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Pentacoordinated Rhodium(I) Complexes Supported by Coumarin-Functionalized *N*-Heterocyclic Carbene Ligands

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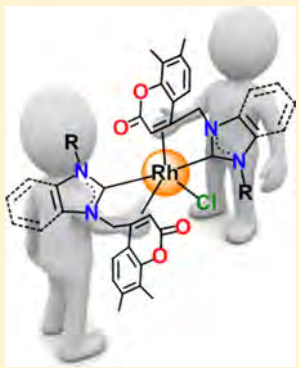
Supporting Information

ABSTRACT: New coumarin-tethered benzimidazolium ($BzICou^RHCl$) and imidazolium ($ICou^RHCl$) salts have been prepared as precursors for coumarin−NHC rhodium(I) complexes RhCl(NHC)(cod). Trigonal bypiramidal pentacoordinated bis-coumarin−NHC rhodium(I) species, $RhCl(NHC)_2$, can be obtained by heating rhodium-cod derivatives in the presence of coumarin−azolium salts and a base. These unusual species are stabilized by coordination of the unsaturated bond of both coumarin moieties by the same enantioface. The allyl substituent on doubly functionalized NHC competes for coordination with coumarin wingtips. DFT calculations upon coordination of the olefin moieties support the experimental results.



INTRODUCTION

Shortly after the first report on the isolation of a free *N*-heterocyclic carbene (NHC) by Arduengo's group,[1] exploitation of their potential in organometallic chemistry and catalysis began. NHCs provide two major advantages for catalyst design: ease in synthesis, which allows for structural tunability, and, more importantly, a high electron σ-donor capacity ensuing stronger metal−ligand bonds, thereby resulting in the stabilization of highly reactive intermediates which could enhance catalytic performances.[2] Consequently, a myriad of modifications within the basic NHC scaffold has been undertaken in recent years.[3] Particularly, a pendant donating group may offer advantages for the improvement of catalytic activity and the control of the selectivity outcome. In some instances, functionalized NHCs can stabilize low-coordinate highly reactive species through the formation of stable chelates or pincers, while in others, they behave as hemilabile ligands which enable the interaction of the substrates and the metal center in saturated derivatives, with relevant implications in catalytic activity.[4] In this context, several NHC-functionalized metal complexes ranging from alkenyl,[5] amine,[6] pyridyl,[7] phosphine,[8] carbonyl,[9] alcohol,[10] ether,[11] or thio,[12] among others,[13] have been reported.

Coumarins consist of fused α-pyron and benzene rings. Their utility spans luminescence, polymeric materials, and biological applications.[14−17] Introduction of an electron-releasing group at 7-position and/or an electron-withdrawing substituent at 3-position results in fluorescence enhancement which has been applied for laser dyes and sensors.[14] Coumarin derivatives have also been shown a broad spectrum of biological activity,[15] including anti-HIV,[15a] anticancer,[15b] and enzyme inhibition.[15c,d] Well-known clinically used examples include warfarin as anticoagulant[16] or novobiocin as antibiotic.[17] Due to a synergistic effect, a coumarin framework has been incorporated into different ligands for a wide array of metal complexes that results in the improvement of biological[18] or photophysical properties.[19] Moreover, coumarin-based complexes have also found application as catalysts for cross-coupling,[20] polymerization,[21] or olefin metathesis,[22] but to the best of our knowledge, coumarin-containing rhodium complexes have not been reported so far.

In recent years, our research interests have been focused in the development of the organometallic chemistry of Rh−NHC complexes[23] and their catalytic applications.[24] We envisage that modification of the NHC framework by the introduction of a pendant coumarin moiety that can potentially interact with the metallic center or a substrate through its unsaturated lactonic ring entails interesting implications on catalytic applications (Chart 1).[25,26] In this regard, biological applications of coumarin-functionalized NHC silver and gold complexes have been previously studied by some of us and others.[27] Now, we aim to synthesize for the first time coumarin-substituted NHC rhodium complexes and study their coordination behavior.

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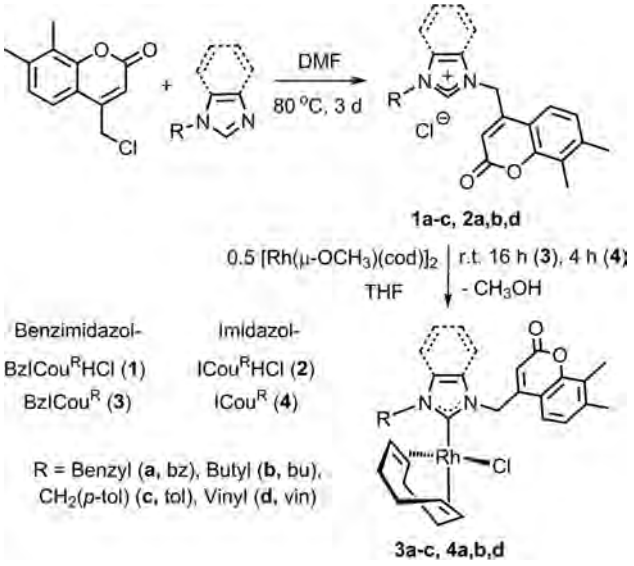
Chart 1. Potential Interactions of a Coumarin-Functionalized NHC−Rh Framework

RESULTS AND DISCUSSION

Synthesis of Coumarin−NHC Rhodium(I) Complexes. Coumarin-tethered azolium salts **1** [1-*R*,3-{(7,8-dimethyl-2*H*-chromen-2-one-4-yl)methyl}benzimidazolium chloride = BzICou^{R}HCl] and **2** [1-*R*,3-{(7,8-dimethyl-2*H*-chromen-2-one-4-yl)methyl}imidazolium chloride = ICou^{R}HCl] were prepared in good to excellent yields as previously described[27b] starting from 4-chloromethyl-7,8-dimethyl coumarin[28] and the corresponding nitrogenated heterocycle (Scheme 1). The synthesis of

Scheme 1. Synthesis of Coumarin-Functionalized NHC−Rh Complexes 3 and 4



rhodium coumarin−NHC complexes was accomplished directly by treatment of **1** or **2** with $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (cod = 1,5-cyclooctadiene) in THF at room temperature to yield RhCl(BzICou^{R})(cod) (**3**) or RhCl(ICou^{R})(cod) (**4**), thus avoiding a preliminary deprotonation step or the preparation of the corresponding Ag−NHC complexes. The formation of benzimidazolin-2-carbene complexes **3** required a reaction time of 16 h. However, similar reaction conditions for the preparation of imidazolin-2-carbene species **4** resulted in the formation of an additional minor species (see below). Shorter reaction time (4 h) and filtration from THF allowed the isolation of complexes **4** in a pure form. As far as we know, **3** and **4** constitute the first rhodium complexes bearing a coumarin-functionalized NHC ligand.

The solid state structures of **3b**, **3c**, and **4a** have been determined by X-ray diffraction analyses on single crystals obtained by slow evaporation of $CDCl_3$ solutions (Figure 1, see the Supporting Information for **3b**). For all complexes, a

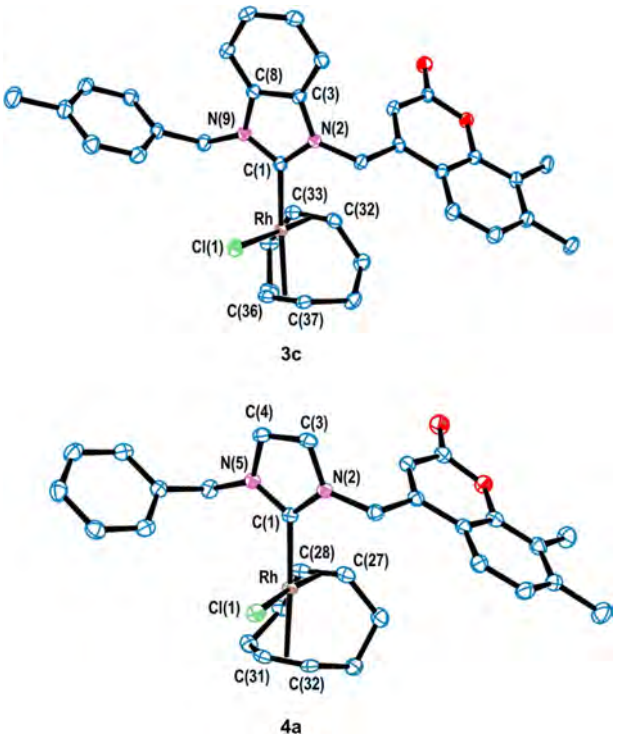


Figure 1. ORTEP views of **3c** and **4a**. Ellipsoids are at 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **3c**: Rh−C(1) 2.010(2), Rh−ct[C(32)−C(33)] 1.9963(2), Rh−ct[C(36)−C(37)] 2.1054(2), Rh−Cl(1) 2.3814(6), C(3)−C(8) 1.396(3), C(32)−C(33) 1.399(3), C(36)−C(37) 1.371(3), C(1)−Rh−Cl(1) 86.34(6), C(1)−Rh−ct[C(32)−C(33)] 94.03(6), C(1)−Rh−ct[C(36)−C(37)] 175.92(6), Cl(1)−Rh−ct[C(32)−C(33)] 177.07(2); **4a**: Rh−C(1) 2.0337(19), Rh−ct[C(27)−C(28)] 1.9921(2), Rh−ct[C(31)−C(32)] 2.0892(2), Rh−Cl(1) 2.3942(5), C(3)−C(4) 1.340(3), C(27)−C(28) 1.400(3), C(31)−C(32) 1.374(3), C(1)−Rh−Cl(1) 87.88(5), C(1)−Rh−ct-[C(27)−C(28)] 94.09(5), C(1)−Rh−ct[C(31)−C(32)] 177.08(6), Cl(1)−Rh−ct[C(27)−C(28)] 173.13(2). ct[C(X)−C(Y)], centroid of the C(X)−C(Y) bond.

distorted square-planar geometry around the metal center is observed. The rhodium−carbene separations lie in the range typically observed for a Rh−NHC single bond.[4c,5c,g,h,7c,9,12b,13a,f,23,24] Furthermore, a slightly distorted coordination of the carbene moiety is reflected in the in-plane bending of the nitrogenated plane with respect to the Rh−NHC axis, described as the yaw angle (ψ 7.4°, **3c**; 9.0°, **4a**).[29,24f] A slightly shorter Rh−NHC distance is observed in benzimidazolin−NHC complex **3c** compared to that in imidazolin−NHC complex **4a**, {Rh−C(1) 2.010(2) (**3c**), 2.0337(19) Å (**4a**)}. The higher trans-influence of the carbene versus the chlorido ligand results in a longer separation from the metal center for the coordinated double bond opposite to the NHC ligand {Rh−ct[C(36)−C(37)] = 2.1054(2) vs Rh−ct[C(32)−C(33)] = 1.9963(2) for **3c** or Rh−ct[C(31)−C(32)] = 2.0892(2) vs Rh−ct[C(27)−C(28)] = 1.9921(2) for **4a** (ct[C(X)−C(Y)], centroid of the C(X)−C(Y) bond)}.

The NMR spectroscopic data show that the structures of **3** and **4** in solution are similar to those found in the solid state. A prototypical signal for the identification of the coumarin moiety is the olefinic proton of the lactonic ring, which appears as a singlet between δ 5.65 and 5.97 ppm. In stark contrast to azolium salts **1** and **2**, the methylene protons connecting NHC

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and the coumarin framework are diastereotopic, as a consequence of the coordination to the metal center. Thus, two doublets with a geminal coupling constant of about 18 Hz are displayed at around 7.1 and 5.6 ppm for complexes **3**. The separation between methylene signals is reduced to about 0.8 ppm in imidazolin-2-carbene complexes **4**. Furthermore, methylene protons of the benzyl substituents are also diastereotopic but smaller separation are observed (Figure 2).

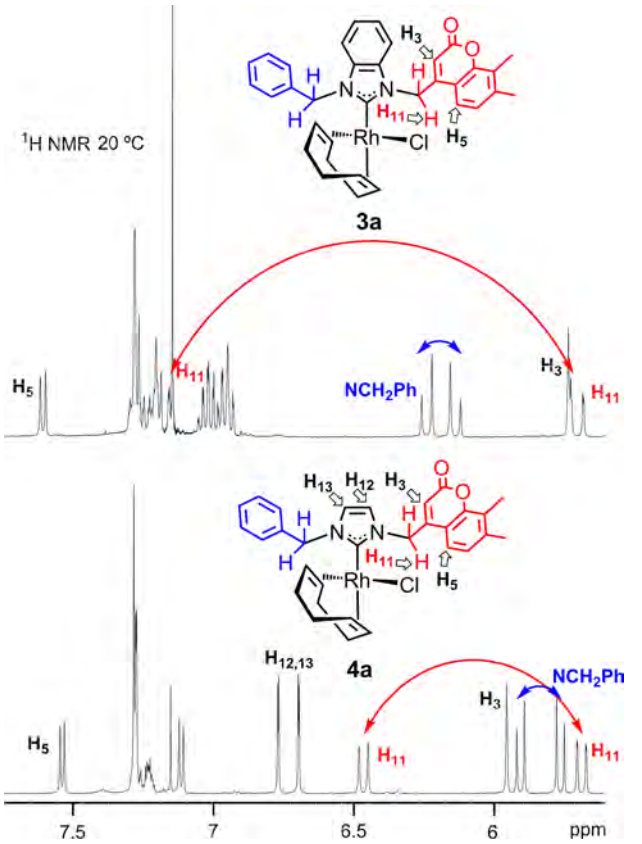
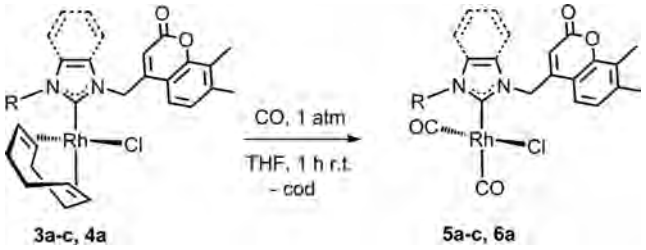


Figure 2. Comparison of the ^{1}H NMR resonances of methylene protons for **3a** (top) and **4a** (bottom).

The differences between benzimidazolin- and imidazolin-2-carbene complexes are also evident in the ^{13}C{^{1}H}-APT NMR spectra. The signals corresponding to carbene carbon atoms of **3** appear as doublets around δ 198 ppm ($J_{C-Rh} \approx 51$ Hz), whereas those for the imidazolin derivatives **4** are about 13 ppm more shielded. Two pairs of doublets are observed for the η^2-alkene carbon atoms of cod ligand around 100 and 70 ppm, which is in agreement with the lack of a plane of symmetry and with a hindered rotation of the carbene ligand around the Rh–C axis. The doublets around 100 ppm exhibit smaller coupling constants {$J_{C-Rh} \approx 11$ (**3**), 7 (**4**) Hz)} than those around 70 ppm ($J_{C-Rh} \approx 14$ Hz); therefore, the former doublets are ascribed to the double bond located opposite to the carbene due to the higher trans-influence of NHC compared to that of chlorido ligand.[30b]

Similar coumarin–NHC ligands have been previously prepared,[27] but their donor properties have not been studied in detail. In this regard, IR spectroscopy is a valuable method for describing the bonding situation of a NHC ligand within rhodium bis-carbonyl complexes. Bubbling carbon monoxide through a solution of **3a–c** or **4a** resulted in the replacement of the cod ligand to yield the bis-carbonyl species RhCl(BzICou^R)(CO)$_2$ (**5a–c**) and RhCl(ICou^{bz})(CO)$_2$ (**6a**), respectively (Scheme 2). The values for the symmetric CO

Scheme 2. Synthesis of Coumarin-Functionalized NHC–Rh Bis-carbonyl Complexes



stretching mode, 2083 cm^{-1} for **5a** versus 2075 cm^{-1} for **6a**, gives TEP parameters similar to that found in related symmetrically substituted azole carbenes, showing slightly higher electro-donating capacity for imidazolin-carbenes.[30]

The substitution of the diolefin ligand by CO results in closer resonances for the diasterotopic methylene protons in the ^{1}H NMR spectra. The more interesting feature of the ^{13}C{^{1}H}-APT NMR spectra is the shielding of rhodium-carbene carbon resonances by about 8–11 ppm compared to cod derivatives, with concomitant reduction of the J_{C-Rh} of about 10 ppm (Figure 3). Two doublets at around δ 184 ppm ($J_{C-Rh} \approx 53$

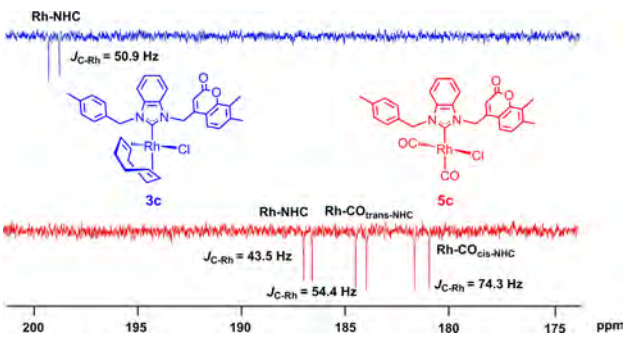


Figure 3. Selected areas of the ^{13}C{^{1}H}-APT NMR spectra of **3c** (top) and **5c** (bottom).

Hz) and 181 ppm ($J_{C-Rh} \approx 73$ Hz) were observed for the nonequivalent carbonyl ligands, the first signal corresponding to the CO located trans to the NHC. As observed for cod complexes, the higher trans-influence of NHC elongates the Rh–CO bond opposite to it, resulting in a decrease of the J_{C-Rh} coupling constant.

Synthesis of Pentacoordinated Bis-Coumarin–NHC Rhodium(I) Complexes. During the preparation of complexes **4**, the formation of an additional minor species was observed (see above). These species could be isolated from the reaction mixture as white solids. Unexpectedly, the ^{1}H NMR spectra showed no resonances for the cod ligand and then the formation of a bis-coumarin–NHC rhodium(I) species was envisioned. These new complexes have been prepared in acceptable yields (38–66%) by refluxing a THF solution of the precursor [Rh(μ-OCH$_3$)(cod)]$_2$ and 2 equiv of the corresponding azolium salts in the presence of sodium methoxide for 24 h (Scheme 3). Cooling the reaction mixture gave the crude compounds as white solids which were washed with cold THF to remove unreacted cod complexes **3** and **4**. Recrystallization from CH_2Cl_2/hexane afforded the pentacoordinated bis-NHC

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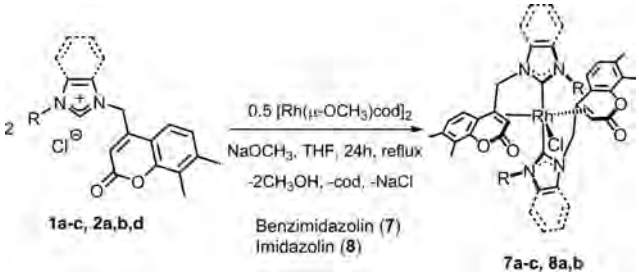
Scheme 3. Synthesis of Bis-Coumarin−NHC Pentacoordinated Rh^{I} Complexes



derivatives RhCl(κ-C,η^2-BzICou^{R})$_2$ (**7a−c**) and RhCl(κ-C,η^2-ICou^{R})$_2$ (**8a,b**). It is noticeable that the formation of **8** proceeds faster than that of **7**, likely due to the slightly higher electron-donor capacity of imidazolin-2-carbenes. Pentacoordinate rhodium(I) complexes **7** and **8** are quite stable and unreactive. For example, compound **7a** does not react with either methanol or aniline after 5 h at room temperature. However, heating at 80 °C for 1 night resulted in decomposition of the complex. Abstraction of the chlorido ligand by treatment with thallium hexafluorophosphate resulted in a mixture of unidentified species.

The solid state structures of **7b** and **8b** have been determined by X-ray diffraction analyses on single crystals obtained by slow evaporation of CH_2Cl_2 (**7b**) or $CDCl_3$ (**8b**) solutions (Figure 4). For both complexes, the coordination polyhedron of the

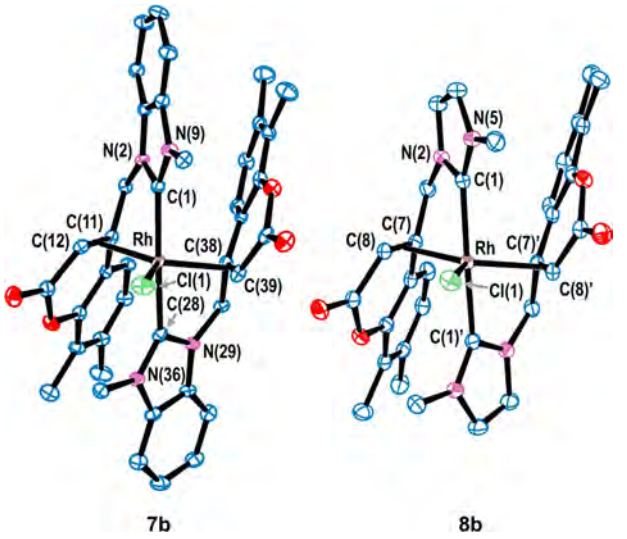


Figure 4. ORTEP views of **7b** and **8b**. Ellipsoids are at 50% probability. Hydrogen atoms and butyl substituent of NHC are omitted for clarity. Selected bond lengths (Å) and angles (deg): **7b**: Rh−C(1) 2.042(3), Rh−C(28) 2.043(3), Rh−ct[C(11)−C(12)] 2.0525(3), Rh−ct[C(38)−C(39)] 2.0677(3), C(11)−C(12) 1.429(4), C(38)−C(39) 1.430(4), C(1)−Rh−C(28) 172.25(13), ct[C(11)−C(12)]−Rh−ct[C(38)−C(39)] 133.52(1), Cl(1)−Rh−ct-[C(11)−C(12)] 114.84(2), Cl(1)−Rh−ct[C(38)−C(39)] 111.65(2), C(1)−Rh−ct[C(11)−C(12)] 79.29(9), C(1)−Rh−ct[C(38)−C(39)] 97.05(9), C(1)−Rh−Cl(1) 95.02(9), C(28)−Rh−Cl(1) 92.73(10); **8b**: Rh−C(1) 2.0579(19), Rh−ct[C(7)−C(8)] 2.0513(1), C(7)−C(8) 1.429(3), C(1)−Rh−C(1)′ 172.90(11), ct[C(7)−C(8)]−Rh−ct[C(7)′−C(8)′] 133.82(10), Cl(1)−Rh−ct[C(7)−C(8)] 113.09(1), C(1)−Rh−ct[C(7)−C(8)] 79.29(5), C(1)−Rh−ct[C(7)′−C(8)′] 97.90(5), C(1)−Rh−Cl(1) 93.55(6). ct[C(X)−C(Y)], centroid of the C(X)−C(Y) bond.

rhodium atom is a distorted trigonal bipyramid[31] (τ = 0.64 for **7b** and τ = 0.65 for **8b**) with the carbene carbon atoms in the apical positions {C(1)−Rh−C(28) = 172.25(13) (**7b**), C(1)−Rh−C(1)′ = 172.90(11) (**8b**)}. The η^2-carbon−carbon bonds of the coumarin moieties lie in the equatorial plane, disposed in an in-plane fashion, in accordance to expectations based on orbital energy for the more π-acceptor ligands.[32] The rhodium−carbene bond slightly elongates in comparison with those in square-planar cod complexes {Rh−C(1) = 2.042(3) Å in **7b** vs 2.010(2) Å in **3c** and Rh−C(1) = 2.0579(19) Å in **8b** vs 2.0337(19) Å in **4a**}. This fact reasonably reflects the strain within the κ-C,η^2-olefin ligand, since generally that distance shortens upon the formation of a chelate.[5e] Alternatively, the possibility that the lengthening of the Rh(I)−NHC bond was caused by a change in coordination number cannot be ruled out. The chelate formation results in higher yaw angles for the heterocyclic ring in **7b** (ψ 12.4°) and **8b** (ψ 12.2°) compared to those in **3c** (ψ 7.4°) and **4a** (ψ 9.0°). In addition, the elongation of the double bond within the lactonic ring, around 0.08 Å, is in accordance with a coordinated olefin but not enough that the Rh(η^2-C═C) fragment should be considered a metalacyclopropane. Remarkably, the κ-C,η^2-CC coordination of the NHC ligand gives rise to a chiral environment around the metal center for both **7b** and **8b**. According to the skew line system,[33] the enantiomers shown in Figure 4 exhibit a Δ configuration. Nevertheless, due to the centrosymmetric space-groups of **7b** ($P2_1/n$) and **8b** ($C2/c$), both enantiomers Λ and Δ are present in the unit cell. Further, different diasteroisomers can form for configurations Λ and Δ of the metal center depending on which enantioface of the C^3═C^4 double bond of the coumarin moiety coordinates to the metal center, namely, 3*si*,4*re* or 3*re*,4*si*. Notably, each coumarin wingtip coordinate by the same 3*si*,4*re* enantioface in both **7b** and **8b**. Neither intra- or intermolecular interactions have been observed between the oxygen atom of the carbonyl groups and the metallic center.

The solid-state structure observed for **7b** and **8b** is maintained in solution. As a consequence of the C_2 symmetry of the complexes, only one set of resonances are observed for both NHC-coumarin ligands in the NMR spectra. Complex **8a** is quite insoluble in chlorinated solvents and only fairly soluble in DMSO-d_6 even at 90 °C, which prevents the observation of some quaternary carbons in the $^{13}C\{^1H\}$-APT NMR spectrum. The coordination of the coumarin moiety is reflected in a shift to a more shielded region of the signals corresponding to the olefinic proton (H_3) and the methylene protons connecting the coumarin moiety to the NHC (H_{11}), with concomitant reduction on the geminal coupling constant (Figure 5). In agreement with this coordination, the $^{13}C\{^1H\}$-APT NMR spectra display two doublets at about δ 73 ppm ($J_{C-Rh} \approx 12$ Hz) and 51 ppm ($J_{C-Rh} \approx 7$ Hz) corresponding to the quaternary and ═CH olefinic carbon atoms, respectively. The resonances corresponding to the carbene carbon atoms of **7** and **8** also appear shielded by about 10−15 compared to Rh−cod derivatives. In addition, the J_{C-Rh} values are reduced to about 34 Hz, reflecting the lengthening of the Rh−NHC bond.

Derivatives **7** and **8** belong to the selected club of pentacoordinated rhodium(I) complexes. In spite of the huge development of Rh−NHC organometallic chemistry, examples of this family remain scarce,[5h,13a,34] likely due to the powerful electron-donor ability of NHC ligands that favor a square-planar environment over pentacoordinated structures. A complex containing two ligands bearing an unsaturated pendant group coordinated in a chelate fashion is unprecedented for

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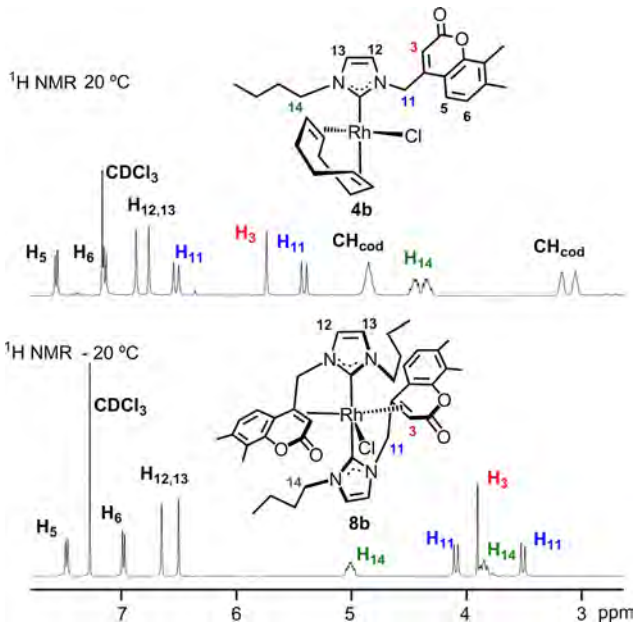


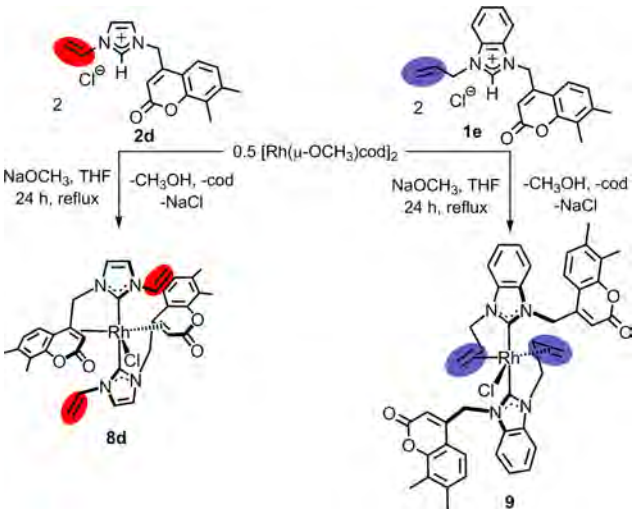
Figure 5. ^{1}H NMR spectra of **4b** (top) and **8b** (bottom).

Rh−NHC systems, although similar examples have been described in rhodium−phosphine and amine chemistry.[35] It is also worth noting that the formation of complexes **7** and **8** involves the replacement of a rather strong coordinating diolefin such as cod by two trisubstituted carbon−carbon double bonds bearing an electron-withdrawing group. Notably, only the diastereoisomer in which both coumarin coordinates by the 3*si*,4*re* enantioface is encountered for complexes **7** and **8**. Remarkably, this preferred coordination triggers that both carbonyl groups were located at the same side of the chlorido ligand, which might have interesting implications on potential catalytic activity.

With the aim of evaluating the bonding strength of the η^2-lactonic ring and studying the competitive coordination with other unsaturated functions, new precursors for NHC−coumarin ligands bearing vinyl (**2d**) and allyl (**1e**) substituents have been designed. Applying the synthetic protocol described above, the η^2-coumarin Rh^I-pentacoordinated complex RhCl(κ-C,η^2-ICou^{vin})$_2$ (**8d**) was prepared from **2d** and isolated as a white solid in moderate yield (Scheme 4). Complex **8d** is sparely soluble in chlorinated solvents and was characterized in DMSO-d_6. The presence of uncoordinated vinyl group in **8d** is clearly established from the ^{1}H NMR spectrum that shows a typical deshielded doublet of doublets at δ 8.01 ppm and two doublets at 5.37 and 4.79 ppm with J_{H-H} of 16.0 Hz (trans), 9.0 Hz (cis) and 1.6 Hz (gem). Moreover, the coumarin olefinic proton resonates at 3.64 ppm as a doublet with a small J_{H-Rh} (1.2 Hz), whereas a broad signal at δ 72.9 ppm and a doublet at 51.1 ppm (J_{C-Rh} = 6.2 Hz) are observed in the ^{13}C{^{1}H}-APT NMR spectrum, in agreement with a η^2-coumarin coordination. Certainly, this result is not surprising since a chelate vinyl−NHC framework has not been described so far, although we have observed a κ-N,η^2-vinyl coordination for 1-vinylpyrazol with a highly similar structure.[24e]

In contrast to **8d**, treatment of the doubly functionalized benzimidazolium salt **1e** with [Rh(μ-OCH$_3$)(cod)]$_2$ in the presence of sodium methoxide resulted in the formation of a η^2-allyl derivative RhCl(κ-C,η^2-BzICou^{all})$_2$ (**9**). The η^2-coordination of both allyl moieties within the NHC framework was

Scheme 4. Competitive Coordination of η^2-Coumarin Moieties in Pentacoordinated Bis-NHC Rhodium(I) Complexes



corroborated by an X-ray diffraction analysis on a single crystal of **9** (Figure 6). Similar to **7b** and **8b**, a distorted trigonal

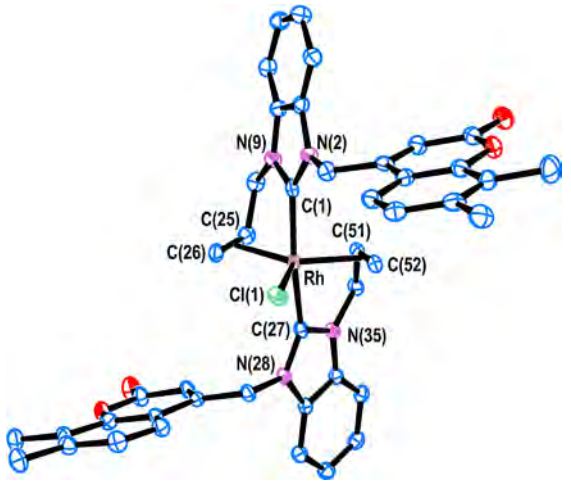


Figure 6. ORTEP view of **9**. Ellipsoids are at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−C(1) 2.010(4), Rh−C(27) 2.031(3), Rh−ct-[C(25)−C(26)] 2.0296(3), Rh−ct[C(51)−C(52)] 2.0341(3), C(25)−C(26) 1.406(5), C(51)−C(52) 1.395(5), C(1)−Rh−C(27) 168.09(13), ct[C(25)−C(26)]−Rh−ct[C(51)−C(52)] 131.17(1), Cl(1)−Rh−ct[C(25)−C(26)] 113.77(2), Cl(1)−Rh−ct[C(51)−C(52)] 115.05(2), C(1)−Rh−ct[C(25)−C(26)] 81.95(9), C(1)−Rh−ct[C(51)−C(52)] 91.30(9), C(1)−Rh−Cl(1) 96.72(9), C(27)−Rh−Cl(1) 94.92(9), ct[C(X)−C(Y)], centroid of the C(X)−C(Y) bond.

bipyramidal environment (τ 0.62) around the metal atom in **9** was observed. The axial positions are occupied by NHC carbon atoms C(1) and C(27) {Figure 6, C(1)−Rh−C(27) 168.09(13)°}, whereas allyl and chlorido ligands occupy the equatorial positions, rendering a chiral environment at the metal center. The Δ configuration is shown in Figure 6; nevertheless, as a consequence of the centrosymmetric $P\bar{1}$ space group, both configurations are present in the crystal. Also, considering the Δ enantiomer, only the diasteroisomer resulting from the coordination of rhodium to the 2*si*

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enantioface of the allyl moiety is observed. Notably similar yaw angles are observed for the two NHC ligands ($\psi_{C(1)}$ 11.0°, $\psi_{C(27)}$ 11.5°) in **9**, but rhodium−carbon bond lengths are different (Figure 6). These differences arise from the different patterns of interatomic contacts observed for the two nonequivalent NHC ligands of **9** (see the Supporting Information).

The NMR data for **9** agree with the structure described in the solid state. The C_2 symmetry results in the appearance of only one set of signals for the equivalent doubly functionalized NHC ligands. Coordination of the allyl group is supported by the observation of a set of shielded resonances at δ 3.01 ppm (d, J_{H-H} = 7.8 Hz) and 2.64 ppm (d, J_{H-H} = 11.0 Hz), corresponding to the terminal protons of the bonded olefin, which correlate each other in the $^1H-^1H$ COSY NMR spectrum and with a broad signal at 4.33 ppm ascribed to the internal proton of the double bond. Moreover, the olefinic proton of the coumarin moiety is observed at δ 5.46 ppm, within the expected range for the unbonded moiety. In addition, the two doublets at δ 59.3 ppm (J_{C-Rh} = 12.7 Hz) and 49.2 ppm (J_{C-Rh} = 5.6 Hz) in the $^{13}C\{^1H\}$-APT NMR spectrum, correlate respectively with the =CH and $=CH_2$ proton resonances of the coordinated allyl moiety in the $^1H-^{13}C$ HSQC NMR experiment. The carbene carbon atom is observed as a doublet at δ 195.6 ppm with a J_{C-Rh} coupling constant of 35.7 Hz.

DFT Calculations on the Coordination of the Olefin Moiety. In order to shed light onto the coordination behavior of coumarin-functionalized NHC ligand, a DFT computational analysis has been carried out using the B3LYP method. Full NHC-coumarin and cod, have been explicitly considered. Substitution of cod by a coumarin-functionalized NHC ligand results in a net stabilization by 6.8 kcal mol^{-1}, in accordance with the experimental results (Figure 7). As discussed previously, only the diastereoisomer in which both coumarin coordinates by the 3*si*,4*re* enantioface is encountered for complexes **7** and **8**.

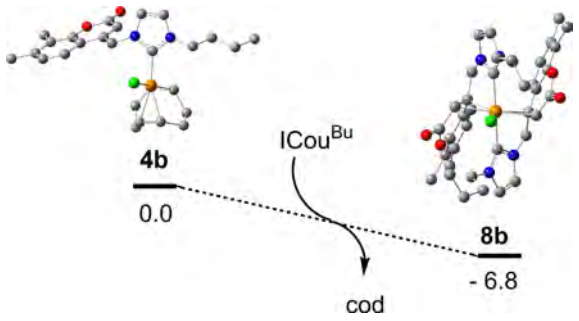

Figure 7. Energy profile for the formation of **8b** from **4b** and coumarin-functionalized NHC (Δ*G*, kcal mol^{-1}).

Putative complex **8b′**, with one coumarin coordinated by 3*si*,4*re* and the other by 3*re*,4*si*, has been calculated to be less stable than **8b** by 4.8 kcal mol^{-1} (Figure 8), probably as a consequence of a more crowded environment around the metal center. Moreover, a minimum for the isomer bearing both coumarin ligands coordinated by its 3*re*,4*si* enantioface could not be located in the potential energy surface.

Coordination of a rather electron-poor trisubstituted olefin fragment found in complexes **7** and **8** is intriguing. The allyl substituent in the coumarin−NHC framework competes for the

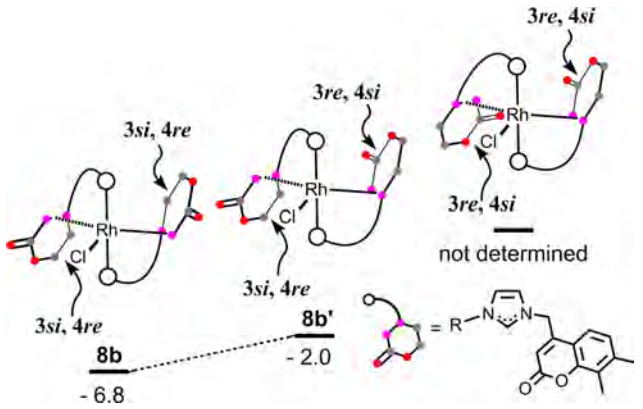

Figure 8. DFT-computed energies for coumarin coordination by different enantiofaces in RhCl(κ−C,η^2-ICou^{bu})$_2$ (Δ*G*, kcal mol^{-1}).

coordination site at the metal center resulting in the formation of **9**. DFT calculations are in agreement with this experimental result, showing that **9** is predicted to be 14.7 kcal mol^{-1} more stable than putative complex **9′** bearing the coordinated coumarin moieties (Figure 9). Derivative **9′′** with a "mixed"

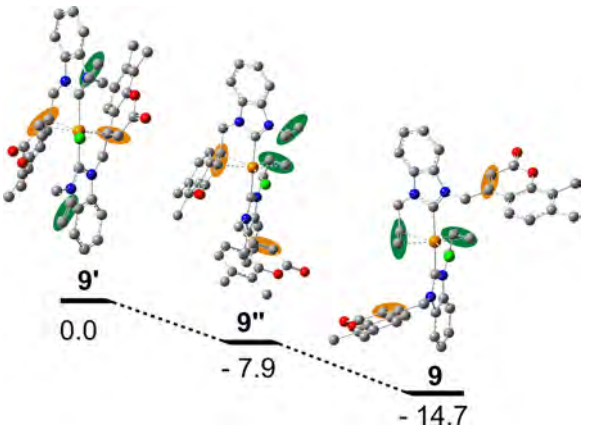

Figure 9. DFT-computed energies for coordination of coumarin versus allyl moieties (Δ*G*, kcal mol^{-1}).

set of coordinated olefin moieties is also 6.8 kcal mol^{-1} less stable than **9**. Similar to **7** and **8**, both allyl fragments within **9** coordinate by the same 2*si* enantioface. Coordination either by two 2*re* enantiofaces or by one 2*si* and one 2*re* enantionfaces results in disfavored species (see the Supporting Information).

CONCLUSION

The synthesis of coumarin-functionalized NHC−rhodium complexes has been described for the first time. Introduction of coumarin-substituted benzimidazolin and imidazolin-carbene ligands can be achieved easily from [Rh(μ-OCH$_3$)(cod)]$_2$ without the need of isolation of free carbene or the use of silver salts. The electron-donor ability of the new ligands, determined from bis-carbonyl rhodium complexes, is similar to that found for related azole carbenes, showing a slightly higher electron-donor capacity for imidazolin-carbenes. Trigonal bypiramidal pentacoordinated bis-coumarin−NHC complexes RhCl(κ-C,η^2-NHC)$_2$ have been prepared by heating the rhodium-cod derivatives in the presence of coumarin-azolium salts and sodium methoxide. It is noticeable that coordination of the carbon−carbon double bond of the lactonic ring in these

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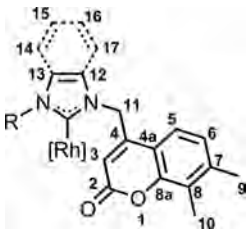
complexes takes place by the same enantioface for both NHC ligands, resulting in a particular disposition of carbonyl groups and chlorido ligand of potential interest for catalysis. Studies on doubly functionalized coumarin−NHC derivatives have shown the preferential diastereoselective coordination of an allyl wingtip over the lactonic ring. DFT calculations on the coordination of the olefin moieties in these complexes support the experimental results. An important effort is currently being done in our laboratories in order to develop the potential of these complexes for catalytic, biological, or photophysical applications.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out with rigorous exclusion of air using Schlenk tube techniques. The reagents were purchased from commercial sources and were used as received. 4-Chloromethyl-7,8-dimethyl-2*H*-chromene-2-one[28] and $[Rh(\mu\text{-}OCH_3)(cod)]_2$[36] were synthesized by the procedures described in literature. Organic solvents were dried by standard methods and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). Chemical shifts (expressed in parts per million (ppm)) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$). Coupling constants, *J*, are given in Hz. Spectral assignments were achieved by combination of $^1H-^1H$ COSY, $^{13}C\{^1H\}$-APT and $^1H-^{13}C$ HSQC/HMBC experiments. H, C, and N analysis were carried out in a PerkinElmer 2400 CHNS/O analyzer. Infrared spectra were recorded on a PerkinElmer Spectrum 100 spectrometer, using an Universal ATR Sampling Accessory (neat samples).

Chart 2. Numbering Scheme for the NHC−Coumarin Ligand.



RhCl(BzlCou^{bz})(cod) (3a). A yellow solution of $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol) in 20 mL of THF was treated with **1a** (173 mg, 0.4 mmol) and was stirred at room temperature for 16 h. After this period, the solution was filtered through Celite and concentrated to ca. 1 mL. Then, *n*-hexane was added to induce the precipitation of an orange solid which was washed with *n*-hexane (3 × 5 mL) and dried in vacuo. Yield: 190 mg (74%). Anal. Calcd for $C_{34}H_{34}N_2O_2RhCl$: C, 63.71; H, 5.35; N, 4.37. Found: C, 64.07; H, 5.44; N, 4.06. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.76 (d, J_{H-H} = 8.1, 1H, H_5), 7.4−7.0 (11H, $H_{6,11,14-17}$, H_{Ph}), 6.28 and 6.17 (both d, J_{H-H} = 15.8, 2H, NCH_2Ph), 5.73 (s, 1H, H_3), 5.70 (d, J_{H-H} = 18.5, 1H, H_{11}), 5.14 and 3.39 (both m, 4H, CH_{cod}), 2.49 (s, 3H, H_9), 2.45 (s, 3H, H_{10}), 2.4−1.7 (m, 8H, CH_{2cod}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 298 K): δ 199.1 (d, J_{C-Rh} = 51.2, Rh−C_{NHC}), 160.9 (C═O), 151.9 (s, C_{8a}), 150.9 (s, C_4), 142.9 (s, C_7), 135.8 (s, $C_{q\text{-}Ph}$), 135.0 and 134.9 (both s, $C_{12,13}$), 129.2 (s, $C_{m\text{-}Ph}$), 128.2 (s, $C_{p\text{-}Ph}$), 127.2 (s, $C_{o\text{-}Ph}$), 126.5 (s, C_6), 125.6 (s, C_8), 123.4 (s, $C_{15,16}$), 120.5 (s, C_5), 115.1 (s, C_{4a}), 111.6 and 110.2 (both s, $C_{14,17}$), 111.2 (s, C_3), 101.4 and 101.3 (both d, J_{C-Rh} = 11.8, ═CH_{cod}), 69.6 (d, J_{C-Rh} = 14.1, ═CH_{cod}), 53.2 (s, NCH_2Ph), 49.2 (s, C_{11}), 33.2, 32.7, 28.8, and 28.5 (all s, CH_{2cod}), 20.7 (C_9), 11.9 (C_{10}).

RhCl(BzlCou^{bu})(cod) (3b). The complex was prepared as described for **3a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol) and **1b** (159 mg, 0.4 mmol). Yield: 170 mg (70%). Anal. Calcd for $C_{31}H_{36}N_2O_2RhCl$: C, 61.34; H, 5.98; N, 4.62. Found: C, 61.03; H, 5.72; N, 4.37. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.73 (d, J_{H-H} = 8.1, 1H, H_5), 7.38 (d, J_{H-H} = 8.1, 1H, H_{17}), 7.30 (d, J_{H-H} = 8.1, 1H, H_6), 7.25 (m, 1H, H_{16}), 7.21 and 5.62 (both d, J_{H-H} = 18.1, 2H, H_{11}), 7.16 (m, 1H, H_{15}), 7.03 (d, J_{H-H} = 8.1, 1H, H_{14}), 5.65 (s, 1H, H_3), 5.16, 5.09, 4.44, and 3.38 (all m, 4H, CH_{cod}), 4.86 (m, 2H, $NC\underline{H}_2CH_2$), 2.48 (s, 3H, H_9), 2.43 (s, 3H, H_{10}), 2.4−1.7 (m, 10H, CH_{2cod}, $NCH_2C\underline{H}_2$), 1.62 (m, 2H, $C\underline{H}_2CH_3$), 1.13 (t, J_{H-H} = 7.4, 3H, $CH_2C\underline{H}_3$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 298 K): δ 197.8 (d, J_{C-Rh} = 51.2, Rh−C_{NHC}), 160.9 (C═O), 151.9 (s, C_{8a}), 151.0 (s, C_4), 142.9 (s, C_7), 134.9 and 134.7 (both s, $C_{12,13}$), 126.4 (s, C_6), 125.5 (s, C_8), 123.2 (s, $C_{15,16}$), 120.4 (s, C_5), 115.1 (s, C_{4a}), 111.2 (s, C_3), 110.6 (s, C_{17}), 110.3 (s, C_{14}), 101.0 and 100.9 (both d, J_{C-Rh} = 9.5, ═CH_{cod}), 69.5 and 68.8 (both d, J_{C-Rh} = 14.6, ═CH_{cod}), 49.1 (s, C_{11}), 48.9 (s, $N\underline{C}H_2CH_2$), 33.4, 32.7, 29.1, and 28.3 (all s, CH_{2cod}), 31.8 (s, $NCH_2\underline{C}H_2$), 20.6 (s, $\underline{C}H_2CH_3$), 20.5 (C_9), 13.9 (s, $CH_2\underline{C}H_3$), 11.9 (C_{10}).

RhCl(BzlCou^{tol})(cod) (3c). The complex was prepared as described for **3a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol) and **1c** (178 mg, 0.4 mmol). Yield: 200 mg (76%). Anal. Calcd for $C_{35}H_{36}N_2O_2RhCl$: C, 64.18; H, 5.54; N, 4.28. Found: C, 63.88; H, 5.13; N, 4.32. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.76 (d, J_{H-H} = 8.1, 1H, H_5), 7.3−7.1 (6H, $H_{6,11}$, H_{tol}), 7.08 (m, 4H, H_{14-17}), 6.24 and 6.12 (both d, J_{H-H} = 15.6, 2H, NCH_2Ph), 5.73 (s, 1H, H_3), 5.70 (d, J_{H-H} = 18.5, 1H, H_{11}), 5.14 and 3.39 (both m, 4H, CH_{cod}), 2.49 (s, 3H, H_9), 2.44 (s, 3H, H_{10}), 2.4−1.7 (m, 8H, CH_{2cod}), 2.35 (s, 3H, Me_{tol}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 298 K): δ 198.9 (d, J_{C-Rh} = 50.9, Rh−C_{NHC}), 160.9 (C═O), 151.9 (s, C_{8a}), 151.0 (s, C_4), 142.9 (s, C_7), 137.9 (s, $\underline{C}_qMe$), 135.0 and 134.9 (both s, $C_{12,13}$), 132.7 (s, $\underline{C}_qCH_2CN$), 129.8 and 127.1 (both s, CH_{tol}), 126.5 (s, C_6), 125.6 (s, C_8), 123.3 (s, $C_{15,16}$), 120.5 (s, C_5), 115.1 (s, C_{4a}), 111.7 and 110.2 (both s, $C_{14,17}$), 111.2 (s, C_3), 101.3 and 101.2 (both d, J_{C-Rh} = 11.3, ═CH_{cod}), 69.6 (d, J_{C-Rh} = 14.4, ═CH_{cod}), 53.1 (s, NCH_2Ph), 49.2 (s, C_{11}), 33.2, 32.6, 28.9, and 28.3 (all s, CH_{2cod}), 21.4 (s, Me_{tol}), 20.7 (C_9), 11.9 (C_{10}).

RhCl(ICou^{bz})(cod) (4a). A yellow solution of $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol) in 20 mL of THF was treated with **2a** (152 mg, 0.4 mmol) and stirred at room temperature for 4 h. After this period, the mixture was cooled into an ice bath, filtered through Celite, and concentrated to ca. 1 mL. Then, *n*-hexane was added to induce the precipitation of a yellow solid which was washed with *n*-hexane (3 × 5 mL) and dried in vacuo. Yield: 190 mg (80%). Anal. Calcd for $C_{30}H_{32}N_2O_2RhCl$: C, 60.97; H, 5.46; N, 4.74. Found: C, 60.88; H, 5.30; N, 4.91. ^1H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.68 (d, J_{H-H} = 8.1, 1H, H_5), 7.4−7.3 (5H, H_{Ph}), 7.22 (d, J_{H-H} = 8.1, 1H, H_6), 6.85 and 6.77 (both d, J_{H-H} = 2.0, 2H, $H_{12,13}$), 6.52 and 5.67 (both d, J_{H-H} = 17.2, 2H, H_{11}), 5.97 (s, 1H, H_3), 5.91 and 5.76 (both d, J_{H-H} = 14.9, 2H, NCH_2Ph), 5.07, 3.35, and 3.28 (all m, 4H, CH_{cod}), 2.43 (s, 3H, H_9), 2.40 (s, 3H, H_{10}), 2.4−1.7 (m, 8H, CH_{2cod}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 298 K): δ 185.6 (d, J_{C-Rh} = 52.1, Rh−C_{NHC}), 160.9 (C═O), 151.9 (s, C_{8a}), 151.8 (s, C_4), 142.8 (s, C_7), 136.1 (s, $C_{q\text{-}Ph}$), 129.1 (s, $C_{m\text{-}Ph}$), 128.5 (s, $C_{p\text{-}Ph}$), 128.3 (s, $C_{o\text{-}Ph}$), 126.5 (s, C_6), 125.3 (s, C_8), 121.8 and 121.6 (both s, $C_{12,13}$), 121.0 (s, C_5), 115.1 (s, C_{4a}), 112.2 (s, C_3), 99.8 and 99.7 (both d, J_{C-Rh} = 7.0, ═CH_{cod}), 69.0 and 68.7 (both d, J_{C-Rh} = 14.3, ═CH_{cod}), 54.9 (s, NCH_2Ph), 51.3 (s, C_{11}), 33.1, 32.9, 28.8, and 28.7 (all s, CH_{2cod}), 20.6 (C_9), 11.8 (C_{10}).

RhCl(ICou^{bu})(cod) (4b). The complex was prepared as described for **4a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol) and **2b** (139 mg, 0.4 mmol). Yield: 140 mg (63%). Anal. Calcd for $C_{27}H_{34}N_2O_2RhCl$: C, 58.23; H, 6.15; N, 5.03. Found: C, 57.88; H, 6.43; N, 5.41. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.66 (d, J_{H-H} = 8.1, 1H, H_5), 7.22 (d, J_{H-H} = 8.1, 1H, H_6), 6.96 and 6.86 (both d, J_{H-H} = 2.0, 2H, $H_{12,13}$), 6.57 and 5.60 (both d, J_{H-H} = 17.4, 2H, H_{11}), 5.90 (s, 1H, H_3), 5.03, 3.32, and 3.27 (all m, 4H, CH_{cod}), 4.55 (m, 2H, $NC\underline{H}_2CH_2$), 2.43 (s, 3H, H_9), 2.40 (s, 3H, H_{10}), 2.4−1.7 (m, 10H, CH_{2cod}, $NCH_2C\underline{H}_2$), 1.52 (m, 2H, $C\underline{H}_2CH_3$), 1.03 (t, J_{H-H} = 7.4, 3H, $CH_2C\underline{H}_3$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 298 K): δ 183.8 (d, J_{C-Rh} = 51.1, Rh−C_{NHC}), 161.3 (C═O), 152.5 (s, C_{8a}), 151.4 (s, C_4), 142.9 (s, C_7), 126.5 (s, C_6), 125.2 (s, C_8), 121.5 and 121.2 (both s, $C_{12,13}$), 120.7 (s, C_5), 114.7 (s, C_{4a}), 111.3 (s, C_3), 99.1 and 99.2 (both d, J_{C-Rh} = 6.5, = CH_{cod}), 68.7 and 68.5 (both d, J_{C-Rh} = 14.3, ═

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CH_{cod}), 51.0 (s, C_{11}), 50.7 (s, N$\underline{C}H_2CH_2$), 33.2, 32.7, 28.9, and 28.6 (all s, CH_{2cod}), 33.0 (s, $NCH_2\underline{C}H_2$), 20.8 (C_9), 20.1 (s, $\underline{C}H_2CH_3$), 14.0 (s, $CH_2\underline{C}H_3$), 11.9 (C_{10}).

RhCl(ICou^{vin})(cod) (4d). The complex was prepared as described for **4a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol) and **2d** (127 mg, 0.4 mmol). Yield: 110 mg (52%). Satisfactory elemental analysis could not be obtained. HRMS (ESI) *m/z* Calcd for $RhC_{25}H_{28}N_2O_2$ ($M - Cl^-$): 491.1200. Found: 491.1197. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.15 (dd, J_{H-H} = 15.8, 8.7, 1H, NC$\underline{H}$=CH_2), 7.66 (d, J_{H-H} = 8.3, 1H, H_5), 7.30 (d, J_{H-H} = 2.0, 1H, H_{13}), 7.23 (d, J_{H-H} = 8.3, 1H, H_6), 6.92 (d, J_{H-H} = 2.0, 1H, H_{12}), 6.57 and 5.63 (both d, J_{H-H} = 17.4, 2H, H_{11}), 5.89 (s, 1H, H_3), 5.38 (dd, J_{H-H} = 15.8, 1.8, 1H, NCH=C$\underline{H}_2$), 5.12 (dd, J_{H-H} = 8.7, 1.8, 1H, NCH=C$\underline{H}_2$), 5.02, 3.38, and 3.20 (all m, 4H, CH_{cod}), 2.42 (s, 3H, H_9), 2.38 (s, 3H, H_{10}), 2.4–1.7 (m, 8H, CH_{2cod}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 298 K): δ 187.6 (d, J_{C-Rh} = 51.5, Rh–C_{NHC}), 161.1 (C=O), 151.7 (s, C_{8a}), 151.4 (s, C_4), 143.0 (s, C_7), 133.7 (s, N$\underline{C}$H=CH_2), 126.6 (s, C_6), 125.2 (s, C_8), 121.8 (s, C_{12}), 120.8 (s, C_5), 117.9 (s, C_{13}), 114.6 (s, C_{4a}), 111.6 (s, C_3), 102.4 (s, NCH=$\underline{C}H_2$), 100.2 and 100.0 (both d, J_{C-Rh} = 6.8, =CH_{cod}), 70.1 and 68.8 (both d, J_{C-Rh} = 14.4, =CH_{cod}), 51.5 (s, C_{11}), 33.00, 32.7, 28.8, and 28.6 (all s, CH_{2cod}), 20.8 (C_9), 11.9 (C_{10}).

RhCl(BzlCou^{bz})(CO)$_2$ (5a). Carbon monoxide was bubbled through an orange solution of **3a** (100 mg, 0.16 mmol) in 20 mL of THF at room temperature for 1 h. Then, the solution was filtered through Celite and the filtrate concentrated to ca. 1 mL. Addition of *n*-hexane induced the precipitation of an orange solid which was washed with *n*-hexane (3 × 5 mL) and dried in vacuo. Yield: 70 mg (73%). Anal. Calcd for $C_{28}H_{22}N_2O_4RhCl$: C, 57.11; H, 3.77; N, 4.76. Found: C, 56.83; H, 3.56; N, 4.68. IR (cm^{-1}): 2083 $\nu(CO)_{sym}$, 2010 $\nu(CO)_{asym}$, 1735 $\nu(C{=}O)_{coumarin}$. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.58 (d, J_{H-H} = 8.0, 1H, H_5), 7.4–7.2 (10H, $H_{6,14-17}$, H_{Ph}), 6.54 and 5.73 (both d, J_{H-H} = 18.0, 2H, H_{11}), 5.95 (m, 2H, NCH_2Ph), 5.62 (s, 1H, H_3), 2.46 (s, 3H, H_9), 2.43 (s, 3H, H_{10}). $^{13}C\{^1H\}$-APT NMR (125.6 MHz, $CDCl_3$, 298 K): δ 188.4 (d, J_{C-Rh} = 43.6, Rh–C_{NHC}), 184.7 (d, J_{C-Rh} = 53.7, Rh–$CO_{trans\text{-}NHC}$), 181.6 (d, J_{C-Rh} = 73.8, Rh–$CO_{cis\text{-}NHC}$), 160.5 (C=O), 152.0 (s, C_{8a}), 148.9 (s, C_4), 142.9 (s, C_7), 134.6 (s, $C_{q\text{-}Ph}$), 134.5 and 134.4 (both s, $C_{12,13}$), 129.3 (s, $C_{m\text{-}Ph}$), 128.7 (s, $C_{p\text{-}Ph}$), 127.6 (s, $C_{o\text{-}Ph}$), 126.4 (s, C_6), 125.7 (s, C_8), 124.7 and 124.6 (both s, $C_{15,16}$), 120.3 (s, C_5), 115.0 (s, C_{4a}), 112.4 and 111.0 (both s, $C_{14,17}$), 111.6 (s, C_3), 53.5 (s, NCH_2Ph), 48.9 (s, C_{11}), 20.6 (C_9), 11.9 (C_{10}).

RhCl(BzlCou^{bu})(CO)$_2$ (5b). The complex was prepared as described for **5a** starting from **3b** (100 mg, 0.18 mmol). Yield: 80 mg (82%). Anal. Calcd for $C_{25}H_{24}N_2O_4RhCl$: C, 54.12; H, 4.36; N, 5.05. Found: C, 54.10; H, 4.11; N, 5.39. IR (cm^{-1}): 2076 $\nu(CO)_{sym}$, 1995 $\nu(CO)_{asym}$, 1737 ν $(C{=}O)_{coumarin}$. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.53 (m, 2H, $H_{5,17}$), 7.41 (m, 1H, H_{16}), 7.32 (m, 1H, H_{15}), 7.25 (d, J_{H-H} = 8.0, 1H, H_6), 7.21 (d, J_{H-H} = 8.1, 1H, H_{14}), 6.49 and 5.67 (both d, J_{H-H} = 17.9, 2H, H_{11}), 5.54 (s, 1H, H_3), 4.76 and 4.57 (both m, 2H, $NC\underline{H}_2CH_2$), 2.46 (s, 3H, H_9), 2.41 (s, 3H, H_{10}), 2.06 (m, 2H, $NCH_2C\underline{H}_2$), 1.57 (m, 2H, $C\underline{H}_2CH_3$), 1.06 (t, J_{H-H} = 7.3, 3H, $CH_2C\underline{H}_3$). $^{13}C\{^1H\}$-APT NMR (75.1 MHz, $CDCl_3$, 298 K): δ 187.3 (d, J_{C-Rh} = 43.0, Rh–C_{NHC}), 184.9 (d, J_{C-Rh} = 54.0, Rh–$CO_{trans\text{-}NHC}$), 182.1 (d, J_{C-Rh} = 73.3, Rh–$CO_{cis\text{-}NHC}$), 160.5 (C=O), 152.0 (s, C_{8a}), 149.1 (s, C_4), 142.7 (s, C_7), 134.4 (s, C_{12}), 134.3 (s, C_{13}), 126.3 (s, C_6), 125.7 (s, C_8), 124.5 and 124.4 (both s, $C_{15,16}$), 120.2 (s, C_5), 115.0 (s, C_{4a}), 111.6 (s, C_{17}), 111.5 (s, C_3), 111.0 (s, C_{14}), 49.2 (s, C_{11}), 48.7 (s, N$\underline{C}H_2CH_2$), 31.9 (s, $NCH_2\underline{C}H_2$), 20.6 (C_9), 20.4 (s, $\underline{C}H_2CH_3$), 13.9 (s, $CH_2\underline{C}H_3$), 11.9 (C_{10}).

RhCl(BzlCou^{tol})(CO)$_2$ (5c). The complex was prepared as described for **5a** starting from **3c** (100 mg, 0.15 mmol). Yield: 75 mg (83%). Anal. Calcd for $C_{29}H_{24}N_2O_4RhCl$: C, 57.78; H, 4.01; N, 4.65. Found: C, 57.61; H, 4.18; N, 4.47. IR (cm^{-1}): 2081 $\nu(CO)_{sym}$, 2003 $\nu(CO)_{asym}$, 1735 $\nu(C{=}O)_{coumarin}$. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.56 (d, J_{H-H} = 8.2, 1H, H_5), 7.4–7.2 (9H, $H_{6,14-17}$, H_{Ph}), 6.54 and 5.73 (both d, J_{H-H} = 18.4, 2H, H_{11}), 5.90 (m, 2H, NCH_2Ph), 5.54 (s, 1H, H_3), 2.47 (s, 3H, H_9), 2.41 (s, 3H, H_{10}). 2.34 (s, 3H, Me_{tol}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 298 K): δ 187.3 (d, J_{C-Rh} = 43.5, Rh–C_{NHC}), 184.6 (d, J_{C-Rh} = 54.4, Rh–$CO_{trans\text{-}NHC}$), 181.5 (d, J_{C-Rh} = 74.3, Rh–$CO_{cis\text{-}NHC}$), 160.9 (C=O), 151.6 (s, C_{8a}), 149.2 (s, C_4), 143.0 (s, C_7), 138.4 (s, $\underline{C}_qMe$), 134.2 and 134.0 (both s, $C_{12,13}$), 131.3 (s, $\underline{C}_qCH_2CN$), 129.9 and 127.2 (both s, CH_{tol}), 126.4 (s, C_6), 125.6 (s, C_8), 124.6 (s, $C_{15,16}$), 120.2 (s, C_5), 114.7 (s, C_{4a}), 112.3 and 110.9 (both s, $C_{14,17}$), 110.8 (s, C_3), 53.1 (s, NCH_2Ph), 48.5 (s, C_{11}), 21.4 (s, Me_{tol}), 20.8 (C_9), 11.8 (C_{10}).

RhCl(ICou^{bz})(CO)$_2$ (6a). The complex was prepared as described for **5a** starting from **4a** (100 mg, 0.17 mmol). Yield: 70 mg (71%). Anal. Calcd for $C_{24}H_{20}N_2O_4RhCl$: C, 53.50; H, 3.74; N, 5.20. Found: C, 53.12; H, 4.08; N, 5.19. IR (cm^{-1}): 2075 $\nu(CO)_{sym}$, 1994 $\nu(CO)_{asym}$, 1724 ν $(C{=}O)_{coumarin}$. ^{1}H NMR (400 MHz, CD_2Cl_2, 233 K): δ 7.46 (d, J_{H-H} = 7.9, 1H, H_5), 7.4–7.3 (m, 5H, H_{Ph}), 7.18 (d, J_{H-H} = 7.9, 1H, H_6), 7.01 and 7.03 (both d, J_{H-H} = 2.0, 2H, $H_{12,13}$), 5.97 and 5.52 (both d, J_{H-H} = 17.8, 2H, H_{11}), 5.70 (s, 1H, H_3), 5.64 and 5.46 (both d, J_{H-H} = 15.3, 2H, NCH_2Ph), 2.39 (s, 3H, H_9), 2.34 (s, 3H, H_{10}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, CD_2Cl_2, 298 K): δ 186.0 (d, J_{C-Rh} = 54.4, Rh–$CO_{trans\text{-}NHC}$), 182.8 (d, J_{C-Rh} = 73.5, Rh–$CO_{cis\text{-}NHC}$), 177.4 (d, J_{C-Rh} = 44.1, Rh–C_{NHC}), 160.7 (C=O), 152.3 (s, C_{8a}), 150.1 (s, C_4), 143.2 (s, C_7), 136.0 (s, $C_{q\text{-}Ph}$), 129.6 (s, $C_{m\text{-}Ph}$), 129.2 (s, $C_{p\text{-}Ph}$), 128.9 (s, $C_{o\text{-}Ph}$), 126.5 (s, C_6), 125.7 (s, C_8), 123.2 and 123.1 (both s, $C_{12,13}$), 121.1 (s, C_5), 115.5 (s, C_{4a}), 113.6 (s, C_3), 55.8 (s, NCH_2Ph), 51.2 (s, C_{11}), 20.7 (C_9), 12.0 (C_{10}).

RhCl(κ-C,η^2-BzlCou^{bz})$_2$ (7a). A yellow solution of $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol) in 20 mL of THF was treated with **1a** (356 mg, 0.8 mmol) and $NaOCH_3$ (22 mg, 0.4 mmol) and heated at 70 °C for 24 h. After this period, the mixture was cooled to 0 °C which resulted in the formation of a precipitate. The mother liquor was removed and the solid washed with cold THF (2 × 5 mL). Then, the solid was dissolved in 20 mL of CH_2Cl_2 and filtered through Celite. The solution was concentrated to ca. 1 mL, and *n*-hexane was added to induce the precipitation of a white solid which was washed with *n*-hexane (3 × 5 mL) and dried in vacuo. Yield: 140 mg (38%). Anal. Calcd for $C_{52}H_{44}N_4O_4RhCl$: C, 67.35; H, 4.78; N, 6.04. Found: C, 67.28; H, 4.75; N, 6.13. ^{1}H NMR (400 MHz, $CDCl_3$, 253 K) δ 7.73 (d, J_{H-H} = 7.8, 2H, H_5), 7.5–6.8 (20H, $H_{6,14-17}$, H_{Ph}), 7.27 and 5.28 (both d, J_{H-H} = 15.0, 4H, NCH_2Ph), 4.42 (s, 2H, H_3), 4.30 and 3.81 (both d, J_{H-H} = 13.2, 4H, H_{11}), 1.82 (s, 6H, H_9), 1.40 (s, 6H, H_{10}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 253 K): δ 184.7 (d, J_{C-Rh} = 33.8, Rh–C_{NHC}), 168.9 (C=O), 146.8 (s, C_{8a}), 138.6 (s, C_7), 136.4 (s, $C_{q\text{-}Ph}$), 134.3 and 132.0 (both s, $C_{12,13}$), 128.5 and 128.4 (both s, $C_{o\text{-}m\text{-}Ph}$), 127.6 (s, $C_{p\text{-}Ph}$), 124.5 (s, C_8), 124.3 (s, C_6), 123.2 and 123.1 (both s, $C_{15,16}$), 120.6 (s, C_{4a}), 119.1 (s, C_5), 112.3 and 109.4 (both s, $C_{14,17}$), 73.8 (d, J_{C-Rh} = 11.9, C_4), 52.0 (d, J_{C-Rh} = 7.6, C_3), 51.9 (s, NCH_2Ph), 46.6 (s, C_{11}), 20.1 (C_9), 11.0 (C_{10}).

RhCl(κ-C,η^2-BzlCou^{bu})$_2$ (7b). The complex was prepared as described for **7a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol), **1b** (317 mg, 0.8 mmol), and $NaOCH_3$ (22 mg, 0.4 mmol). Yield 160 mg (47%). Anal. Calcd for $C_{46}H_{48}N_4O_4RhCl$: C, 64.30; H, 5.63; N, 6.52. Found: C, 64.18; H, 5.32; N, 6.37. ^{1}H NMR (400 MHz, $CDCl_3$, 253 K): δ 7.73 (d, J_{H-H} = 8.3, 2H, H_5), 7.37 (d, J_{H-H} = 8.5, 2H, H_{17}), 7.25 (m, 2H, H_{16}), 7.16 (m, 2H, H_{15}), 6.89 (d, J_{H-H} = 8.3, 2H, H_6), 7.86 (d, J_{H-H} = 8.5, 2H, H_{14}), 5.41 and 4.09 (both m, 4H, $NC\underline{H}_2CH_2$), 4.28 and 3.75 (both d, J_{H-H} = 12.7, 4H, H_{11}), 4.16 (s, 2H, H_3), 1.95 (m, 4H, $NCH_2C\underline{H}_2$), 1.72 (s, 6H, H_9), 1.57 (m, 4H, $NCH_2C\underline{H}_2$), 1.32 (s, 6H, H_{10}), 1.03 (t, J_{H-H} = 7.2, 6H, $CH_2C\underline{H}_3$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 253 K): δ 184.5 (d, J_{C-Rh} = 34.7, Rh–C_{NHC}), 168.9 (C=O), 146.5 (s, C_{8a}), 138.1 (s, C_7), 134.0 (s, C_{13}), 131.8 (s, C_{12}), 124.4 (s, C_8), 124.1 (s, C_6), 123.0 (s, C_{15}), 123.1 (s, C_{16}), 120.7 (s, C_{4a}), 118.8 (s, C_5), 111.4 (s, C_{17}), 109.5 (s, C_{14}), 73.0 (d, J_{C-Rh} = 11.7, C_4), 51.6 (d, J_{C-Rh} = 7.5, C_3), 47.4 (s, N$\underline{C}H_2CH_2$), 46.6 (s, C_{11}), 32.1 (s, $NCH_2\underline{C}H_2$), 20.1 (s, $\underline{C}H_2CH_3$), 20.0 (C_9), 14.1 (s, $CH_2\underline{C}H_3$), 11.0 (C_{10}).

RhCl(κ-C,η^2-BzlCou^{tol})$_2$ (7c). The complex was prepared as described for **7a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol), **1c** (356 mg, 0.8 mmol), and $NaOCH_3$ (22 mg, 0.4 mmol). Yield: 170 mg (45%). Anal. Calcd for $C_{54}H_{48}N_4O_4RhCl$: C, 67.89; H, 5.06; N, 5.86. Found: C, 67.52; H, 4.97; N, 5.75. ^{1}H NMR (400 MHz, $CDCl_3$, 253 K): δ 7.73 (d, J_{H-H} = 8.0, 2H, H_5), 7.5–6.8 (18H, $H_{6,14-17}$, H_{Ph}), 7.15 and 5.21 (both d, J_{H-H} = 14.7, 4H, NCH_2Ph), 4.40 (s, 2H, H_3), 4.30 and 3.83 (both d, J_{H-H} = 13.2, 4H, H_{11}), 2.24 (s, 6H, Me_{tol}),

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1.82 (s, 6H, H_9), 1.41 (s, 6H, H_{10}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 253 K): δ 184.7 (d, J_{C-Rh} = 34.3, Rh−C_{NHC}), 168.7 (C═O), 146.7 (s, C_{8a}), 138.5 (s, C_7), 137.1 (s, $\underline{C}_qMe$), 134.2 and 132.1 (both s, $C_{12,13}$), 133.5 (s, $\underline{C}_qCH_2CN$), 129.1 and 128.4 (both s, CH_{tol}), 124.5 (s, C_8), 124.2 (s, C_6), 123.1 and 123.0 (both s, $C_{15,16}$), 120.7 (s, C_{4a}), 119.1 (s, C_5), 112.4 and 109.3 (both s, $C_{14,17}$), 73.5 (d, J_{C-Rh} = 11.6, C_4), 52.0 (d, J_{C-Rh}= 7.2, C_3), 51.7 (s, NCH_2Ph), 46.6 (s, C_{11}), 21.4 (s, Me_{tol}), 20.0 (C_9), 10.9 (C_{10}).

RhCl(κ-C,η²-ICou^{bz})$_2$ (8a). The complex was prepared as described for **7a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol), **2a** (305 mg, 0.8 mmol), and $NaOCH_3$ (22 mg, 0.4 mmol). Yield: 210 mg (63%). Satisfactory elemental analysis could not be obtained. HRMS (ESI) *m/z* Calcd for $RhC_{44}H_{40}N_4O_4$ (M − Cl^-): 791.2099. Found: 791.2082. ^1H NMR (400 MHz, DMSO-d_6, 363 K): δ 7.64 (d, J_{H-H} = 8.0, 2H, H_5), 7.50 (d, J_{H-H} = 7.0, 4H, $H_{o\text{-}Ph}$), 7.34 (vt, *N* = 14.7, 4H, $H_{m\text{-}Ph}$), 7.29 (t, J_{H-H} = 7.0, 2H, $H_{p\text{-}Ph}$), 7.12 (d, J_{H-H} = 8.0, 2H, H_6), 6.83 and 6.70 (both d, J_{H-H} = 2.0, 4H, $H_{12,13}$), 6.48 and 4.89 (both d, J_{H-H} = 14.3, 4H, NCH_2Ph), 4.10 and 3.81 (both d, J_{H-H} = 15.1, 4H, H_{11}), 3.84 (s, 2H, H_3), 2.23 (s, 6H, H_9), 2.05 (s, 6H, H_{10}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, DMSO-d_6, 363 K): δ 168.0 (C═O), 147.7 (s, C_{8a}), 138.2 (s, C_7), 137.6 (s, $C_{q\text{-}Ph}$), 129.5 and 128.6 (both s, $C_{o\text{-}m\text{-}Ph}$), 128.0 (s, $C_{p\text{-}Ph}$), 124.7 (s, C_6), 123.9 (s, C_8), 122.0 and 119.6 (both s, $C_{12,13}$), 121.6 (s, C_{4a}), 120.2 (s, C_5), 112.3 and 109.4 (both s, $C_{14,17}$), 52.6 (s, NCH_2Ph), 49.6 (s, C_{11}), 19.8 (C_9), 11.4 (C_{10}).

RhCl(κ-C,η²-ICou^{bu})$_2$ (8b). The complex was prepared as described for **7a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol), **2b** (277 mg, 0.8 mmol), and $NaOCH_3$ (22 mg, 0.4 mmol). Yield: 200 mg (66%). Anal. Calcd for $C_{38}H_{44}N_4O_4RhCl$: C, 60.12; H, 5.84; N, 7.38. Found: C, 59.70; H, 5.83; N, 7.10. ^1H NMR (400 MHz, $CDCl_3$, 253 K): δ 7.46 (d, J_{H-H} = 8.0, 1H, H_5), 6.97 (d, J_{H-H} = 8.0, 1H, H_6), 6.63 and 6.49 (both d, J_{H-H} = 1.8, 3H, $H_{12,13}$), 5.03 and 3.85 (both m, 2H, $NC\underline{H}_2CH_2$), 4.10 and 3.52 (both d, J_{H-H} = 13.8, 2H, H_{11}), 3.91 (s, 1H, H_3), 2.18 (s, 3H, H_9), 1.96 (s, 3H, H_{10}), 1.70 (m, 2H, $NCH_2C\underline{H}_2$), 1.44 (m, 2H, $NCH_2C\underline{H}_2$), 0.95 (t, J_{H-H} = 7.2, 3H, $CH_2C\underline{H}_3$). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 253 K): δ 172.4 (d, J_{C-Rh} = 34.7, Rh−C_{NHC}), 169.6 (C═O), 147.1 (s, C_{8a}), 137.7 (s, C_7), 124.7 (s, C_8), 124.3 (s, C_6), 121.3 (s, C_{4a}), 121.0 and 117.8 (both s, $C_{12,13}$), 118.8 (s, C_5), 71.9 (d, J_{C-Rh} = 12.7, C_4), 50.9 (d, J_{C-Rh} = 7.7, C_3), 49.3 (s, $N\underline{C}H_2CH_2$), 49.0 (s, C_{11}), 33.6 (s, $NCH_2\underline{C}H_2$), 20.5 (C_9), 19.9 (s, $\underline{C}H_2CH_3$), 14.3 (s, $CH_2\underline{C}H_3$), 11.7 (C_{10}).

RhCl(κ-C,η²-ICou^{vin})$_2$ (8d). The complex was prepared as described for **7a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol), **2d** (254 mg, 0.8 mmol), and $NaOCH_3$ (22 mg, 0.4 mmol). Yield: 160 mg (57%). Anal. Calcd for $C_{34}H_{32}N_4O_4RhCl$: C, 58.42; H, 4.61; N, 8.02. Found: C, 58.25; H, 4.49; N, 7.84. ^1H NMR (300 MHz, DMSO-d_6, 298 K): δ 8.01 (dd, J_{H-H} = 16.0, 9.0, 2H, $NC\underline{H}$=CH_2), 7.62 (d, J_{H-H} = 8.0, 2H, H_5), 7.57 and 6.98 (both d, J_{H-H} = 2.1, 4H, $H_{12,13}$), 7.08 (d, J_{H-H} = 8.0, 2H, H_6), 5.37 (dd, J_{H-H} = 16.0, 1.6, 2H, NCH═$C\underline{H}_2$), 4.79 (dd, J_{H-H} = 9.0, 1.6, 2H, NCH═$C\underline{H}_2$), 4.02 and 3.78 (both d, J_{H-H} = 14.1, 4H, H_{11}), 3.64 (d, J_{H-Rh} = 1.2, 2H, H_3), 2.18 (s, 6H, H_9), 1.89 (s, 6H, H_{10}). $^{13}C\{^1H\}$-APT NMR (75.1 MHz, DMSO-d_6, 298 K): δ 171.1 (d, J_{C-Rh} = 35.5, Rh−C_{NHC}), 166.7 (C═O), 146.6 (s, C_{8a}), 136.8 (s, C_7), 134.1 (s, $N\underline{C}H$=CH_2), 124.0 (s, C_6), 123.3 (s, C_8), 120.7 (s, C_5), 119.4 and 117.0 (both s, $C_{12,13}$), 117.0 (s, C_{4a}), 99.2 (s, NCH═$\underline{C}H_2$), 72.9 (br, C_4), 51.1 (d, J_{C-Rh} = 6.2, C_3), 48.7 (s, C_{11}), 19.3 (C_9), 10.5 (C_{10}).

RhCl(κ-C,η²-BzlCou^{all})$_2$ (9). The complex was prepared as described for **7a** starting from $[Rh(\mu\text{-}OCH_3)(cod)]_2$ (106 mg, 0.2 mmol), **1e** (305 mg, 0.8 mmol), and $NaOCH_3$ (22 mg, 0.4 mmol). Yield: 120 mg (32%). Satisfactory elemental analysis could not be obtained. HRMS (ESI) *m/z* Calcd for $RhC_{40}H_{40}N_4O_4$ (M − Cl^-): 791.2099. Found: 791.210. ^1H NMR (400 MHz, $CDCl_3$, 253 K): δ 7.71 (d, J_{H-H} = 8.2, 2H, H_5), 7.63 and 5.37 (both d, J_{H-H} = 18.4, 4H, H_{11}), 7.4−7.0 (10H, $H_{6,14-17}$), 5.46 (s, 2H, H_3), 4.33 (m, 6H, NCH_2CH═), 3.01 (d, J_{H-H} = 7.8, 2H, NCH_2CH═$C\underline{H}_2$), 2.64 (d, J_{H-H} = 11.0, 2H, NCH_2CH═$C\underline{H}_2$), 2.44 (s, 6H, H_9), 2.41 (s, 6H, H_{10}). $^{13}C\{^1H\}$-APT NMR (100.4 MHz, $CDCl_3$, 253 K): δ 195.6 (d, J_{C-Rh} = 35.7, Rh−C_{NHC}), 161.5 (C═O), 152.8 (s, C_4), 151.3 (s, C_{8a}), 142.8 (s, C_7), 134.7 and 133.0 (both s, $C_{12,13}$), 126.6 (s, C_6), 125.0 (s, C_8), 123.6 and 123.0 (both s, $C_{15,16}$), 121.0 (s, C_5), 115.0 (s, C_{4a}), 110.5 and 110.4 (both s, $C_{14,17}$), 109.6 (s, C_3), 59.3 (d, J_{C-Rh} = 12.7, $NCH_2\underline{C}H$═), 50.4 (s, $N\underline{C}H_2CH$═), 49.2 (d, J_{C-Rh} = 5.6, NCH_2CH═$\underline{C}H_2$), 47.2 (s, C_{11}), 20.7 (C_9), 11.8 (C_{10}).

Crystal Structure Determination. Single crystals for the X-ray diffraction studies were grown by slow evaporation of $CDCl_3$ (**3c**, **4a**, and **8b**) or CH_2Cl_2 (**7b** and **9**) solutions. X-ray diffraction data were collected at 100(2) K on a Bruker APEX SMART CCD diffractometer with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å) using narrow ω rotations(0.3−0.6°). Intensities were integrated and corrected for absorption effects with SAINT+[37] and SADABS[38] programs, both included in APEX2 package. The structures were solved by the Patterson method with SHELXS-97[39] and refined by full matrix least-squares on F^2 with SHELXL-2014,[40] under WinGX.[41]

Crystal Data for ***3c****.* $C_{35}H_{36}ClN_2O_2Rh{\cdot}CHCl_3$; *M* = 774.38 g·mol^{-1}; triclinic, $P\bar{1}$; *a* = 12.3496(7) Å, *b* = 12.3541(7) Å, *c* = 13.3569(8) Å, α = 106.6520(10)°, β = 109.7080(10)°, γ = 107.9120(10)°, *V* = 1643.12(17) Å^3; *Z* = 2; D_c = 1.565 g Cm^{-3}; μ = 0.882 mm^{-1}; *F*(000) = 792; yellow prism, 0.300 × 0.150 × 0.130 mm; ϑ_{min} = 1.799°, ϑ_{max} = 28.553°; limiting indexes $-15 \le h \le 16$, $-16 \le k \le 15$, $-17 \le l \le 17$; reflections collected/unique 19 234/7636 (R_{int} = 0.0236); data/restraints/parameters 7636/0/409; GOF 1.059; R_1 = 0.0303 [$I > 2\sigma(I)$], 0.0367 (all data); wR^2 = 0. 0733 [$I > 2\sigma(I)$], 0. 0779 (all data); largest diff. peak/hole 0.554 and −0.402 e·Å^{-3}. CCDC deposit number: 1569679.

Crystal Data for ***4a****.* $C_{30}H_{32}ClN_2O_2Rh{\cdot}2CHCl_3$; *M* = 829.67 g·mol^{-1}; triclinic, $P\bar{1}$; *a* = 11.3385(6) Å, *b* = 11.9379(6) Å, *c* = 14.9149(11) Å, α = 98.3830(10)°, β = 105.5410(10)°, γ = 115.1550(10)°, *V* = 1680.71(18) Å^3, *Z* = 2; D_c = 1.639 g Cm^{-3}; μ = 1.098 mm^{-1}; *F*(000) = 840; yellow prism, 0.220 × 0.200 × 0.120 mm; ϑ_{min} = 1.974°, ϑ_{max} = 27.103°; limiting indexes $-14 \le h \le 14$, $-15 \le k \le 15$, $-19 \le l \le 19$; reflections collected/unique 27 191/7387 (R_{int} = 0.0245); data/restraints/parameters 7387/0/399; GOF 1.028; R_1 = 0.0276 [$I > 2\sigma(I)$], 0.0310(all data); wR^2 = 0.0659 [$I > 2\sigma(I)$], 0.0683 (all data); largest diff. peak/hole 1.259/−0.718 e·Å^{-3}. CCDC deposit number: 1569680.

Crystal Data for ***7b****.* $C_{46}H_{48}ClN_4O_4Rh{\cdot}CH_2Cl_2$; *M* = 944.17 g·mol^{-1}; monoclinic, $P2_1/n$; *a* = 12.5553(9) Å, *b* = 12.9395(9) Å, *c* = 26.0875(18) Å, β = 99.0930(10)°, *V* = 4184.9(5) Å^3; *Z* = 4; D_c = 1.499 g Cm^{-3}; μ = 0.650 mm^{-1}; *F*(000) = 1952; yellow prism, 0.210 × 0.160 × 0.050 mm; ϑ_{min} = 2.231°, ϑ_{max} = 28.674°; limiting indexes $-16 \le h \le 16$, $-15 \le k \le 16$, $-35 \le l \le 34$; reflections collected/unique 35 830/9975 (R_{int} = 0.0614); data/restraints/parameters 9975/0/538; GOF 1.146; R_1 = 0.0521 [$I > 2\sigma(I)$], 0.0773 (all data); wR^2 = 0.0845 [$I > 2\sigma(I)$], 0.0920 (all data); largest diff. peak/hole 0.762/−0.715 e·Å^{-3}. CCDC deposit number: 1569681.

Crystal Data for ***8b****.* $C_{38}H_{44}ClN_4O_4Rh{\cdot}4CHCl_3$; *M* = 1236.60 g·mol^{-1}; monoclinic, *C*2/*c*; *a* = 19.6171(11) Å, *b* = 17.6333(11) Å, *c* = 15.1016(9) Å, β = 98.1160(10)°, *V* = 5171.5(5) Å^3; *Z* = 4; D_c = 1.588 g Cm^{-3}; μ = 1.046 mm^{-1}; *F*(000) = 2504; yellow prism, 0.250 × 0.175 × 0.150 mm; ϑ_{min} = 2.097°, ϑ_{max} = 28.620°; limiting indexes $-25 \le h \le 25$, $-23 \le k \le 23$, $-19 \le l \le 19$; reflections collected/unique 29 801/6241 (R_{int} = 0.0338); data/restraints/parameters 6241/30/328; GOF 1.026; R_1 = 0.0318 [$I > 2\sigma(I)$], 0.0410 (all data); wR^2 = 0.0658 [$I > 2\sigma(I)$], 0.0706 (all data); largest diff. peak/hole 1.031/−0.650 e·Å^{-3}. CCDC deposit number: 1569682.

Crystal Data for ***9****.* $C_{44}H_{40}ClN_4O_4Rh{\cdot}3CH_2Cl_2$; *M* = 1081.94 g·mol^{-1}; triclinic, $P\bar{1}$; *a* = 12.5925(9) Å, *b* = 13.9807(10) Å, *c* = 15.0183(18) Å, α = 102.9200(10)°, β = 93.5190(10)°, γ = 115.0090(10)°, *V* = 2298.8(4) Å^3; *Z* = 2; D_c = 1.563 g Cm^{-3}; μ = 0.828 mm^{-1}; *F*(000) = 1104; colorless prism, 0.250 × 0.120 × 0.070 mm; ϑ_{min} = 1.413°; ϑ_{max} = 26.370°; limiting indexes $-15 \le h \le 15$, $-17 \le k \le 17$, $-18 \le l \le 18$; reflections collected/unique 24 768/9342 (R_{int} = 0.0364); data/restraints/parameters 9342/0/596; GOF 1.052; R_1 = 0. 0437 [$I > 2\sigma(I)$], 0. 0585 (all data); wR^2 = 0. 0991 [$I > 2\sigma(I)$], 0. 1065 (all data); largest diff. peak/hole 0.575 /−0. 896 e·Å^{-3}. CCDC deposit number: 1569683.

Computational Details. All DFT theoretical calculations have been carried out using the Gaussian program package.[42] The B3LYP method[43] has been employed, for both energies and gradient calculations, and the "ultrafine" grid has been used in all cases. The

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def2-SVP basis set[44] has been selected for all atoms. The nature of the stationary points has been confirmed by analytical frequency analysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00750.

Experimental procedures for the preparation of azolium salts **1** and **2**, intermolecular contacts within **9**, and NMR spectra for compounds (PDF)

Cartesian coordinates for theoretical calculations (XYZ)

Accession Codes

CCDC 1569678−1569683 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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