at 2065 and 1999 cm^{-1} ($\nu_{(CO)av}$ 2032 cm^{-1}) in the latter case, both corresponding to the two carbonyl stretching modes. The carbene carbon signal for complex **3a** [Rh$_2$(cod)$_2$Cl$_2$(μ-**COC**)] is observed as a doublet at 176.1 ppm (J = 46.8 Hz). The carbene carbon atom resonance for the bimetallic tetracarbonyl complex **4a** [Rh$_2$(CO)$_4$Cl$_2$(μ-**COC**)] appears as a doublet at 170.0 ppm (J = 41.1 Hz), similar to that of **4b** [Ir$_2$(CO)$_4$Cl$_2$(μ-**COC**)], appearing as a singlet at 170.5 ppm. The carbonyl ligands for **4a** are observed as two doublets in the ^{13}C NMR spectrum, one at 183.4 ppm (J = 74.6 Hz), representing the carbonyl trans to the chlorido, and the other at 185.8 ppm (J = 54.5 Hz), representing the carbonyls trans to the carbene. Similarly to **4a**, compound **4b** also displays two carbonyl resonances, resonating as singlets at 168.6 ppm (trans Cl) and 181.4 (trans carbene) (see Figures S18 and S20, SI).

The IR spectra for both **4a** and **4b** display two strong bands at 2076 and 1995 cm^{-1} ($\nu_{(CO)av}$ 2035 cm^{-1}) for the former and at 2063 and 1978 cm^{-1} ($\nu_{(CO)av}$ 2020 cm^{-1}) for the latter, which are in agreement with the values previously reported for the related complexes [M(CO)$_2$Cl(MIC)] (with M = Rh or Ir; MIC = 1,2,3-triazolylidene).[3b,c] The structures of **1b**, **2a**, **2b**, **3a**, and **4a** were confirmed by X-ray diffraction studies, and are shown in Figures 1–5.
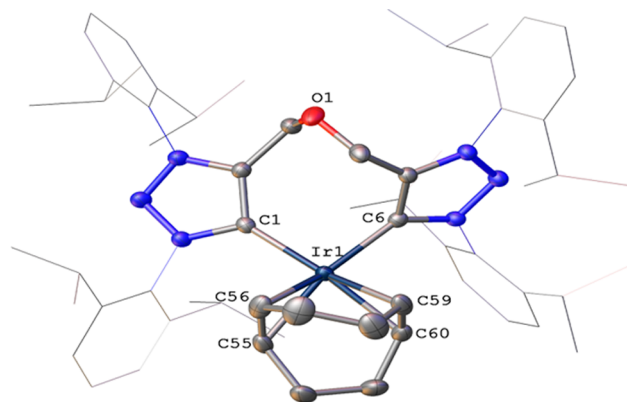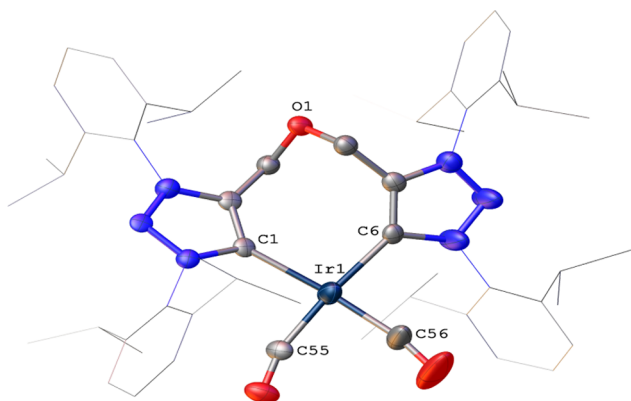

Figure 1. X-ray crystal structure of complex **1b** [Ir(cod)(**COC**)]-(PF$_6$) (50% displacement ellipsoids). [Counteranion (PF$_6^-$), hydrogen atoms and solvent molecules (dichloromethane) omitted for clarity.] Selected bond distances (Å) and angles (deg): Ir1–C1 2.102(2), Ir1–C6 2.055(2), Ir1–C55 2.223(2), Ir1–C56 2.162(2), Ir1–C59 2.177(2), Ir1–C60 2.152(2), C1–Ir1–C6 92.74(8), C1–Ir1–C55 98.27(8), C1–Ir1–C56 91.90(9), C1–Ir1–C59 159.12(10), C1–Ir1–C60 163.36(10), C6–Ir1–C55 168.04(9), C6–Ir1–C56 147.91(10), C6–Ir1–C59 84.29(9), C6–Ir1–C60 89.29(9).

Complex **1b** [Ir(cod)(**COC**)](PF$_6$) displays a single Ir(I) metal center, which is bound to two 1,2,3-triazol-5-ylidene ligands, and a 1,5-cyclooctadiene (cod). The Ir–C$_{carbene}$ bond distances are 2.102(2) and 2.055(2) Å, respectively.

The bond angle between the two carbenic carbons and the iridium center was found to be 92.7(8)°, which confirms the pseudo-square planar geometry of the Ir(I) center. Complex
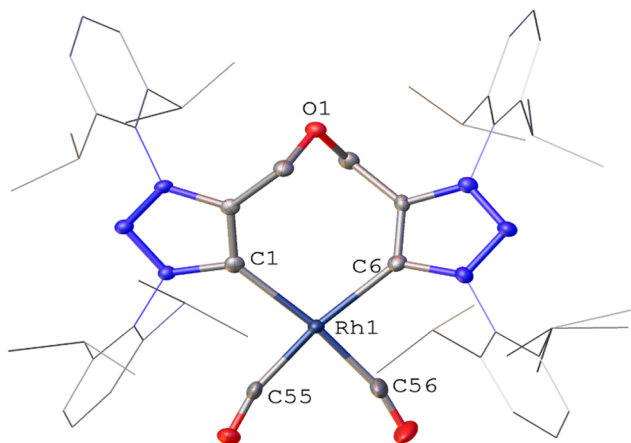
Figure 2. X-ray crystal structure of complex **2a** [Rh(CO)$_2$(**COC**)]-(PF$_6$) (50% displacement ellipsoids). [Counteranion (PF$_6^-$) and hydrogen atoms omitted for clarity.] Selected bond distances (Å) and angles (deg): Rh1−C1 2.122(4), Rh1−C6 2.110(4), Rh1−C55 1.878(4), Rh1−C56 1.878(4), C1−Rh1−C6 95.24(14), C1−Rh1−C55 93.09(15), C1−Rh1−C56 167.67(17), C6−Rh1−C55 167.76(15), C6−Rh1−C56 90.90(16).
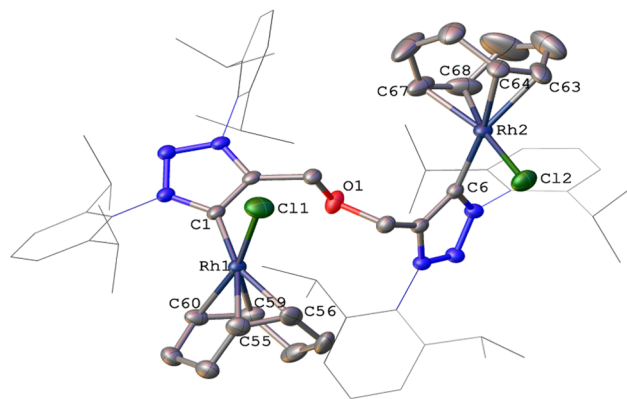

Figure 3. X-ray crystal structure of complex **2b** [Ir(CO)$_2$(**COC**)]-(PF$_6$) (50% displacement ellipsoids). [Counteranion (PF$_6^-$) and hydrogen atoms omitted for clarity.] Selected bond distances (Å) and angles (deg): Ir1−C1 2.110(16), Ir1−C6 2.059(15), Ir1−C55 1.824(17), Ir1−C56 1.868(19), C1−Ir1−C6 93.7(6), C1−Ir1−C55 91.5(7), C1−Ir1−C56 169.2(8), C6−Ir1−C55 172.6(7), C6−Ir1−C56 92.7(7).

2a, [Rh(CO)$_2$(**COC**)](PF$_6$), displays a single Rh(I) metal center in a slightly distorted square planar geometry bound to two 1,2,3-triazol-5-ylidene ligands, and two carbonyls groups. The Rh−C$_{carbene}$ bond distances are 2.122(4) and 2.110(4) Å, respectively. The bond angle between the two carbenic carbons and the rhodium center was found to be 93.09(15)°, which confirms the pseudo-square planar geometry of the Rh(I) center.

Complex **2b** [Ir(CO)$_2$(**COC**)](PF$_6$) shows a single Ir(I) metal center in a slightly distorted square planar geometry, which are coordinated to two 1,2,3-triazol-5-ylidene moieties, and two carbonyls. The Ir−C$_{carbene}$ bond distances are 2.110(16) and 2.059(15) Å, respectively. The bond angle of 93.7(6)° between the two carbenic carbons and the iridium center confirms the pseudo-square planar geometry of the Ir(I) center.

The molecular structure of complex **3a** [Rh$_2$(cod)$_2$Cl$_2$(μ-**COC**)] (Figure 4) shows two Rh(I) centers, each bound to a

Figure 4. X-ray crystal structure of complex **3a** [Rh$_2$(cod)$_2$Cl$_2$(μ-**COC**)] (50% displacement ellipsoids). (Hydrogen atoms and solvent molecules (dichloromethane) omitted for clarity.) Selected bond distances (Å) and angles (deg): Rh1−C1 2.030(2), Rh1−Cl1 2.3927(7), Rh1−C55 2.197(3), Rh1−C56 2.177(3), Rh1−C59 2.099(3), Rh1−C60 2.089(2), Rh2−C6 2.043(2), Rh2−Cl2 2.3741(7), Rh2−C63 2.167(3), Rh2−C64 2.205(2), Rh2−C67 2.087(3), Rh2−C68 2.087(3), C1−Rh1−Cl1 86.46(7), C55−Rh1−C1 165.77(10), C56−Rh1−C1 157.78(10), C59−Rh1−C1 94.40(10), C60−Rh1−C1 93.06(9), C6−Rh2−Cl2 87.31(7), C6−Rh2−C63 155.92(11), C6−Rh2−C64 167.10(10), C6−Rh2−C67 95.81(10), C6−Rh2−C68 93.60(11).
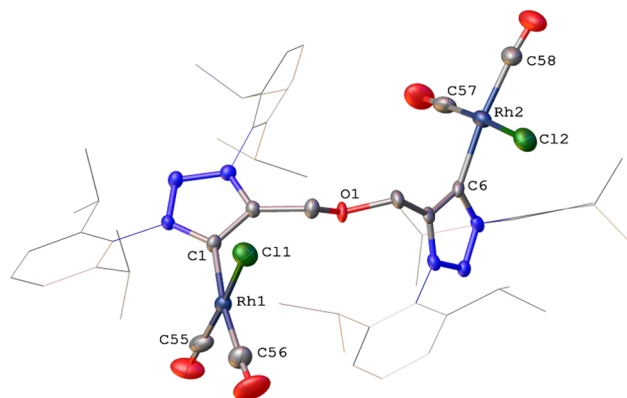

Figure 5. X-ray crystal structure of complex **4a** [Rh$_2$(CO)$_4$Cl$_2$(μ-**COC**)] (50% displacement ellipsoids). (Hydrogen atoms omitted for clarity.) Selected bond distances (Å) and angles (deg): Rh1−C1 2.054(5), Rh1−Cl1 2.3434(16), Rh1−C55 1.831(7), Rh1−C56 1.899(7), Rh2−C6 2.041(5), Rh2−Cl2 2.3672(17), Rh2−C57 1.812(7), Rh2−C58 1.905(6), C1−Rh1−Cl1 87.50(15), C55−Rh1−C1 93.1(2), C56−Rh1−C1 172.9(2), C6−Rh2−Cl2 85.70(15), C6−Rh2−C57 91.6(2), C6−Rh2−C58 174.0(2).

1,2,3-triazol-5-ylidene, a 1,5-cyclooctadiene (cod), and a chlorido ligand. The Rh−C$_{carbene}$ bond distances are 2.043(2) and 2.030(2) Å, respectively. Interestingly, the metal centers and the (cod) ligands are facing in opposite directions (isomer DL) probably due to steric constraints imparted by the bulky ligand substituents. Related examples in the literature of bis-NHC Rh(I) complexes linked by an aliphatic chain indicate the possibility of forming different isomers meso and DL.[10] In our case, we only observed one set of NMR resonances confirming the presence of only one of the isomers. In complex **4a** [Rh$_2$(CO)$_4$Cl$_2$(μ-**COC**)] (Figure 5), two Rh(I) centers are present, each one is bound to a 1,2,3-triazol-5-ylidene ligand, two carbonyls, and a chlorido. The

Scheme 3. Synthesis of Metal Complexes 6−9

Dipp = 2,6-diisopropylphenyl; cod = 1,5-cyclooctadiene
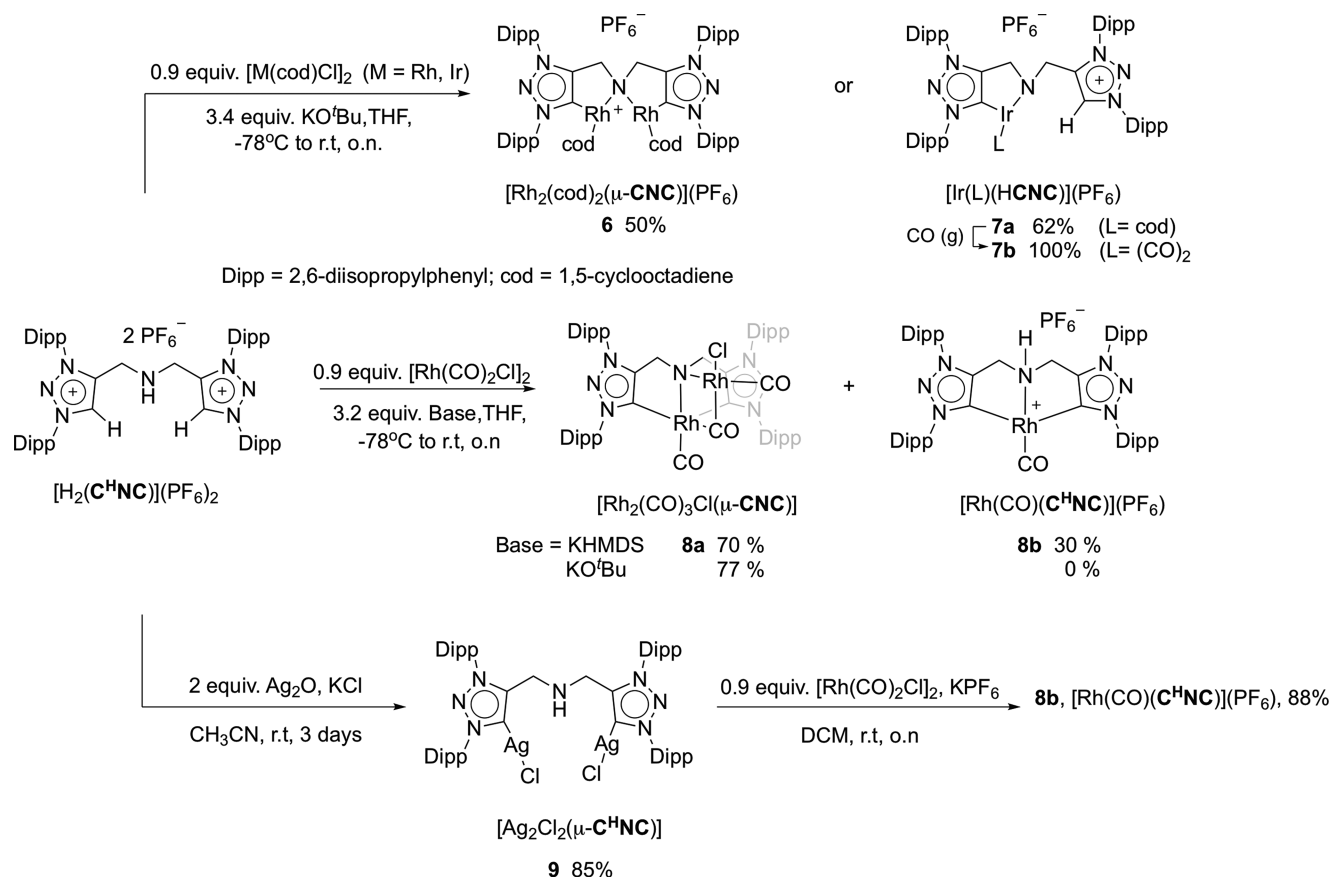
Rh−$C_{carbene}$ bond distances are 2.054(5) and 2.041(5) Å, respectively.

Based on the reactivity observed for the ligand salt [H$_2$(**COC**)](PF$_6$)$_2$, we decided to explore the coordination versatility of the ligand precursor [H$_2$(**C^{H}NC**)](PF$_6$)$_2$ toward two different Rh(I) metal precursors, [Rh(cod)Cl]$_2$ and [Rh(CO)$_2$Cl]$_2$, and also an Ir(I) metal precursor, [Ir(cod)-Cl]$_2$, with the ultimate goal of obtaining a pincer complex analogous to the CNC-bis(triazolylidene) pincer ligand based on a rigid carbazole scaffold.[6j] In this case, when KO^{t}Bu was used as base in the presence of [Rh(cod)Cl]$_2$, complex **6** [Rh$_2$(cod)$_2$(μ-**CNC**)](PF$_6$) (Scheme 3) was obtained in 50% yield as the only product of the reaction. Conversely, when [Ir(cod)Cl]$_2$ dimer was used as metal precursor and KO^{t}Bu as base, cationic monometallic Ir(I) complex **7a** [Ir(cod)-(**HCNC**)](PF$_6$) (Scheme 3) was obtained in 62% yield. The carbene carbon atom resonance for complex **7a** appears at 166.5 ppm. The related dicarbonylated derivative **7b** [Ir-(CO)$_2$(**HCNC**)](PF$_6$) could be easily obtained in 100% yield after bubbling CO(g) through a dichloromethane solution containing **7a**. The carbene carbon atom resonance for the dicarbonyl complex **7b** appears at 174.1 ppm, while the carbonyl ligands give rise to two signals at 186.5 and 178.8 ppm. The IR spectrum displayed two strong bands at 2035 and 1964 cm^{-1} (ν(CO)$_{av}$ = 1999.5 cm^{-1}) corresponding to the two carbonyl stretching modes. These bands occur at frequencies significantly higher than the 2032.5 cm^{-1} observed for the cationic **2b** and related examples in the literature, reflecting the donating character of the amido group.[11,18] In these two complexes, the metal is bonded to only two of the three possible coordinating sites of the CNC ligand [H$_2$(**C^{H}NC**)]-

(PF$_6$)$_2$ featuring a pendant triazolium salt. All our attempts using KHMDS as base resulted in the formation of untreatable mixtures; similarly, attempts at a subsequent deprotonation and metalation step after isolation of **7a/b** did not proceed smoothly.

These observations reflect the marked differences in reactivity and coordination modes for ligand precursor [H$_2$(**C^{H}NC**)](PF$_6$)$_2$ with a N−H bridge, compared to [H$_2$(**COC**)](PF$_6$)$_2$ with the ether bridge, even though the ligand scaffolds share the same linker length. MIC-anchored/pendant-triazolium species are not accessible via trans-metallation reactions and isolation often occurs serendipitously and is hard to predict. In contrast to their NHCs analogues, only two examples are known.[12] Such examples are however useful for the preparation of homo- and heterobimetallic complexes. In addition, the availability of Ir(I) complexes bearing an N-donor-functionalized 1,2,3-triazolylidene ligands is very appealing for comparative reasons, since the related Rh(I) derivatives have recently shown hemilability and cooperativity in alkyne hydrothiolation reactions.[16]

When [Rh(CO)$_2$Cl]$_2$ was employed as metal precursor in combination with KHMDS as base, an inseparable mixture of complexes **8a** [Rh$_2$(CO)$_3$Cl(μ-**CNC**)] and **8b** [Rh(CO)-(**C^{H}NC**)](PF$_6$) in a 70/30% ratio (Scheme 3), where complex **8a** is the major product (see Figures S31 and S32, SI) was obtained. Conversely, when KO^{t}Bu was used instead, the reaction produces selectively the bimetallic **8a** [Rh$_2$(CO)$_3$Cl-(μ-**CNC**)] in 77% yield as the only product. The potential noninnocent/hemilabile implication of the monometallic complex **8b** [Rh(CO)(**C^{H}NC**)](PF$_6$) in catalysis piqued our interest in the isolation of this complex featuring the CNC

ligand coordinated in a pincer manner. Thus, we decided to attempt an alternative preparatory route, namely, the transmetallation from silver.[3b,9,13] Treatment of [H$_2$(C^{H}NC)]-(PF$_6$)$_2$ with Ag$_2$O in the presence of KCl as halide source in acetonitrile afforded the bimetallic complex 9 [Ag$_2$Cl$_2$(μ-C^{H}NC)] in 85% yield after 3 days at room temperature.[9e] Next, 9 was reacted with [Rh(CO)$_2$Cl]$_2$ in dichloromethane at room temperature to afford the desired cationic monometallic complex 8b [Rh(CO)(C^{H}NC)](PF$_6$) in 88% yield as the only product (Scheme 3). The ^{1}H NMR spectrum of the cationic complex displays resonance of the N−H group at 6.51 ppm. In the ^{13}C NMR spectrum, the C$_{carbene}$ atom resonates as a doublet at 178.7 ppm (J = 44.2 Hz), while the carbonyl ligand trans to the N−H group resonates as a doublet at 192.3 ppm (J = 81.5 Hz). Also in the IR spectrum, the ν_{NH} and ν_{CO} bands are observed at 3256 and 1974 cm^{-1}, respectively (see Experimental Section, and Figures S33 and S34, SI). Despite all our efforts, single crystals of 8b, suitable for X-ray analysis, could not be obtained. Attempts to extend this methodology for the preparation of the Ir(I) analogue [Ir(CO)(C^{H}NC)]-(PF$_6$) employing several metal precursors such as [Ir(cod)Cl]$_2$, [Ir(μ-OMe)(cod)]$_2$, [Ir(coe)$_2$Cl]$_2$, or Ir(CO)$_2$(acac) were unsuccessful. The difficulty in isolating the iridium complexes might be due to the difference in the stability of the metal−carbon bonds for iridium compared to rhodium, or due to the larger size of the metal center along with the steric hindrance imposed by the bulky wingtips of the 1,2,3-triazolylidene ligands. Complexes 6, 7a, 7b, 8a, 8b, and 9 were spectroscopically characterized by NMR, HRMS, and FTIR analyses. The molecular structures of complexes 6, 7b, and 8a were confirmed by X-ray diffraction studies, and are shown in Figures 6−8, respectively.

The structure of the cationic complex 6 [Rh$_2$(cod)$_2$(CNC)]-(PF$_6$) comprises two Rh(I) atoms, each one bound to a 1,2,3-triazolylidene ligand and a 1,5-cyclooctadiene (cod). The two metal centers are bridged by the amido functionality with a
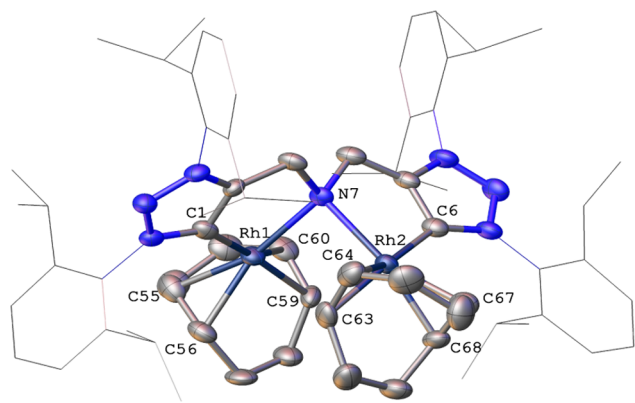
Figure 6. X-ray crystal structure of complex 6 [Rh$_2$(cod)$_2$(μ-CNC)](PF$_6$) (50% displacement ellipsoids). [Counteranion (PF$_6^-$), hydrogen atoms, and solvent molecules (dichloromethane) omitted for clarity.]. Selected bond distances (Å) and angles (deg): Rh1−Rh2 3.1963(12), Rh1−C1 2.035(11), Rh2−C6 2.037(10), Rh1−N7 2.209(8), Rh2−N7 2.217(8), Rh1−C55 2.125(12), Rh1−C56 2.136(11), Rh1−C59 2.223(11), Rh1−C60 2.191(11), Rh2−C63 2.207(11), Rh2−C64 2.179(12), Rh1−N7−Rh2 92.5(3), C1−Rh1−N7 80.8(4), C1−Rh1−C55 93.9(4), C1−Rh1−C56 94.7(4), C1−Rh1−C59 169.6(4), C1−Rh1−C60 153.9(4), C6−Rh2−C63 167.9(4), C6−Rh2−C64 156.4(4), C6−Rh2−C67 95.4(5), C6−Rh2−C68 95.3(4).
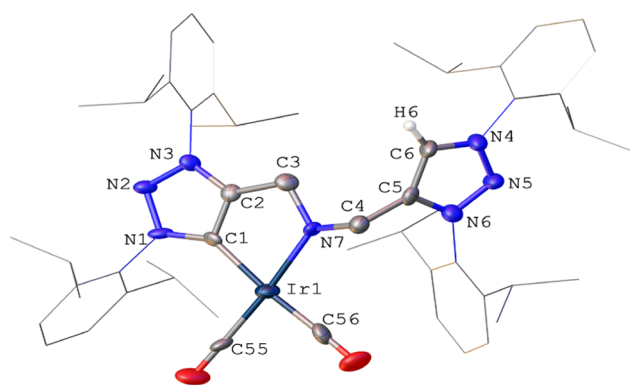
Figure 7. X-ray crystal structure of complex 7b [Ir(CO)$_2$(HCNC)]-(PF$_6$) (50% displacement ellipsoids). (Hydrogen atoms, counteranion (PF$_6^-$), and solvent molecules (dichloromethane) omitted for clarity.) Selected bond distances (Å) and angles (deg): Ir1−C1 2.032(9), Ir1−N7 2.048(7), Ir1−C55 1.865(9), Ir1−C56 1.866(11), C1−Ir1−N7 78.0(3), C1−Ir1−C55 97.2(3), C1−Ir1−C56 174.3(4), N7−Ir1−C55 175.3(3), N7−Ir1−C56 96.3(3).
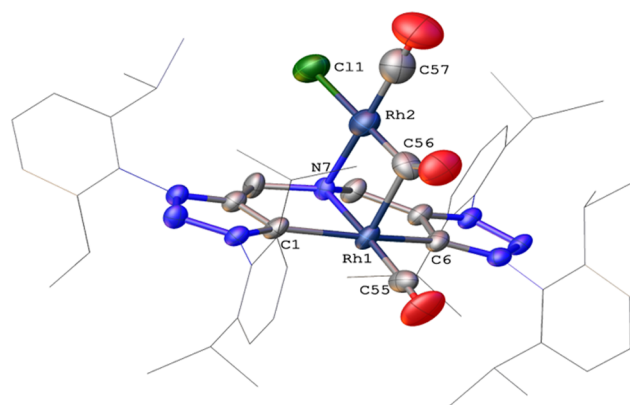
Figure 8. X-ray crystal structure of complex 8a [Rh$_2$(CO)$_3$Cl(μ-CNC)] (50% displacement ellipsoids). [Hydrogen atoms omitted for clarity.] Selected bond distances (Å) and angles (deg): Rh1−Rh2 2.9698(12), Rh1−C1 2.046(8), Rh1−C6 2.029(8), Rh1−N7 2.113(6), Rh1−C55 51.846(10), Rh1−C56 2.211(10), Rh2−N7 2.189(7), Rh2−C56 1.909(11), Rh2−C57 1.819(15), Rh2−Cl1 2.385(3), C1−Rh1−C6 157.3(3), C1−Rh1−N7 79.3(3), C1−Rh1−C55 100.0(3), N7−Rh1−C56 87.3(3), Rh1−N7−Rh2 56 47.41(18), N7−Rh2−C57 177.7(4).

short Rh−Rh distance of 3.196 Å, slightly shorter than the 3.226 Å observed for a related bimetallic Rh(I) complex described by Bertrand and co-workers, which features an anionic 1,2,3-triazolylidene ligand example.[15] The structure of the cationic monometallic Ir(I) complex 7b [Ir-(CO)$_2$(HCNC)](PF$_6$), featuring a pendant triazolium salt, displays a pseudo-square planar geometry around the Ir(I) center (Figure 7). The metal is bonded to one 1,2,3-triazolylidene ligand, the bridging nitrogen acting as a one-electron donor, and two carbonyls completing the 16VE coordination sphere. The Ir−C and Ir−N bond distances of [2.032(9) Å, Ir1−N7 2.032(9) and 2.048(7) Å] Å (Ir1−N7) are within the expected range. The structure of the binuclear complex 8a [Rh$_2$(CO)$_3$Cl(CNC)] consists of two Rh(I) atoms bridged by the N atom of the CNC ligand and a carbonyl group. The Rh−Rh distance (2.9698 Å) between the two metal centers of 8a is within the range for related amido-bridged rhodium complexes.[15]

The first rhodium atom shows a slightly distorted square planar geometry featuring a pincer ligand with a central amido-ligating atom and the two 1,2,3-triazol-5-ylidene ligand units. A carbonyl ligand completes the coordination sphere around the metal center. The second rhodium atom displays a square planar geometry bound to the nitrogen atom of the CNC ligand, two carbonyls, and a chloride. In solution, however, there is no evidence for the presence of a bridging carbonyl ligand between the two rhodium metal centers.

Both the ^{13}C NMR and FTIR spectra are consistent with the presence of three terminal CO ligands. In the ^{13}C NMR spectrum, the $C_{carbene}$ atom resonates as a doublet at 173.7 ppm (J = 44.5 Hz), while the carbonyl ligand trans to the chlorido resonates as a doublet at 187.4 ppm (J = 75.7 Hz). The two CO ligands, both trans to ligand-N, are observed at 193.7 ppm (J = 71.7 Hz). Also in the IR spectrum, only two bands are observed at 2019 and 1981 cm^{-1}.

What is especially noteworthy is the different bonding modes displayed by the coordinated [H$_2$($\mathbf{C^HNC}$)](PF$_6$)$_2$ for complexes **6−8**, with either a trivalent or a tetravalent central nitrogen atom. In the case of symmetric **6** [Rh$_2$(cod)$_2$(μ-**CNC**)](PF$_6$), the positive charge is presumably located on the ammonium-type N-atom, acting as a one electron donor to each of the Rh metal centers.[14] In contrast, **8a** [Rh$_2$(CO)$_3$Cl-(μ-**CNC**)] also displays a tetravalent N-atom, but in this case, the bonding can be better described as a neutral amino ligand that binds via a one electron donation to the bis-(triazolylidene)(CO)$_2$-Rh metal and a lone pair donation to the Rh(CO)$_2$Cl fragment. In **8b** [Rh(CO)($\mathbf{C^HNC}$)](PF$_6$), the protonated nitrogen atom acts exclusively as a neutral two-electron donor, while in the case of **7a/7b**, the trivalent nitrogen exhibits anionic bonding (one electron donor) to iridium. Finally, absence of base in the reaction of [H$_2$($\mathbf{C^HNC}$)](PF$_6$)$_2$ with Ag$_2$O provides access to a bimetallic metal complex **9** [Ag$_2$Cl$_2$(μ-**CNC**)], where the nitrogen is not coordinated.

CONCLUSIONS

In summary, we have reported the synthesis of both ether- and amine-linked bis(1,2,3-triazolylidene) ligand salt precursors via a 1,3-dipolar cycloaddition between 1,3-bis-(2,6-diisopropylphenyl)triaz-1-ene and the corresponding bisalkyne. We have studied their coordination versatility preferentially by reacting the in situ deprotonated salt precursor with either KHMDS or ^{t}BuOK as a base, and with Rh(I) or Ir(I) metal precursors. Both COC- and CNC-bis(1,2,3-triazol-5-ylidene) ligands displayed very different reactivities and coordination modes, which are strongly influenced by the base employed. Exceptionally, when the desired monometallic complexes could not be accessible via in situ deprotonation, the transmetallation route from silver was employed instead. We found that the COC ligand can act as either a chelating ligand or a bridging ligand, yielding either mono- or bimetallic Rh(I) and Ir(I) complexes showing no preference between the metals. In contrast, the CNC ligand revealed a coordination inclination toward rhodium complexes. Two unusual bimetallic Rh(I) complexes where the metal centers are bridged by the central amido functionality of the anionic CNC ligand, along with a cationic monometallic Rh(I) complex bearing a neutral CNC bis(1,2,3-triazol-5-ylidene)-based pincer ligand, were obtained. However, only a monometallic Ir(I) complex with a pendant uncoordinated triazolium arm could be isolated. The

catalytic performances of the mono- and bimetallic complexes are currently under investigation in our laboratories.

EXPERIMENTAL SECTION

General Experimental Procedures. All synthetic manipulations, unless otherwise stated, were performed under a N$_2$(g) or Ar(g) atmosphere using standard Schlenk line techniques. Air-sensitive solids were stored and handled in an InertLab glovebox. Preparation of NMR and crystallization samples that also require an inert atmosphere were performed in a glovebox.

The following ligand and metal precursors were synthesized in this study according to known synthetic procedures: 1,3-bis-(2,6-diisopropylphenyl)triaz-1-ene,[16] sodium hypochlorite,[17] N-(tert-butyloxy)carbonyl dipropargylamine,[18] di-μ-chloro-bis-(1,5-cyclooctadiene)dirhodium(I),[19] di-μ-chloro-bis(1,5-cyclooctadiene)dirhodium(I),[20] and di-μ-chloro-bis(1,5-cyclooctadiene)diiridium(I).[21] All other reagents were obtained from commercial sources and were used without any further purification.

Unless otherwise stated, only anhydrous solvents were used for the experimental procedures. Anhydrous tetrahydrofuran (THF) and diethyl ether (DEE) were obtained after distillation over sodium wire Na(s) and benzophenone under a N$_2$ atmosphere. Anhydrous toluene and hexane were obtained after distillation over sodium wire under N$_2$ atmosphere. Anhydrous dichloromethane was obtained after distillation over calcium hydride (CaH$_2$) under N$_2$ atmosphere. Deuterated benzene was dried over sodium and distilled under Ar atmosphere. Deuterated acetonitrile, chloroform, and dichloromethane were dried over calcium hydride under Ar(g) atmosphere.

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AVANCE-III-300 operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 121.49 MHz for ^{31}P, and 282.40 MHz for ^{19}F; AVANCE-III-400 operating at 400.21 MHz for ^{1}H, 100.64 MHz for ^{13}C, 162.01 MHz for ^{31}P, and 376.57 MHz for ^{19}F; or AVANCE-III-500 operating at 500.13 MHz for ^{1}H, 125.31 MHz for ^{13}C, 202.46 MHz for ^{31}P, and 470.59 MHz for ^{19}F. ^{1}H Chemical shifts are reported as δ (ppm) values downfield from Me$_4$Si, and chemical shifts were referenced to residual nondeuterated solvent peaks (CDCl$_3$: 7.260 ppm, C$_6$D$_6$: 7.160 ppm; CD$_2$Cl$_2$: 5.32 ppm; and CD$_3$CN: 1.940 ppm). ^{13}C chemical shifts are also reported as δ (ppm) values downfield from Me$_4$Si, and chemical shifts were referenced to residual nondeuterated solvent peaks (CDCl$_3$: 77.160 ppm, C$_6$D$_6$: 128.060 ppm; CD$_2$Cl$_2$: 54.00 ppm; and CD$_3$CN: 118.260 ppm). Proton coupling constants (J) are given in hertz. The spectral coupling patterns are designated as follows: s/S—singlet; d/D—doublet; t/T—triplet; q/Q—quartet; quint—quintet; sept—septet; hept—heptet; m—multiplet; dd—doublet of doublets; dt—doublet of triplets; td—triplet of doublets; and br—broad signal. Quaternary carbons are designated as C$_q$.

Chemical shift assignment in the ^{1}H NMR spectra is based on first-order analysis experiments. The ^{13}C shifts were obtained from proton-decoupled ^{13}C NMR spectra. Where necessary, the multiplicities of the ^{13}C signals were deduced from proton-decoupled DEPT-135 spectra. The resonances of the proton-bearing carbon atoms were correlated with specific proton resonances using two-dimensional (^{13}C−^{1}H) heteronuclear single-quantum coherence experiments. Standard

Bruker pulse programs (298 K) were used in the experiments, while low-temperature (243 K) NMR experiments were run for all of the fluxional 1,5-cyclooctadiene metal complexes.

Solution IR spectra (ν(CO)) were recorded on a Bruker α FTIR spectrophotometer with CH_2Cl_2 as solvent. The range of absorption measured was 4000−400 cm^{-1}.

Electrospray mass spectroscopy (ESI-MS) images were recorded on a Bruker Q-TOF mass spectrometer with positive electron spray as the ionization techniques; nitrogen was employed as drying and nebulizing gas at a flow rate of 4 L/min. The m/z values were measured in the range of 100−1500 with acetonitrile as solvent. Accurate mass measurements were performed by using a Q-TOF premier mass spectrometer with electrospray source (Waters, Manchester, U.K.) operating at a resolution of ca. 16 000 (full width at half-maximum).

Synthesis of 1a [Rh(cod)(COC)](PF$_6$). Note: Attempts to obtain **1a** via in situ deprotonation produced only traces of the desired compound. Herein, the entitled compound was obtained in two steps via transmetallation reaction from its corresponding bimetallic silver derivative **5** [Ag$_2$Cl$_2$(COC)] (see vida infra).

To a Schlenk tube loaded with **5** [Ag$_2$Cl$_2$(μ-COC)] (165 mg, 0.15 mmol), KPF$_6$ (55 mg, 0.30 mmol), and [Rh(cod)Cl]$_2$ (73 mg, 0.15 mmol), dichloromethane (ca. 50 mL) was added via cannula in a dark environment under stirring. The initial clear golden brown solution eventually changes to a murky orange solution over time. The reaction vessel was capped and the mixture was stirred overnight in the dark resulting in a murky orange solution the following morning. The solvent was removed in vacuo. By means of cannula filtration, the reaction mixture was washed with hexane and diethyl ether. Finally, compound **1a** [Rh(cod)(COC)](PF$_6$) was extracted with dichloromethane, resulting in an orange solid (108 mg, 0.09 mmol, 62%) after solvent evaporation. The product was dried under vacuum at 50 °C overnight for NMR analysis.

^{1}H NMR: δ_H (CDCl$_3$, 500.13 MHz) 7.60 (m, 4H, ArH$_{Dipp}$), 7.40 (d, 4H, J = 7.8 Hz, ArH$_{Dipp}$), 7.33 (d, 4H, J = 7.9 Hz, ArH$_{Dipp}$), 4.93 (br s, 4H, O(CH$_2$)$_2$), 4.82 (br s, 2H, cod-CH), 3.27 (br s, 2H, cod-CH), 2.11 (sept, J = 6.5 Hz, 8H, CH(CH$_3$)$_2$), 1.77 (br s, 4H, cod-CH$_2$), 1.64 (br s, 4H, cod-CH$_2$), 1.38 (s, 12H, CH(CH$_3$)$_2$), 1.19 (s, 12H, CH(CH$_3$)$_2$), 1.10 (d, 12H, J = 6.7 Hz, CH(CH$_3$)$_2$), 1.07 (d, 12H, J = 6.8 Hz, CH(CH$_3$)$_2$). ^{13}C NMR: δ_C (CDCl$_3$, 125.31 MHz) 169.37 (d, J = 41.2 Hz, C$_{carbene}$), 145.56 (C$_{q\ Trz}$), 144.79 (ArC$_q$), 144.72 (ArC$_q$), 135.15 (ArC$_q$), 132.34 (ArCH), 131.56 (ArCH), 130.16 (ArC$_q$), 124.74 (ArCH), 124.51 (ArCH), 97.30 (cod-CH), 69.39 (d, J = 13.9 Hz, cod-CH), 57.88 (O(CH$_2$)$_2$), 32.86 (cod-CH$_2$), 29.30 (CH(CH$_3$)$_2$), 29.23 (CH(CH$_3$)$_2$), 28.42 (cod-CH$_2$), 25.94 (CH(CH$_3$)$_2$), 25.84 (CH(CH$_3$)$_2$), 23.72 (CH(CH$_3$)$_2$), 22.81 (CH(CH$_3$)$_2$). ^{19}F NMR: δ_F (CDCl$_3$, 470.59 MHz) −73.64 (d, J = 712.6 Hz, PF$_6$). ^{31}P NMR: δ_P (CDCl$_3$, 202.46 MHz) −144.31 (sept, J = 712.6 Hz, PF$_6$). HRMS (flow injection analysis (FIA)-ESI): calcd for [C$_{62}$H$_{84}$N$_6$ORh]$^+$ [M − PF$_6$]$^+$: 1031.5761; found: 1031.5783.

Synthesis of 1b [Ir(cod)Cl$_2$(COC)]. An oven-dried Schlenk tube was loaded with [H$_2$(COC)](PF$_6$)$_2$ (369 mg, 0.33 mmol), KHMDS (165 mg, 0.83 mmol), and [Ir(cod)Cl]$_2$ (222 mg, 0.33 mmol). Dry THF (ca. 50 mL) was added to the reaction mixture at −78 °C under stirring in an inert atmosphere for 30 min, whereafter the septum was removed and the Schlenk was capped. The reaction mixture was allowed to gradually warm to RT overnight. The reaction mixture

turned from yellow-orange to a darker yellow-brown upon overnight reaction. The solvent was evaporated under reduced pressure followed by several washings with hexane and DEE, followed by cannula extraction with dichloromethane to afford compound **1b** [Ir(cod)Cl$_2$(COC)] (0.26 g, 0.21 mmol, 50%) as a bright orange solid. The product was dried overnight, under vacuum, at 50 °C for NMR analysis. Crystallization from a toluene/dichloromethane mixture yielded single crystals suitable for XRD analysis.

^{1}H NMR: δ_H (CD$_2$Cl$_2$, 400.21 MHz) 7.65 (t, 2H, J = 7.8 Hz, ArH$_{Dipp}$), 7.59 (t, 2H, J = 7.8 Hz, ArH$_{Dipp}$), 7.40 (d, 6H, J = 7.2 Hz, ArH$_{Dipp}$), 7.32 (d, 2H, J = 7.7 Hz, ArH$_{Dipp}$), 5.13 (d, 2H, J = 13.6 Hz, O(CH$_2$)$_2$), 4.35 (d, 2H, J = 13.6 Hz, O(CH$_2$)$_2$), 4.06 (br s, 2H, cod-CH), 2.54 (m, 4H, cod-CH$_2$), 2.22 (m, 4H, CH(CH$_3$)$_2$), 2.01 (m, 4H, CH(CH$_3$)$_2$), 1.82 (m, 2H, cod-CH), 1.44 (m, 2H, cod-CH$_2$), 1.31 (d, 6H, J = 6.3 Hz, CH(CH$_3$)$_2$), 1.25 (d, 6H, J = 6.3 Hz, CH(CH$_3$)$_2$), 1.19 (d, 6H, J = 6.4 Hz, CH(CH$_3$)$_2$), 1.12 (m, 26H, CH(CH$_3$)$_2$ [24H], cod-CH$_2$[2H]), 0.93 (d, 6H, J = 6.2 Hz, CH(CH$_3$)$_2$). ^{13}C NMR: δ_C (CD$_2$Cl$_2$, 100.64 MHz) 166.68 (C$_{carbene}$), 145.74 (C$_{q\ Trz}$), 145.63 (ArC$_q$), 144.95 (ArC$_q$), 144.00 (ArC$_q$) 141.89 (ArC$_q$), 135.04 (ArC$_q$), 132.78 (ArCH), 131.76 (ArCH), 128.59 (ArC$_q$), 125.37 (ArCH), 125.08 (ArCH), 124.87 (ArCH), 124.30 (ArCH), 73.77 (cod-CH), 73.11 (cod-CH), 57.01 (O(CH$_2$)$_2$), 35.17 (cod-CH$_2$), 29.53 (CH(CH$_3$)$_2$), 29.53 (CH(CH$_3$)$_2$), 29.47 (CH(CH$_3$)$_2$), 29.28 (CH(CH$_3$)$_2$), 27.06 (cod-CH$_2$), 26.00 (CH(CH$_3$)$_2$), 25.53 (CH(CH$_3$)$_2$), 24.71 (CH(CH$_3$)$_2$), 24.47 (CH(CH$_3$)$_2$), 23.73 (CH(CH$_3$)$_2$), 23.66 (CH(CH$_3$)$_2$), 23.11 (CH(CH$_3$)$_2$), 21.56 (CH(CH$_3$)$_2$). ^{19}F NMR: δ_F (CD$_2$Cl$_2$, 376.57 MHz) −73.64 (d, J = 710.0 Hz, PF$_6$). ^{31}P NMR: δ_P (CD$_2$Cl$_2$, 162.01 MHz) −144.52 (sept, J = 710.24 Hz, PF$_6$). HRMS (FIA-ESI): calcd for [C$_{62}$H$_{84}$N$_6$OIr]$^+$ [M − PF$_6$]$^+$: 1121.6336; found: 1121.6274.

Synthesis of 2a [Rh(CO)$_2$(COC)](PF$_6$). The entitled compound was synthesized according to the same procedure described for compound **1a** [Rh(cod)(COC)](PF$_6$). To a Schlenk tube loaded with **5** [Ag$_2$Cl$_2$(COC)] (206 mg, 0.18 mmol), KPF$_6$ (68 mg, 0.37 mmol), and [Rh(CO)$_2$Cl]$_2$ (72 mg, 0.18 mmol), dichloromethane (ca. 50 mL) was added via cannula in a dark environment. The color of the reaction contents changed from the initial dark brown to orange-brown within a few minutes. The reaction vessel was capped and the reaction was stirred overnight, resulting in a yellow-brown solution the following morning. The solvent was removed in vacuo. By means of cannula filtration, the reaction mixture was washed with hexane and diethyl ether. Finally, compound **2a** was extracted with dichloromethane, resulting in an orange-brown solid (142 mg, 0.13 mmol, 68%) after solvent evaporation.

Trace amounts of **2a** could also be isolated from the reaction procedure to prepare **4a** [Rh$_2$(CO)$_4$Cl$_2$(μ-COC)], using 0.5 equiv of metal precursor [Rh(cod)Cl]$_2$, followed by treatment with CO(g) as described above. After cannula extraction of **4a** [Rh$_2$(CO)$_4$Cl$_2$(μ-COC)] from the reaction mixture in solvents hexane and DEE, the residue was extracted with dichloromethane to yield a mixture of unreacted [H$_2$(COC)](PF$_6$)$_2$ and **2a**. Recrystallization of this fraction yielded single crystals of **2a** [Rh(CO)$_2$(COC)](PF$_6$), which were analyzed by X-ray diffraction, HRMS, and FTIR spectroscopy.

^{1}H NMR: δ_H (CDCl$_3$, 500.13 MHz) 7.66 (m, 4H, ArH$_{Dipp}$), 7.40 (m, 8H, ArH$_{Dipp}$), 4.29 (d, 2H, J = 13.6 Hz, O(CH$_2$)$_2$), 4.24 (d, 2H, J = 13.5 Hz, O(CH$_2$)$_2$), 2.69 (sept, 2H, J = 6.8 Hz, CH(CH$_3$)$_2$), 2.31 (sept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 2.14

(sept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 1.96 (sept, 2H, J = 6.7 Hz, C**H**(CH$_3$)$_2$), 1.42 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.27 (d, 6H, J = 6.9 Hz, CH(C**H**$_3$)$_2$), 1.25 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.20 (dd, 12H, J = 7.1, 7.1 Hz, CH(C**H**$_3$)$_2$), 1.14 (d, 6H, J = 6.7 Hz, CH(C**H**$_3$)$_2$), 1.09 (dd, 12H, J = 6.9, 6.8 Hz, CH(C**H**$_3$)$_2$). ^{13}C NMR: δ_C (CDCl$_3$, 125.31 MHz) 183.82 (d, J = 56.4 Hz, Rh−(**C**O)$_2$), 167.59 (**C**$_{carbene}$), 146.48 (**C**$_{q\,Trz}$), 146.38 (**C**$_{q\,Trz}$) 145.53(Ar**C**$_q$), 144.67 (Ar**C**$_q$) 143.57 (Ar**C**$_q$), 143.54 (Ar**C**$_q$), 135.44 (Ar**C**$_q$), 133.22 (Ar**C**H), 132.79 (Ar**C**H), 128.44 (Ar**C**$_q$), 125.39 (Ar**C**H), 124.98 (Ar**C**H), 124.98 (Ar**C**H), 124.98 (Ar**C**H), 55.44 (O(**C**H$_2$)$_2$), 29.85 (**C**H(CH$_3$)$_2$), 29.77 (**C**H(CH$_3$)$_2$), 29.51 (**C**H(CH$_3$)$_2$), 29.23 (**C**H(CH$_3$)$_2$), 26.38 (**C**H(CH$_3$)$_2$), 25.58 (**C**H(CH$_3$)$_2$), 24.89 (**C**H(CH$_3$)$_2$), 24.69 (**C**H(CH$_3$)$_2$), 23.52 (**C**H(CH$_3$)$_2$), 23.41 (**C**H(CH$_3$)$_2$), 22.54 (**C**H(CH$_3$)$_2$), 22.51 (**C**H(CH$_3$)$_2$). ^{19}F NMR: δ_F (CDCl$_3$, 470.59 MHz) −73.54 (d, J = 712.3 Hz, P**F**$_6$). ^{31}P NMR: δ_P (CDCl$_3$, 202.46 MHz) −144.33 (sept, J = 712.9 Hz, **P**F$_6$). HRMS (FIA-ESI): calcd for [C$_{62}$H$_{84}$N$_6$ORh]$^+$ [M − PF$_6$]$^+$: 979.4721; found: 979.4963. FTIR ν_{CO} (CH$_2$Cl$_2$): 2016, 1998 cm^{-1}.

Synthesis of 2b [Ir(CO)$_2$(COC)](PF$_6$). Compound **2b** was obtained by substitution of the 1,5-cyclooctadiene (cod) ligand of **1b** [Ir(cod)(**COC**)](PF$_6$). A dichloromethane solution of compound **1b** (0.26 g, 0.21 mmol) was treated with CO(g) for 1 h, resulting in a color change from an intense red-orange to yellow-green. After solvent removal, product **2b** [Ir-(CO)$_2$(**COC**)](PF$_6$) (0.25 g, 0.21 mmol, 100%) was obtained as a light yellow-green solid. The product was dried under vacuum at 50 °C overnight for NMR analysis. Crystallization from CDCl$_3$ yielded single crystals suitable for XRD analysis.

^{1}H NMR: δ_H (CD$_2$Cl$_2$, 500.13 MHz) 7.71 (d, 2H, J = 7.9 Hz, Ar**H**$_{Dipp}$), 7.67 (d, 2H, J = 7.9 Hz, Ar**H**$_{Dipp}$), 7.47 (d, 4H, J = 7.8 Hz, Ar**H**$_{Dipp}$), 7.43 (d, 4H, J = 7.8 Hz, Ar**H**$_{Dipp}$), 4.35 (d, 2H, J = 13.5 Hz, O(C**H**$_2$)$_2$), 4.22 (d, 2H, J = 13.5 Hz, O(C**H**$_2$)$_2$), 2.63 (sept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 2.31 (sept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 2.14 (sept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 1.97 (sept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 1.40 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.27 (dd, 12H, J = 6.9, 6.9 Hz, CH(C**H**$_3$)$_2$), 1.21 (dd, 12H, J = 6.7, 6.7 Hz, CH(C**H**$_3$)$_2$), 1.14 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.11 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.08 (d, 6H, J = 6.9 Hz, CH(C**H**$_3$)$_2$). ^{13}C NMR: δ_C (CD$_2$Cl$_2$, 125.31 MHz) 176.46 (Ir−(**C**O)$_2$), 166.17 (**C**$_{carbene}$), 146.83 (**C**$_{q\,Trz}$), 146.79 (Ar**C**$_q$), 146.28 (Ar**C**$_q$) 145.17 (Ar**C**$_q$), 144.74 (Ar**C**$_q$), 135.25 (Ar**C**$_q$), 133.77 (Ar**C**H), 133.40 (Ar**C**H), 128.65 (Ar**C**$_q$), 125.91 (Ar**C**H), 125.62 (Ar**C**H), 125.56 (Ar**C**H), 125.42 (Ar**C**H), 55.63 (O(**C**H$_2$)$_2$), 30.48 (**C**H(CH$_3$)$_2$), 30.26 (**C**H(CH$_3$)$_2$), 30.08 (**C**H(CH$_3$)$_2$), 29.73 (**C**H(CH$_3$)$_2$), 25.78 (**C**H(CH$_3$)$_2$), 25.12 (**C**H(CH$_3$)$_2$), 24.98 (**C**H(CH$_3$)$_2$), 23.72 (**C**H(CH$_3$)$_2$), 23.72 (**C**H(CH$_3$)$_2$), 23.72 (**C**H(CH$_3$)$_2$) 22.79 (**C**H(CH$_3$)$_2$), 22.67 (**C**H(CH$_3$)$_2$). ^{19}F NMR: δ_F (CDCl$_3$, 470.59 MHz) −73.53 (d, J = 712.4 Hz, P**F**$_6$). ^{31}P NMR: δ_P (CDCl$_3$, 202.46 MHz) −144.38 (sept, J = 712.3 Hz, **P**F$_6$). HRMS (FIA-ESI): calcd for [C$_{56}$H$_{72}$N$_6$O$_3$Ir]$^+$ [M − PF$_6$]$^+$: 1069.5295; found: 1069.5167. FTIR ν_{CO} (CH$_2$Cl$_2$): 2065, 1999 cm^{-1}.

Synthesis of 3a [Rh$_2$(cod)$_2$Cl$_2$(μ-COC)]. Complex **3a** could be prepared using either one of two different synthetic methods: (1) a one-pot deprotonation and metallation approach and (2) generation of the free carbene with subsequent metallation.

Method 1. An oven-dried Schlenk tube was loaded with [H$_2$(**COC**)](PF$_6$)$_2$ (532 mg, 0.48 mmol), KHMDS (238 mg, 1.19 mmol) (KHMDS = potassium hexamethyldisilazide), and

[Rh(cod)Cl]$_2$ (283 mg, 0.57 mmol). Dry THF (ca. 50 mL) was added to the dry contents at −78 °C under stirring in an inert atmosphere for 30 min, whereafter the septum was removed and the Schlenk tube was capped. The reaction mixture was allowed to gradually warm to RT overnight. The reaction mixture turned from orange-brown to bright yellow upon overnight reaction.

Method 2. An oven-dried Schlenk tube was loaded with [H$_2$(**COC**)](PF$_6$)$_2$ (479 mg, 0.41 mmol) and KHMDS (215 mg, 1.08 mmol), to which was added degassed dry THF (ca. 40 mL) at −78 °C under stirring, and the color of the solution changed to dark purple upon triazolium deprotonation and in situ generation of the free biscarbene. After stirring for 2 min, [Rh(cod)Cl]$_2$ (255 mg, 0.52 mmol) dissolved in THF (ca. 10 mL) was transferred to the reaction mixture at low temperature. The reaction mixture changed color from purple to orange-brown. The reaction was allowed to react for 30 min before the septum was removed and the Schlenk tube was capped for overnight reaction, gradually heating to RT. The color again changed from orange-brown to bright yellow upon overnight reaction.

For both methods 1 and 2, the reaction workup involved evaporation of the solvent and washing with solvents hexane and diethyl ether. Extraction with dichloromethane afforded compound **3a** [Rh$_2$(cod)$_2$Cl$_2$(μ-**COC**)] (0.4 g, 0.32 mmol, 66%—method 1; 0.4 g, 0.30 mmol, 69%—method 2) as a bright yellow solid. Crystallization from CDCl$_3$ yielded single crystals suitable for XRD analysis.

^{1}H NMR: δ_H (CDCl$_3$, 400.21 MHz) 7.56 (dd, 4H, J = 7.5 Hz, Ar**H**$_{Dipp}$), 7.44 (d, 2H, J = 7.3 Hz, Ar**H**$_{Dipp}$), 7.30 (d, 4H, J = 7.1 Hz, Ar**H**$_{Dipp}$), 7.25 (d, 2H, J = 8.6 Hz, Ar**H**$_{Dipp}$), 5.68 (d, 2H, J = 11.4 Hz, O(C**H**$_2$)$_2$), 4.77 (br s, 2H, cod-C**H**), 4.67 (d, 4H, J = 11.5 Hz, cod-C**H** [2H], O(C**H**$_2$)$_2$ [2H]), 3.30 (br s, 2H, cod-C**H**$_2$), 3.25 (t, 2H, J = 6.0 Hz, cod-C**H**$_2$), 2.85 (br s, 2H, cod-C**H**), 2.45 (t, 2H, J = 5.4 Hz, cod-C**H**$_2$), 1.95 (sept, 4H, J = 6.2 Hz C**H**(CH$_3$)$_2$), 1.86 (sept, 4H, J = 7.2 Hz, C**H**(CH$_3$)$_2$), 1.58 (br s, 2H, cod-C**H**$_2$), 1.53 (d, 6H, J = 6.0 Hz, cod-C**H**$_2$), 1.45 (br s, 4H, cod-C**H**$_2$), 1.26 (br s, 5H, CH(C**H**$_3$)$_2$), 1.19 (dd, 12H, J = 6.2, 6.3 Hz, CH(C**H**$_3$)$_2$), 1.13 (d, 7H, J = 6.5 Hz, CH(C**H**$_3$)$_2$), 1.07 (br s, 12H, CH(C**H**$_3$)$_2$), 1.01 (dd, 12H, J = 9.1, 7.2 Hz, CH(C**H**$_3$)$_2$). ^{13}C NMR: δ_C (CDCl$_3$, 100.64 MHz) 176.08 (d, J = 46.8 Hz, **C**$_{carbene}$), 147.29 (**C**$_{q\,Trz}$), 146.65 (Ar**C**$_q$), 145.90 (Ar**C**$_q$), 144.91 (Ar**C**$_q$) 144.59 (Ar**C**$_q$), 135.17 (Ar**C**$_q$), 132.10 (Ar**C**H), 130.74 (Ar**C**H), 129.74 (Ar**C**$_q$), 124.73 (Ar**C**H), 124.54 (Ar**C**H), 124.20 (Ar**C**H), 122.88 (Ar**C**H), 95.77 (d, J = 7.2 Hz, cod-**C**H), 94.96 (d, J = 7.0 Hz, cod-**C**H), 67.47 (dd, J = 14.8, 13.8 Hz, cod-**C**H), 64.56 (O(**C**H$_2$)$_2$), 33.12 (cod-**C**H$_2$), 32.38 (cod-**C**H$_2$), 28.84 (**C**H(CH$_3$)$_2$), 28.84 (**C**H(CH$_3$)$_2$), 28.73 (cod-**C**H$_2$), 28.64 (**C**H(CH$_3$)$_2$), 28.64 (cod-**C**H$_2$), 28.34 (**C**H(CH$_3$)$_2$), 26.99 (**C**H(CH$_3$)$_2$), 25.99 (**C**H(CH$_3$)$_2$), 25.58 (**C**H(CH$_3$)$_2$), 25.16 (**C**H(CH$_3$)$_2$), 24.32 (**C**H(CH$_3$)$_2$), 24.32 (**C**H(CH$_3$)$_2$), 24.03 (**C**H(CH$_3$)$_2$), 22.95 (**C**H(CH$_3$)$_2$). HRMS (FIA-ESI): calcd for [C$_{70}$H$_{96}$N$_6$ORh$_2$]$^{2+}$ [M − 2Cl]$^{2+}$: 621.2877; found: 621.2769, and [C$_{70}$H$_{96}$N$_6$OClRh$_2$] [M − Cl]$^+$: 1277.5444; found: 1277.5303.

Synthesis of 4a [Rh$_2$(CO)$_4$Cl$_2$(μ-COC)]. Compound **4a** could be prepared from either of two synthetic pathways: (1) directly from [Rh(CO)$_2$Cl]$_2$ and (2) by substitution of the 1,5-cyclooctadiene (cod) ligand of compound **3a** [Rh$_2$(cod)$_2$Cl$_2$(μ-**COC**)] with two carbonyl ligands. For synthetic pathway 1, a one-pot deprotonation and metallation

approach as well as the generation of the free carbene with subsequent metallation led to the formation of product **4a**.

Method 1. An oven-dried Schlenk tube was loaded with $[H_2(\mathbf{COC})](PF_6)_2$ (524 mg, 0.47 mmol), KHMDS (207 mg, 1.04 mmol), and $[Rh(CO)_2Cl]_2$ (169 mg, 0.44 mmol) and submerged in a cold bath at −78 °C under stirring. Anhydrous THF (ca. 50 mL) was transferred via cannula to the Schlenk tube under stirring in an inert atmosphere. The reaction was allowed to react for 30 min before the septum was removed, and the Schlenk tube was capped for overnight reaction, gradually heating to RT. The reaction mixture turned from dark brown to orange-brown. The product was isolated by evaporating the solvent and cannula extraction with dichloromethane following washing with hexane and DEE. Compound **4a** $[Rh_2(CO)_4Cl_2(\mu\text{-}\mathbf{COC})]$ (0.3 g, 0.25 mmol, 53%) was isolated as a light yellow solid. Crystallization from $CDCl_3$ yielded single crystals suitable for XRD analysis.

Method 2. Compound **4a** could also be obtained by converting compound **3a** $[Rh_2(cod)_2Cl_2(\mu\text{-}\mathbf{COC})]$ by bubbling $CO(g)$ through a dichloromethane solution of compound **3a** (0.41 g, 0.32 mmol) for 1 h, resulting in a color change from light orange to yellow. After solvent removal, product **4a** $[Rh_2(CO)_4Cl_2(\mu\text{-}\mathbf{COC})]$ (0.38 g, 0.32 mmol, 100%) was obtained as a yellow solid. Crystallization from $CDCl_3$ yielded single crystals suitable for XRD analysis.

^1H NMR: δ_H ($CDCl_3$, 500.13 MHz) 7.57 (m, 4H, Ar$\mathbf{H}_{Dipp}$), 7.35 (dd, 8H, J = 6.7, 6.7 Hz, Ar$\mathbf{H}_{Dipp}$), 4.62 (s, 4H, O($\mathbf{CH}_2)_2$), 2.57 (sept, 4H, J = 6.1 Hz, $\mathbf{CH}(CH_3)_2$), 2.23 (sept, 4H, J = 6.1 Hz, $\mathbf{CH}(CH_3)_2$), 1.37 (d, 12H, J = 5.8 Hz, $CH(\mathbf{CH}_3)_2$), 1.19 (d, 12H, J = 5.9 Hz, $CH(\mathbf{CH}_3)_2$), 1.09 (dd, 24H, J = 7.2, 7.2 Hz, $CH(\mathbf{CH}_3)_2$). ^{13}C NMR: δ_C ($CDCl_3$, 125.31 MHz) 185.75 (d, J = 54.5 Hz, Rh−$\mathbf{CO}_{trans\ carbene}$), 183.40 (d, J = 74.6 Hz, Rh−$\mathbf{CO}_{trans\ Cl}$), 170.00 (d, J = 41.1 Hz, $\mathbf{C}_{carbene}$), 146.35 ($\mathbf{C}_{q\ Trz}$), 145.89 (Ar$\mathbf{C}_q$) 145.68 (Ar$\mathbf{C}_q$), 135.45 (Ar$\mathbf{C}_q$), 132.28 (Ar$\mathbf{CH}$), 131.45 (Ar$\mathbf{CH}$), 129.88 (Ar$\mathbf{C}_q$), 124.78 (Ar$\mathbf{CH}$), 124.20 (Ar$\mathbf{CH}$), 63.41 (O($\mathbf{CH}_2)_2$), 29.05 ($\mathbf{CH}(CH_3)_2$), 28.99 ($\mathbf{CH}(CH_3)_2$), 26.59 ($CH(\mathbf{CH}_3)_2$), 25.83 ($CH(\mathbf{CH}_3)_2$), 23.29 ($CH(\mathbf{CH}_3)_2$), 23.12 ($CH(\mathbf{CH}_3)_2$). HRMS (FIA-ESI): calcd for $C_{57}H_{72}N_6O_4ClRh_2$ [M − Cl − CO]$^+$: 1145.3414; found: 1145.3220, $C_{56}H_{72}N_6O_3Cl_2Rh_2$ [M − 2CO]$^+$: 1152.3153; found: 1152.3556, $C_{56}H_{72}N_6O_3ClRh_2$ [M − Cl − 2CO]$^+$: 1117.3464; found: 1117.3301. FTIR ν_{CO} (CH_2Cl_2): 2076, 1995 cm^{-1}.

Synthesis of 4b $[Ir_2(CO)_4Cl_2(\mu\text{-}\mathbf{COC})]$. Complex **4b** was synthesized in a one-pot synthetic approach, using the metal precursor $[Ir(cod)Cl]_2$, followed by 1,5-cyclooctadiene (cod) substitution with $CO(g)$. An oven-dried Schlenk tube was loaded with $[H_2(\mathbf{COC})](PF_6)_2$ (369 mg, 0.33 mmol), KHMDS (165 mg, 0.83 mmol), and $[Ir(cod)Cl]_2$ (222 mg, 0.33 mmol) and submerged in a cold bath at −78 °C under stirring. Anhydrous THF (ca. 50 mL) was transferred via a cannula to the Schlenk tube under stirring in an inert atmosphere. The reaction was allowed to react for 30 min before the septum was removed, and the Schlenk was capped for overnight reaction, gradually heating to RT before allowing to reach RT. The reaction mixture turned from yellow-orange to a darker yellow-brown upon overnight reaction. The solvent was removed under reduced pressure, followed by hexane extraction. The hexane fraction was dried and redissolved in anhydrous dichloromethane, after which $CO(g)$ was bubbled through the solution for 1 h. The product was isolated by evaporating the solvent, extracting compound **4b**

$[Ir_2(CO)_4Cl_2(\mu\text{-}\mathbf{COC})]$ with hexane, and drying the light brown solid overnight (0.22 g, 0.16 mmol, 48%).

^1H NMR: δ_H ($CDCl_3$, 500.13 MHz) 7.57 (m, 4H, Ar$\mathbf{H}_{Dipp}$), 7.35 (dd, 8H, J = 7.9, 7.8 Hz Ar$\mathbf{H}_{Dipp}$), 4.59 (s, 4H, O($\mathbf{CH}_2)_2$), 2.51 (sept, 4H, J = 6.7 Hz, $\mathbf{CH}(CH_3)_2$), 2.22 (sept, 4H, J = 6.7 Hz, $\mathbf{CH}(CH_3)_2$), 1.37 (d, 12H, J = 6.7 Hz, $CH(\mathbf{CH}_3)_2$), 1.20 (d, 12H, J = 6.8 Hz, $CH(\mathbf{CH}_3)_2$), 1.09 (dd, 24H, J = 6.8, 6.8 Hz, $CH(\mathbf{CH}_3)_2$). ^{13}C NMR: δ_C ($CDCl_3$, 125.31 MHz) δ 181.35 (Ir−$\mathbf{CO}_{trans\ carbene}$), 170.46 ($\mathbf{C}_{carbene}$), 168.62 (Ir−$\mathbf{CO}_{trans\ Cl}$), 147.16 ($\mathbf{C}_{q\ Trz}$), 145.83 (Ar$\mathbf{C}_q$) 145.62 (Ar$\mathbf{C}_q$), 135.11 (Ar$\mathbf{C}_q$), 132.46 (Ar$\mathbf{CH}$), 131.59 (Ar$\mathbf{CH}$), 129.68 (Ar$\mathbf{C}_q$), 124.90 (Ar$\mathbf{CH}$), 124.19 (Ar$\mathbf{CH}$), 63.10 (O($\mathbf{CH}_2)_2$), 29.22 ($\mathbf{CH}(CH_3)_2$), 29.06 ($\mathbf{CH}(CH_3)_2$), 26.62 ($CH(\mathbf{CH}_3)_2$), 25.82 ($CH(\mathbf{CH}_3)_2$), 23.31 ($CH(\mathbf{CH}_3)_2$), 22.98($CH(\mathbf{CH}_3)_2$). HRMS (FIA-ESI): calcd for $C_{56}H_{73}N_6O_3Cl_2Ir_2$ [M − 2CO +H]$^+$: 1333.4357; found: 1333.3364 and also $C_{56}H_{72}N_6O_3Cl_2Ir_2$ [M − 2CO]$^+$: 1332.4279; found: 1332.3394. FTIR ν_{CO} (CH_2Cl_2): 2063, 1978 cm^{-1}.

Synthesis of 5 $[Ag_2Cl_2(\mu\text{-}\mathbf{COC})]$. To a Schlenk tube loaded with $[H_2(\mathbf{COC})](PF_6)_2$ (496 mg, 0.45 mmol), KCl (74 mg, 1.11 mmol), and Ag_2O (206 mg, 0.89 mmol) was added acetonitrile (ca. 50 mL) and stirred in a dark environment for 3 days. The reaction mixture was filtered. The filtrate was collected and evaporated to dryness under vacuum to perform a cannula filtration with dichloromethane. After cannula filtration and evaporation of the solvent under reduced pressure, compound **5** $[Ag_2Cl_2(\mu\text{-}\mathbf{COC})]$ (404 mg, 0.36 mmol, 82%) was obtained as a gray solid. The product was dried under vacuum at 50 °C overnight for NMR analysis.

^1H NMR: δ_H ($CDCl_3$, 500.13 MHz) 7.83 (t, 1H, J = 6.4 Hz, Ar$\mathbf{H}_{Dipp}$), 7.67 (t, 1H, J = 8.4 Hz, Ar$\mathbf{H}_{Dipp}$), 7.56 (dd, 2H, J = 6.7 Hz, Ar$\mathbf{H}_{Dipp}$), 7.47 (d, 2H, J = 7.5 Hz, Ar$\mathbf{H}_{Dipp}$), 7.39 (t, 1H, J = 8.1 Hz, Ar$\mathbf{H}_{Dipp}$), 7.32 (d, 4H, J = 7.9 Hz, Ar$\mathbf{H}_{Dipp}$), 7.21 (t, 1H, J = 8.4 Hz, Ar$\mathbf{H}_{Dipp}$), 4.47 (m, 2H, O−($\mathbf{CH}_2)_2$), 4.05 (s, 2H, O−($\mathbf{CH}_2)_2$), 2.23 (sept, 4H, J = 5.8 Hz, $\mathbf{CH}(CH_3)_2$), 2.06 (sept, 4H, J = 6.8 Hz, $\mathbf{CH}(CH_3)_2$), 1.30 (d, 12H, J = 6.8 Hz, $CH(\mathbf{CH}_3)_2$), 1.23 (m, 6H, $CH(\mathbf{CH}_3)_2$), 1.14 (d, 12H, J = 6.8 Hz, $CH(\mathbf{CH}_3)_2$), 1.08 (d, 12H, J = 6.7 Hz, $CH(\mathbf{CH}_3)_2$), 1.04 (d, 6H, J = 6.5 Hz, $CH(\mathbf{CH}_3)_2$). ^{13}C NMR: δ_C ($CDCl_3$, 125.31 MHz) 172.51 ($\mathbf{C}_{carbene}$), 160.12 ($\mathbf{C}_{q\ Trz}$), 145.22 (Ar$\mathbf{C}_q$), 145.02 (Ar$\mathbf{C}_q$), 144.97 (Ar$\mathbf{C}_q$), 135.35 (Ar$\mathbf{C}_q$), 135.29 (Ar$\mathbf{C}_q$), 133.90 (Ar$\mathbf{CH}$), 131.81 (Ar$\mathbf{CH}$), 129.16 (Ar$\mathbf{C}_q$) 125.55 (Ar$\mathbf{CH}$), 125.06 (Ar$\mathbf{CH}$), 124.97 (Ar$\mathbf{CH}$), 124.54 (Ar$\mathbf{CH}$), 63.54 (O−($\mathbf{CH}_2)_2$), 29.50 ($\mathbf{CH}(CH_3)_2$), 29.22 ($\mathbf{CH}(CH_3)_2$), 28.99 ($\mathbf{CH}(CH_3)_2$), 28.73 ($\mathbf{CH}(CH_3)_2$), 25.97 ($CH(\mathbf{CH}_3)_2$), 25.91 ($CH(\mathbf{CH}_3)_2$), 25.77 ($CH(\mathbf{CH}_3)_2$), 25.70 ($CH(\mathbf{CH}_3)_2$), 24.62 ($CH(\mathbf{CH}_3)_2$), 24.56 ($CH(\mathbf{CH}_3)_2$), 24.43 ($CH(\mathbf{CH}_3)_2$), 22.80 ($CH(\mathbf{CH}_3)_2$). HRMS (FIA-ESI): calcd for $[C_{54}H_{75}N_6OCl_2Ag_2]$; 1107.3481; found: 1107.3492.

Synthesis of 6 $[Rh_2(cod)_2(\mu\text{-}\mathbf{CNC})](PF_6)$. An oven-dried Schlenk tube was loaded with $[H_2(\mathbf{C^HNC})](PF_6)$ (206 mg, 0.19 mmol), KO^{t}Bu (72 mg, 0.65 mmol), and $[Rh(cod)Cl]_2$ (82 mg, 0.17 mmol) and submerged in a cold bath at −78 °C under stirring. Anhydrous THF (ca. 50 mL) was transferred via a cannula to the Schlenk tube under stirring for 30 min in an inert atmosphere before the septum was removed, and the Schlenk tube was sealed. The reaction mixture was stirred overnight while gradually warming to RT. The reaction mixture turned from light yellow to light brown. After solvent evaporation, the residue was washed with hexanes, followed by DEE. Extraction with dichloromethane afforded compound **6** $[Rh_2(cod)_2(\mu\text{-}\mathbf{CNC})](PF_6)$ (150 mg, 0.11 mmol, 58%) as a deep orange solid. Crystallization from a toluene/dichloro-

methane mixture yielded single crystals suitable for XRD analysis.

^{1}H NMR: δ_H (CD$_2$Cl$_2$, 400.21 MHz) 7.54 (m, 4H, ArH$_{Dipp}$), 7.34 (t, 4H, J = 7.6 Hz, ArH$_{Dipp}$), 7.27 (t, 4H, J = 8.9 Hz, ArH$_{Dipp}$), 6.28 (d, 2H, J = 6.5 Hz, cod-CH), 4.76 (d, 2H, J = 18.1 Hz, N(CH$_2$)$_2$), 3.74 (s, 1H, cod-CH), 3.68 (d, 2H, J = 12.4 Hz, N(CH$_2$)$_2$), 3.53 (br s, 2H, cod-CH), 3.45 (br s, 2H, cod-CH), 2.46 (m, 4H, CH(CH$_3$)$_2$), 2.32 (br s, 2H, cod-CH$_2$), 2.13 (m, 12H, CH(CH$_3$) [4H], cod-CH$_2$ [8H]), 1.76 (m, 2H, cod-CH$_2$), 1.53 (br s, 3H, cod-CH$_2$), 1.36−0.97 (overlapping d, 49H, J = 5.5 Hz, CH(CH$_3$) [48H], underlying cod-CH$_2$ [1H]). ^{13}C NMR: δ_C (CD$_2$Cl$_2$, 100.64 MHz) 161.54 (C$_{carbene}$), 156.29 (C$_{q \, Trz}$), 145.27 (ArC$_q$), 145.12 (ArC$_q$), 144.78 (ArC$_q$), 144.71 (ArC$_q$), 133.78 (ArC$_q$), 132.29 (ArCH), 131.67 (ArCH), 129.69 (ArC$_q$), 125.27 (ArCH), 125.20 (ArCH), 124.12 (ArCH), 123.95 (ArCH), 97.02 (d, J = 9.4 Hz, cod-CH), 89.01 (d, J = 6.9 Hz, cod-CH), 68.12 (d, J = 11.8 Hz, cod-CH), 67.83 (d, J = 13.0 Hz, cod-CH), 61.99 (N(CH$_2$)$_2$), 35.01 (cod-CH$_2$), 32.27 (cod-CH$_2$), 29.35 (CH(CH$_3$)$_2$), 29.20 (CH(CH$_3$)$_2$), 29.03 (CH(CH$_3$)$_2$), 28.85 (CH(CH$_3$)$_2$), 28.31 (cod-CH$_2$), 28.01 (cod-CH$_2$), 26.81 (CH(CH$_3$)$_2$), 26.63 (CH(CH$_3$)$_2$), 26.45 (CH(CH$_3$)$_2$), 25.93 (CH(CH$_3$)$_2$), 24.04 (CH(CH$_3$)$_2$), 23.48 (CH(CH$_3$)$_2$), 22.59 (CH(CH$_3$)$_2$), 22.17 (CH(CH$_3$)$_2$). ^{19}F NMR: δ_F (CD$_2$Cl$_2$, 376.57 MHz) −73.28 (d, J = 711.0 Hz, PF$_6$). ^{31}P NMR: δ_P (CD$_2$Cl$_2$, 162.01 MHz) −144.71 (sept, J = 710.9 Hz, PF$_6$). HRMS (FIA-ESI): calcd for [C$_{70}$H$_{96}$N$_7$Rh$_2$]$^+$ [M − PF$_6$]: 1240.5837; found: 1240.4195.

Synthesis of 7a [Ir(cod)(HCNC)](PF$_6$). An oven-dried Schlenk tube was loaded with [H$_2$(C^{H}NC)](PF$_6$) (179 mg, 0.16 mmol), KO^{t}Bu (72 mg, 0.64 mmol), and [Ir(cod)Cl]$_2$ (129 mg, 0.19 mmol) and submerged in a cold bath at −78 °C under stirring. Anhydrous THF (ca. 50 mL) was transferred via a cannula to the Schlenk tube under stirring for 30 min in an inert atmosphere before the septum was removed, and the Schlenk tube was sealed. The reaction mixture was stirred overnight under gradual warming to RT. The reaction mixture turned from bright orange to deeper red-orange. After solvent evaporation, the residue was washed with hexanes, followed by diethyl ether. Extraction with dichloromethane afforded compound 7a [Ir(cod)(HCNC)](PF$_6$) (124 mg, 0.09 mmol, 62%) as an orange solid.

^{1}H NMR: δ_H (CD$_2$Cl$_2$, 500.13 MHz) 8.54 (s, 1H, CH$_{Trz}$), 7.71 (dt, 2H, J = 7.8 Hz, ArH$_{Dipp}$), 7.60 (t, 1H, J = 7.8 Hz, ArH$_{Dipp}$), 7.54 (t, 1H, J = 7.8 Hz, ArH$_{Dipp}$), 7.47 (d, 2H, J = 7.8 Hz, ArH$_{Dipp}$), 7.43 (t, 2H, J = 8.0 Hz, ArH$_{Dipp}$), 7.39 (d, 2H, J = 7.9 Hz, ArH$_{Dipp}$), 7.29 (d, 2H, J = 7.8 Hz, ArH$_{Dipp}$), 4.42 (s, 2H, N(CH$_2$)$_2$), 3.72 (s, 2H, N(CH$_2$)$_2$), 3.22 (br s, 2H, J = 7.8, cod-CH), 2.55 (br s, 2H, cod-CH), 2.46 (hept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 2.32 (hept, 2H, J = 6.8 Hz, CH(CH$_3$)$_2$), 2.09 (hept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 1.98 (hept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 1.79 (br t, 3H, J = 11.3 Hz, cod-CH$_2$), 1.54 (br s, 1H, cod-CH$_2$), 1.42 (m, 4H, cod-CH$_2$), 1.33 (dd, 10H, J = 6.7 Hz, CH(CH$_3$)), 1.28 (dd, 3H, J = 6.6 Hz, CH(CH$_3$)), 1.22 (d, 6H, J = 6.8 Hz, CH(CH$_3$)), 1.15 (m, 17H, CH(CH$_3$)), 1.10 (d, 6H, J = 6.8 Hz, CH(CH$_3$)), 1.07 (d, 6H, J = 6.9 Hz, CH(CH$_3$)) ^{13}C NMR: δ_C (CD$_2$Cl$_2$, 125.31 MHz) 166.45 (C$_{carbene}$), 162.07 (C$_{q \, Trz−Ir}$), 150.23 (C$_{q \, Trz−H}$), 146.31 (ArC$_q$), 146.29 (ArC$_q$), 146.18 (ArC$_q$), 145.80 (ArC$_q$), 145.71 (ArC$_q$), 145.60 (ArC$_q$), 145.47 (ArC$_q$), 135.14 (ArC$_q$), 134.13 (ArCH), 133.98 (ArCH), 133.59 (ArCH), 133.21 (ArCH), 132.78 (ArCH), 132.33 (Trz−CH), 131.94 (ArCH), 130.99 (ArC$_q$), 130.84 (ArC$_q$), 128.93 (ArC$_q$), 128.65 (ArC$_q$), 125.82

(ArCH), 125.64 (ArCH), 125.57 (ArCH), 125.46 (ArCH), 125.32 (ArCH), 124.27 (ArCH), 75.45 (cod-CH), 56.68 (N(CH$_2$)$_2$), 49.99 (N(CH$_2$)$_2$), 46.33 (cod-CH), 33.48 (cod-CH$_2$), 31.17 (CH(CH$_3$)$_2$), 30.81 (cod-CH$_2$), 30.23 (CH(CH$_3$)$_2$), 30.09 (CH(CH$_3$)$_2$), 29.88 (CH(CH$_3$)$_2$), 29.72 (CH(CH$_3$)$_2$), 29.60 (CH(CH$_3$)$_2$), 29,43 (CH(CH$_3$)$_2$), 29.24 (CH(CH$_3$)$_2$), 26.61 (CH(CH$_3$)$_2$), 25.70 (CH(CH$_3$)$_2$), 25.64 (CH(CH$_3$)$_2$), 25.57 (CH(CH$_3$)$_2$), 25.26 (CH(CH$_3$)$_2$), 25.22 (CH(CH$_3$)$_2$), 24.87 (CH(CH$_3$)$_2$), 24.82 (CH(CH$_3$)$_2$), 24.38 (CH(CH$_3$)$_2$), 24.08 (CH(CH$_3$)$_2$), 24.02 (CH(CH$_3$)$_2$), 23.80 (CH(CH$_3$)$_2$), 23.66 (CH(CH$_3$)$_2$), 23.41 (CH(CH$_3$)$_2$), 23.16 (CH(CH$_3$)$_2$), 22.55 (CH(CH$_3$)$_2$) ^{19}F NMR: δ_F (CD$_2$Cl$_2$, 470.59 MHz) −73.07 (d, J = 711.1 Hz, PF$_6$). ^{31}P NMR: δ_P (CD$_2$Cl$_2$, 202.46 MHz) −144.50 (sept, J = 711.0 Hz, PF$_6$). HRMS (FIA-ESI): calcd for [C$_{62}$H$_{85}$N$_7$Ir]$^+$ [M − PF$_6$]: 1120.6495; found: 1120.6492.

Synthesis of 7b [Ir(CO)$_2$(HCNC)](PF$_6$). Compound 7b was obtained by substitution of the 1,5-cyclooctadiene ligand (cod) of 7a [Ir(cod)(HCNC)](PF$_6$). A dichloromethane solution of compound 7a (124 mg, 0.09 mmol) was treated with CO(g) for 1 h, resulting in no observable color change. After solvent removal, product 7b [Ir(CO)$_2$(HCNC)](PF$_6$) (118 g, 0.09 mmol, 100%) was obtained as a dark orange-brown solid. The product was dried under vacuum at 50 °C overnight for NMR analysis. Single crystals suitable for XRD analysis were obtained from dichloromethane/hexane by slow vapor diffusion.

^{1}H NMR: δ_H (CD$_2$Cl$_2$, 500.13 MHz) 8.75 (s, 1H, CH$_{Trz}$), 7.72 (dt, 2H, J = 7.8 Hz, ArH$_{Dipp}$), 7.65 (t, 1H, J = 7.6 Hz, ArH$_{Dipp}$), 7.59 (t, 1H, J = 7.6 Hz, ArH$_{Dipp}$), 7.47 (d, 2H, J = 8.0 Hz, ArH$_{Dipp}$), 7.43 (dd, 4H, J = 7.9 Hz, ArH$_{Dipp}$), 7.37 (d, 2H, J = 7.8 Hz, ArH$_{Dipp}$), 5.01 (s, 2H, N(CH$_2$)$_2$), 3.95 (s, 2H, N(CH$_2$)$_2$), 2.35 (hept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 2.28 (hept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 2.13 (hept, 2H, J = 6.5 Hz, CH(CH$_3$)$_2$), 2.05 (hept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 1.33 (dd, 12H, J = 8.3 Hz, CH(CH$_3$)), 1.29 (d, 2H, J = 6.7 Hz, CH(CH$_3$)), 1.26 (d, 4H, J = 6.8 Hz, CH(CH$_3$)), 1.23 (d, 2H, J = 7.0 Hz, CH(CH$_3$)), 1.18 (dd, 12H, J = 5.7 Hz, CH(CH$_3$)), 1.15 (d, 8H, J = 6.9 Hz, CH(CH$_3$)), 1.12 (d, 6H, J = 6.8 Hz, CH(CH$_3$)), 1.08 (d, 2H, J = 7.2 Hz, CH(CH$_3$)) ^{13}C NMR: δ_C (CD$_2$Cl$_2$, 125.31 MHz) 186.55.45 (Ir−CO$_{trans \, carbene}$), 178.85 (Ir−CO$_{trans \, N}$), 174.07 (C$_{carbene}$), 161.97 (C$_{q \, Trz−Ir}$), 155.28 (C$_{q \, Trz−H}$), 149.36 (ArC$_q$), 145.99 (ArC$_q$), 145.92 (ArC$_q$), 145.52 (ArC$_q$), 145.42 (ArC$_q$), 135.29 (ArC$_q$), 134.44 (ArC$_q$), 134.09 (ArCH), 134.02 (ArCH), 133.96 (ArCH), 133.58 (ArCH), 133.18 (ArCH), 132.95 (ArC$_q$), 132.55 (ArCH), 132.30 (Trz−CH), 131.57 (ArC$_q$), 130.80 (ArC$_q$), 130.65 (ArC$_q$), 129.02 (ArC$_q$), 126.11 (ArCH), 125.81 (ArCH), 125.58 (ArCH), 125.44 (ArCH), 125.32 (ArCH), 124.81 (ArCH), 58.55 (N(CH$_2$)$_2$), 55.66 (N(CH$_2$)$_2$), 30.23 (CH(CH$_3$)$_2$), 30.04 (CH(CH$_3$)$_2$), 29.91 (CH(CH$_3$)$_2$), 29.84 (CH(CH$_3$)$_2$), 29.77 (CH(CH$_3$)$_2$), 29.71 (CH(CH$_3$)$_2$), 29.63 (CH(CH$_3$)$_2$), 29.44 (CH(CH$_3$)$_2$), 25.89 (CH(CH$_3$)$_2$), 25.70 (CH(CH$_3$)$_2$), 25.64 (CH(CH$_3$)$_2$), 25.52 (CH(CH$_3$)$_2$), 25.22 (CH(CH$_3$)$_2$), 25.14 (CH(CH$_3$)$_2$), 25.10 (CH(CH$_3$)$_2$), 24.87 (CH(CH$_3$)$_2$), 24.60 (CH(CH$_3$)$_2$), 24.43 (CH(CH$_3$)$_2$), 24.12 (CH(CH$_3$)$_2$), 24.04 (CH(CH$_3$)$_2$), 23.81 (CH(CH$_3$)$_2$), 23.65 (CH(CH$_3$)$_2$), 23.16 (CH(CH$_3$)$_2$), 23.10 (CH(CH$_3$)$_2$). ^{19}F NMR: δ_F (CD$_2$Cl$_2$, 470.59 MHz) −70.86 (d, J = 711.4 Hz, PF$_6$). ^{31}P NMR: δ_P (CD$_2$Cl$_2$, 202.46 MHz) −143.44 (sept, J = 711.3 Hz, PF$_6$). HRMS (FIA-ESI): calcd for [C$_{56}$H$_{73}$N$_7$ O$_2$Ir]$^+$ [M − PF$_6$]: 1068.5454; found: 1068.5450. FTIR ν_{CO} (CH$_2$Cl$_2$): 2035, 1964 cm^{-1}.

Synthesis of 8a [Rh$_2$(CO)$_3$Cl(μ-CNC)]. Addition of THF (ca. 50 mL) at −78 °C to a Schlenk tube loaded with [H$_2$(**C^{H}NC**)](PF$_6$) (208 mg, 0.19 mmol), KO^{t}Bu (67 mg, 0.60 mmol), and [Rh(CO)$_2$Cl]$_2$ (65 mg, 0.17 mmol) was followed by stirring the reaction mixture for 30 min at low temperature, whereafter the septum was removed and the reaction vessel was sealed. The reaction mixture was stirred overnight while warming up to RT. The reaction mixture turned from orange-brown to yellow-brown upon overnight reaction. The solvent was evaporated and the reaction mixture was washed with hexane. Cannula extraction with diethyl ether, followed by extraction with dichloromethane ensued. Both fractions were evaporated and combined to afford compound **8a** [Rh$_2$(CO)$_3$Cl(μ-**CNC**)] as a yellow solid (165 mg, 0.14 mmol, 77%). Crystallization from toluene yielded single crystals suitable for XRD analysis.

^{1}H NMR: δ_H (C$_6$D$_6$, 400.21 MHz) 7.16 (m, 6H, Ar**H**$_{Dipp}$), 7.09 (dd, 2H, J = 7.6, 7.5 Hz, Ar**H**$_{Dipp}$), 7.06 (dd, 2H, J = 7.4, 7.5 Hz, Ar**H**$_{Dipp}$), 6.95 (dd, 2H, J = 7.6, 7.6 Hz, Ar**H**$_{Dipp}$), 5.29 (d, 1H, J = 2.2 Hz, N(C**H**$_2$)$_2$), 5.25 (d, 1H, J = 2.2 Hz, N(C**H**$_2$)$_2$), 3.82 (s, 1H, N(C**H**$_2$)$_2$), 3.78 (s, 1H, N(C**H**$_2$)$_2$) 3.21 (hept, 2H, J = 6.7 Hz, C**H**(CH$_3$)$_2$), 3.03 (hept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 2.86 (hept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 2.39 (hept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 1.74 (d, 6H, J = 6.7 Hz, CH(C**H**$_3$)$_2$), 1.52 (d, 6H, J = 6.7 Hz, CH(C**H**$_3$)$_2$), 1.28 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.21 (d, 6H, J = 6.9 Hz, CH(C**H**$_3$)$_2$), 1.12 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 1.01 (d, 6H, J = 6.9 Hz, CH(C**H**$_3$)$_2$), 0.99 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$), 0.88 (d, 6H, J = 6.8 Hz, CH(C**H**$_3$)$_2$). ^{13}C NMR: δ_C (C$_6$D$_6$, 100.64 MHz) 193.70 (d, J = 71.7 Hz, Rh−**C**O), 187.40 (d, J = 75.7 Hz, Rh−**C**O), 173.74 (d, J = 44.5 Hz, **C**$_{carbene}$), 155.68 (**C**$_{q\ Trz}$), 146.84 (Ar**C**$_q$), 146.77 (Ar**C**$_q$) 145.23 (Ar**C**$_q$), 144.29 (Ar**C**$_q$), 135.71 (Ar**C**$_q$), 132.06 (Ar**C**H), 131.51 (Ar**C**$_q$), 131.22 (Ar**C**H), 125.42 (Ar**C**H), 124.54 (Ar**C**H), 123.96 (Ar**C**H), 123.87 (Ar**C**H), 57.65 (N(**C**H$_2$)$_2$), 29.26 (**C**H(CH$_3$)$_2$), 29.29 (**C**H(CH$_3$)$_2$), 29.08 (**C**H(CH$_3$)$_2$), 28.99 (**C**H(CH$_3$)$_2$), 26. 91 (**C**H(CH$_3$)$_2$), 25.97 (**C**H(CH$_3$)$_2$), 25.56 (**C**H(CH$_3$)$_2$), 25.50 (**C**H(CH$_3$)$_2$), 24.55 (**C**H(CH$_3$)$_2$), 23.38 (**C**H(CH$_3$)$_2$), 22.77 (**C**H(CH$_3$)$_2$), 22.73 (**C**H(CH$_3$)$_2$). HRMS (FIA-ESI): calcd for C$_{57}$H$_{72}$N$_7$O$_3$Rh$_2$ [M − Cl]$^+$: 1108.3801; found: 1108.3755 and also C$_{56}$H$_{72}$N$_7$O$_2$Rh$_2$ [M − Cl − CO]$^+$: 1080.3852; found: 1080.5378 and also C$_{55}$H$_{72}$N$_7$ORh [M − Cl − 2CO − Rh]$^+$: 949.4847; found: 949.4938. FTIR ν_{CO} (CH$_2$Cl$_2$): 2019, 1981 cm^{-1}.

Synthesis of 8b [Rh(CO)(C^{H}NC)](PF$_6$) (via in Situ Deprotonation). To a Schlenk tube loaded with [H$_2$(**C^{H}NC**)](PF$_6$) (185 mg, 0.17 mmol), KHMDS (65 mg, 0.33 mmol), and [Rh(CO)$_2$Cl]$_2$ (58 mg, 0.15 mmol), −78 °C anhydrous THF (ca. 50 mL) was added, followed by stirring the reaction mixture for 30 min at the same temperature. The septum was removed and the reaction vessel was sealed. The reaction mixture was stirred overnight while warming up to RT. The reaction mixture turned from dark brown to yellow-orange upon overnight reaction. The solvent was removed under reduced pressure, and the reaction mixture was washed with hexane. Extraction with diethyl ether and dichloro-methane followed. NMR analysis showed that both fractions contained a mixture of complexes **8a** [Rh$_2$(CO)$_3$Cl(μ-**CNC**)] and **8b** [Rh(CO)(**C^{H}NC**)](PF$_6$), with **8a** being the major product (ca. 70%) and **8b** the minor product (ca. 30%), based on NMR intensity (see Figures S31 and S32). Attempts to separate the two complexes were unsuccessful.

^{1}H NMR: δ_H (C$_6$D$_6$, 500.13 MHz) 7.14 (m, 4H, Ar**H**$_{Dipp}$), 6.99 (d, 4H, J = 7.2, 7.5 Hz, Ar**H**$_{Dipp}$), 6.95 (d, 4H, J = 7.6, 7.6 Hz, Ar**H**$_{Dipp}$), 6.52 (pent, 1H, J = 6.4 Hz, N**H**(CH$_2$)$_2$), 3.94 (d, 1H, J = 5.8 Hz, N**H**(CH$_2$)$_2$), 3.91 (d, 1H, J = 5.6 Hz, N**H**(CH$_2$)$_2$), 3.27 (s, 1H, N**H**(CH$_2$)$_2$), 3.26 (s, 1H, N**H**-(CH$_2$)$_2$), 3.28 (hept, 2H, J = 7.0 Hz, C**H**(CH$_3$)$_2$), 2.92 (hept, 2H, J = 6.8 Hz, C**H**(CH$_3$)$_2$), 2.76 (hept, 2H, J = 6.9 Hz, C**H**(CH$_3$)$_2$), 2.24 (hept, 2H, J = 6.7 Hz, C**H**(CH$_3$)$_2$), 1.70 (d, 12H, J = 6.5 Hz, CH(C**H**$_3$)$_2$), 1.20 (dd, 24H, J = 6.8, 6.6 Hz, CH(C**H**$_3$)$_2$), 1.08 (d, 12H, J = 6.9 Hz, CH(C**H**$_3$)$_2$). ^{13}C NMR: δ_C (C$_6$D$_6$, 125.31 MHz) 194.94 (d, J = 68.1 Hz, Rh−**C**O), 178.73 (d, J = 44.1 Hz, **C**$_{carbene}$), 152.15 (**C**$_{q\ Trz}$), 147.31 (Ar**C**$_q$), 147.29 (Ar**C**$_q$) 144.89 (Ar**C**$_q$), 144.34 (Ar**C**$_q$), 135.51 (Ar**C**$_q$), 132.33 (Ar**C**H), 131.26 (Ar**C**$_q$), 131.07 (Ar**C**H), 125.60 (Ar**C**H), 124.86 (Ar**C**H), 123.90 (Ar**C**H), 123.43 (Ar**C**H), 49.88 (N(**C**H$_2$)$_2$), 29.36 (**C**H(CH$_3$)$_2$), 29.25 (**C**H(CH$_3$)$_2$), 29.20 (**C**H(CH$_3$)$_2$), 28.08 (**C**H(CH$_3$)$_2$), 26. 27 (**C**H(CH$_3$)$_2$), 25.32 (**C**H(CH$_3$)$_2$), 24.85 (**C**H(CH$_3$)$_2$), 24.56 (**C**H(CH$_3$)$_2$), 24.25 (**C**H(CH$_3$)$_2$), 23.51 (**C**H(CH$_3$)$_2$), 23.24 (**C**H(CH$_3$)$_2$), 23.10 (**C**H(CH$_3$)$_2$). ^{19}F NMR: δ_F (C$_6$D$_6$, 470.59 MHz) −71.59 (d, J = 714.3 Hz, P**F**$_6$). ^{31}P NMR: δ_P (C$_6$D$_6$, 202.46 MHz) −141.46 (sept, J = 713.7 Hz, **P**F$_6$). HRMS (FIA-ESI): calcd for C$_{54}$H$_{73}$N$_7$Rh [M − CO − PF$_6$]$^+$: 950.4926; found: 950.3512. FTIR ν_{CO} (CH$_2$Cl$_2$): 2019 or 1981 cm^{-1} (overlapping with ν_{CO} of **8a**).

Synthesis of 8b [Rh(CO)(C^{H}NC)](PF$_6$) (via Trans-metallation from Silver). The entitled compound was obtained in two steps via transmetallation reaction from its corresponding bimetallic silver derivative **9** [Ag$_2$Cl$_2$(μ-**CNC**)] (see vida infra), which was prepared following a reported method.[9c] To a Schlenk tube loaded with [H$_2$(**C^{H}NC**)](PF$_6$) (731 mg, 0.66 mmol), KCl (122 mg, 1.64 mmol), and Ag$_2$O (305 mg, 1.32 mmol) was added acetonitrile (ca. 50 mL) and stirred in a dark environment for 3 days. The reaction mixture was filtered. The filtrate was collected and evaporated to dryness under vacuum to perform a cannula filtration with dichloromethane. After cannula filtration and evaporation of the solvent under reduced pressure, compound **9** [Ag$_2$Cl$_2$(μ-**CNC**)] (619 mg, 0.56 mmol, 85%) was obtained as a pure white solid.

^{1}H NMR: δ_H (CD$_2$Cl$_2$, 500.13 MHz) 7.56 (m, 4H, Ar**H**$_{Dipp}$), 7.34 (m, 8H, Ar**H**$_{Dipp}$), 3.75 (d, 4H, J = 6.9 Hz, N**H**(CH$_2$)$_2$), 2.71 (s, 1H, N**H**(CH$_2$)$_2$), 2.35 (sept, 4H, J = 6.6 Hz, C**H**(CH$_3$)$_2$), 2.26 (sept, 4H, J = 6.3 Hz, C**H**(CH$_3$)$_2$), 1.39 (d, 3H, J = 6.7 Hz, CH(C**H**$_3$)$_2$), 1.34 (d, 3H, J = 6.6 Hz, CH(C**H**$_3$)$_2$), 1.15 (m, 42H, CH(C**H**$_3$)$_2$). ^{13}C NMR: δ_C (CD$_2$Cl$_2$, 125.31 MHz) 149.82 (**C**$_{carbene}$), 149.68 (**C**$_{carbene}$), 145.99 (**C**$_{q\ Trz}$), 145.85 (**C**$_{q\ Trz}$), 145.34 (Ar**C**$_q$), 145.12 (Ar**C**$_q$), 145.01 (Ar**C**$_q$), 135.84 (Ar**C**$_q$), 132.34 (Ar**C**H), 131.65 (Ar**C**H), 131.53 (Ar**C**H), 129.66 (Ar**C**$_q$), 125.11 (Ar**C**H), 124.79 (Ar**C**$_q$), 124.48 (Ar**C**H), 124.27 (Ar**C**H), 45.64 (N**H**(**C**H$_2$)$_2$), 29.28 (**C**H(CH$_3$)$_2$), 29.06 (**C**H(CH$_3$)$_2$), 28.93 (**C**H(CH$_3$)$_2$), 28.58 (**C**H(CH$_3$)$_2$), 25.74 (**C**H(CH$_3$)$_2$), 25.67 (**C**H(CH$_3$)$_2$), 25.66 (**C**H(CH$_3$)$_2$), 24.69 (**C**H(CH$_3$)$_2$), 24.63 (**C**H(CH$_3$)$_2$), 24.52 (**C**H(CH$_3$)$_2$), 23.91 (**C**H(CH$_3$)$_2$), 23.10 (**C**H(CH$_3$)$_2$). HRMS (FIA-ESI): calcd for [C$_{54}$H$_{76}$N$_7$Cl$_2$Ag$_2$] 1106.3403; found: 1106.3446.

To a Schlenk tube loaded with **9** [Ag$_2$Cl$_2$(μ-**CNC**)] (135 mg, 0.12 mmol), KPF$_6$ (45 mg, 0.24 mmol), and [Rh(CO)$_2$Cl]$_2$ (38 mg, 0.10 mmol), dichloromethane (ca. 50 mL) was added. The reaction vessel was capped and the reaction was stirred overnight. The reaction mixture turned from brown to a murky khaki color upon overnight reaction. The solvent

was removed under reduced pressure, and the reaction mixture was washed with cold hexane. Washing was continued with RT hexane, followed by extraction with diethyl ether, which resulted in the isolation of compound **8b** [Rh(CO)($\mathbf{C^H NC}$)]-(PF$_6$) as a yellow solid (118 mg, 0.11 mmol, 88%).

^{1}H NMR: δ_H (C$_6$D$_6$, 500.13 MHz) 7.16 (m, 6H, ArH$_{Dipp}$), 7.10 (dd, 2H, J = 7.8, 7.8 Hz, ArH$_{Dipp}$), 6.99 (dd, 2H, J = 7.7, 7.7 Hz, ArH$_{Dipp}$), 6.96 (dd, 2H, J = 7.5, 7.5 Hz, ArH$_{Dipp}$), 6.51 (pent, 1H, J = 7.4 Hz, NH(CH$_2$)$_2$), 3.94 (dd, 1H, J = 6.0, 6.0 Hz, NH(CH$_2$)$_2$), 3.91 (dd, 1H, J = 6.0, 5.8 Hz, NH(CH$_2$)$_2$), 3.29 (d, 1H, J = 9.2 Hz, NH(CH$_2$)$_2$), 3.26 (d, 1H, J = 9.2 Hz, NH(CH$_2$)$_2$), 2.90 (hept, 2H, J = 6.7 Hz, CH(CH$_3$)$_2$), 2.83 (hept, 2H, J = 6.8 Hz, CH(CH$_3$)$_2$), 2.76 (hept, 2H, J = 6.9 Hz, CH(CH$_3$)$_2$), 2.25 (hept, 2H, J = 6.8 Hz, CH(CH$_3$)$_2$), 1.67 (dd, 12H, J = 6.6, 6.7 Hz, CH(CH$_3$)$_2$), 1.29 (d, 6H, J = 6.8 Hz, CH(CH$_3$)$_2$), 1.18 (dd, 12H, J = 6.9, 6.8 Hz, CH(CH$_3$)$_2$), 1.06 (d, 6H, J = 6.9 Hz, CH(CH$_3$)$_2$), 0.98 (dd, 12H, J = 6.8, 6.8 Hz, CH(CH$_3$)$_2$). ^{13}C NMR: δ_C (C$_6$D$_6$, 125.31 MHz) 192.33 (d, J = 81.5 Hz, Rh−CO), 178.67 (d, J = 44.2 Hz, C$_{carbene}$), 152.19 (C$_{q\ Trz}$), 147.22 (ArC$_q$), 147.18 (ArC$_q$) 144.92 (ArC$_q$), 144.39 (ArC$_q$), 135.50 (ArC$_q$), 132.38 (ArCH), 131.26 (ArCH), 131.04 (ArC$_q$), 125.57 (ArCH), 124.83 (ArCH), 123.98 (ArCH), 123.46 (ArCH), 49.88 (N(CH$_2$)$_2$), 29.35 (CH(CH$_3$)$_2$), 29.23 (CH(CH$_3$)$_2$), 29.09 (CH(CH$_3$)$_2$), 29.09 (CH(CH$_3$)$_2$), 26.26 (CH(CH$_3$)$_2$), 25.33 (CH(CH$_3$)$_2$), 24.87 (CH(CH$_3$)$_2$), 24.56 (CH(CH$_3$)$_2$), 24.26 (CH(CH$_3$)$_2$), 23.51 (CH(CH$_3$)$_2$), 23.23 (CH(CH$_3$)$_2$), 23.12 (CH(CH$_3$)$_2$). ^{19}F NMR: δ_F (C$_6$D$_6$, 470.59 MHz) −71.23 (d, J = 713.0 Hz, PF$_6$). ^{31}P NMR: δ_P (C$_6$D$_6$, 202.46 MHz) −143.27 (sept, J = 713.0 Hz, PF$_6$). HRMS (FIA-ESI): calcd for C$_{55}$H$_{73}$N$_7$ORh [M − PF$_6$]$^+$: 950.4931; found: 950.4931. FTIR ν_{CO} (CH$_2$Cl$_2$): 1974 cm^{-1}. FTIR ν_{NH} (CH$_2$Cl$_2$): 3256 cm^{-1}.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsome-ga.9b00514.

Synthesis and characterization of [H$_2$(**COC**)](PF$_6$)$_2$, [H$_2$(**C^{Boc}NC**)](PF$_6$)$_2$, and [H$_2$(**C^{H}NC**)](PF$_6$)$_2$; NMR spectra of ligand precursor salts: [H$_2$(**COC**)](PF$_6$)$_2$, [H$_2$(**C^{Boc}NC**)](PF$_6$)$_2$, and [H$_2$(**C^{H}NC**)](PF$_6$)$_2$; and details of complexes **1a**, **1b**, **2a**, **2b**, **3a**, **4a**, **4b**, **5**, **6**, **7a**, **7b**, **8a**, **8b**, and **9** for the crystal structure determinations of [H$_2$(**COC**)](PF$_6$)$_2$, [H$_2$(**C^{Boc}NC**)]-(PF$_6$)$_2$, [H$_2$(**C^{H}NC**)](PF$_6$)$_2$, **1b**, **2a**, **2b**, **3a**, **4a**, **6**, **7b**, and **8a** (PDF)

Crystallographic data (CIF)

Accession Codes

CCDC numbers 1874026−1874035 and 1890712 contain the supporting crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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