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Fine-Tunable 3,4-Dihydroquinazol-2-ylidene Carbenes: Synthesis, Rhodium(I) Complexes, and Reactivity

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Supporting Information

ABSTRACT: The design and synthesis of various new six-membered cyclic formamidinium salts with a 3,4-dihydroquinazoline core have been reported in this paper. Our synthetic strategy allows access to a kind of tailor-made 3,4-dihydroquinazolinium salts bearing different substituent combinations. A series of novel 3,4-dihydroquinazolin-2-ylidene-based rhodium(I) complexes were prepared by the reaction of $[Rh(cod)Cl]_2$ with the free carbene obtained in situ from the deprotonation of the corresponding 3,4-dihydroquinazolinium salts with $KN(SiMe_3)_2$. The NHCs prepared in situ can also react with S_8 or CS_2 to afford the corresponding thiones or NHC−CS_2 adducts, respectively. The rhodium(I) complexes were transformed to the corresponding dicarbonyl complexes, and the ν(CO) values of the corresponding dicarbonyl Rh complexes indicate the 3,4-dihydroquinazol-2-ylidenes are stronger electron donors than normal five-membered NHCs. The Rh complexes are highly active in the arylation of carbonyl compounds, and the 3,4-dihydroquinazolin-2-ylidenes prepared in situ upon deprotonation are powerful in palladium-catalyzed Suzuki cross-coupling reactions at room temperature with a ppm scale catalyst loading with TONs of up to 425 000.

R^1, R^2 = Aryl or Alkyl;
R^3 = H or ^{n}Bu; R^4 = H or OMe

INTRODUCTION

Over the past decade, N-heterocyclic carbenes (NHCs) have received much attention mainly due to their widespread and spectacular applications as organocatalysts and as ligands for organometallic catalysis.[1] Because the steric and electronic properties of NHCs play a prominent role in catalysis, a variety of NHCs with different N-heterocycle scaffolds have been developed, among which of special interest are electronic and steric variations resulting from different backbone structures and different N-substituents on the NHCs.[2]

The vast majority of NHCs are based on five-membered-ring systems, such as imidazol-2-ylidenes (**A**), imidazolidin-2-ylidenes (**B**), and benzimidazol-2-ylidenes (**C**) (Figure 1).

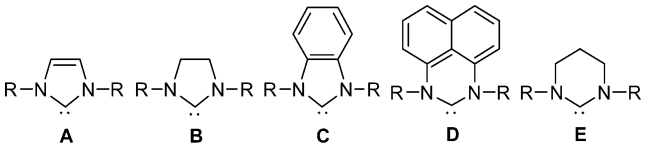

Figure 1. Selected five- and six- membered N-heterocyclic carbenes.

Although, compared with five-membered NHCs, six-membered NHCs such as perimidine-based carbenes (**D**) and tetrahydropyrimidin-2-ylidenes (**E**) have rarely been reported, these ligands afford new possibilities for carbene design.[3] This six-membered NHC scaffold directs the N-bound groups closer to the carbene atom, which increases the steric impact on both the carbene and a coordinated metal center, thus providing steric protection not offered by five-membered NHCs. In particular, as for six-membered NHC **D**, placing the carbene center in the perimidine-based six-membered ring leaves the divalent carbon as part of a formally 7π-electron, six-membered heterocyclic ring, while the more stable unsaturated species **A** possess the 6π-electron structure expected for aromatic systems.[3c,h] On the basis of the ν(CO) values of the corresponding $(CO)_2RhCl$(**D**) (R = ^{i}Pr) complex, carbene **D** is an even stronger electron donor than the imidazolidin-2-ylidene **B**.[3c] The NHC **D** prepared in situ upon deprotonation of a novel lutidine-bridged bis-perimidinium dibromide has been reported as a potent precatalyst in palladium-catalyzed Heck and Suzuki cross-coupling reactions under aerobic conditions and is efficient in Suzuki cross-coupling of aryl iodide and phenylboronic acid at 140 °C even with a ppm scale catalyst loading.[3i] Its stronger σ-donor character is responsible for its superior catalytic performance. The palladium complexes based on NHC **E** were found highly active in Heck-type reactions, which could efficiently catalyze the coupling of aliphatic and aromatic vinyl compounds with aryl bromides and chlorides with high turnover numbers (TONs) up to 2 000 000.[3d] Stabilities of these NHC Pd complexes under Heck-couplings conditions were correlated with their molecular structure. The NHCs **E** are also found to be reactive in other organometallic catalyses, such as Rh- or Ir-catalyzed arylation of carbonyl compounds using equimolar amounts of arylboronic acid and carbonyl compound in the presence of 0.08−1 mol % catalyst,[3j] Ru-catalyzed olefin metathesis,[3l] Pd-catalyzed Suzuki cross-

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coupling reactions,[3m] Pt-catalyzed hydrosilylation of alkynes, alkenes, and ketones,[3n] and Cu-catalyzed carbonyl hydrosilylation and cyanosilylation reactions.[3o]

Carbene **D** displays a planar molecular geometry, while, in the scaffold of carbene **E**, only five atoms, i.e., two N atoms, 4- and 6-position C atoms, and a carbene C atom, are almost in one plane, and the middle 5-position C atom is out of the plane (Figure 2). As part of our studies on the design and synthesis of

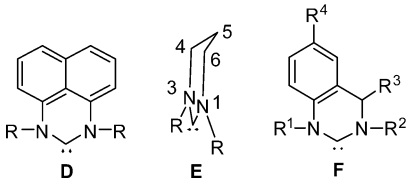
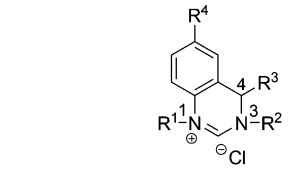


Figure 2. Six-membered cyclic NHCs **D**, **E**, and targeted **F**.

novel NHC ligands for transition metal-based catalysis,[4] we have undertaken the design of new stable carbenes combining the scaffolds of the NHCs **D** and **E**, and herein we report the synthesis of various new six-membered cyclic formamidinium salts with a 3,4-dihydroquinazoline core. A series of novel 3,4-dihydroquinazolin-2-ylidene-based rhodium(I) complexes were prepared by the reaction of $[Rh(cod)Cl]_2$ with the free carbene synthesized in situ. We observed that the 3,4-dihydroquinazolin-2-ylidenes showed high efficiency not only in Rh-cataylzed arylation of carbonyl compounds using arylboronic acid but also in palladium-catalyzed Suzuki cross-coupling reactions at room temperature with a ppm scale catalyst loading with TONs of up to 425 000.

RESULTS AND DISCUSSION

We first attempted to synthesize a 3,4-dihydroquinazolinium salt, with two aryl substitutes on the N1 atom and N3 atom, respectively (Figure 4). According to a literature method,[5] the



R^1, R^2 = Aryl or Alkyl; R^3 = H or ^{n}Bu; R^4 = H or OMe

Figure 3. Targeted substituted 3,4-dihydroquinazolinium salts.

condensation of 2-fluorobenzaldehyde with mesitylaniline ($MesNH_2$) afforded Schiff base **1**, which was treated with LiNHMes (Mes = mesityl) and subsequently reduced by $LiAlH_4$ to give diamine **2**. Diamine **2** underwent cyclization to produce the corresponding 3,4-dihydroquinazolinium salt **3** in 44% yield using triethyl orthoformate in the presence of NH_4Cl (Scheme 1).

Next we tried to prepare a 3,4-dihydroquinazolinium salt with an alkyl substituent on the N3 atom using the aforementioned method. Unfortunately, the condensation of 2-fluorobenzaldehyde with various aliphatic amines such as ^{i}PrNH$_2$, CyNH$_2$ (Cy = cyclohexyl), and PhCH$_2$NH$_2$ (BnNH$_2$) failed to give the desired product (Scheme 2). Therefore, we examined an alternative method starting from 2-bromobenzaldehyde diethylacetal,[6] which was subjected to a palladium-catalyzed coupling with mesityl-NH$_2$, 3,5-Me$_2$-phenyl-NH$_2$,

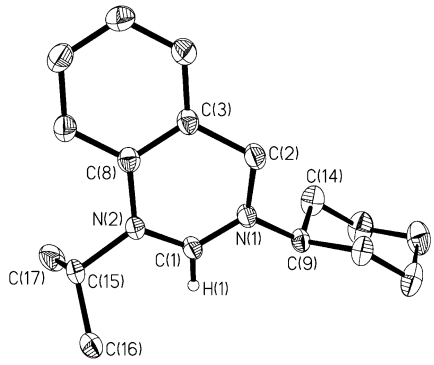
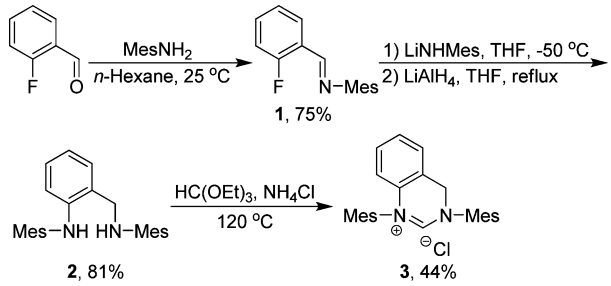
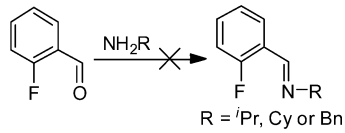


Figure 4. Molecular structure of **11c′** with 30% probability ellipsoids. The anion (I^-) has been omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)–C(1) 1.302(4), N(1)–C(2) 1.459(5), N(1)–C(9) 1.477(4), N(2)–C(1) 1.331(4), N(2)–C(8) 1.414(4), N(2)–C(15) 1.501(4), C(2)–C(3) 1.500(5), C(3)–C(8) 1.386(5), C(1)–N(1)–C(2) 120.7(3), C(1)–N(1)–C(9) 118.9(3), C(2)–N(1)–C(9) 120.1(3), C(1)–N(2)–C(8) 119.2(3), C(1)–N(2)–C(15) 117.9(3), C(8)–N(2)–C(15) 121.7(3), N(1)–C(1)–N(2) 124.1(3), N(1)–C(2)–C(3) 110.6(3), C(7)–C(8)–N(2) 122.3(3), C(3)–C(8)–N(2) 118.2(3).

Scheme 1. Synthesis of 3,4-Dihydroquinazolinium Salt 3



Scheme 2. Attempt to Condense 2-Fluorobenzaldehyde with Alkyl Amine



BnNH$_2$, and CyNH$_2$, respectively, and, after deprotection by *p*-toluenesulfonic acid, was converted to the aldehydes **4a–d** in 70–74% yields. The condensation reaction of **4a–d** with the corresponding amines and subsequent reduction by $LiAlH_4$ afforded the desired diamines **5a–d** in 63–84% yields, which underwent cyclization to give the corresponding 3,4-dihydroquinazolinium salts **6a–d** [**6a** (R^1 = Mes, R^2 = Bn, X = H), **6b** (R^1 3,5-Me$_2$-phenyl, R^2 = ^{i}Pr, X = H), **6c** (R^1, R^2 = Bn, X = H), and **6d** (R^1, R^2 = Cy, X = OMe)] in 55–92% yields using the typical method[2] (Scheme 3). Following this route, the synthesis of chiral 3,4-dihydroquinazolinium salts has been also developed. For example, 2-bromobenzaldehyde diethylacetal underwent a palladium-catalyzed coupling with (*S*)-phenylethylamine and, after deprotection, was converted to the aldehyde **7** in 84% yield. Further condensation with a second (*S*)-phenylethylamine followed by reduction with $LiAlH_4$ afforded the chiral diamine **8** in 90% yield, which then underwent cyclization to produce the desired chiral 3,4-dihydroquinazolinium salt **9** in 31% yield using the typical method[2] (Scheme 4).

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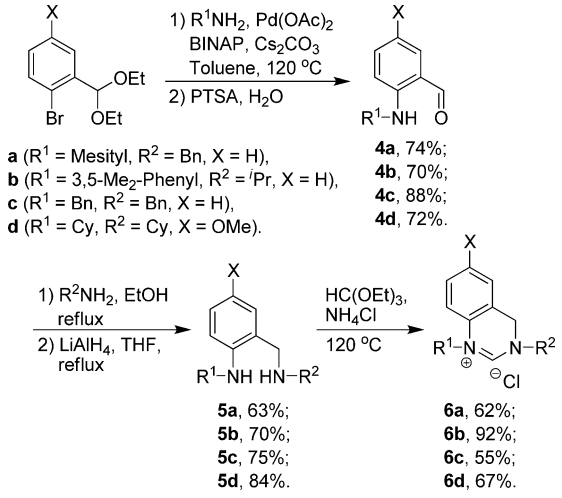
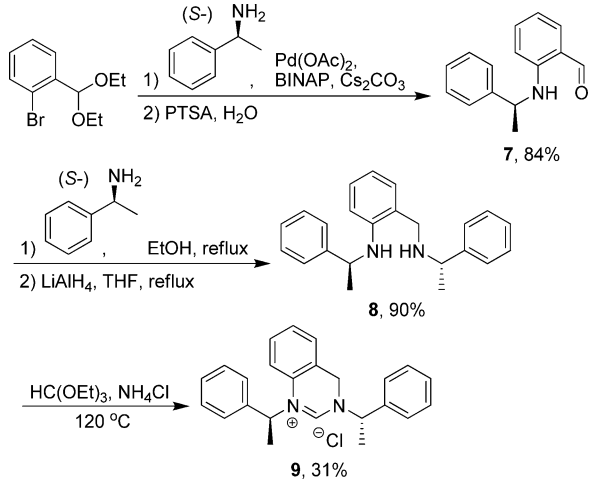
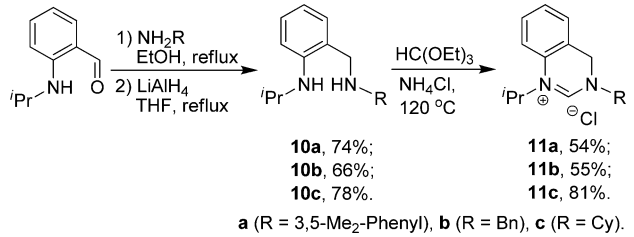
Scheme 3. Synthesis of 3,4-Dihydroquinazolinium Salts 6a–d



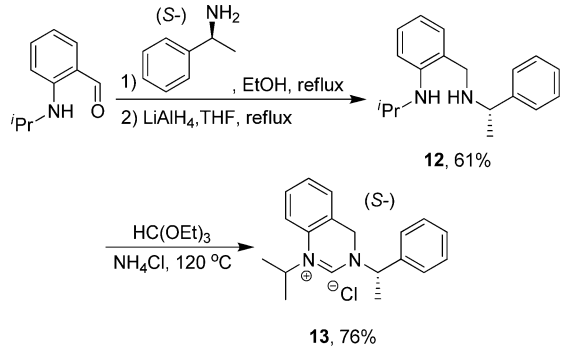
Scheme 4. Synthesis of Chiral 3,4-Dihydroquinazolinium Salt 9



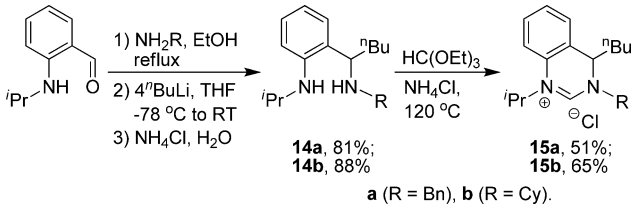
Scheme 5. Synthesis of 3,4-Dihydroquinazolinium Salts 11a–c



Scheme 6. Synthesis of Chiral 3,4-Dihydroquinazolinium Salt 13



Scheme 7. Synthesis of 3,4-Dihydroquinazolinium Salts 15a,b



The isopropyl group is often chosen as a sterically demanding N-substituent in the design of NHCs. Due to low boiling point of the volatile $^{i}PrNH_2$, a 3,4-dihydroquinazolinium salt with an isopropyl substituent on the N1 atom was prepared from the 2-isopropylaminobenzaldehyde, obtained from 2-aminobenzyl alcohol by a literature method.[7] The condensation of 2-(isopropylamino)benzaldehyde with NH_2R (R = 3,5-Me_2-phenyl, Bn, or Cy) and subsequent reduction afforded the corresponding diamines **10a–c** in 66–78% yields, which underwent cyclization to give 3,4-dihydroquinazolinium salts **11a–c** [**11a** (R = 3,5-Me_2-phenyl), **11b** (R = Bn), and **11c** (R = Cy)] in 54–81% yield, respectively (Scheme 5). Chiral 3,4-dihydroquinazolinium salt **13** with an isopropyl substituent was also prepared in 76% yield by the cyclization of diamine **12**, which was obtained in 61% yield starting from the condensation of 2-(isopropylamino)benzaldehyde with (*S*)-phenylethylamine (Scheme 6).

We further synthesized 3,4-dihydroquinazolinium salts with an *n*-butyl substituent on the C4 atom. The addition of *n*-butyllithium to the corresponding Schiff bases, prepared from the condensation of 2-(isopropylamino)benzaldehyde with the corresponding amines (Scheme 7), afforded diamines **14a,b** in 81–88% yields. **14a,b** underwent cyclization to afford the expected 3,4-dihydroquinazolinium salt **15a,b** in 51–65% yields.

The dihydroquinazoline scaffold structure of these 3,4-dihydroquinazolinium salts was confirmed by the X-ray crystal structure of 1-isopropyl-3-cyclohexyl-3,4-dihydroquinazolinium iodide salt (**11c′**), which was obtained by treatment of **11c** with excess NaI (Figure 4).

Our successful synthetic strategy allows access to the preparation of a novel kind of tailor-made 3,4-dihydroquinazolinium salts bearing different substituent combinations, where the rational changes of different substituent combinations might be applied to fine-tune the corresponding NHCs, exhibiting different steric impact and electron-donating ability, and thus these properties manifest themselves in the behavior of the NHC–metal complexes. More noticeable is the formation of chiral 3,4-dihydroquinazolinium salts **9** and **13**. Considering that this six-membered dihydroquinazoline scaffold directs the N-bound groups closer to the carbene atom as the perimidine scaffold does in E-type NHC complexes,[3c,h] which might increase the chiral control on both the carbene and a coordinated metal, the NHC derived from **9** and **13** could provide potential applications in asymmetric catalysis.

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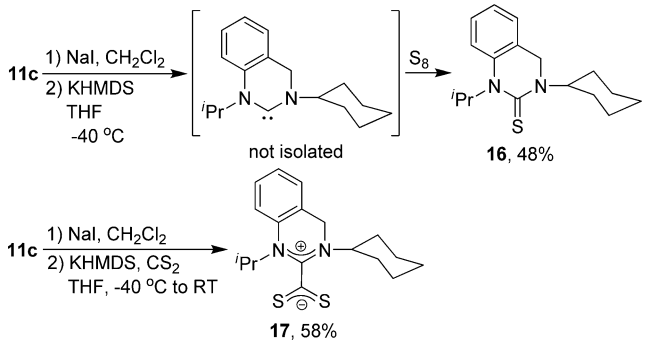
Free NHCs are able to react with S_8 and CS_2 to form thiones and NHC−CS_2 adducts, which are very useful compounds in many organic reactions.[8,9] For example, imidazolidin-2-thione could be used as a synthetic precursor for a Liebeskind−Srogl cross-coupling reaction to prepare the corresponding 2-aryl-2-imidazoline,[8] and a wide range of stable benzimidazolium or imidazol(in)ium−CS_2 adducts have been studied as novel ionic liquids[10] or organocatalysts in the cyanosilylation of aldehydes[11] and in the Staudinger reaction for the preparation of β-lactams.[12] Furthermore, they can be also used as intermediates for sulfur heterocycles,[13] ligands for gold complexes, surface units for gold nanoparticles,[14] and promising antifungal and antibacterial agents.[15]

With these 3,4-dihydroquinazolinium salts in hand, we could investigate the reactivity of their corresponding NHCs with elemental sulfur (S_8) and carbon disulfide (CS_2). In practice, the representative salt **11c** was selected as starting material. These transformations have been carried out from the reactions of S_8 or CS_2 with the free carbene in situ prepared from deprotonation of **11c** by $KN(SiMe_3)_2$ (KHMDS). Thereby, the thione **16** and NHC−CS_2 adduct **17** were prepared in moderate yields (48% for **16**, 58% for **17**), respectively, and their structures have been confirmed by NMR and ESI analyses (Scheme 8). The ^{13}C NMR signals for C=S appear at δ = 181.9 ppm for **16**, and in **17**, the ^{13}C NMR signals for C-2 and CS_2 appear at δ = 162.5 and 232.7 ppm, respectively.

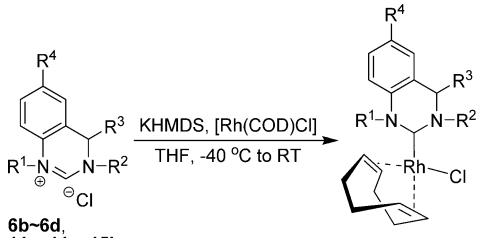
Scheme 8. Synthesis of the Thione 16 and NHC−CS_2 Adduct 17 from 3,4-Dihydroquinazolinium Salt 11c



The ability of the new NHCs to ligate a transition metal fragment was also evaluated. The reaction between the in situ generated carbene and $[(COD)RhCl]_2$ led to the formation of the expected NHC complexes **18a−g**, which were isolated in 34−65% yield as air-stable yellow solids (Scheme 9). Both mass and NMR spectra, and in particular the X-ray diffraction analyses of **18e−g** (Figures 5 and 6), confirmed the formation of these NHC Rh complexes. The Rh−C_{NHC} bond distances of 2.055(3), 2.051(2), and 2.051(3) Å for **18e**, **18f**, and **18g**, respectively, are shorter than that reported for (COD)RhBr(**E**) (R = ^{i}Pr) (2.0896(18) Å),[3d] similar to that of (COD)RhCl(**D**) (R = ^{i}Pr) (2.056(11) Å),[3h] and longer than that of five-membered (COD)RhCl(**B**) (R = Me) (2.023(2) Å) (NHC = 1,3-dimethylimidiazolin-2-ylidene).[16]

The existence of weak interactions between the Rh atom and H atom in these Rh complexes is confirmed by the observation of the short Rh---H distances (Rh(1)---H(16A) 2.4138(2) Å and Rh(1)---H(9A) 2.4973(2) Å for **18e**, Rh(1)---H(5) 2.4757(9) Å and Rh(1)---H(12) 2.4861(6) Å for **18f**, Rh(1)---H(19) 2.4818(9) Å and Rh(1)---H(9) 2.5458(6) Å for **18g**) in their solid structures. In solution, the interaction is also apparent in the ^1H NMR spectrum. For example, the chemical shift for the methine septet in N^{i}Pr moves from 4.52 ppm in precursor **11c** to 7.04 ppm for **18f**, and that in NCy moves from 4.85 ppm in **11c** to 6.64 ppm for **18f**. The existence of weak interactions between the Rh atom and H atom is probably attributed to a direct effect of the six-membered heterocyclic structure enforcing a close approach of the N-bonded groups to the metal center, which could bring additional stabilization to the metal center. Such weak interactions between the Rh atom and H atom were also observed in (COD)RhCl(**D**).[3c,h]

Scheme 9. Synthesis of Rh Complexes 18a−g Based on 3,4-Dihydroquinazol-2-ylidene



18a (R^1 = 3,5-Me_2-Phenyl, R^2 = ^{i}Pr, R^3, R^4 = H), 34%
18b (R^1, R^2 = Bn, R^3, R^4 = H), 59%
18c (R^1, R^2 = Cy, R^3 = H, R^4 = OMe), 39%
18d (R^1 = ^{i}Pr, R^2 = 3,5-Me_2-Phenyl, R^3, R^4 = H), 40%
18e (R^1 = ^{i}Pr, R^2 = Bn, R^3, R^4 = H), 65%
18f (R^1 = ^{i}Pr, R^2 = Cy, R^3, R^4 = H), 50%
18g (R^1 = ^{i}Pr, R^2 = Cy, R^3 = ^{n}Bu, R^4 = H), 49%

To evaluate the electron-donating ability of these new NHCs, **18c−f** were treated with excess carbon monoxide, which afforded the Rh dicarbonyl species **19a−e** in 67−83% yield, respectively (Scheme 10). The average CO vibration frequency of the Rh carbonyl complexes **19a−e** (ν_{av} = 2028−2031) indicates that the corresponding 3,4-dihydroquinazol-2-ylidenes are stronger electron donors than normal five-membered NHCs (ν_{av} = 2038−2041),[17] weaker than the six-membered NHCs of type **E** (ν_{av} = 2023),[3d] and similar to the six-membered NHCs of type **D** (R = ^{i}Pr, ν_{av} = 2031).[3h]

The catalytic activity of the Rh complexes was studied in detail. The Rh complexes are highly active in the arylation of carbonyl compounds using equimolar amounts of arylboronic acid and carbonyl compound in the presence of 0.1−1 mol % catalyst (Table S1, see Supporting Information). Moreover the 3,4-dihydroquinazolin-2-ylidenes prepared in situ upon deprotonation are proved to be powerful in palladium-catalyzed Suzuki cross-coupling reactions at room temperature with a ppm scale catalyst loading with TONs of up to 425 000 (Table S2, see Supporting Information).

■ CONCLUSION

In conclusion, we have described the design and synthesis of various novel six-membered formamidinium salts with a substituted 3,4-dihydroquinazoline core. Particularly, by a successful synthetic strategy, we could make the rational changes of different substituent combinations in 3,4-dihydroquinazolinium salts, which might be applied to fine-tune the corresponding NHCs exhibiting different steric impact and electron-donating ability. In the presence of KHMDS as a base, NHCs prepared in situ from three representative formamidinium salts can react with S_8 or CS_2 to afford the corresponding thiones or NHC−CS_2 adducts, respectively, and several Rh

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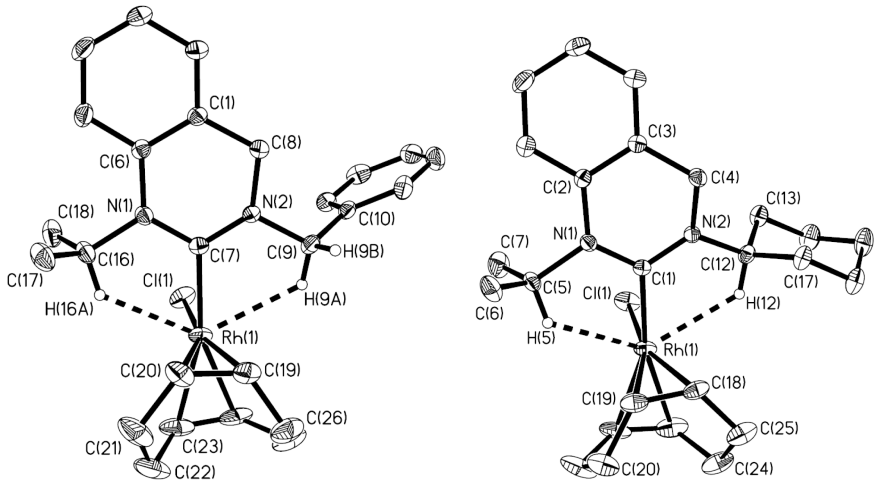


Figure 5. Molecular structure of **18e** (left) and **18f** (right) with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): **18e**: Rh(1)−C(7) 2.055(3), Rh(1)−Cl(1) 2.3718(7), N(1)−C(7) 1.365(3), N(2)−C(7) 1.329(3), C(1)−C(6) 1.384(4), C(7)−Rh(1)−Cl(1) 87.72(7), C(7)−N(2)−C(8) 126.0(2), C(7)−N(2)−C(9) 120.7(2), C(6)−C(1)−C(8) 121.2(2), C(1)−C(6)−N(1) 118.8(2), N(2)−C(7)−N(1) 118.4(2), N(2)−C(7)−Rh(1) 119.81(18), N(1)−C(7)−Rh(1) 121.77(19), N(2)−C(8)−C(1) 112.2(2), Rh(1)---H(16A) 2.4138(2), Rh(1)---H(9A) 2.4973(2); **18f**: Rh(1)−C(1) 2.051(2), Rh(1)−Cl(1) 2.3833(10), N(1)−C(1) 1.372(3), N(1)−C(2) 1.416(3), N(2)−C(1) 1.335(3), N(2)−C(4) 1.462(3), C(2)−C(3) 1.394(3), C(3)−C(4) 1.481(3), C(1)−Rh(1)−Cl(1) 89.62(7), C(1)−N(1)−C(2) 121.90(19), C(2)−N(1)−C(5) 120.1(2), C(1)−N(2)−C(4) 123.51(19), N(2)−C(1)−N(1) 117.1(2), N(2)−C(1)−Rh(1) 120.35(16), N(1)−C(1)−Rh(1) 122.58(16), C(2)−C(3)−C(4) 118.6(2), N(2)−C(4)−C(3) 110.81(18), Rh(1)---H(5) 2.4757(9), Rh(1)---H(12) 2.4861(6).

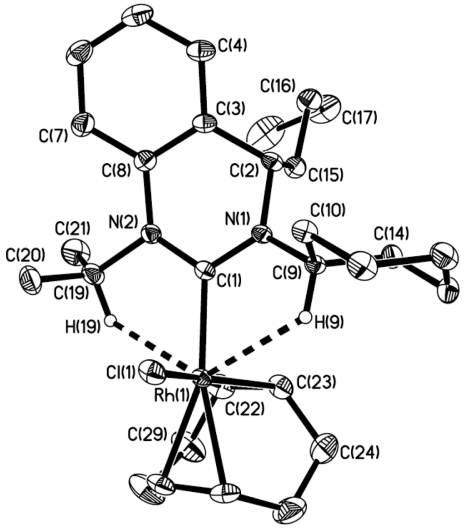
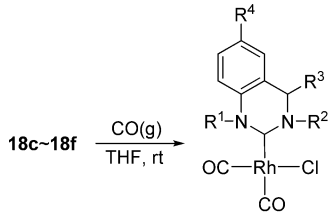


Figure 6. Molecular structure of **18g** with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Rh(1)−C(1) 2.051(3), Rh(1)−Cl(1) 2.3772(10), N(1)−C(1) 1.333(3), N(1)−C(2) 1.487(3), N(2)−C(1) 1.368(3) N(2)−C(8) 1.423(3), C(3)−C(8) 1.386(4), C(3)−C(2) 1.489(4), C(1)−Rh(1)−Cl(1) 90.04(8), C(1)−N(1)−C(2) 121.0(2), C(1)−N(2)−C(8) 120.8(2), C(1)−N(2)−C(19) 116.7(2), C(1)−N(1)−C(9) 120.1(2), N(1)−C(1)−N(2) 117.2(2), N(1)−C(1)−Rh(1) 120.72(18), N(2)−C(1)−Rh(1) 122.10(18), Rh(1)---H(19) 2.4818(9), Rh(1)---H(9) 2.5458(6).

complexes based on NHC 3,4-dihydroquinazol-2-ylidene were also prepared by the method. On the basis of the ν(CO) values of the corresponding dicarbonyl Rh complex, the 3,4-dihydroquinazol-2-ylidenes are stronger electron donors than normal five-membered NHCs. The 3,4-dihydroquinazolin-2-ylidenes showed high efficiency not only in Rh-cataylzed arylation of carbonyl compounds using arylboronic acid but also in palladium-catalyzed Suzuki cross-coupling reactions at room temperature with a ppm scale catalyst loading with TONs of up to 425 000. These results render the 3,4-dihydroquinazol-2-ylidene a promising NHC ligand for further development in metal-catalyzed reactions.

Scheme 10. Synthesis of Dicarbonyl Rh Complexes 19a−e



19a (R^1, R^2 = Cy, R^3 = H, R^4 = OMe), 68%
19b (R^1 = ^{i}Pr, R^2 = 3,5-Me_2-Phenyl, R^3, R^4 = H), 83%
19c (R^1 = ^{i}Pr, R^2 = Bn, R^3, R^4 = H), 72%
19d (R^1 = ^{i}Pr, R^2 = Cy, R^3, R^4 = H), 82%
19e (R^1 = ^{i}Pr, R^2 = Cy, R^3 = ^{n}Bu, R^4 = H), 67%

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^{1}H NMR $CDCl_3$: 7.26 ppm; ^{13}C NMR $CDCl_3$: 77.0 ppm). Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer 341 MC digital polarimeter with a 10 cm cell (c given in g per 100 mL), and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer.

2-Fluorobenzaldehyde and KHMDS are commercially available and were used as received without further purification. The following compounds have been previously reported, and their spectra were consistent with that of the published data: 2-(isopropylamino)-benzaldehyde.[12]

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*3-Cyclohexyl-1-isopropyl-3,4-dihydroquinazoline-2-thione (**16**).* **11c** (58 mg, 0.2 mmol) was treated with NaI (240 mg, 1.6 mmol) in acetone (5 mL). After the mixture was stirred for 8 h, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (2 × 20 mL). After removal of solvent, the resulting residue was suspended in THF (5 mL), and S_8 (12.8 mg, 0.4 mmol) and KHMDS (1.0 M in hexane, 0.22 mL, 0.22 mmol) were added dropwise at −40 °C. After 1 h, the mixture was warmed to room temperature and stirred for 1 h. The solvent was evacuated in vacuo, and the residue was purified by column chromatography on silica gel (PE/EtOAc = 10:1) to give the product **16** as a white powder (28 mg, 48%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.23 (m, 2H), 7.11−7.05 (m, 2H), 5.54 (sept, J = 7.2 Hz, 1H), 5.27−5.20 (m, 1H), 4.07 (s, 2H), 1.84−1.81 (m, 4H), 1.71−1.68 (m, 1H), 1.62 (d, J = 7.2, 6H), 1.47−1.40 (m, 4H), 1.18−1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 137.4, 127.5, 124.6, 124.5, 123.6, 116.2, 60.0, 53.8, 43.7, 29.8, 25.5, 25.4, 21.3; IR (KBr disk) ν 3121, 2968, 2920, 2851, 1668, 1437, 1400, 1215, 1100, 751 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{24}N_2S$ [M + H]$^+$ 288.1660, found 288.1657.

*1-Isopropyl-3-cyclohexyl-3,4-dihydroquinazolinium-2-dithiocarboxylate (**17**).* **11c** (58 mg, 0.2 mmol) was treated with NaI (240 mg, 1.6 mmol) in acetone (5 mL). After the mixture was stirred for 8 h, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (2 × 20 mL). After removal of solvent, the resulting residue was suspended in THF (5 mL), and CS_2 (30 mg, 0.4 mmol) and KHMDS (1.0 M in hexane, 0.22 mL, 0.22 mmol) were added dropwise at −40 °C. After 1 h, the mixture was warmed to room temperature and stirred for 1 h. The solvent was evacuated in vacuo, and the residue was purified by column chromatography on silica gel (PE/EtOAc = 10:1) to give the product **17** as an orange powder (45 mg, 58%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8 Hz, 1H), 7.35 (t, J = 8 Hz, 1H), 7.25 (t, J = 6.8 Hz, 1H), 7.15 (d, J = 6.8 Hz, 1H), 5.46 (sept, J = 7.0 Hz,1H), 4.54 (tt, J_1 = 11.8 Hz, J_2 = 3.8 Hz, 1H), 4.46 (s, 2H), 2.05−2.03 (m, 2H), 1.83−1.79 (m, 2H), 1.70−1.60 (m, 1H), 1.64 (d, J = 7.2 Hz, 6H), 1.55−1.51 (m, 2H), 1.40−1.33 (m, 2H), 1.14−1.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.7, 162.5, 133.8, 128.6, 126.4, 126.3, 120.4, 118.3, 61.5, 52.9, 43.0, 28.8, 25.0, 24.9, 21.0; IR (KBr disk) ν 3122, 2974, 2920, 1745, 1608, 1551, 1466, 1396, 1365, 1344, 1204, 1088, 1064, 852, 694 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{24}N_2S_2$ [M + H]$^+$ 332.1381, found 332.1386.

*(1,5-Cyclooctadiene)(1-(3,5-dimethylphenyl)-3-isopropyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Chloride (**18a**).* KHMDS (1.0 M in hexane, 0.35 mL, 0.35 mmol) was added dropwise to a solution of **6b** (100 mg, 0.32 mmol) and $[(COD)RhCl]_2$ (78 mg, 0.16 mmol) in THF (5 mL) at −78 °C. After 30 min, the mixture was warmed to room temperature and stirred for 2 h. The solvent was evacuated in vacuo, and the residue was purified by column chromatography on silica gel (PE/EA = 10:1) to give the product **18a** as an orange powder (58 mg, 34%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.15 (s, 1H), 7.06−7.00 (m, 4H), 6.49 (sept, J = 6.8 Hz, 1H), 6.37 (d, J = 7.2 Hz, 1H), 4.73 (t, J = 6.8 Hz, 1H), 4.62 (q, J = 7.6 Hz, 1H), 4.47 (d, J = 14.4 Hz, 1H), 4.24 (d, J = 14.4 Hz, 1H), 3.48−3.44 (m, 1H), 2.64−2.62 (m, 1H), 2.48−2.46 (m, 1H), 2.44 (s, 6H), 2.04−1.97 (m, 2H), 1.71−1.63 (m, 2H), 1.49 (d, J = 6.4 Hz, 6H), 1.29−1.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5 (d, $^1J_{RhC}$ = 45.7 Hz, C_{carb}Rh), 141.1, 138.8, 137.2, 129.2, 128.1, 125.4, 124.2, 118.6, 115.7, 115.2, 96.4 (d, $^1J_{RhC}$ = 6.2 Hz, CH_{cod}), 95.7 (d, $^1J_{RhC}$ = 7.4 Hz, CH_{cod}), 68.8 (d, $^1J_{RhC}$ = 16.4 Hz, CH_{cod}), 66.5 (d, $^1J_{RhC}$ = 14.7 Hz, CH_{cod}), 58.2, 41.6, 34.9, 29.2, 26.4, 22.4, 21.3, 21.2, 20.2, 19.8; mp 207.7−208.0 °C; HRMS (ESI) m/z [M]$^+$ calcd for $C_{27}H_{34}ClN_2Rh$ 524.1466; found 524.1468.

*(1,5-Cyclooctadiene)(1,3-dibenzyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Chloride (**18b**).* Following the procedure for the synthesis of **18a**, KHMDS (1.0 M in hexane, 0.32 mL, 0.32 mmol), **6c** (100 mg, 0.29 mmol), and $[(COD)RhCl]_2$ (70 mg, 0.145 mmol) afforded **18b** as an orange powder (95 mg, 59%), which was purified by column chromatography on silica gel (PE/EA = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.48 (m, 4H), 7.40 (t, J = 8.4 Hz, 2H), 7.35−7.31 (m, 3H), 7.23 (t, J = 7.2 Hz, 2H), 7.08 (t, J = 8.0 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 7.2 Hz, 1H), 6.46 (d, J = 14.2 Hz, 1H), 6.25 (d, J = 14.2 Hz, 1H), 6.13 (d, J = 14.8 Hz, 1H), 4.99 (m, 2 H), 4.24 (s, 2H), 3.48−3.79 (m, 2H), 2.33−2.14 (m, 4H), 1.90−1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4 (d, $^1J_{RhC}$ = 47.4 Hz, C_{carb}Rh), 136.9, 135.5, 134.2, 128.9, 128.3, 127.9, 127.8, 127.2, 126.8, 125.7, 124.5, 120.5, 114.6, 98.1 (d, $^1J_{RhC}$ = 3.7 Hz, CH_{cod}), 98.0 (d, $^1J_{RhC}$ = 2.9 Hz, CH_{cod}), 69.8 (d, $^1J_{RhC}$ = 4.7 Hz, CH_{cod}), 69.6 (d, $^1J_{RhC}$ = 3.7 Hz, CH_{cod}), 61.9, 58.1, 46.6, 32.5, 32.4, 28.7, 28.6; mp 200.4−200.7 °C; HRMS (ESI) m/z [M]$^+$ calcd for $C_{30}H_{32}ClN_2Rh$ 558.1309; found 558.1334.

*(1,5-Cyclooctadiene)(1,3-dicyclohexyl-6-methoxy-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Chloride (**18c**).* Following the procedure for the synthesis of **18a**, KHMDS (1.0 M in hexane, 0.33 mL, 0.33 mmol), **6d** (100 mg, 0.30 mmol), and $[(COD)RhCl]_2$ (74 mg, 0.15 mmol) in THF (5 mL) afforded **18c** as an orange powder (64 mg,39%), which was purified by column chromatography on silica gel (PE/EA = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 9.2 Hz, 1H), 6.71−6.68 (m, 2H), 6.51−6.45 (m, 2H), 4.96−4.90 (m, 2H), 4.21 (d, J = 14.4 Hz, 1H), 4.10 (d, J = 14.4 Hz, 1H), 3.75 (s, 3H), 3.42-.341 (m, 2H), 2.52−2.43 (m, 2H), 2.42−2.32 (m, 5H), 2.21 (m, 1H), 2.07−1.89 (m, 8H), 1.85−1.71 (m, 6H), 1.67−1.60 (m, 2H), 1.50−1.40 (m, 1H), 1.32−1.14 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7 (d, $^1J_{RhC}$ = 47.0 Hz, C_{carb}Rh), 155.8, 128.6, 122.8, 117.3, 112.7, 110.9, 95.76 (d, $^1J_{RhC}$ = 3.7 Hz, CH_{cod}), 95.69 (d, $^1J_{RhC}$ = 4.0 Hz, CH_{cod}), 69.2 (d, $^1J_{RhC}$ = 15.4 Hz, CH_{cod}), 67.6 (d, $^1J_{RhC}$ = 13.3 Hz, CH_{cod}), 65.7, 55.4, 43.0, 33.4, 32.1, 30.8, 30.3, 29.3, 28.2, 27.3, 26.8, 26.2, 25.9, 25.7; mp 203.3−203.6 °C; HRMS (ESI) m/z [M]$^+$ calcd for $C_{29}H_{42}ClON_2Rh$ 572.2041; found 572.2040.

*(1,5-Cyclooctadiene)(3-(3,5-dimethylphenyl)-1-isopropyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Chloride (**18d**).* Following the procedure for the synthesis of **18a**, KHMDS (1.0 M in hexane, 0.35 mL, 0.35 mmol), **11a** (100 mg, 0.32 mmol), and $[(COD)RhCl]_2$ (78 mg, 0.16 mmol) afforded **18d** as an orange powder (67 mg, 40%), which was purified by column chromatography on silica gel (PE/EA = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.25 (t, J = 6.4 Hz, 1H), 7.10−7.06 (m, 3H), 6.96 (d, J = 7.6 Hz, 1H), 4.79−4.69 (m, 4H), 3.49 (m, 1H), 2.63 (m, 1H), 2.44 (s, 6H), 2.08−1.93 (m, 3H), 1.83 (d, J = 7.2 Hz, 3H), 1.82 (d, J = 7.2 Hz, 3H), 1.68−1.64 (m, 2H), 1.53−1.44 (m, 1H), 1.30−1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.9 (d, $^1J_{RhC}$ = 46.2 Hz, C_{carb}Rh), 145.5, 138.5, 132.9, 128.4, 127.8, 126.1, 124.4, 121.5, 115.9, 96.6 (d, $^1J_{RhC}$ = 6.8 Hz, CH_{cod}), 95.3 (d, $^1J_{RhC}$ = 7.7 Hz, CH_{cod}), 68.3 (d, $^1J_{RhC}$ = 14.1 Hz, CH_{cod}), 68.0 (d, $^1J_{RhC}$ = 5.2 Hz, CH_{cod}), 59.4, 51.1, 34.4, 29.6, 28.9, 26.7, 22.0, 21.2, 21.0; mp 207.9−208.1 °C; HRMS (ESI) m/z [M]$^+$ calcd for $C_{27}H_{34}ClN_2Rh$ 524.1466; found 524.1459.

*(1,5-Cyclooctadiene)(1-isopropyl-3-benzyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Chloride (**18e**).* Following the procedure for the synthesis of **18a**, KHMDS (1.0 M in hexane, 0.24 mL, 0.24 mmol), **11b** (65 mg, 0.215 mmol), and $[(COD)RhCl]_2$ (36.5 mg, 0.074 mmol) afforded **18e** as yellow solids (70 mg, 65%), which was purified by column chromatography on silica gel (PE/EtOAc = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.8 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.33−7.18 (m, 4H), 6.99 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.32 (d, J = 14.8, 2H), 6.01 (d, J = 14.8, 2H), 4.96−4.94 (m, 2H), 4.14 (dd, J_1 = 19.2, J_2 = 14.8 Hz, 2H), 3.55−3.53 (m, 1H), 3.48−3.44 (m, 1H), 2.42−2.36 (m, 2H), 2.26−2.19 (m, 2H), 1.95−1.90 (m, 2H), 1.91 (d, J = 6.8 Hz, 3H), 1.86−1.80 (m, 2H), 1.70 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6 (d, $^1J_{RhC}$ = 46.9 Hz, C_{carb}Rh), 135.6, 133.2, 128.8, 127.7, 126.3, 124.1, 121.5, 115.8, 97.1 (d, $^1J_{RhC}$ = 6.3 Hz, CH_{cod}), 96.7(d, $^1J_{RhC}$ = 6.0 Hz, CH_{cod}), 70.1 (d, $^1J_{RhC}$ = 14.3 Hz, CH_{cod}), 68.5 (d, $^1J_{RhC}$ = 14.3 Hz, CH_{cod}), 61.9, 58.8, 46.6, 32.7, 32.1, 30.7, 29.3, 28.9, 28.4, 22.6, 20.3; IR (KBr disk) ν = 3551, 3474, 3413, 3131, 1637, 1617, 1528, 1795, 1410, 1284, 1125, 760 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{32}ClN_2Rh$ [M]$^+$ 510.1309, found 510.1312.

*(1,5-Cyclooctadiene)(1-isopropyl-3-cyclohexyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Chloride (**18f**).* Following the procedure for the synthesis of **18a**, KHMDS (1.0 M in hexane, 0.37 mL, 0.37 mmol), **11c** (100 mg, 0.34 mmol), and $[(COD)RhCl]_2$ (84 mg, 0.17 mmol) afforded **18f** as an orange powder (85 mg, 50%), which was purified by column chromatography on silica gel (PE/EA = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.17 (m, 2H), 7.05−7.00 (m, 2H),

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6.95 (d, J = 7.2 Hz, 1H), 6.68−6.60 (m, 1H), 5.03−4.98 (m, 1H), 4.91−4.86 (m, 1H), 4.19 (s, 2H), 3.39 (m, 1H), 3.38 (m, 1H), 2.47−2.30 (m, 5H), 2.01−1.92 (m, 5H), 1.85−1.63 (m, 11H), 1.49−1.43 (m, 2H), 1.24−1.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9 (d, $^1J_{RhC}$ = 45.5 Hz, $C_{carb}Rh$), 134.0, 127.6, 126.1, 123.8, 121.5, 115.4, 96.6 (d, $^1J_{RhC}$ = 7.2 Hz, CH_{cod}), 95.4 (d, $^1J_{RhC}$ = 7.6 Hz, CH_{cod}), 68.7 (d, $^1J_{RhC}$ = 14.4 Hz, CH_{cod}), 68.3 (d, $^1J_{RhC}$ = 5.4 Hz, CH_{cod}), 66.0, 58.2, 42.7, 32.9, 32.3, 30.7, 29.3, 28.1, 26.1, 25.9, 22.8, 20.4; mp 202.8−203.2 °C; HRMS (ESI) m/z $[M]^+$ calcd for $C_{25}H_{36}ClN_2Rh$ 502.1622; found 502.1602.

*(1,5-Cyclooctadiene)(1-isopropyl-3-cyclohexyl-4-butyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Chloride (**18g**).* Following the procedure for the synthesis of **18a**, KHMDS (1.0 M in hexane, 0.32 mL, 0.32 mmol), **15b** (100 mg, 0.29 mmol), and $[(COD)RhCl]_2$ (71 mg, 0.145 mmol) afforded **18g** as an orange powder (80 mg, 49%), which was purified by column chromatography on silica gel (PE/EA = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.4 Hz, 1H), 7.22−7.15 (m, 2H), 7.03 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 7.2 Hz, 1H), 6.32−6.27 (m, 1H), 4.99−4.94 (m, 2H), 4.18 (t, J = 6.4 Hz, 1H), 3.36 (m, 1H), 3.23 (m, 1H), 2.51−2.36 (m, 4H), 2.28−2.26 (m, 1H), 2.04−2.00 (m, 2H), 1.98 (d, J = 7.2 Hz, 3H), 1.92 (m, 1H), 1.76 (m, 2H), 1.66 (d, J = 7.2 Hz, 3H), 1.62 (m, 1H), 1.34−1.24 (m, 3H), 1.23−0.85 (m, 6H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0 (d, $^1J_{RhC}$ = 47.0 Hz, $C_{carb}Rh$), 133.6, 127.2, 126.3, 124.9, 123.5, 115.8, 96.9 (d, $^1J_{RhC}$ = 6.4 Hz, CH_{cod}), 96.8 (d, $^1J_{RhC}$ = 7.2 Hz, CH_{cod}), 71.2 (d, $^1J_{RhC}$ = 15.3 Hz, CH_{cod}), 66.1, 57.6, 53.4, 37.0, 32.9, 32.7, 32.4, 32.1, 29.1, 28.6, 26.8, 26.4, 25.7, 22.3, 21.9, 20.0, 13.9; mp: 216.7−217.0 °C; HRMS (ESI) m/z $[M]^+$ calcd for $C_{29}H_{44}ClN_2Rh$ 558.2248; found 558.2216.

*(1,3-Dicyclohexyl-6-methoxy-3,4-dihydroquinazolin-2-ylidene)-rhodium(I) Biscarbonyl Chloride (**19a**).* Rh complex **18c** (40 mg, 0.07 mmol) was dissolved in dried CH_2Cl_2 (3 mL), and carbon monoxide was bubbled through the solution for 1 h at room temperature. A color change from yellow to pale yellow was observed during this time. The solvent was evacuated in vacuo, and the residue was purified by column chromatography on silica gel (PE/EtOAc = 12:1) to give the product **19a** as an orange powder (25 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.8 Hz), 6.78 (dd, J^1 = 2.8 Hz, J^2 = 8.8 Hz, 1H), 6.54 (d, J = 2.8 Hz, 1H), 5.54−5.45 (m, 2H), 4.26 (d, J = 3.2 Hz, 2H), 3.78 (s, 3H, OCH_3), 2.26−2.08 (m, 5H), 1.96−1.85 (m, 4H), 1.78−1.64 (m, 6H), 1.60−1.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3 (d, $^1J_{RhC}$ = 38.4 Hz, $C_{carb}Rh$), 186.3 (d, $^1J_{RhC}$ = 54.4 Hz, OCRh), 183.3 (d, $^1J_{RhC}$ = 73.4 Hz, OCRh), 156.6, 128.2, 122.8, 117.9, 113.0, 111.2, 67.7, 66.6, 55.5, 43.4, 30.9, 29.9, 29.7, 29.6, 28.8, 26.6, 26.3, 25.6, 25.4, 25.2; IR (KBr disk) 2069, 1989 cm $^{-1}$.

*(3-(3,5-Dimethylphenyl)-1-isopropyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Biscarbonyl Chloride (**19b**).* Following the procedure for the synthesis of **19a**, **18d** (40 mg, 0.076 mmol) afforded **19b** as an orange powder (30 mg, 83%), which was purified by column chromatography on silica gel (PE/EA = 12:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.18−7.00 (m, 5H), 6.18 (sept, 1H, NCH), 4.80 (d, J^1 = 14.8 Hz, 1H), 4.74 (d, J^1 = 14.8 Hz, 1H), 2.37 (s, 6H), 1.71 (t, J = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0 (d, $^1J_{RhC}$ = 39.6 Hz, $C_{carb}Rh$), 186.2 (d, $^1J_{RhC}$ = 53.8 Hz, OCRh), 182.9 (d, $^1J_{RhC}$ = 77.0 Hz, OCRh), 144.9, 139.3, 132.7, 129.8, 128.2, 126.4, 125.4, 125.2, 121.5, 116.7, 59.8, 51.8, 29.7, 21.3, 20.7, 20.1; IR (KBr disk) 2067, 1989 cm $^{-1}$.

*(3-Benzyl-1-isopropyl-3,4-dihydroquinazolin-2-ylidene)rhodium-(I) Biscarbonyl Chloride (**19c**).* Following the procedure for the synthesis of **19a**, **18e** (54 mg, 0.17 mmol) afforded **19c** as an orange powder (35 mg, 72%), which was purified by column chromatography on silica gel (PE/EA = 12:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.32 (m, 1H), 7.24−7.18 (m, 1H, Ar-H), 7.08 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 6.8 Hz, 1H), 6.19 (sept, J = 7.2 Hz, 1H), 6.13 (d, 1H, J = 14.8 Hz), 5.07 (d, J = 15.2 Hz, 1H), 4.34−4.23 (m, 2H, NCH_2), 1.75 (d, J = 7.2 Hz, 3H), 1.67 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4 (d, $^1J_{RhC}$ = 39.7 Hz, $C_{carb}Rh$), 185.7 (d, $^1J_{RhC}$ = 54.2 Hz, OCRh), 182.7 (d, $^1J_{RhC}$ = 76.0 Hz, OCRh), 134.3, 132.7, 128.9, 128.3, 128.0, 127.7, 126.6, 125.2, 121.1, 116.5, 62.3, 59.5, 47.0, 20.8, 19.7; IR (KBr disk) 2071, 1992 cm $^{-1}$.

*(3-Cyclohexyl-1-isopropyl-3,4-dihydroquinazolin-2-ylidene)-rhodium(I) Biscarbonyl Chloride (**19d**).* Following the procedure for the synthesis of **19a**, **18f** (50 mg, 0.1 mmol) afforded **19d** as an orange powder (37 mg, 82%), which was purified by column chromatography on silica gel (PE/EA = 12:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.27 (m, 2H), 7.14−7.10 (m, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.02 (sept, J = 7.2 Hz, 1H), 5.52−5.46 (m, 1H), 4.34 (d, J = 14.8 Hz, 1H), 4.25 (d, J = 14.8 Hz, 1H), 2.22−2.19 (m, 1H), 1.92−1.76 (m, 4H), 1.70 (d, J = 7.2 Hz, 3H), 1.62 (d, J = 7.2 Hz, 3H), 1.52−1.45 (m, 3H), 1.31−1.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3 (d, $^1J_{RhC}$ = 38.4 Hz, $C_{carb}Rh$), 186.1 (d, $^1J_{RhC}$ = 52.7 Hz, OCRh), 182.9 (d, $^1J_{RhC}$ = 76.6 Hz, OCRh), 133.8, 127.9, 126.4, 124.8, 121.2, 116.2, 66.8, 58.6, 43.2, 29.6, 28.8, 25.4, 20.9, 19.9; IR (KBr disk) 2070, 1991 cm $^{-1}$.

*(4-Butyl-3-cyclohexyl-1-isopropyl-3,4-dihydroquinazolin-2-ylidene)rhodium(I) Biscarbonyl Chloride (**19e**).* Following the procedure for the synthesis of **19a**, **18g** (35 mg, 0.062 mmol) afforded **19e** as an orange powder (21 mg, 67%), which was purified by column chromatography on silica gel (PE/EA = 12:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.30 (m, 2H), 7.17−7.13 (m, 1H), 7.03−6.97 (m, 1H), 5.89−5.78 (m, 1H), 5.47−5.41 (m, 1H), 4.21 (t, J = 7.0 Hz, 1H), 2.44 (m, 1H), 2.17−2.08 (m, 1H), 1.96−1.89 (m, 2H), 1.78 (d, J = 7.2 Hz, 3H), 1.60−1.54 (m, 5H), 1.51 (d, J = 6.8 Hz, 3H), 1.25 (m, 2H), 1.18−0.81 (m, 5H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9 (d, $^1J_{RhC}$ = 41.1 Hz, $C_{carb}Rh$), 186.2 (d, $^1J_{RhC}$ = 46.3 Hz, OCRh), 183.3 (d, $^1J_{RhC}$ = 76.4 Hz, OCRh), 133.7, 127.6, 126.1, 124.2, 116.3, 66.7, 57.4, 54.3, 35.1, 31.9, 30.8, 27.3, 25.5, 25.2, 22.3, 22.2, 21.8, 19.3, 13.9; IR (KBr disk) 2071, 1991 cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving experimental procedures for the synthesis of the ligands and CIF files giving crystal data for the complexes described herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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