New Rhodium(I) Carbene Complexes from Carbene Transfer Reactions

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The Rh(I) complexes RhCl(diene)(NHC) have been synthesized from Ag(I) carbene precursors, where NHC is one of the *N*-heterocyclic carbenes 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), 3-methyl-1-phenacylimidazol-2-ylidene (MAI), and 3-methyl-1-picolylimidazol-2-ylidene (MPI), and diene is either NBD or COD. The complexes are characterized by elemental analysis, ^{1}H NMR and IR spectroscopies, mass spectrometry, and, in the case of RhCl(NBD)(IMes) and RhCl(COD)(MAI), X-ray crystallography. The new Ag(I) carbene complexes [Ag(IPr)$_2$]PF$_6$ and [Ag(IMes)$_2$]PF$_6$ are also reported.

Introduction

N-Heterocyclic carbenes (NHC) derived from imidazolium ions continue to attract general attention as efficient ligands in transition-metal-catalyzed processes,[1,2] including hydrogenation,[3] hydroformylation,[4] Heck, Suzuki, and Stille couplings,[5,6] olefin metathesis, and hydrosilylation.[7] Metal NHC complexes can be synthesized directly from the free NHC ligands prepared by deprotonation of the corresponding imidazolium salts,[8] but synthesis of the free NHC requires strictly anaerobic conditions, and difficulties have arisen from the use of a strong base to generate functionalized carbene ligands that contain acidic protons within the functional group. For example, McGuinness and Cavell[9] have reported that attempts to prepare the free carbenes 3-methyl-1-phenacylimidazol-2-ylidene (MAI) and 3-methyl-1-picolylimidazol-2-ylidene (MPI) (Figure 1) by deprotonation of imidazolium salts failed because of the high acidity of the methylene protons; thus the “direct synthetic method” is not suitable for a metal complex with such funtionalized carbene ligands.

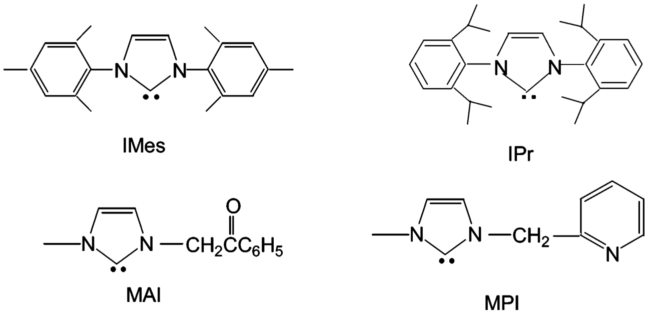

Figure 1. The carbene ligands used.

Silver(I) complexes of NHCs, which are readily made from Ag$_2$O and in situ deprotonation of precursor imidazolium halides,[1,10] can function as effective carbene transfer reagents, and thus provide a convenient entry point into other metal carbene chemistry without the need for the anaerobic conditions required for syntheses of a free NHC.[11] This carbene transfer method has been reported for synthesis of Rh−NHC complexes with 1,3-bisbutylimidazol-2-ylidene,[12a] a pincer carbene ligand,[12b] an imino-carbene ligand,[12c] a biscarbene ligand,[12d] and a tricarbene ligand.[12e] We were interested in synthesizing complexes of the type RhCl(diene)(NHC) and report here on the eight complexes where diene = COD or NBD, and NHC = IMes, IPr, MAI, or MPI. X-ray structures of RhCl(NBD)(IMes) and RhCl(COD)(MAI) are presented. One of this series of complexes, RhCl(COD)(IMes), has been synthesized previously via the known AgCl(IMes)[13] and directly via the free carbene[14] and has been shown to catalyze carbocyclization reactions[13b]

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and hydroamination of olefins.[14] Our ongoing studies on the interaction of the rhodium(I)−NHC complexes with H_2 and O_2 and their use in catalytic hydrogenations and oxidations will be reported later.[15] Carbene transfer from Ag(I) species is not always successful, and, for example, Herrmann's group, while attempting to use a Ag(I) complex with dimesityltetrahydropyrimid-2-ylidene for carbene transfer to Pd(II), generated instead a Ag(I)−biscarbene complex.[16] We note here also the synthesis of the PF_6^- salts of $[Ag(IPr)_2]^+$ and $[Ag(IMes)_2]^+$.

Results and Discussion

Rhodium(I)−Carbene Complexes. The eight complexes (**1**−**8**) of the type RhCl(diene)(NHC), where diene = NBD or COD, and NHC = IMes (**1** and **2**), IPr (**3** and **4**), MAI (**5** and **6**), or MPI (**7** and **8**), were isolated in good yield and characterized, two of them, RhCl(NBD)(IMes) (**1**) and RhCl(COD)(MAI) (**6**), by crystallography. As described in the Introduction, Ag−NHC complexes can provide effective carbene transfer reagents, particularly when functional groups in carbenes such as MAI and MPI are base-sensitive. We find that rhodium complexes containing MAI and MPI are readily synthesized by reacting the appropriate Ag−carbene with the familiar $[RhCl(diene)]_2$ precursors[17] in CH_2Cl_2 at room temperature.

The monomeric Ag(I)−carbenes AgCl(IPr)[1,18] and AgCl(IMes),[13a] with relatively strong Ag−C bonds, are rather stable and do not readily transfer the carbenes. Thus, no reaction with $[RhCl(diene)]_2$ complexes was evident at room temperature even after 12 h, and treatment at 85 °C in toluene for 6 h was found necessary for production of the Rh(I)−diene−carbene complexes in good yield; this is the first report on the use of AgCl(IPr) as a carbene transfer agent. Reactions of $[RhCl(diene)]_2$ with free IMes and IPr in THF were also studied, and complexes **1**−**4** were afforded in good yield at room temperature by this method. Nolan's group has reported that reaction of $[RhCl(COE)_2]_2$ (COE = cyclooctene) with IMes forms (with loss of COE) a chloro(hydrido)-orthometalated complex through intramolecular C−H activation of one of the Me groups.[19] The COD ligand is more strongly coordinating than COE and results in complexes **1**−**8**, showing no C−H activation. All these Rh complexes were characterized as monomeric species by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, mass spectrometry, and elemental analyses. Our syntheses of complexes **1**−**8**, which were developed independently, turn out to be modifications of the literature methods reported for RhCl(COD)(IMes) (**2**) by Evans et al.[13b] (using AgCl(IMes)) and Beller's group (using free IMes).[14]

There are notable differences in the NMR spectra for the corresponding NBD and COD complexes **1** and **2**. For RhCl(NBD)(IMes) (**1**), the ^1H NMR spectrum shows singlets at δ 2.14 and 2.30 for the *p*-Me and *o*-Me groups, respectively, and one singlet at 6.84 for the *m*-protons of mesityl groups. For RhCl(COD)(IMes) (**2**), three methyl ^1H signals at δ 1.97, 2.14, and 2.67, as well as singlets at δ 6.81 and 6.86 for the *m*-protons, reveal inequivalent *o*-Me groups and *m*-protons, presumably because of restricted rotation around the $Rh-C_{carbene}$ bond[20,21] and/or less likely the $N_{imid}-C_{mesityl}$ bond. $^{13}C\{^1H\}$ NMR data for **1** and **2** lead to the same conclusion. For **1**, only two methyl signals are seen, one for the *o*-Me groups at δ 18.9 and one for the *p*-Me at δ 21.1; singlets at δ 136.1 and 129.4 are assigned, respectively, to the two equivalent aryl C-*o*-CH_3 C atoms and the aryl *m*-CH carbon. For **2**, the $^{13}C\{^1H\}$ NMR spectrum displays inequivalent *o*-Me carbon signals at δ 17.9 and 20.1 and the *p*-Me singlet at δ 20.8, as well as singlets for two different aryl C-*o*-CH_3 carbons (δ 134.1 and 136.7) and two different aryl *m*-CH carbons (δ 128.1 and 130.0). For **1** and **2**, the $^{13}C\{^1H\}$ NMR doublets for the carbenic carbons appear at δ 186.0 (J_{RhC} = 59 Hz) and 184.8 (J_{RhC} = 53 Hz), upfield from the corresponding resonance for the free carbene at δ 219.2; the δ values are 4−6 ppm downfield from those observed for a Rh(I)−diene complex with 1,3-dicyclohexylimidazol-2-ylidene.[20] Our NMR data in C_6D_6 for complex **2** are in reasonable agreement with those reported earlier in $CDCl_3$,[13b,14] but our spectra are better resolved and more definitively assigned.

Similar differences are seen in the NMR spectra of **3** and **4**, with the NBD analogue again showing "more equivalence". For RhCl(NBD)(IPr) (**3**), a single septet ^1H NMR resonance for the α-protons of the *i*Pr groups is seen at δ 3.26, downfield from the value of 2.96 for free IPr, while two sets of doublet Me resonances are seen at δ 1.04 and 1.59; the corresponding $^{13}C\{^1H\}$ NMR spectrum shows one methine signal at δ 29.0 and two Me signals at δ 26.1 and 23.6. In the COD analogue (**4**), the methine protons are inequivalent (two broad ^1H septets at δ 2.54 and 4.12), and there are two sets of inequivalent methyl protons at δ 0.96 and 1.72; however, only two $^{13}C\{^1H\}$ singlets are seen at δ 26.7 and 29.1, implying that the resonances of the methine and methyl carbons overlap. For both **3** and **4**, the $^{13}C\{^1H\}$ NMR doublet for the carbenic carbon appears at δ 187.7 (J_{RhC} = 59 and 53 Hz, respectively), 33 ppm upfield from the corresponding resonance for free IPr and ~7 ppm downfield of the values in other Rh(I)−diene−carbene complexes.[20,21]

In complexes **5**−**8**, containing the functionalized carbenes MAI and MPI, the carbenes remain as monodentate ligands; there is no evidence for interaction with the phenacyl or pyridyl groups. For the MAI complexes **5** and **6**, the carbenic-carbon $^{13}C\{^1H\}$ NMR doublets appear at δ 181.2 and 180.2, respectively. Complexes **7** and **8**, containing the picolyl functionality, have limited solubility in common solvents, and their ^1H NMR spectra show broad signals; satisfactory ^{13}C NMR spectra could not be obtained.

The X-ray crystallographic, solid structures of complexes RhCl(NBD)(IMes) (**1**) and RhCl(COD)(MAI) (**6**), shown in Figures 2 and 3, respectively (with selected bond distances and angles in Tables 2 and 3), were the same as those indicated in solution by the NMR studies. Complex **1** crystallizes with two molecules in the asymmetric unit and shows typical square-planar Rh(I) geometry where two *cis* sites are each considered as the center of an olefinic bond; the corresponding structure of RhCl(COD)(IMes) (**2**) was reported recently.[13b] The structure of **6** is the first reported for a metal complex containing MAI. The $Rh-C_{carbene}$, Rh−Cl, $Rh-C_{diene}$, and $C_{carbene}-N$ bond lengths for **2** and **6** are in the range observed for other Rh(I)−

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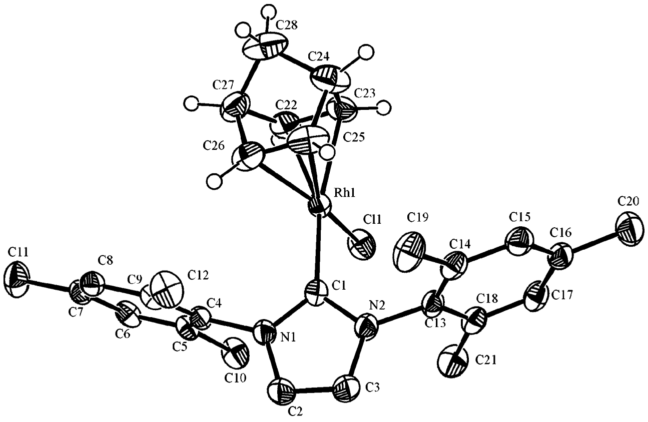

Figure 2. ORTEP diagram of RhCl(NBD)(IMes) (**1**) with 50% probability thermal ellipsoids.

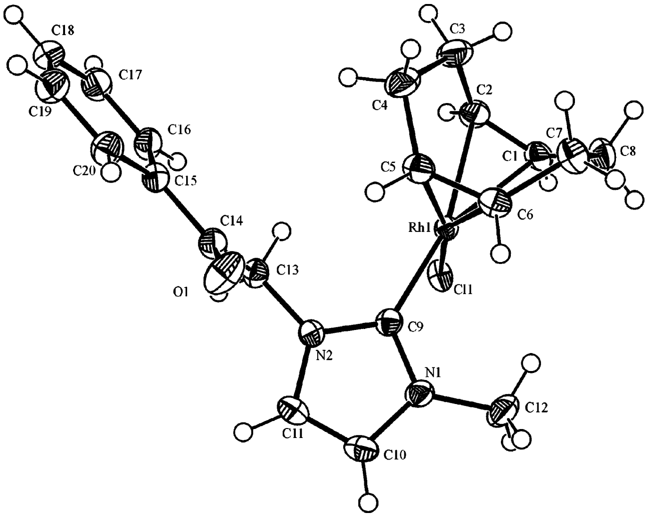

Figure 3. ORTEP diagram of RhCl(COD)(MAI) (**6**) with 50% probability thermal ellipsoids.

Table 1. Crystallographic Data for RhCl(NBD)(IMes) (1) and RhCl(COD)(MAI) (6)

data	**1**	**6**
formula	$C_{28}H_{32}N_2RhCl$	$C_{20}H_{24}N_2ORhCl$
fw	534.92	446.77
cryst color, habit	yellow, tablet	yellow, irregular
cryst size (mm)	0.50 × 0.25 × 0.20	0.25 × 0.20 × 0.15
cryst syst	monoclinic	monoclinic
space group	*C*2/c (#15)	*P*2$_1$/*n* (#14)
a (Å)	35.387(3)	9.9376(3)
b (Å)	17.511(1)	9.7772(3)
c (Å)	16.885(1)	19.4287(6)
β (deg)	103.882(3)	96.898(1)
V (Å^3)	1015.7(1)	1874.1(1)
μ (mm^{-1})	0.795	1.064
no. of total reflns	91 201	30 342
no. of unique reflns	11 895	4501
R_{int}	0.030	0.028
no. of variables	621	243
R1 ($I > 2\sigma(I)$)	0.044 (all data)	0.030 (all data)
wR2^a	0.087 (all data)	0.077 (all data)
gof	1.07 (all data)	1.10 (all data)

^{a} $w = 1/[\sigma^2(F_o^2) + (0.0627P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Distances and Angles for RhCl(NBD)(IMes) (1) with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
Rh(1)−C(22)	2.174(3)	C(1)−Rh(1)−Cl(1)	94.15(7)
Rh(1)−C(23)	2.196(3)	C(1)−Rh(1)−C(22)	157.78(10)
Rh(1)−C(25)	2.111(3)	C(1)−Rh(1)−C(23)	163.02(10)
Rh(1)−C(26)	2.098(3)	C(1)−Rh(1)−C(25)	101.81(10)
Rh(1)−C(1)	2.069(2)	C(1)−Rh(1)−C(26)	99.49(10)
Rh(1)−Cl(1)	2.3570(7)	C(22)−Rh(1)−Cl(1)	91.99(8)
C(1)−N(1)	1.369(3)	C(23)−Rh(1)−Cl(1)	93.67(8)
C(1)−N(2)	1.363(3)	C(25)−Rh(1)−Cl(1)	157.21(9)
C(2)−N(1)	1.394(3)	C(26)−Rh(1)−Cl(1)	153.29(9)
C(3)−N(2)	1.396(3)	N(2)−C(1)−N(1)	103.5(2)

Table 3. Selected Bond Distances and Angles for RhCl(COD)(MAI) (6) with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
Rh(1)−C(1)	2.194(2)	C(9)−Rh(1)−Cl(1)	88.44(6)
Rh(1)−C(2)	2.212(2)	C(9)−Rh(1)−C(1)	160.40(9)
Rh(1)−C(5)	2.097(2)	C(9)−Rh(1)−C(2)	163.34(9)
Rh(1)−C(6)	2.109(2)	C(9)−Rh(1)−C(5)	90.54(9)
Rh(1)−C(9)	2.016(2)	C(9)−Rh(1)−C(6)	93.76(9)
Rh(1)−Cl(1)	2.4016(5)	C(1)−Rh(1)−Cl(1)	88.71(7)
C(9)−N(1)	1.355(3)	C(2)−Rh(1)−Cl(1)	94.63(7)
C(9)−N(2)	1.356(3)	C(5)−Rh(1)−Cl(1)	162.74(7)
C(10)−N(1)	1.384(3)	C(6)−Rh(1)−Cl(1)	158.30(7)
C(11)−N(2)	1.384(3)	N(2)−C(9)−N(1)	103.91(18)

diene−carbene complexes.[20−22] Minor differences between the structure of **1** and those of closely analogous complexes must be caused by the presence of the bulky mesityl groups; data on a Rh(I)−diene complex with a bulky perimidine-based carbene show similar effects.[22]

The positive ion ESI-MS analyses for complexes **1**−**4** and **6**−**8** in each case showed a major *m*/*z* peak corresponding to the $[M - Cl]^+$ fragment; for complex **5**, the most intense peak appeared at *m*/*z* $[MAI + H]^+$ (201).

During our studies to generate silver(I) carbene reagents, we synthesized AgCl(IPr), $[Ag(IPr)_2]PF_6$, and $[Ag(IMes)_2]PF_6$ by the standard reaction of the imidazolium salt with silver oxide. The first of these complexes was reported very recently by Nolan's group and structurally characterized as AgCl(IPr)·$1.86CH_2Cl_2$;[1] the X-ray analysis of our product revealed no solvent molecules in the unit cell, and there are differences in the crystal systems (orthorhombic vs monoclinic for the solvated species), space groups, and geometric parameters (corresponding bond angles and lengths show differences of up to 2° and 0.09 Å). Because of these differences and minor differences in the NMR spectral data of the two complexes, our data on AgCl(IPr) are given in the Supporting Information. Salts of $[Ag(IPr)_2]^+$ have not been previously reported, while the $[Ag(IMes)_2]^+$ cation has been structurally characterized previously within salts having the anions $[CF_3SO_3]^-$,[23] $[AgCl_2]^-$, and $[Ag_4I_6]^{2-}$.[1] Structural data on $[Ag(IMes)_2]PF_6$ are given in the Supporting Information; the PF_6^- anion results in many weak H···F interactions (Table S1), and these cause significant differences from the structure of the triflate salt. For example, the planar imidazole rings of the IMes ligands in the PF_6^- salt are twisted from coplanarity by 70.6°, much more than that of ∼40° in the triflate salt.[23] The syntheses and characterization of $[Ag(IPr)_2]PF_6$ and $[Ag(IMes)_2]PF_6$ are also given in the Supporting Information.

Conclusions

The AgCl(IPr) and AgCl(IMes) species are efficient carbene transfer agents at 85 °C and have been used to synthesize RhCl-

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(diene)(NHC) complexes, which were isolated also from reaction of the free carbene with a Rh precursor; analogous Rh complexes containing the functionalized carbene ligands MAI and MPI were obtained in high yields using known [Ag(NHC)$_2$]$^+$ species as carbene transfer agents. The complexes RhCl(NBD)(IMes) and RhCl(COD)(MAI) were characterized structurally. The syntheses and characterization of AgCl(IPr), [Ag(IPr)$_2$]PF$_6$, and [Ag(IMes)$_2$]PF$_6$ are presented in the Supporting Information.

Experimental Section

All manipulations were performed under Ar, using standard Schlenk techniques. Reagent grade solvents (Fisher Scientific) were dried using standard procedures and prior to use were purged with Ar. Deuterated solvents (Cambridge Isotope Laboratories) were similarly dried and then distilled under N$_2$ prior to use. Common chemicals, including Ag$_2$O, were obtained from Fisher Scientific; these and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes•HCl) (Strem) were used as received. 1,3-Bis(2,6-diisopropylphenyl)-imidazolium chloride (IPr•HCl),[24] IPr,[24] IMes,[25] AgCl(IMes),[13] [Ag(MAI)$_2$][AgBr$_2$] and [Ag(MPI)$_2$I][0.4AgI$_2$][9] (MAI = 3-methyl-1-phenacylimidazol-2-ylidene, and MPI = 3-methyl-1-picolylimidazol-2-ylidene), and the [RhCl(diene)]$_2$ precursors[17] were synthesized according to the reported procedures. Our syntheses of AgCl(IPr),[1] [Ag(IMes)$_2$]PF$_6$, and [Ag(IPr)$_2$]PF$_6$ are given in the Supporting Information.

NMR spectra were recorded at room temperature (~20 °C) on a Bruker AV 300 spectrometer (300.0 MHz for ^{1}H, 121.4 MHz for ^{31}P{^{1}H}, and 75.0 MHz for ^{13}C{^{1}H} NMR). Shifts are relative to external TMS or 85% aqueous H$_3$PO$_4$; residual protonated species in deuterated solvents were used as internal references for ^{1}H data (δ 7.15 for C$_6$D$_6$ and δ 7.24 for CDCl$_3$), with J values given in Hz (s = singlet, d = doublet, m = multiplet, spt = septet, br = broad). Mass spectral data (reported as *m*/*z* values) were acquired on a Bruker Esquire ES spectrometer in this department (Dr. Y. Ling). IR spectra (KBr) were recorded on ATI Mattson Genesis or Bomem-Michelson MB-100 FT-IR spectrometers. Elemental analyses were performed by Mr. M. Lakha of this department on a Carlo Erba EA 1108 analyzer.

Crystal Structure Determinations. Measurements were made on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation (0.71069 Å). Some crystallographic data for **1** and **6** are shown in Tables 1−3. The structures were solved using direct methods[26] and expanded using Fourier techniques.[27] For all structures, all non-H atoms were refined anisotropically; all H atoms on coordinated carbons were located in difference maps and refined isotropically, while all other H atoms were included in calculated positions but not refined.

RhCl(NBD)(IMes) (1). *Method 1*: A suspension of [RhCl(NBD)]$_2$ (0.023 g, 0.050 mmol) and AgCl(IMes) (0.045 g, 0.100 mmol) in toluene (10 mL) was stirred for 6 h at 85 °C. The resulting yellowish suspension was cooled to room temperature and filtered through Celite, and the yellow filtrate was concentrated. Addition of hexane (10 mL) precipitated a yellow powder, which was collected and dried in vacuo. Yield: 0.049 g (91%). *Method 2*: A suspension of [RhCl(NBD)]$_2$ (0.023 g, 0.050 mmol) and free IMes (0.030 g, 0.100 mmol) in THF (10 mL) was stirred for 2 h at room temperature to give a yellowish solution, which was concentrated. Addition of hexane (10 mL) precipitated a yellow powder, which was collected and dried in vacuo. Yield: 0.046 g (86%). ^{1}H NMR (C$_6$D$_6$): δ 6.84 (s, 4H, *m*-Ar*H*), 6.08 (s, 2H, NC*H*), 4.56 (s, 2H, CH$_2$C*H*), 3.19 (m, 4H, =C*H* of NBD), 2.30 (s, 12H, *o*-C*H*$_3$), 2.14 (s, 6H, *p*-C*H*$_3$), 0.95 (d, 1H, J = 15, C*H*$_2$), 0.83 (d, 1H, J = 15, C*H*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 186.0 (d, J_{RhC} = 59, N*C*N), 138.6 (s, N*C*), 136.8 (s, *C*-*p*-CH$_3$), 136.1 (s, *C*-*o*-CH$_3$), 129.4 (s, *m*-*C*H), 123.0 (s, N*C*H), 75.7 (d, J_{RhC} = 6, =*C*H of NBD), 62.7 (d, J_{RhC} = 5, CH*C*H$_2$), 50.4 (s, *C*HCH$_2$), 46.7 (d, J_{RhC} = 12, =*C*H of NBD), 21.1 (s, *p*-*C*H$_3$), 18.9 (s, *o*-*C*H$_3$). ESI-MS (MeOH): 499, [M − Cl]$^+$ (100%); 305, [IMes + H]$^+$ (56%). Anal. Calcd for C$_{28}$H$_{32}$N$_2$RhCl: C, 62.87; H, 6.03; N, 5.24. Found: C, 62.98; H, 6.20; N, 5.27.

RhCl(COD)(IMes) (2). This complex was prepared by methods analogous to those described for **1**. *Method 1*: 0.044 g (0.090 mmol) of [RhCl(COD)]$_2$ and 0.081 g (0.181 mmol) of AgCl(IMes) were used. Yield: 0.084 g (85%). *Method 2*: 0.044 g (0.090 mmol) of [RhCl(COD)]$_2$ and 0.055 g (0.181 mmol) of IMes were used. Yield: 0.084 g (90%). ^{1}H NMR (C$_6$D$_6$): δ 6.86 (s, 2H, *m*-Ar*H*), 6.81 (s, 2H, *m*-Ar*H*), 6.12 (s, 2H, NC*H*), 5.07 (m, 2H, =C*H* of COD), 3.46 (m, 2H, =C*H* of COD), 2.67 (s, 6H, *o*-C*H*$_3$), 2.14 (s, 6H, *o*-C*H*$_3$), 1.97 (s, 6H, *p*-C*H*$_3$), 1.82 (m, 2H, C*H*$_2$), 1.56 (m, 2H, C*H*$_2$), 1.45 (m, 2H, C*H*$_2$), 1.29 (m, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 184.8 (d, J_{RhC} = 53, N*C*N), 138.3 (s, N*C*), 138.0 (s, *C*-*p*-CH$_3$), 136.7 (s, *C*-*o*-CH$_3$), 134.1 (s, *C*-*o*-CH$_3$), 130.0 (s, *m*-*C*H), 128.1 (s, *m*-*C*H), 123.1 (s, N*C*H), 96.2 (d, J_{RhC} = 7, =*C*H of COD), 67.1 (d, J_{RhC} = 14, =*C*H of COD), 32.9 (s, *C*H$_2$), 28.5 (s, *C*H$_2$), 20.8 (s, *p*-*C*H$_3$), 20.1 (s, *o*-*C*H$_3$), 17.9 (s, *o*-*C*H$_3$). ESI-MS (MeOH): 515, [M − Cl]$^+$ (100%); 407, [M − Cl − COD]$^+$ (10%); 305, [IMes + H]$^+$ (12%). Anal. Calcd for C$_{29}$H$_{36}$N$_2$RhCl•0.5H$_2$O: C, 62.20; H, 6.66; N, 5.00. Found: C, 62.61; H, 6.86; N, 5.10.

RhCl(NBD)(IPr) (3). This complex was prepared by methods analogous to those used for **1**. *Method 1*: 0.023 g (0.050 mmol) of [RhCl(NBD)]$_2$ and 0.053 g (0.100 mmol) of AgCl(IPr) were used. Yield: 0.055 g (89%). *Method 2*: 0.023 g (0.050 mmol) of [RhCl(NBD)]$_2$ and 0.039 g (0.100 mmol) of IPr were used. Yield: 0.057 g (92%). ^{1}H NMR (C$_6$D$_6$): δ 7.28−7.18 (m, 6H, *m*, *p*-C*H*), 6.48 (s, 2H, NC*H*), 4.56 (m, 2H, CH$_2$C*H*), 3.26 (spt, 4H, J = 6, C*H*(CH$_3$)$_2$), 3.16 (br, 2H, =C*H* of NBD), 2.86 (m, 2H, =C*H* of NBD), 1.59 (d, 12H, J = 6, C*H*$_3$), 1.04 (d, 12H, J = 6, C*H*$_3$), 0.90 (d, 1H, J = 8, C*H*$_2$), 0.85 (d, 1H, J = 12, C*H*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 187.7 (d, J_{RhC} = 59, N*C*N), 146.7 (s, N*C*), 136.8 (s, NC*C*), 130.0 (s, *p*-CH), 128.3 (s, *m*-*C*H), 124.1 (d, J_{RhC} = 7, N*C*H), 75.6 (d, J_{RhC} = 6, = *C*H of NBD), 62.9 (d, J_{RhC} = 5, CH*C*H$_2$), 50.5 (d, J_{RhC} = 2, *C*HCH$_2$), 47.3 (d, J_{RhC} = 12, =*C*H of NBD), 29.0 (s, *C*H(CH$_3$)$_2$), 26.1 (s, *C*H$_3$), 23.6 (s, *C*H$_3$). ESI-MS (MeOH): 583, [M − Cl]$^+$ (100%). Anal. Calcd for C$_{34}$H$_{44}$N$_2$RhCl: C, 66.00; H, 7.17; N, 4.53. Found: C, 66.30; H, 7.36; N, 4.82.

RhCl(COD)(IPr) (4). This complex was prepared by methods analogous to those used for **1**. *Method 1*: 0.025 g (0.050 mmol) of [RhCl(COD)]$_2$ and 0.053 g (0.100 mmol) of AgCl(IPr) were used. Yield: 0.052 g (82%). *Method 2*: 0.025 g (0.050 mmol) of [RhCl(COD)]$_2$ and 0.039 g (0.100 mmol) of IPr were used. Yield: 0.056 g (88%). ^{1}H NMR (C$_6$D$_6$): δ 7.31−7.19 (m, 6H, *m*, *p*-C*H*), 6.59 (s, 2H, NC*H*), 5.04 (s, 2H, =C*H* of COD), 4.12 (br, 2H, C*H*(CH$_3$)$_2$), 3.41 (s, 2H, =C*H* of COD), 2.54 (br, 2H, C*H*(CH$_3$)$_2$),1.72 (d, 12H, J = 6, C*H*$_3$), 1.44 (m, 2H, C*H*$_2$), 1.42 (m, 2H, C*H*$_2$), 1.38 (m, 2H, C*H*$_2$), 1.30 (m, 2H, C*H*$_2$), 0.96 (d, 12H, J = 6, C*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 187.7 (d, J_{RhC} = 53, N*C*N), 146.8 (s, N*C*), 136.9 (s, NC*C*), 130.1 (s, *p*-*C*H), 128.3 (s, *m*-CH), 124.7 (s, N*C*H), 96.4 (d, J_{RhC} = 7, =*C*H of COD), 67.4 (d, J_{RhC} = 14, =*C*H of COD), 33.1 (s, *C*H$_2$), 29.1 (s, *C*H(CH$_3$)$_2$), 28.6 (s, *C*H$_2$), 26.7 (s, *C*H$_3$). ESI-MS (MeOH): 599, [M − Cl]$^+$ (100%); 389, [IPr + H]$^+$ (35%).

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Anal. Calcd for $C_{35}H_{48}N_2RhCl$: C, 66.22; H, 7.63; N, 4.42. Found: C, 66.51; H, 7.71; N, 4.70.

RhCl(NBD)(MAI) (5). An orange suspension of $[RhCl(NBD)]_2$ (0.023 g, 0.050 mmol) and $[Ag(MAI)_2][AgBr_2]$ (0.039 g, 0.050 mmol) in CH_2Cl_2 (10 mL) was stirred overnight at room temperature. The mixture was then filtered through Celite, and the yellow filtrate was concentrated. Addition of hexane (10 mL) precipitated a yellow powder, which was collected and dried in vacuo. Yield: 0.036 g (84%). ^{1}H NMR (C_6D_6): δ 8.19 (s, 1H, NC*H*), 8.17 (s, 1H, NC*H*), 7.18−7.11 (m, 5H, C*H*), 6.23 (d, 1H, *J* = 2, NC*H*$_2$), 5.92 (d, 1H, *J* = 2, NC*H*$_2$), 4.98 (s, 2H, CH$_2$C*H*), 3.37 (s, 3H, C*H*$_3$), 3.19 (m, 4H, ═C*H* of NBD), 1.52 (d, 1H, *J* = 8, C*H*$_2$), 1.50 (d, 1H, *J* = 8, C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 190.8 (s, *C*O), 181.2 (d, J_{RhC} = 56, N*C*N), 136.8 (s, CO*C*), 134.0 (s, *p*-*C*H), 129.4 (s, *m*-*C*H), 127.5 (s, *o*-*C*H), 121.2 (s, N*C*H), 120.9 (s, N*C*H), 76.8 (d, J_{RhC} = 6, = *C*H of NBD), 63.7 (s, CH*C*H$_2$), 56.8 (s, N*C*H$_2$), 50.5 (s, *C*HCH$_2$), 45.6 (d, J_{RhC} = 12, = *C*H of NBD), 37.2 (s, N*C*H$_3$). ESI-MS (MeOH): 201, [MAI + H]$^+$ (100%). Anal. Calcd for $C_{19}H_{20}N_2RhClO\cdot 2H_2O$: C, 48.89; H, 5.18; N, 6.00. Found: C, 48.35; H, 5.01; N, 6.55. IR (KBr): 1686 cm^{-1} (ν_{CO}).

RhCl(COD)(MAI) (6). This complex was prepared in a manner analogous to that described for **5**, but using $[RhCl(COD)]_2$ (0.022 g, 0.045 mmol) and $[Ag(MAI)_2][AgBr_2]$ (0.035 g, 0.045 mmol). Yield: 0.038 g (95%). ^{1}H NMR (C_6D_6): δ 8.18 (d, 1H, *J* = 2, NC*H*), 8.16 (s, 1H, *J* = 2, NC*H*), 7.71 (m, 1H, *p*-C*H*), 7.65 (m, 2H, *m*-C*H*), 6.96 (m, 2H, *o*-C*H*), 5.48 (s, 1H, NC*H*$_2$), 5.43 (s, 1H, NC*H*$_2$), 4.92 (m, 2H, ═C*H* of COD), 4.06 (s, 3H, C*H*$_3$), 3.38 (m, 1H, ═C*H* of COD), 3.06 (m, 1H, ═C*H* of COD), 2.38 (m, 2H, C*H*$_2$), 2.05 (m, 1H, C*H*$_2$), 1.88 (m, 4H, C*H*$_2$), 1.70 (m, 1H, C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 190.5 (s, *C*O), 180.2 (d, J_{RhC} = 53, N*C*N), 137.6 (s, CO*C*), 134.2 (s, *p*-*C*H), 129.0 (s, *m*-*C*H), 128.1 (s, *o*-*C*H), 122.4 (s, N*C*H), 122.1 (s, N*C*H), 98.5 (d, J_{RhC} = 8, ═*C*H of COD), 68.0 (d, J_{RhC} = 14, ═*C*H of COD), 56.6 (s, N*C*H$_2$), 37.4 (s, N*C*H$_3$), 32.7 (d, J_{RhC} = 28, *C*H$_2$), 28.6 (d, J_{RhC} = 24, *C*H$_2$). ESI-MS (MeOH): 411, [M − Cl]$^+$ (100%); 201, [MAI + H]$^+$ (71%). Anal. Calcd for $C_{20}H_{24}N_2RhClO\cdot H_2O$: C, 51.68; H, 5.64; N, 6.03. Found: C, 51.80; H, 5.33; N, 6.07. IR (KBr): 1690 cm^{-1} (ν_{CO}).

RhCl(NBD)(MPI) (7). This complex was prepared in a manner analogous to that described for **5**, but using $[RhCl(NBD)]_2$ (0.023 g, 0.050 mmol) and $[Ag(MPI)_2I][0.4AgI_2]$ (0.034 g, 0.050 mmol). Yield: 0.033 g (82%). ^{1}H NMR (C_6D_6): δ 8.35 (m, 1H, C*H*), 7.72 (m, 1H, C*H*), 7.41 (s, 1H, NC*H*), 6.97 (m, 1H, C*H*), 6.85 (s, 1H, NC*H*), 6.45 (m, 1H, C*H*), 5.80 (s, 2H, NC*H*$_2$), 4.26 (s, 2H, CH$_2$C*H*), 3.72 (m, 2H, ═C*H* of NBD), 3.51 (s, 3H, C*H*$_3$), 3.20 (m, 2H, ═C*H* of NBD), 1.19 (d, 1H, *J* = 6, C*H*$_2$), 0.86 (d, 1H, *J* = 6, C*H*$_2$). ESI-MS (MeOH): 368, [M − Cl]$^+$ (100%); 174, [MPI + H]$^+$ (23%). Anal. Calcd for $C_{17}H_{19}N_3RhCl\cdot 0.5CH_2Cl_2\cdot H_2O$: C, 45.28; H, 4.77; N, 9.05. Found: C, 45.55; H, 4.98; N, 8.88.

RhCl(COD)(MPI) (8). This complex was prepared in a manner analogous to that described for **5**, but using $[RhCl(COD)]_2$ (0.022 g, 0.045 mmol) and $[Ag(MPI)_2I][0.4AgI_2]$ (0.031 g, 0.046 mmol). Yield: 0.033 g (88%). ^{1}H NMR (C_6D_6): δ 8.25 (m, 1H, C*H*), 7.22 (m, 1H, C*H*), 7.41 (s, 1H, NC*H*), 6.88 (s, 1H, NC*H*), 6.78 (m, 1H, C*H*), 6.45 (m, 1H, C*H*), 5.82 (s, 2H, NC*H*$_2$), 5.50 (s, 2H, ═C*H* of COD), 5.18 (s, 1H, ═C*H* of COD), 5.01 (s, 1H, ═C*H* of COD), 3.49 (s, 3H, C*H*$_3$), 2.52 (m, 2H, C*H*$_2$), 2.20 (m, 1H, C*H*$_2$), 2.05 (m, 4H, C*H*$_2$), 1.80 (m, 1H, C*H*$_2$). ESI-MS (MeOH): 384, [M − Cl]$^+$ (100%); 174, [MPI + H]$^+$ (35%). Anal. Calcd for $C_{18}H_{23}N_3RhCl\cdot 2.5CH_2Cl_2$: C, 38.95; H, 4.46; N, 6.65. Found: C, 38.56; H, 4.68; N, 6.59.

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Supporting Information Available: Preparation of AgCl(IPr), $[Ag(IMes)_2]PF_6$, and $[Ag(IPr)_2]PF_6$, C−H···F contacts and interaction dimensions for $[Ag(IMes)_2]PF_6$ in Angstroms and degrees, and crystallographic data for AgCl(IPr), $[Ag(IMes)_2]PF_6$, RhCl(NBD)(IMes) (**1**), and RhCl(COD)(MAI) (**6**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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