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Synthesis and Complexation Behavior of Indenyl and Cyclopentadienyl Ligands Functionalized with a Naphthyridine Unit

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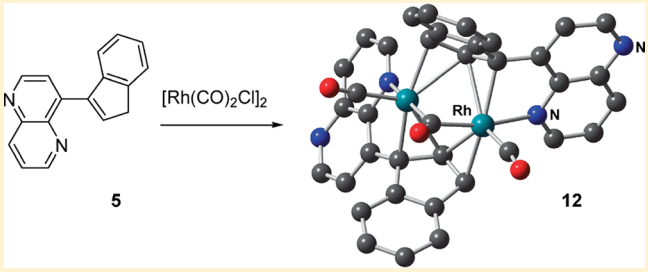
Supporting Information

ABSTRACT: Lithium indenide (Li-Ind) or cyclopentadienide (Li-Cp) derivatives react as nucleophiles with 8-(methylsulfinyl)-1,5-naphthyridine (Naph), leading to donor-functionalized ligands Ind^{Naph} or Cp^{Naph}, respectively. The new ligands comprise two N-donor atoms, which, for geometric reasons, cannot bind to the same metal atom. In complexes, where the metal atom is bound by the Cp or Ind moiety, the N5-donor atom is located in a distal position. The coordination behavior to Rh or Zr metal centers has been investigated. The Cp-based ligands show the expected chelating coordination mode with η^5-Cp and N coordination, whereas the indenyl units act as dihapto, trihapto, or pentahapto ligands. The dinuclear Rh(I) complex **12** shows a rare coordination geometry with two η^3 ligands bridging a $Rh_2(CO)_3$ fragment.



INTRODUCTION

Donor-functionalized cyclopentadienides or indenides play an important role as spectator ligands in organometallic chemistry.[1] The combination of anionic cyclopentadienides or indenides (Cp^- or Ind^-) with a neutral donor function leads to systems that can act as chelating ligands or as hemilabile ligands, depending on the metal atom used. The spacer between the donor function and the C_5 ring has to be of suitable length and geometry. By incorporation of the spacer and the donor atom into an aromatic ring system, rigid and well-coordinating chelate ligands are obtained. Therefore, the C_5 ring has to be directly connected to an aromatic group. Cyclopentadienides or indenides (e.g., LiC_5H_5 or LiC_9H_7) are easily available compounds, but unfortunately, they rarely react with aromatic rings. We have used and developed several routes for the synthesis of aromatically substituted cyclopentadienes and indenes.[2]

In previous work, we have incorporated a C_2 spacer as well as an sp^2 nitrogen atom into a rigid heterocycle by using 8-quinolyl-functionalized Cp and Ind ligands. Their predefined geometry allows the coordination of the N atom to the cyclopentadienyl- or indenyl-bonded metal center.[3] We have also prepared a number of 9-(1-naphthyl)-9*H*-fluorene and 3-(1-naphthyl)-1*H*-indene ligand precursors containing an additional coordinating group at the naphthalene 2-position through the use of various synthetic approaches, including the use of ligand-coupling reactions of 1-naphthyl sulfoxides, activated by carboxylate esters at the naphthalene 2-position, with fluorenyl and indenyllithiums.[4] We also described how ligand-coupling reactions of 1-isoquinolinyl and 2-pyridyl sulfoxides with 1-naphthyl Grignard reagents could be used to obtain axially chiral isoquinoline and pyridine ligands.[5] A logical extension of this work is the potential for ligand-coupling reactions of azaheterocyclic sulfoxides with fluorenides, indenides, or cyclopentadienides.

Since the nitrogen atom in an 8-quinolyl sulfoxide is not in a position to activate a ligand-coupling reaction, we decided to examine the reactions of 8-sulfinyl-1,5-naphthyridenes, where N5 is in a position to activate potential ligand-coupling reactions, while N1 can coordinate to a metal in a manner analogous to 8-quinolyl-functionalized Cp and Ind ligands. Metal complexes of 1,5-naphthyriden-8-yl-functionalized Cp and Ind ligands would be of particular interest as the distal N5 is in strong electronic communication with the coordinating Cp or Ind group, whereas N1 may coordinate to the same metal as the five-membered ring. This opens up interesting possibilities to "tune" the reactivity of the metal complex through the coordination of a Lewis acid to the 5-nitrogen.

There have been only a few examples of cyclopentadienides or indenides being involved in aromatic substitution reactions, and in those examples, strong electron-withdrawing groups are required to facilitate the reaction.[2c,6] While sulfoxide ligand-coupling reactions also require the presence of electron-withdrawing groups at positions consistent with an S_NAr mechanism,

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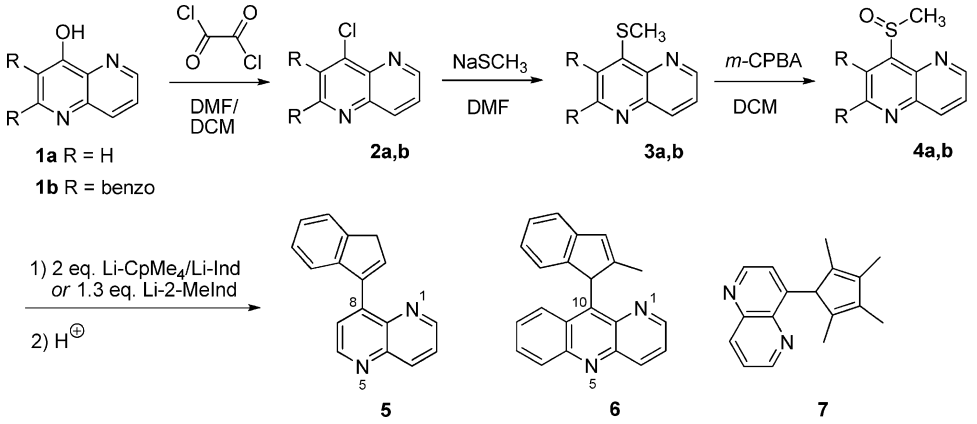
Scheme 1. Synthetic Route to the Ligands 5−7



Oae and Furakawa and their co-workers have carried out extensive studies that demonstrate that these reactions proceed through the intermediacy of hypervalent σ-sulfuranes formed through initial nucleophilic attack at sulfur.[7] Apicophilic groups that can stabilize this intermediate greatly facilitate the reaction, making the method ideally suited for stabilized carbanions, such as cyclopentadienides or indenides. In addition to preparing 1,5-naphthyriden-8-yl-functionalized Cp and Ind ligands, we were also interested in preparing benzo[*b*][1,5]naphthyridin-10-yl-functionalized Ind ligands with a view to generating systems with a stable rotational axis around the heteroaryl−indene bond that could then be used to generate planar-chiral metal complexes stereospecifically[2a,b] or to constrain the coordination of the 1-nitrogen to metals coordinating the Ind moiety.[8]

RESULTS AND DISCUSSION

Ligand Synthesis. The synthesis of the required sulfoxides commenced with 8-hydroxy-1,5-naphthyridine (**1a**)[9] and benzo[*b*][1,5]naphthyridin-10(5*H*)-one (**1b** drawn as the hydroxy tautomer in Scheme 1 for convenience),[10] which were prepared following literature procedures. Both **1a** and **1b** have been previously converted into the corresponding chloro derivatives (**2a**, **2b**), using either phosphorus oxychloride[8] or thionyl chloride,[9] respectively; however, we found it more convenient to use the Vilsmeier reagent generated from oxalyl chloride and DMF (Scheme 1). In the case of **1a**, the chloro derivative **2a** was isolated and subsequently treated with sodium methanethiolate to furnish the methylsulfanyl derivative **3a**. In the case of **1b**, the chlorination and subsequent reaction with methanethiolate to provide **3b** were carried out in the one pot, since the chloro derivative **2b** proved too reactive to isolate without significant conversion back to **1b**. The sulfides **3a** and **3b** were then oxidized to the sulfoxides **4a** and **4b**, respectively, by using 1 equiv of *m*-CPBA. The sulfoxide **4a** rapidly reacts with either Li-Ind or lithium 1,2,3,4-tetramethylcyclopentadienide (Li-CpMe$_4$) at −78 °C in THF solution. While the initial ligand-coupling product in the reaction with Li-Ind is the 1-heteroaryl-1*H*-indene tautomer, the presence of the heteroaryl substituent appears to lead to an increased acidity of the indene so that the product is deprotonated by the starting Li-Ind present in the reaction mixture, as evident by a deeply violet color (the same color develops when the isolated ligand **5** is reacted with *n*-BuLi in THF). When using only a slight excess of Li-Ind, the reaction fails to go to completion, and on hydrolysis, the ligand-coupling product is isolated as a mixture of the 1-heteroaryl-1*H*- and 3-heteoaryl-1*H*-indene tautomers. However, when 2 equiv of Li-Ind are used, together with a longer reaction time (1 h), only the 3-heteroaryl-1*H*-indene tautomer **5** is isolated in a yield of 85%. The reaction of **4a** with 2 equiv of Li-CpMe$_4$, which also results in the formation of an intensely violet solution of the lithium salt of **7**, affords on hydrolysis the ligand **7** in 85% isolated yield. In the case of sulfoxide **4b**, the ligand-coupling reaction was carried out using lithium-2-methylindenide (Li-2-MeInd), the 2-methyl substituent being used to raise the barrier to rotation around the heteroaryl−indene bond. When this reaction was carried out using the same conditions as for **4a**, the 3-heteroaryl-1*H*-indene tautomer of the product was formed, but this proved to be quite unstable to light and air, and underwent substantial decomposition during attempts to purify it. To isolate the 1-heteroaryl-1*H*-indene tautomer, the reaction was carried at −110 °C with 1.3 equiv of Li-2-MeInd for only 30 min. The 1-heteroaryl-1*H*-indene tautomer **6**, which was stable, was isolated in 57% yield.

Formation of Metal Complexes. It is well known that rhodium complexes with a Cp ligand and additional labile ligands can be activated thermally or photochemically. The resulting complexes are highly reactive and can, for example, activate CH bonds in hydrocarbons.[11] It was also shown that hemilabile donors stabilize the reactive intermediates so that cleaner catalytic transformations are possible.[12]

The synthesis of complex **8** is achieved by reaction of the deprotonated ligand **7** with the rhodium precursor di-μ-chlorodicyclooctadienyldirhodium(I) in 45% yield. Exposure to UV light in deuterated chloroform allows the quantitative conversion to the red Rh(III) complex **9** (see Scheme 2). The η^5-hapticity in **8** and in **9** is confirmed by the presence of scalar couplings between the ^{103}Rh nuclei and all five quaternary carbon atoms of the C$_5$ rings (**8**: $^1J_{Rh,C} \approx 8.5$ Hz; **9**: $^1J_{Rh,C} \approx 4.0$ Hz). The coordination of the naphthyridine unit to the Rh atom in **9** is confirmed by ^{15}N NMR. Noncoordinating ^{15}N atoms of the ligand precursors or of the complexes **8** and **9** give rise to signals in the region between δ = 300 and 320 ppm. The ^{15}N−^{1}H correlated spectrum of **9** (see Figure 1) shows two resonances, one at δ = 241.4 ppm for the coordinating N1 atom and the other at δ = 318.0 ppm for the distal N5 atom. The high field shift upon coordination is, therefore, about 70 ppm.

Crystals of the ligand precursor **7** and of the complexes **8** and **9** suitable for single-crystal X-ray diffraction analysis have been obtained from dichloromethane solutions. Their molecular structures are very similar to the corresponding quinoline systems.[12,13]

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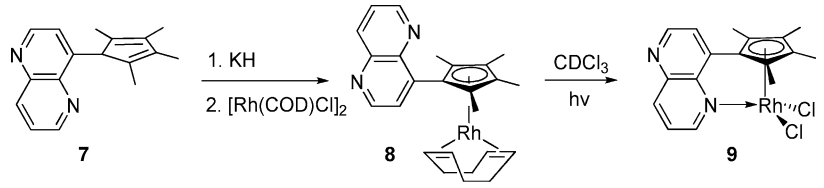
Scheme 2. Synthesis of 8 and 9



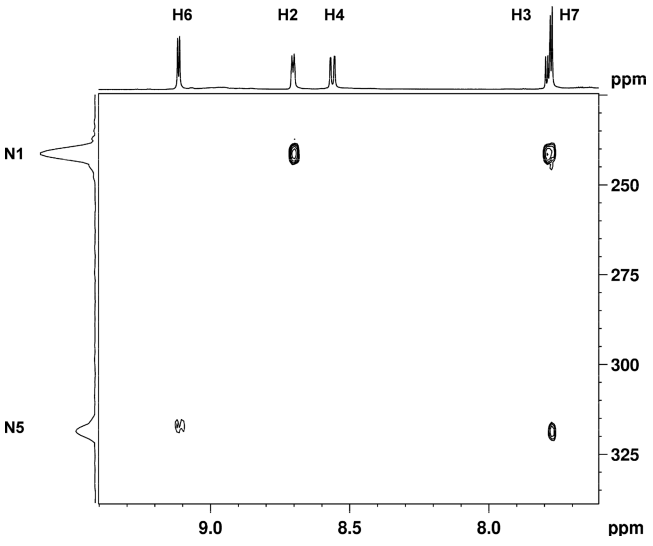
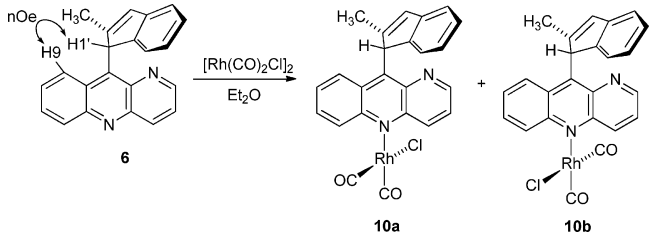


Figure 1. $^{15}N-^{1}H$ correlated NMR spectrum (HMBC) of **9**.

The chelating coordination mode with the well-suited geometry of the new ligand is visible in the molecular structure of complex **9** (see Figure 2).

On the basis of our previous studies with 1- and 3-(1-napthyl)-1*H*-indenes,[2a,c,4b,d] the benzonaphthyridene ligand **6** was expected to exhibit a stable rotational axis around the C−C single bond between the benzonaphthyridene and the indene moieties. The ligand-coupling reaction affords **6** as a single rotational isomer in which the indene H1′ is anti to the benzonaphthyridene N1 atom, as evident from a strong cross-peak in the NOESY spectrum between H1′ of the indene and H9 of the benzonaphthyridene (Scheme 3). Reaction of **6** with

Scheme 3. Synthesis of 10a and 10b



$[Rh(CO)_2Cl]_2$ leads to a product **10**, which shows only coordination to the N5 atom, as evident from the $^{15}N-^{1}H$ correlated HMBC spectrum, no doubt owing to steric hindrance of the N1 atom by the indene moiety. The IR spectrum of **10** shows two signals for the valence vibration of the two carbonyl units at $\tilde{\nu}(CO)$ = 2084 and 2009 cm^{-1}. The almost equal intensity of the two bands is indicative for two CO ligands in a cis arrangement.[14] Compared to other complexes of the type $Rh(CO)_2Cl(L)$ (L = ClPy, HOPy, Py, MePy), the influence of the benzonaphthyridene unit lies between pyridine and methylpyridine.[15] NMR analysis reveals that a 1:1 mixture of very similar compounds has formed. The ^{13}C NMR shows a double set of signals. For instance, there are four CO resonances that are each split into doublets due to coupling to ^{103}Rh ($^{1}J_{Rh,C}$ = 72.2 Hz for two doublets at δ = 180 ppm and 68.6 Hz for two

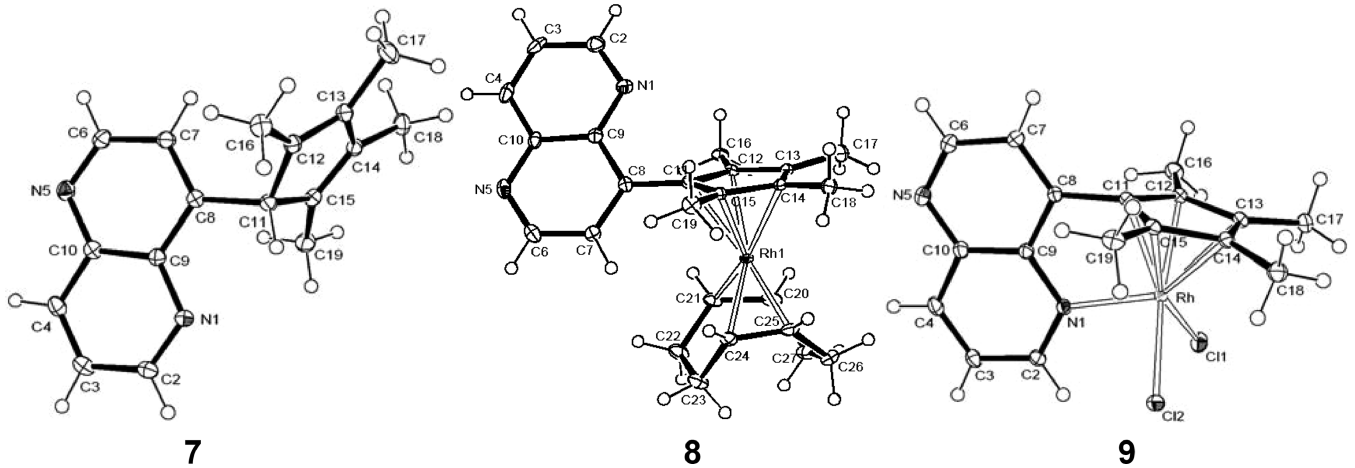


Figure 2. Solid-state molecular structures of **7**, **8**, and **9**. Selected bond lengths [Å] and angles [deg]. **7**: C(11)−C(12) 1.513(2); C(11)−C(15) 1.523(2); C(12)−C(13) 1.350(2); C(13)−C(14) 1.480(2); C(14)−C(15) 1.343(2). **8** (only one of the two independent molecules of **8** is shown; values refer to the molecule shown): Rh(1)−C(11) 2.240(3); Rh(1)−C(12) 2.201(3); Rh(1)−C(13) 2.277(3); Rh(1)−C(14) 2.277(3); Rh(1)−C(15) 2.232(3); Rh(1)−C(20) 2.109(4); Rh(1)−C(21) 2.103(4); Rh(1)−C(24) 2.115(3); Rh(1)−C(25) 2.109(4). **9**: Rh−N(1) 2.101(2); Rh−Cl(1) 2.395(1); Rh−Cl(2) 2.417(1); Rh−C(11) 2.073(2); Rh−C(12) 2.121(2); Rh−C(13) 2.193(2); Rh−C(14) 2.186(2); Rh−C(15) 2.126(2); N(1)−Rh−Cl(1) 91.19(4); N(1)−Rh−Cl(2) 90.07(4); Cl(1)−Rh−Cl(2) 93.19(4); C(11)−C(15) 1.441(2); C(11)−C(12) 1.445(2); C(12)−C(13) 1.454(2); C(13)−C(14) 1.423(3); C(14)−C(15) 1.453(2).

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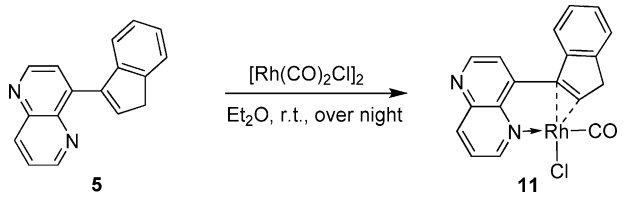
doublets at δ = 183 ppm). Consistent with these data are isomeric structures **10a** and **10b** where the CO ligands are mutually *cis*; however, the structures differ from one another through restricted rotation along the Rh–N bond. The peri-H substituents to 5-nitrogen in the benzonaphthyridene unit are presumably responsible for this behavior. To date, all attempts to prepare complexes of ligand **6** where the metal is coordinated to the indenyl moiety have been unsuccessful.

Whereas the benzonaphthyridene ligand **6** coordinates to the $Rh(CO)_2Cl$ unit with the N5 atom, ligand **5** binds to the same fragment with the N1 atom and additionally by the double bond of the indene unit. The rhodium-η^2-complex **11** could be obtained easily by reaction of **5** with tetracarbonyldi-μ-chlorodirhodium(I) at room temperature (Scheme 4).

Scheme 4. Synthesis of 11



Crystals of **11** were obtained from dichloromethane solutions. Figure 3 shows the well-suited geometry of the ligand for

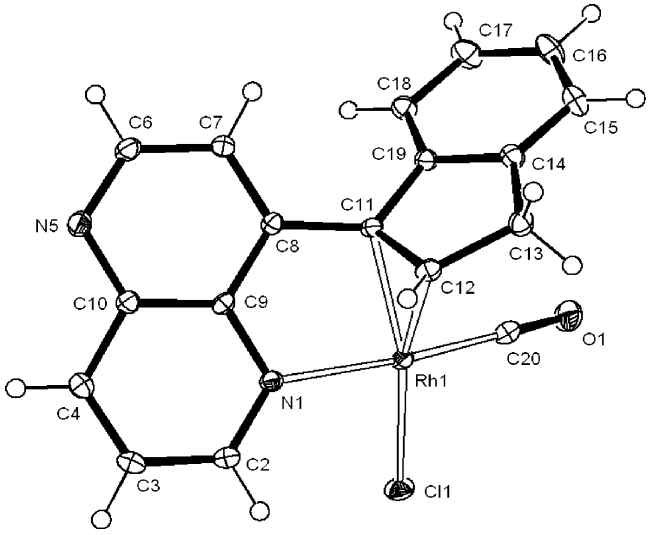
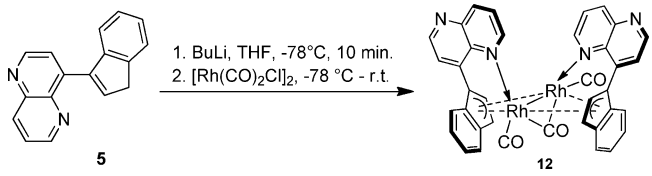


Figure 3. Solid-state molecular structure of **11**. Selected bond lengths [Å] and angles [deg]: Rh(1)–C(11) 2.152(2); Rh(1)–C(12) 2.121(2); Rh(1)–C(20) 1.838(2); Rh(1)–Cl(1) 2.3448(6); Rh(1)–N(1) 2.1004(18); C(20)–O(1) 1.135(1); C(19)–C(11)–Rh(1) 115.2(1); C(13)–C(12)–Rh(1) 119.13(15); C(20)–Rh(1)–N(1) 173.03(9); C(20)–Rh(1)–C(12) 92.57(9); C(20)–Rh(1)–C(11) 96.44(9); N(1)–Rh(1)–C(12) 89.33(8); N(1)–Rh(1)–C(11) 80.86(7); C(12)–Rh(1)–C(11) 38.99(8); C(20)–Rh(1)–Cl(1) 89.91(7); N(1)–Rh(1)–Cl(1) 90.97(5); O(1)–C(20)–Rh(1) 177.6(2).

a chelating coordination. The rhodium atom is in a square-planar coordination environment with the CO ligand in a trans position to the N-donor atom. The angles around N1 add to almost 360° (359.5°), which indicates that the lone pair of the N atom is in an ideal position for the interaction with the Rh center. The bond of Rh to two carbon atoms from the indene leads to doublets in the ^{13}C NMR spectra with $^1J(^{103}Rh,^{13}C)$ of 13.6 and 14.7 Hz, respectively. ^{15}N NMR gives information about the metal–N interaction in solution: whereas the distal N5 atom gives rise to a signal at 308.4 ppm (free ligand **5**: δ = 310.5 and 312.6 ppm), the coordinated N1 atom resonates at 244.9 ppm and is thus shifted by approximately 65 ppm upfield upon complexation.

We attempted to deprotonate complex **11** in order to promote the formation of a η^5-complex. However, reaction with potassium hydride led to the formation of a mixture where no products could be identified. Reaction with silver carbonate or iodine (either alone or in the presence of base) did not lead to the formation of a η^5-complex either. We, therefore, deprotonated ligand **5** with *n*-BuLi and reacted it with $[Rh(CO)_2Cl]_2$. Again, no η^5 Rh complex formed, but the unexpected dinuclear complex **12** was isolated (Scheme 5).

Scheme 5. Formation of Complex 12



Crystal structure analysis as well as NMR analysis confirmed the C_2-symmetric structure of complex **12**, which requires the coordination of the same planar-chiral face of two ligands to the $Rh_2(CO)_3$ fragment. Complex **12** is a coordinatively saturated rhodium dimer containing one metal–metal bond, one bridging CO, and one terminal CO per rhodium. The two deprotonated 8-(1-indenyl)-1,5-naphthyridine ligands are binding each with the N1 atom to one of the rhodium atoms. The indenyl parts of these ligands are both binding with three carbon atoms (η^3) to both rhodium atoms (μ_2) at once. In the $^{13}C\{^1H\}$ NMR spectrum of **12**, the indenyl C1′ and C3′ atoms appear as doublets through scalar couplings to ^{103}Rh, with $^1J_{Rh,C}$ = 10.9 and 9.4 Hz, respectively. The indenyl C2′ atom is, however, a singlet. The terminal CO ligands appear as a doublet with $^1J_{Rh,C}$ = 99.6 Hz, while the bridging CO appears as a triplet with $^1J_{Rh,C}$ = 38.2 Hz. The IR spectrum of **12** shows two signals for the vibrations of the terminal carbonyl units at $\tilde{\nu}$(CO) = 2022 and 1988 cm^{-1}, whereas the bridging carbonyl shows only one signal at $\tilde{\nu}$(CO) = 1776 cm^{-1}.

To date, there are just a few complexes known that contain a bridging η^3-indenyl ligand. The dimeric complex $(indenyl)_3Cr_2Cl$ **A** and its derivative $(indenyl)_4Cr_2$ **B** are representatives of a chromium species (Figure 4). They are available by reduction of chromium(III) chloride with sodium indenide, followed by gradual substitution of chloride with an indenyl group.[16] Complexes representing palladium are the dimeric species $(\mu,\eta^3\text{-Ind})(\mu\text{-Cl})Pd_2(PR_3)_2$ (R = Cy, Ph) **C**, which are accessible via a reversible conproportionation of Ind-Pd(II) and $Pd(0)(PR_3)_n$ species.[17] Figure 5 shows two different views of the complex $[Rh_2(Ind^{Naph})_2(CO)_3]$ **12**.

The formation of an η^5-complex with ligand **5** could be accomplished by reaction with $Zr(NMe)_4$. Both components react quickly at room temperature with formation of complex **13** together with free $HNMe_2$ as the only products. However, after 1 h in a sealed NMR tube, decomposition products are observable in the NMR spectrum and, after one day, **13** is transformed completely into a mixture of unidentified products. Therefore, **13** could be analyzed only by ^1H, ^{13}C, and ^1H–^{13}C correlation NMR spectroscopy. The three NMe_2 groups are

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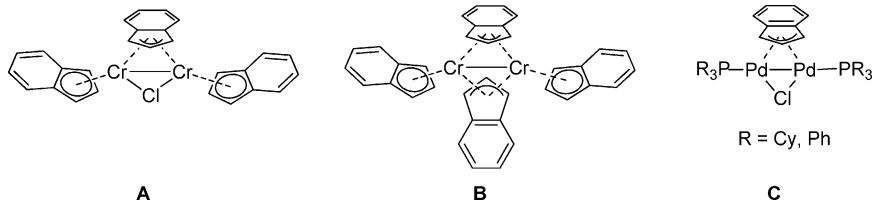


Figure 4. Literature examples of metal complexes with bridging η^3-indenyl ligands.

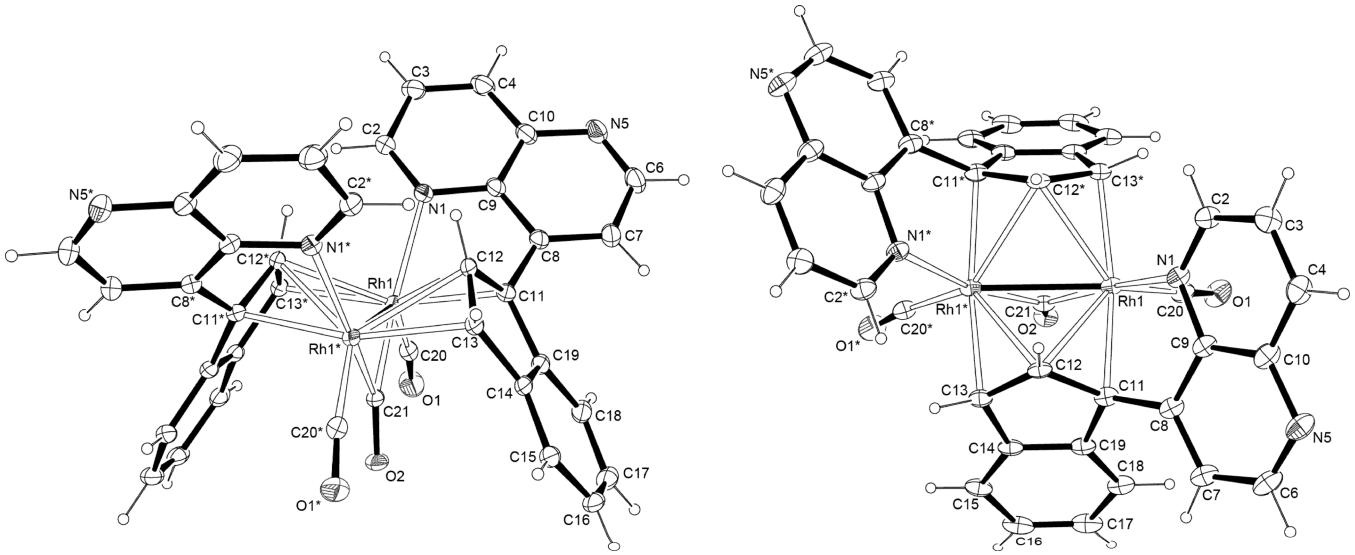
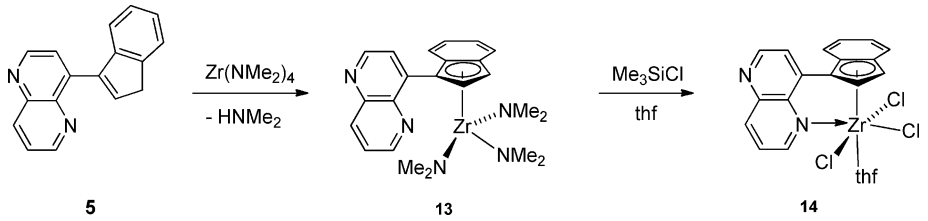


Figure 5. Solid-state molecular structure of $[Rh_2(Ind^{Naph})_2(CO)_3]$ **12** (left: side-view; right: top-view). A molecule of dichloromethane in the asymmetric unit has been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Rh(1)−Rh(1*) 2.7044(6); Rh(1)−C(11) 2.209(4); Rh(1)−C(12) 2.472(4); Rh(1)−C(12*) 2.475(3); Rh(1)−C(13*) 2.203(4); Rh(1)−C(20) 1.871(4); Rh(1)−C(21) 1.979(4); Rh(1)−N(1) 2.250(3); C(20)−O(1) 1.131(5); C(21)−O(2) 1.193(6); C(19)−C(11)−Rh(1) 113.5(2); C(14)−C(13)−Rh(1*) 115.6(2); C(12)−C(11)−Rh(1) 81.9(2); C(12)−C(13)−Rh(1*) 83.0(2); C(11)−Rh(1)−C(13*) 162.3(1); C(11)−Rh(1)−C(12*) 128.8(1); C(8)−C(11)−Rh(1) 105.7(3); N(1)−Rh(1)−C(11) 77.84(13); N(1)−Rh(1)−C(13*) 94.06(13); O(1)−C(20)−Rh(1) 171.2(4); O(2)−C(21)−Rh(1) 136.9(1); C(20)−Rh(1)−C(11) 102.1(2); C(20)−Rh(1)−C(13*) 94.6(2); N(1)−Rh(1)−C(20) 98.6(2); N(1)−Rh(1)−C(21) 168.0(1).

Scheme 6. Formation of Complexes 13 and 14



equivalent in the ^{1}H as well as in the ^{13}C NMR spectra. In addition to that, the ^{1}H NMR shifts of the naphthyridine unit are similar to those of the free ligand **5**. This is in agreement with a noncoordinating naphthyridine unit leading to a three-legged piano stool arrangement.[18] However, we cannot exclude the possibility of a weak naphthyridine−Zr interaction combined with a fast exchange of the NMe_2 units. A similar behavior has been observed by Kol et al. for a closely related zirconium complex where X-ray crystallography showed a very long Zr−N interaction between the additional N-donor and the zirconium atom.[19] Complex **13** can be converted to the stable chloro derivative **14** by addition of Me_3SiCl (see Scheme 6).

The coordination of the naphthyridine unit to the metal center in solution is proven by two well-separated ^{15}N NMR resonances with $\delta(^{15}N)$ = 172.3 ppm for the coordinated N1 and 314.2 ppm for the noncoordinating atom N5 (see Table 1). Therefore, the ^{15}N NMR resonance is shifted 141 ppm upfield upon coordination, a value that is much higher compared with complexation to the more electron-rich Rh(III) or Rh(I) centers in complexes **9**−**12**. Similar upfield shifts are well-documented in the literature.[20]

A single-crystal X-ray analysis of the complex reveals that two molecules of THF are present in the asymmetric unit. One of them is coordinated to the Zr center and thus completes its coordination sphere to an octahedral environment where the indenyl unit occupies one coordination site (see Figure 6). The Zr−N distance is within the usual range of such interactions.[18] We have tested complex **14** as an olefin polymerization catalyst. Addition of 1000 equiv of MAO (Al/Zr ratio) and ethylene saturation of the toluene solution lead to the formation of small

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Table 1. Comparison of the ^{15}N NMR Data of the Free Ligands and upon Ligand Coordination to the Metal Centers

complex	metal center	$\delta(^{15}N1/^{15}N5)$	corresponding ligand	$\delta(^{15}N1/^{15}N5)$	$\Delta\delta(^{15}N$ coord − ^{15}N noncoord)
9	Rh(III)	241/318	7	312/303	−71
10	Rh(I)	318/225	6	319/311	−86
11	Rh(I)	245/308	5	313/310	−68
12	Rh(I)	252/302	5	313/310	−61
14	Zr(IV)	172/314	5	313/310	−141

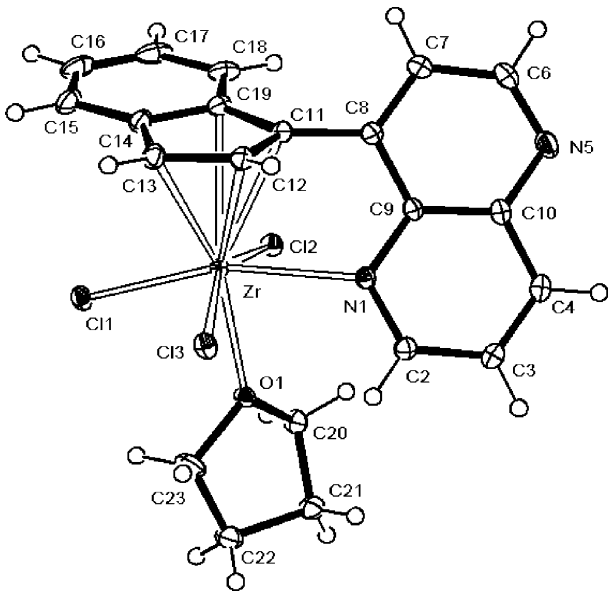

Figure 6. Solid-state molecular structures of **14**. An additional molecule of THF in the asymmetric unit has been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zr−O(1) 2.315(1); Zr−N(1) 2.416(1); Zr−Cl(1) 2.4431(4); Zr−Cl(2) 2.4676(4); Zr−Cl(3) 2.4834(4); Zr−C(12) 2.454(1); O(1)−Zr−N(1) 78.98(4); O(1)−Zr−Cl(1) 82.75(3); O(1)−Zr−Cl(2) 79.35(3); O(1)−Zr−Cl(3) 77.35(3); N(1)−Zr−Cl(1) 161.69(3); Cl(1)−Zr−C(12) 120.54(3).

amounts of linear polyethylene. The activity of 80 (g [polymer] mmol^{-1} [Zr] h^{-1} bar^{-1}) is quite low so that we did not evaluate this reactivity in more detail.

CONCLUSION

The synthesis of N-donor-functionalized indenyl and cyclopentadienyl ligands, where a second N atom is in a distal position, has been demonstrated by the coupling of the naphthyridine unit with the indenyl or the cyclopentadienyl ring, respectively. The coordination behavior of the new ligands has been evaluated in a series of rhodium complexes and two Zr(IV) complexes. Depending on the substitution pattern, Rh coordinates to the ligands in κ^1, η^2, η^3, or η^5 mode. The axially chiral ligand **6** forms two diastereomeric complexes (**10a** and **10b**) due to restricted rotation of the coordinated square-planar $Rh(CO)_2Cl$ unit. The dinuclear complex **12** shows a rare coordination environment where two ligands are bridging a $Rh_2(CO)_3$ unit. Zr complex **14** shows the expected geometry, and it has been evaluated as an olefin polymerization catalyst. ^{15}N NMR spectroscopy was used as a highly reliable tool for the validation of metal−N interactions in solution. This work is the basis for a wider application of donor-functionalized ligands with distal donors to other metal centers and for the investigation of the influence of the distal donor.

EXPERIMENTAL SECTION

Materials and General Considerations. Unless noted otherwise, all manipulations were carried out under an inert argon or nitrogen atmosphere using standard Schlenk techniques. All glassware was heated and dried under vacuum before use. Toluene, THF, dichloromethane, and *n*-hexane were dried using a solvent purifier system based on molecular sieves supplied by VAC and were degassed prior to use.

NMR spectra were recorded on a Bruker DRX 200, Bruker Avance II 400, or Bruker Avance III 600 spectrometer. The latter spectrometer was equipped with a direct detection cryoprobe for maximum sensitivity in the detection of ^{13}C. ^{1}H and ^{13}C NMR chemical shifts were referenced to signals of the solvent. NMR assignments were confirmed by H,H−COSY, HSQC, and HMBC experiments. Mass spectra were recorded on a Finnigan MAT8230 and a JEOL JMS-700 spectrometer. Elemental analyses were performed on a CHN-O-vario EL by the Mikroanalytisches Labor, Organisch-Chemisches Institut, University of Heidelberg. X-ray crystallographic data were collected using a Bruker AXS SMART 1000 CCD diffractometer (**7**−**9**, **11**, **14**) or a Bruker-Nonius Kappa Apex II diffractometer with an FR591 rotating anode source (**12**).

X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are listed in Table 1SI (see the Supporting Information). Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å) (compounds **7**−**9**, **11**, and **14**) or with a Bruker-Nonius Kappa Apex II diffractometer with an FR591 rotating anode source (compound **12**). Data were corrected for air and detector absorption, and Lorentz and polarization effects;[21] absorption by the crystal was treated with a semiempirical multiscan method.[22] The structures were solved by conventional direct methods[23] (**7**, **12**), by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors[24] (**8**, **11**, **14**) or by the charge flip procedure[25] (**13**) and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[26,23b] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data, the positions of some hydrogen atoms (the nonmethyl hydrogens in **7**, those on the carbon atoms involved in coordination to Rh **8** and **12**) were taken from difference Fourier syntheses and refined.

Synthesis of 2a. 8-Hydroxy-1,5-naphthyridine (1.00 g, 6.8 mmol) was suspended in a mixture of dry DMF (10 mL) and dry CH_2Cl_2 (10 mL) and cooled to −10 °C. Oxalyl chloride (700 μL, 8.16 mmol) was added dropwise, and the solution was warmed to rt. The CH_2Cl_2 was removed under vacuum, and the remaining DMF solution was stirred at 50 °C for 4 h. The mixture was diluted with CH_2Cl_2 (100 mL) and washed with dilute NH_3 (100 mL of water + 2 mL of conc. NH_3). The CH_2Cl_2 layer was filtered through Celite 545 to remove insoluble material, and the Celite was washed with further CH_2Cl_2. The combined CH_2Cl_2 filtrate was washed a further four times with water and dried with $MgSO_4$, and the solvent was evaporated. The crude chloride is a tan-colored solid. Yield: 710 mg (4.3 mmol = 63%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (dd, 1H, $^3J_{H2,H3}$ = 4.1 Hz, $^3J_{H3,H4}$ = 8.5 Hz, *H*3), 7.75 (d, 1H, $^3J_{H6,H7}$ = 4.6 Hz, *H*7), 8.34 (dd, 1H, $^3J_{H3,H4}$ = 8.5 Hz, $^4J_{H2,H4}$ = 1.5 Hz, *H*4), 8.84 (d, 1H, $^3J_{H6,H7}$ = 4.6 Hz, *H*6), 9.08 (dd, 1H, $^3J_{H2,H3}$ = 4.1 Hz, $^4J_{H2,H4}$ = 1.5 Hz, *H*2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 124.5, 125.3, 138.0 (3×CH), 140.9, 144.2, 144.9 (3×C_q),

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150.6, 151.6 (2×CH). MS(EI) *m*/*z* (%): 164 (100) $[M]^+$, 129 (45) $[M - Cl]^+$.

Synthesis of 3a. 8-Chloro-1,5-naphthyridine (**1b**) (1.43 g, 8.7 mmol) was dissolved in 10 mL of dry DMF, and 730 mg (10.4 mmol) of NaSMe was added. The reaction was exothermic. The mixture was stirred at rt overnight, then diluted with CH_2Cl_2 and washed five times with water. The organic layer was dried and the solvent evaporated. The crude product was isolated as a brown powder that was dried at 60 °C under high vacuum for 20 min in order to remove the last traces of DMF. Yield: 1.36 g (7.72 mmol = 89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.55 (s, 3H, C*H*$_3$), 7.26 (d, 1H, $^3J_{H6,H7}$ = 4.8 Hz, *H*7), 7.63 (dd, 1H, $^3J_{H2,H3}$ = 4.2 Hz, $^3J_{H3,H4}$ = 8.5 Hz, *H*3), 8.33 (dd, 1H, $^3J_{H3,H4}$ = 8.5 Hz, $^4J_{H2,H4}$ = 1.6 Hz, *H*4), 8.74 (d, 1H, $^3J_{H6,H7}$ = 4.8 Hz, *H*6), 8.91 (dd, 1H, $^3J_{H2,H3}$ = 4.2 Hz, $^4J_{H2,H4}$ = 1.6 Hz, *H*2). ^{13}C{^{1}H} ($CDCl_3$, 100 MHz): δ 13.6 (CH_3), 117.1, 124.9, 137.6 (3×CH), 141.7, 142.3 (2×C_q), 149.4, 150.1 (2×CH), 151.6 (C_q). MS(EI) *m*/*z* (%): 176 (100) $[M]^+$, 129 (45) $[M - SCH_3]^+$.

Synthesis of 3b. Benzo[*b*][1,5]naphthyridin-10(5*H*)-one (2.0 g, 10.2 mmol) was suspended in a mixture of dry DMF (20 mL) and dry CH_2Cl_2 (20 mL) and cooled to −10 °C. Oxalyl chloride (1.45 g, 11.4 mmol) was added dropwise and the solution warmed to rt. The CH_2Cl_2 was removed under vacuum. The solution was cooled to 0 °C, and NaSMe (2.2 g, 31.4 mmol) was added. The mixture was stirred at 0 °C for 10 min and was allowed to warm to rt over 30 min. The mixture was diluted with CH_2Cl_2 (150 mL) and extracted with dilute NH_3 (150 mL of water + 2 mL of conc. NH_3). The CH_2Cl_2 layer was filtered through Celite 545 to remove insoluble material. The combined CH_2Cl_2 filtrate was washed a further four times with water and dried, and the solvent was evaporated. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 15% EtOAc + 1% NEt_3 in CH_2Cl_2 gave the sulfide as a pale yellow solid. Yield: 950 mg (4.2 mmol = 41%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.87 (s, 3H, C*H*$_3$), 7.64 (m, 1H, *H*8), 7.68 (dd, 1H, $^3J_{H3,H4}$ = 8.8 Hz, $^3J_{H2,H3}$ = 3.8 Hz, *H*3), 7.82 (m, 1H, *H*7), 8.20 (d, 1H, $^3J_{H8,H9}$ = 8.8 Hz, *H*9), 8.51 (dd, 1H, $^3J_{H3,H4}$ = 8.8 Hz, $^4J_{H2,H4}$ = 1.5 Hz, *H*4), 8.81 (d, 1H, $^3J_{H6,H7}$ = 8.8 Hz, *H*6), 9.12 (dd, 1H, $^3J_{H2,H3}$ = 3.8 Hz, $^4J_{H2,H4}$ = 1.5 Hz, *H*2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 20.5 (CH_3), 124.7, 126.6, 126.8 (3×CH), 129.8 (C_q), 130.1, 130.9, 138.1 (3×CH), 140.7, 144.3, 148.6, 149.4 (4×C_q), 151.0 (CH). MS (EI) *m*/*z* (%): 226 (10) $[M]^+$, 180 (100) $[M - SCH_3]^+$.

Synthesis of 4a. The sulfide **3a** (1.36 g, 7.7 mmol) was dissolved in 70 mL of CH_2Cl_2, the solution cooled to 0 °C, and *m*-CPBA (2.21 g of 70−75% purity, 9.6 mmol) was added. The mixture was allowed to warm to rt over 10 min. The CH_2Cl_2 solution was washed twice with saturated aqueous $NaHCO_3$ solution and dried with $MgSO_4$, and the solvent was evaporated. The crude sulfoxide is a pale yellow solid. Yield: 1.15 g (6.0 mmol, 78%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.07 (s, 3H, C*H*$_3$), 7.73 (dd, 1H, $^3J_{H2,H3}$ = 4.1 Hz, $^3J_{H3,H4}$ = 8.5 Hz, *H*3), 8.20 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*7), 8.50 (d, 1H, $^3J_{H3,H4}$ = 8.5 Hz, *H*4), 8.94 (d, 1H, $^3J_{H2,H3}$ = 4.1 Hz, *H*2), 9.17 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*6). ^{13}C{^{1}H} ($CDCl_3$, 150 MHz): δ = 41.9 (CH_3), 119.7, 125.2, 137.8 (3×CH), 139.2, 143.2 (2×C_q), 150.7, 151.3 (2×CH), 154.3 (C_q).

Synthesis of 5. A solution of indenyllithium was prepared by dissolving indene (1.65 mL, 14.0 mmol) in 30 mL of THF at 0 °C and adding *n*-BuLi (8.6 mL of 1.6 M, 13.8 mmol) dropwise. The solution was cooled to −78 °C, and the sulfoxide **4a** (1.21 g, 6.3 mmol) dissolved in 15 mL of THF was added dropwise. After 1 h at −78 °C, the reaction was quenched by addition of 10% aqueous NH_4Cl (100 mL). The mixture was diluted with CH_2Cl_2 and the organic layer separated. The CH_2Cl_2 layer was washed a further two times with water and dried with $MgSO_4$, and the solvent was evaporated. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 25% EtOAc in CH_2Cl_2 gave the indene product as a pale pink solid. Yield: 1.31 g (5.36 mmol = 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.69 (d, 2H, $^3J_{H1',H2'}$ = 1.8 Hz, (*H*1′)$_2$), 6.95 (t, 1H, $^3J_{H1',H2'}$ = 1.8 Hz, *H*2′), 7.19−7.26 (m, 3H, *H*4/*H*5/*H*6), 7.56 (m, 1H, *H*7), 7.66 (dd, 1H, $^3J_{H2,H3}$ = 4.1 Hz, $^3J_{H3,H4}$ = 8.5 Hz, *H*3), 7.73 (d, 1H, $^3J_{H6,H7}$ = 4.4 Hz, *H*7), 8.46 (dd, 1H, $^3J_{H3,H4}$ = 8.5 Hz, $^4J_{H2,H4}$ = 1.7 Hz, *H*4), 8.96 (dd, 1H, $^3J_{H2,H3}$ = 4.1 Hz, $^4J_{H2,H4}$ = 1.7 Hz, *H*2), 9.02 (d, 1H, $^3J_{H6,H7}$ = 4.4 Hz, *H*6). ^{13}C{^{1}H} ($CDCl_3$, 100 MHz): δ 38.7 (*C*1′), 120.9 (*C*2′), 123.7 (*C*7), 124.0 (CH_{Ind}), 124.5 (*C*3), 125.7, 126.1 (2×CH_{Ind}), 136.5 (CH_{Ind}), 137.7 (*C*4), 140.8, 142.5, 143.8, 143.9, 144.3, 144.3 (6×C_q), 150.7 (t, $^2J_{H,N}$ = 3.2 Hz, *C*2), 151.1 (t, $^2J_{H,N}$ = 3.0 Hz, *C*6). ^{15}N NMR ($CDCl_3$, 61 MHz): δ 310.5 (*N*5/H4, H6, H7), 312.6 (*N*1/H2, H3, H7). MS(EI) *m*/*z* (%): 243 (100) $[M - H]^+$, 216 (8) $[M - C_2H_3]^+$. $C_{17}H_{12}N_2$ (244.28) Calcd: C, 83.58; H, 4.95; N, 11.47. Found: C, 82.87; H, 4.92; N, 11.35.

Synthesis of 6. The sulfide **3b** (1.0 g, 4.4 mmol) was dissolved in 50 mL of CH_2Cl_2. The solution was cooled to 0 °C, and *m*-CPBA (1.1 g of 70−75% purity, 4.6 mmol) was added. After 15 min, the solution was extracted twice with saturated aqueous $NaHCO_3$ solution and dried with $MgSO_4$, and the solvent was evaporated. The crude product (**4b**) was used directly in the next step. A solution of 2-methylindenyllithium was prepared by dissolving 2-methylindene (710 μL, 5.3 mmol) in 70 mL of THF at 0 °C and adding *n*-BuLi (3.4 mL of 1.6 M, 5.4 mmol) dropwise. The solution was cooled to −110 °C, and the crude sulfoxide **4b** (1.0 g, 4.1 mmol) dissolved in 20 mL of dry CH_2Cl_2 was added dropwise. After 30 min at −110 °C, the reaction was quenched by addition of 10% aqueous NH_4Cl (100 mL). The mixture was diluted with CH_2Cl_2, and the organic layer was separated. The CH_2Cl_2 layer was then washed twice with water and dried with $MgSO_4$, and the solvent was evaporated. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 5% EtOAc in CH_2Cl_2 gave the indene product as a gum contaminated with a bright yellow impurity. The yellow impurity can be removed by dissolving the product in a little CH_2Cl_2 and then adding *n*-hexane: the yellow impurity then precipitates as a gum on the walls of the flask. The mother liquor is separated and heated to boil off the CH_2Cl_2; the pure indene then crystallizes from the *n*-hexane solution as a colorless solid. Yield: 780 mg (2.53 mmol = 58% calculated from **3b**). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.82 (s, 3H, C*H*$_3$), 5.41 (s, 1H, *H*1′), 6.68 (dd, 1H, $^3J_{H3,H4}$ = 8.6 Hz, $^4J_{H2,H3}$ = 3.9 Hz, *H*3), 6.83 (m, 2H, *H*3′/*H*7′), 6.94, (dd, 1H, $^3J_{H4',H5'}$ = 7.5 Hz, $^3J_{H5',H6'}$ = 7.5 Hz, *H*5′), 7.31 (m, 2H, *H*6′/*H*8), 7.54 (m, 2H, *H*4′/*H*7), 8.23 (d, 1H, $^3J_{H8,H9}$ = 8.9 Hz, *H*9), 8.34 (m, 2H, *H*2/*H*4), 8.61 (d, 1H, $^3J_{H6,H7}$ = 8.8 Hz, *H*6). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 15.7 (CH_3), 53.2 (*C*1′), 120.5 (CH), 122.6 (*C*3′), 123.5 (CH_{Ind}), 124.1, 124.6 (2×CH), 126.7, 127.8, 129.6 (3×CH_{Ind}), 130.1, 131.7, 137.5 (3×CH), 129.5, 138.8, 144.7, 144.8, 145.6, 148.8, 150.0, 150.7 (8×C_q), 150.8 (*C*H). ^{15}N-HMBC NMR (C_6D_6, 41 MHz): δ 311.5 (*N*5/H4, H6), 319.1 (*N*1/H2, H3, H4). MS(FAB) *m*/*z* (%): 309 (100) $[M + H]^+$, 293 (53) $[M - CH_3 - H]^+$.

Synthesis of 7. A solution of 1,2,3,4-tetramethylcyclopentadienyllithium was prepared by dissolving 1,2,3,4-tetramethylcyclopentadiene (220 mg, 1.8 mmol, 85% purity) in 10 mL of THF and adding *n*-BuLi (1.2 mL of 1.6 M, 1.9 mmol) dropwise over 10 min at 0 °C. The solution was cooled to −78 °C, and the sulfoxide **4a** (170 mg, 0.9 mmol) dissolved in 10 mL of THF was added dropwise. After 2 h at −78 °C, the reaction was quenched by addition of 10% aqueous NH_4Cl (50 mL). The mixture was diluted with CH_2Cl_2, and the organic layer was separated. The CH_2Cl_2 layer was washed a further two times with water and dried with $MgSO_4$, and the solvent was evaporated. Flash chromatography (silica gel 60, 230−400 mesh) eluting with 25% EtOAc in CH_2Cl_2 gave the product as an orange compound. Yield: 188 mg (0.75 mmol = 83%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.60 (s, 6H, 2×C*H*$_3$), 1.85 (s, 6H, 2×C*H*$_3$), 5.43 (s, 1H, Cp*H*), 6.89 (d, 1H, $^3J_{H7,H6}$ = 4.5 Hz, *H*7), 7.64 (dd, 1H, $^3J_{H3,H4}$ = 8.5 Hz, $^3J_{H3,H2}$ = 4.4 Hz, *H*3), 8.40 (dd, 1H, $^3J_{H4,H3}$ = 8.5 Hz, $^4J_{H4,H2}$ = 1.2 Hz, *H*4), 8.77 (d, 1H, $^3J_{H6,H7}$ = 4.5 Hz, *H*6), 9.01 (dd, 1H, $^3J_{H2,H3}$ = 4.4 Hz, $^4J_{H2,H4}$ = 1.2 Hz, *H*2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 11.1 (CH_3), 11.8 (CH_3), 55.4 (CH_{Cp}), 121.0 (*C*7), 123.9 (*C*3), 136.9 (C_q), 137.4 (*C*4), 137.9 (C_q), 143.6, 143.8, 144.4 (3×C_q), 149.6 (*C*2), 150.9 (*C*6). ^{15}N-HMBC NMR ($CDCl_3$, 41 MHz): δ 302.6 (*N*5/H4, H6, H7), 311.8 (*N*1/H3). MS(EI) *m*/*z* (%): 250 (100) $[M]^+$, 235 (95) $[M - CH_3]^+$, 220 (30) $[M - 2×CH_3]^+$, 205 (12) $[M - 3×CH_3]^+$.

Synthesis of 8. Ligand **7** (497 mg, 1.99 mmol) was dissolved in 100 mL of THF, and KH (84 mg, 2.09 mmol) was added at rt. After stirring overnight, di-μ-chlorodicyclooctadienyldirhodium(I) (490 mg, 0.99 mmol) in 100 mL of toluene was added, and the reaction mixture was stirred for a further 2 days. The solvent was evaporated and the residue extracted with diethylether. Flash chromatography (Alox, 230−400 mesh) eluting with CH_2Cl_2 gave the product as a red solid.

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Yield: 412 mg (0.9 mmol = 45%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.52 (s, 6H, 2×CH_3), 2.02 (m, 4H, $CH_{2\text{-COD}}$), 2.05 (s, 6H, 2×CH_3), 2.32 (m, 4H, $CH_{2\text{-COD}}$), 3.17 (m, 4H, CH_{COD}), 7.62 (dd, 1H, $^3J_{H3,H4}$ = 8.4 Hz, $^3J_{H3,H2}$ = 4.1 Hz, *H*3), 8.32 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*7), 8.45 (dd, 1H, $^3J_{H4,H3}$ = 8.4 Hz, $^4J_{H4,H2}$ = 1.5 Hz, *H*4), 9.01 (dd, 1H, $^3J_{H2,H3}$ = 4.1 Hz, $^4J_{H2,H4}$ = 1.5 Hz, *H*2), 9.05 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*6). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 9.9, 10.6 (2×CH_3), 32.4 ($CH_{2\text{-COD}}$), 71.4 (d, $^1J_{Rh,C}$ = 14.0 Hz, CH_{COD}), 96.8 (d, $^1J_{Rh,C}$ = 4.1 Hz, C_q), 99.6 (d, $^1J_{Rh,C}$ = 4.0 Hz, C_q), 102.3 (d, $^1J_{Rh,C}$ = 4.6 Hz, C_q), 123.8 (*C*3), 130.0 (*C*7), 137.4 (*C*4), 143.9, 144.1, 144.5 (3×C_q), 150.3 (*C*2), 150.6 (*C*6). ^{15}N-HMBC NMR ($CDCl_3$, 61 MHz): δ 306.9 (*N*5/H4, H6, H7), 313.9 (*N*1/H2, H3). MS(EI) *m*/*z* (%): 460 (24) [M]$^+$, 352 (77) [M − COD]$^+$, 249 (49) [M − RhCOD]$^+$. $C_{25}H_{29}N_2Rh$ (460.42 g/mol) Calcd: C, 65.22; H, 6.35; N, 6.08. Found: C, 64.55; H, 6.44; N, 6.49.

Synthesis of 9. An NMR tube was charged with complex **8** (30 mg, 0.07 mmol) in $CDCl_3$ (0.6 mL) and irradiated with ultraviolet light for 7 days. After evaporating the solvent, 28 mg of the crude product was obtained, which showed good NMR spectra, but unsatisfactory elemental analysis data. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.68 (s, 6H, 2×CH_3), 1.83 (s, 6H, 2×CH_3), 7.77 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*7), 7.79 (dd, 1H, $^3J_{H3,H4}$ = 8.7 Hz, $^3J_{H3,H2}$ = 4.9 Hz, *H*3), 8.56 (dd, 1H, $^3J_{H4,H3}$ = 8.7 Hz, $^4J_{H4,H2}$ = 1.0 Hz, *H*4), 8.71 (dd, 1H, $^3J_{H2,H3}$ = 4.9 Hz, $^4J_{H2,H4}$ = 1.0 Hz, *H*2), 9.11 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*6). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 8.8, 9.2 (2×CH_3), 90.0 (d, $^1J_{Rh,C}$ = 9.0 Hz, C_q), 98.7 (d, $^1J_{Rh,C}$ = 7.1 Hz, C_q), 106.3 (d, $^1J_{Rh,C}$ = 8.8 Hz, C_q), 125.6 (*C*7), 127.7 (*C*3), 137.6, 145.1, 153.9 (3×C_q), 139.2 (*C*4), 152.3 (*C*6), 155.2 (*C*2). ^{15}N-HMBC NMR ($CDCl_3$, 61 MHz): δ 241.4 (*N*1/H2, H3), 318.0 (*N*5/H6, H7). MS(EI) *m*/*z* (%): 422 (16) [M]$^+$, 387 (100) [M − Cl]$^+$, 352 (31) [M − 2×Cl]$^+$, 250 (16) [M − $RhCl_2$]$^+$.

Synthesis of 10. Ligand **6** (44 mg, 0.14 mmol) was dissolved in diethylether (10 mL). The solution was added to a solution of tetracarbonyldi-μ-chlorodirhodium(I) (27 mg, 0.07 mmol) in diethylether (10 mL). After stirring overnight, the yellow precipitate was filtered, washed with diethylether, and dried under high vacuum. The product was obtained as a pale yellow powder. Yield: 30 mg (0.06 mmol = 43%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.86 (s, 3H, CH_3), 5.55 (s, 1H, *H*1′), 6.75−6.82 (m, 2H, *H*3′/CH_{Ind}), 6.90 (m, 1H, CH_{Ind}), 7.23 (m, 1H, CH_{Ind}), 7.40 (m, 1H, CH_{Ind}), 7.67 (m, 1H, *H*3), 7.85 (ddd, 1H, $^3J_{H7,H8}$ = 7.6 Hz, $^3J_{H8,H9}$ = 8.8 Hz, $^4J_{H6,H8}$ = 1.1 Hz, *H*8), 8.11 (ddd, 1H, $^3J_{H7,H8}$ = 7.6 Hz, $^3J_{H6,H7}$ = 8.8 Hz, $^4J_{H7,H9}$ = 1.1 Hz, *H*7), 8.69 (dd, 1H, $^3J_{H2,H3}$ = 3.7 Hz, $^4J_{H2,H4}$ = 1.5 Hz, *H*2), 8.76 (broad d, 1H, $^3J_{H8,H9}$ = 8.8 Hz, *H*9), 9.58 (broad d, 1H, $^3J_{H6,H7}$ = 8.8 Hz, *H*6), 9.64 (dd, 1H, $^3J_{H3,H4}$ = 8.7 Hz, $^4J_{H2,H4}$ = 1.5 Hz, *H*4). ^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz) (two isomers): δ 15.81, 15.93 (2×CH_3), 53.03, 53.04 (2×CH_{Cp}), 120.22, 120.34, 121.98, 122.35, 123.58, 123.89, 125.10, 125.15, 126.27, 126.29, 126.52, 126.81, 126.90, 127.71, 129.84, 129.87 (16×CH + 2 overlapping CH signals), 130.04, 130.05 (2×C_q), 132.97, 132.99, 136.13, 136.19 (4×CH), 138.72, 138.73 (2*d*, $J_{Rh,C}$ = 0.9 Hz, 2×C_q), 144.61, 144.65, 144.85, 145.17, 147.42, 147.53, 148.94, 148.96, 149.83, 150.56 5 (10×C_q), 150.64, 150.677, (2×CH), 151.85, 151.89 (2×C_q), 179.93 (d, $^1J_{Rh,C}$ = 72.2 Hz, CO), 180.03 (d, $^1J_{Rh,C}$ = 72.2 Hz, CO), 183.02 (d, $^1J_{Rh,C}$ = 68.6 Hz, CO), 183.03 (d, $^1J_{Rh,C}$ = 68.7 Hz, CO). ^{15}N NMR ($CDCl_3$, 61 MHz): δ 225.5 (*N*5/H4, H6), 318.4 (*N*1/H2, H3). FT-IR (toluene): $\tilde{\nu}$ (cm^{-1}) = 2084 (s, $\nu_{C=O}$), 2009 (s, $\nu_{C=O}$). MS(EI) *m*/*z* (%): 474 (5) [M − CO]$^+$, 410 (50) [M − Cl − 2CO]$^+$, 307 (100) [M − $Rh(CO)_2Cl$]$^+$. $C_{24}H_{16}ClN_2O_2Rh$ (502.75 g/mol) Calcd: C, 57.34; H, 3.21; N, 5.57. Found C, 57.25; H, 3.47; N, 5.36.

Synthesis of 11. Tetracarbonyldi-μ-chlorodirhodium(I) (39 mg, 0.1 mmol) was dissolved in diethylether (10 mL). At rt, ligand **5** (51 mg, 0.21 mmol) was added. The reaction mixture was stirred for 6 h. A yellow precipitate was formed, which was filtered, washed with diethylether, and dried under high vacuum. The product was obtained as pale yellow crystals. Yield: 60 mg (0.15 mmol = 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.46 (d, 2H, $^3J_{H1',H2'}$ = 2.8 Hz, (1′H)$_2$), 5.30 (t, 1H, $^3J_{H1',H2'}$ = 2.8 Hz, *H*2′), 7.37−7.44 (m, 3H, 3×CH_{Ind}), 7.79 (dd, 1H, $^3J_{H2,H3}$ = 4.8 Hz, $^3J_{H3,H4}$ = 8.7 Hz, *H*3), 7.83 (d, 1H, $^3J_{H6,H7}$ = 4.4 Hz, *H*7), 7.95 (d, 1H, $^3J_{H,H}$ = 7.3 Hz, CH_{Ind}), 8.59 (d, 1H, $^3J_{H3,H4}$ = 8.7 Hz, *H*4), 8.96 (d, 1H, $^3J_{H6,H7}$ = 4.4 Hz, *H*6), 9.24 (d, 1H, $^3J_{H2,H3}$ = 4.8 Hz, *H*2). ^{13}C{^{1}H} ($CDCl_3$, 150 MHz): δ 43.8 (C1′), 78.0 (d, $^1J_{Rh,C}$ = 14.7 Hz, *C*2′), 90.7 (d, $^1J_{Rh,C}$ = 13.6 Hz, *C*3′), 120.5 (CH), 122.0 (CH_{Ind}), 125.3 (CH), 126.1, 127.5, 127.8 (3×CH_{Ind}), 139.9 (CH), 142.5, 144.5, 145.2, 145.4, 148.0 (5×C_q), 151.1 (CH), 152.7 (CH), 183.3 (d, $^1J_{Rh,C}$ = 74.7 Hz, CO). ^{15}N-HMBC NMR (C_6D_6, 41 MHz): δ 244.9 (*N*1/H2), 308.4 (*N*5/H6). FT-IR (toluene): $\tilde{\nu}$ (cm^{-1}) = 2034 cm^{-1} (s, $\nu_{C=O}$). MS(EI) *m*/*z* (%): 410 (5) [M]$^+$, 346 (100) [M − Cl − CO]$^+$, 243 (25) [M − Rh(CO)Cl]$^+$. $C_{18}H_{12}ClN_2ORh$ (410.66 g/mol) Calcd: C, 52.69; H, 2.95; N, 6.83. Found: C, 52.16; H, 3.02; N, 6.71.

Synthesis of 12. In a Schlenk flask under an argon atmosphere, **5** (300 mg, 1.23 mmol) was dissolved in degassed THF (30 mL), and the solution was cooled to −78 °C. A solution of *n*-BuLi in *n*-hexane (0.89 mL of 1.53 M, 1.36 mmol) was added dropwise and the mixture stirred for 10 min. At this temperature, $[Rh(CO)_2Cl]_2$ (240 mg, 0.62 mmol) was added. The mixture was stirred under an argon atmosphere overnight, allowing it to warm up slowly to rt in the acetone/dry ice bath. The volatiles were evaporated under vacuum, and the remaining dark, reddish-brown residue was dissolved in degassed CH_2Cl_2 (15 mL) and filtered through Celite 545 under an argon atmosphere. This solution was concentrated to approximately 10 mL under vacuum. Stirring under an argon atmosphere, approximately 5 mL of degassed *n*-hexane was added dropwise. After standing overnight at rt, the supernatant was removed from the red solid via a cannula. The solid was then recrystallized from CH_2Cl_2/*n*-hexane using the same procedure as above. After drying under high vacuum, the product was obtained as an orange solid (200 mg, 0.26 mmol, 42%). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 4.85 (d, 1H, $^3J_{H2',H3'}$ = 4.0 Hz, *H*2′), 6.02 (broad d, 1H, $^3J_{H2',H3'}$ = 4.0 Hz, *H*3′), 7.01 (ddd, 1H, $^3J_{H4',H5'}$ = 7.8 Hz, $^3J_{H5',H6'}$ = 7.2 Hz, $^4J_{H5',H7'}$ = 1.1 Hz, *H*5′), 7.12 (ddd, 1H, $^3J_{H6',H7'}$ = 7.9 Hz, $^3J_{H5',H6'}$ = 7.2 Hz, $^4J_{H5',H7'}$ = 1.1 Hz, *H*6′), 7.52 (broad d, 1H, $^3J_{H4',H5'}$ = 7.8 Hz, *H*4′), 7.55 (dd, 1H, $^3J_{H3,H4}$ = 8.5 Hz, $^3J_{H2,H3}$ = 4.6 Hz, *H*3), 7.87 (broad d, 1H, $^3J_{H6',H7'}$ = 7.9 Hz, *H*7′), 8.12 (dd, 1H, $^3J_{H2,H3}$ = 4.6 Hz, $^4J_{H2,H4}$ = 1.4 Hz, *H*2), 8.18 (d, 1H, $^3J_{H6,H7}$ = 4.6 Hz, *H*7), 8.42 (dd, 1H, $^3J_{H3,H4}$ = 8.5 Hz, $^4J_{H2,H4}$ = 1.4 Hz, *H*4), 8.89 (d, 1H, $^3J_{H6,H7}$ = 4.6 Hz, *H*6). ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz): δ 50.1 (d, $^1J_{C,Rh}$ = 9.4 Hz, *C*3′), 61.0 (d, $^1J_{C,Rh}$ = 10.9 Hz, *C*1′), 82.9 (*C*2′), 121.05 (*C*7′), 122.42 (*C*4′), 122.94 (*C*7), 124.08 (*C*6′), 124.17 (*C*5′), 124.64 (*C*3), 139.22 (*C*4), 139.80 (*C*7a′), 142.48 (*C*3a′), 144.63 (*C*4a), 146.44 (*C*8a), 148.29 (*C*2), 152.34 (*C*6), 154.10 (*C*8), 190.41 (d, $^1J_{C,Rh}$ = 99.6 Hz, terminal CO), 205.68 (t, $^1J_{C,Rh}$ = 38.2 Hz, μ-CO). ^{15}N NMR ($CDCl_3$, 61 MHz): δ 251.6 (*N*1/H2, H3), 302.4 (*N*5/H4, H6, H7). FT-IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2022 (s, terminal $\nu_{C=O}$), 1988 (s, terminal $\nu_{C=O}$), 1776 (m, μ-$\nu_{C=O}$). MS(ESI+) *m*/*z* (%): 777 (8) [M + H]$^+$, 749 (31) [M + H − CO]$^+$, 693 (100) [M + H − 3×CO]$^+$. $C_{37}H_{30}N_4O_3Rh_2$ (776.41) Calcd: C, 57.24; H, 2.86; N, 7.22. Found: C, 57.05; H, 2.90; N, 7.07.

Synthesis of 13. Ligand **5** (5 mg, 0.025 mmol) was dissolved in d^6-benzene (0.5 mL), and tetrakis(dimethylamido)zirconium(IV) (6.6 mg, 0.025 mmol) dissolved in d^6-benzene (0.5 mL) was added. An intense reddish-violet solution formed. The NMR data showed that only one product is formed. Because of the low stability of the compound, the characterization was performed by NMR and by the subsequent derivatization to **14**. ^{1}H NMR (C_6D_6, 600 MHz): δ 2.83 (s, 18H, 3×N(CH_3)$_2$), 6.84 (d, 1H, $^3J_{H2',H3'}$ = 3.5 Hz, *H*2′ or 3′), 6.92−6.94 (m, 2H, *H*3′ or 2′/*H*3), 7.14−7.16 (m, 1H, *H*4′ or 7′), 7.20−7.23 (m, 1H, *H*4′ or 7′), 7.44 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*7), 7.62 (ddd, 1H, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.1 Hz, *H*5′ or 6′), 7.83 (ddd, 1H, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.1 Hz, *H*5′ or 6′), 8.29 (dd, 1H, $^3J_{H2,H3}$ = 4.4 Hz, $^4J_{H2,H4}$ = 1.6 Hz, *H*2), 8.34 (dd, 1H, $^3J_{H3,H4}$ = 8.2 Hz, $^4J_{H2,H4}$ = 1.6 Hz, *H*4), 8.85 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*6). ^{13}C-Dept{^{1}H} NMR (C_6D_6, 150 MHz): δ 44.8 (3×N(CH_3)$_2$), 102.5 (CH_{Cp}), 119.5 (CH_{Cp}), 119.5 (CH_{Ind}), 122.4 (CH_{Ind}), 123.1 (*C*7), 123.4 (2 x CH_{Ind}), 137.9 (*C*4), 148.6 (*C*2), 151.6 (*C*6).

Synthesis of 14. To a stirred solution of Zr(NMe_2)$_4$ (110 mg, 0.41 mmol) in toluene (15 mL) was added a solution of **5** (100 mg, 0.41 mmol) in toluene (15 mL) at −78 °C. The colorless solution immediately turned dark purple and was stirred for 1 h. At −78 °C, the solvent was evaporated to 10 mL, followed by addition of Me_3SiCl (0.2 mL, 1.64 mmol) dropwise over 5 min. After stirring the reaction

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mixture at rt for 18 h, the solution was filtered. The crude product was washed with pentane (3 × 10 mL) and dried under vacuum to yield complex **14** (120 mg, 0.23 mmol, 56%) as a yellow solid. Green single crystals of [Zr(Ind^{Naph})Cl_3(THF)] for X-ray diffraction were grown from a saturated THF solution at rt. The compound cocrystallizes with one additional molecule of THF (see X-ray analysis and elemental analysis). ^{1}H NMR (d_8-THF, 600 MHz): δ 6.93 (d, 1H, $^3J_{H2',H3'}$ = 3.4 Hz, *H*2′ or 3′), 7.15 (d, 1H, $^3J_{H2',H3'}$ = 3.4 Hz, *H*3′ or 2′), 7.24−7.33 (m, 3H, H_{Ind}), 7.77 (d, 1H, $^3J_{H,H}$ = 8.4 Hz, H_{Ind}), 7.93 (dd, 1H, $^3J_{H3,H4}$ = 8.6 Hz, $^3J_{H2,H3}$ = 4.6 Hz, *H*3), 7.97 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*7), 8.72 (d, 1H, $^3J_{H3,H4}$ = 8.6 Hz, *H*4), 9.02 (d, 1H, $^3J_{H2,H3}$ = 4.6 Hz, *H*2), 9.11 (d, 1H, $^3J_{H6,H7}$ = 4.3 Hz, *H*6). ^{13}C{^{1}H} NMR (d_8-THF, 151 MHz): δ 109.2 (CH_{Ind}), 113.9 (C_q), 122.9 (CH_{Ind}), 124.7 (*C*7), 124.9 (*C*3), 125.7 (CH_{Ind}), 126.4 (CH_{Ind}), 126.7, 127.0 (2×CH_{Ind}), 128.2, 129.3 (2×C_q), 141.2 (*C*4), 142.0, 144.2, 147.2 (3×C_q), 151.4 (*C*2), 152.4 (*C*6). ^{15}N-HMBC NMR (d_8-THF, 61 MHz): δ = 172.3 (*N*1), 314.2 (*N*5). $C_{25}H_{27}Cl_3N_2O_2Zr$ (585.06 g/mol) Calcd: C, 51.32; H, 4.65; N, 4.79. Found: C, 49.89; H, 4.39; N, 4.76.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for compounds **7**, **8**, **9**, **11**, **12**, and **14**. Table 1SI with crystal data and structure refinement details of **7**−**9**, **11**, **12**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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